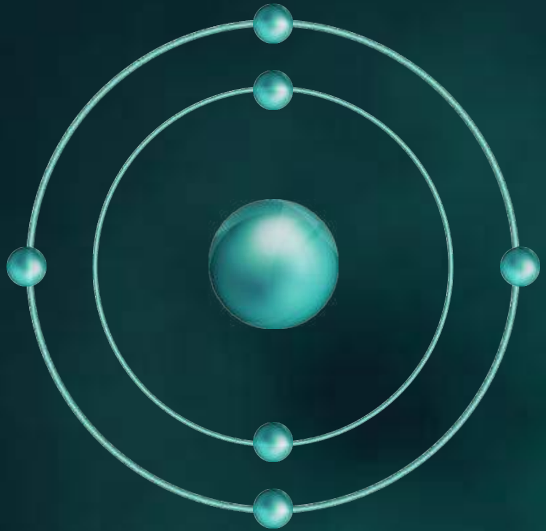
BYJU'S Classes

Alcohols, Phenols, and Ethers



Introduction

Importance of alcohols in our daily life

1) Ethanol is the only alcohol which is used for the drinking purpose.

2) Alcohols have insecticidal property, so they are used for sanitization. Alcohol used for this purpose are methanol, ethanol, and isopropyl alcohol.

3) Alcohol is present in table sugar.

4) Alcohols are used in making paints, varnishes, paper, and fabrics.

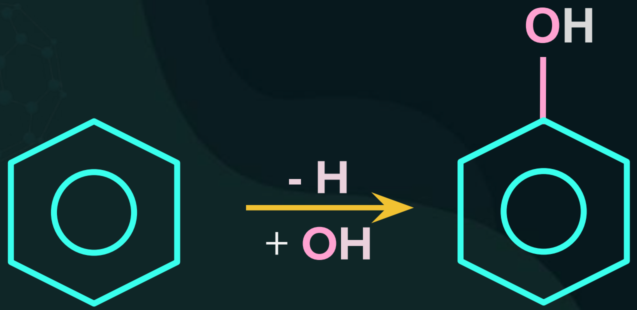
Introduction

$$R-H \xrightarrow[+\,OH]{-\,H} R-OH$$

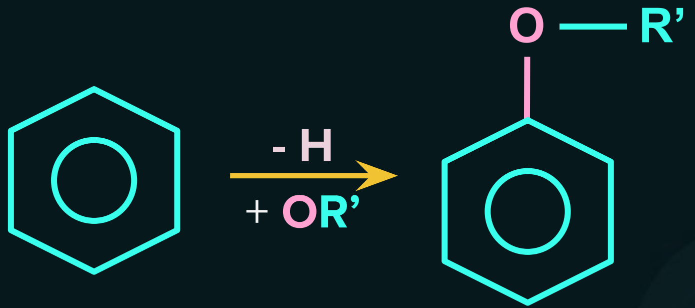
Alcohol

$$R-H \xrightarrow[+\,OR']{-\,H} R-O-R'$$

Alkyl ether

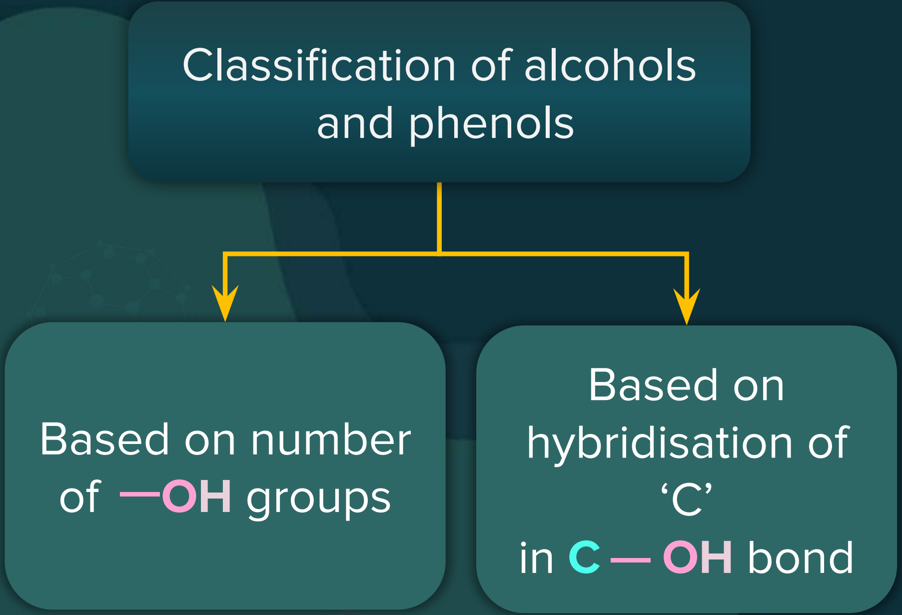


Phenol



Aryl ether

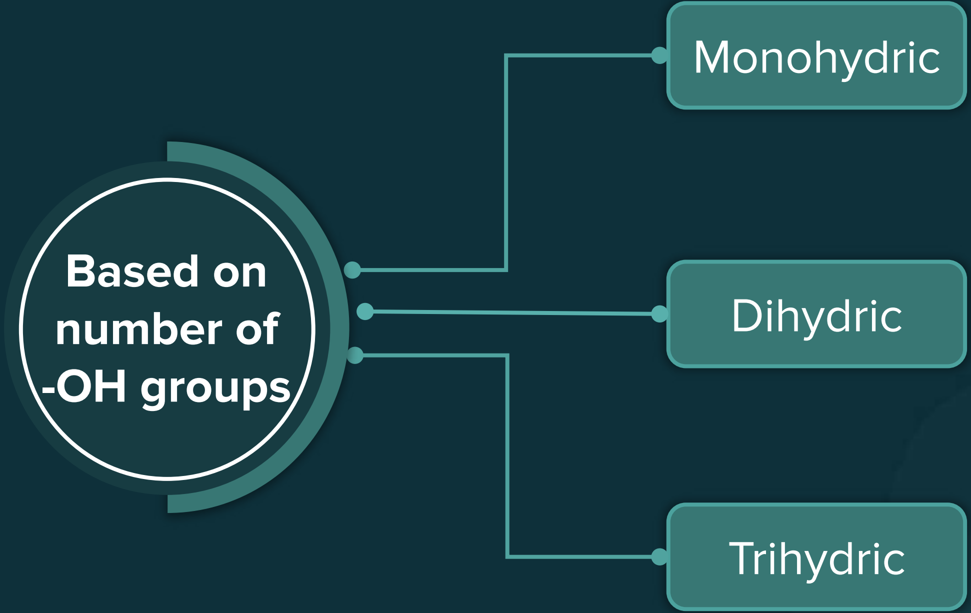
Classification of Alcohols and Phenols



Classification of alcohols and phenols

Based on number of —**OH** groups

Based on hybridisation of ‘C’ in **C** — **OH** bond



Based on number of -OH groups

Monohydric

Dihydric

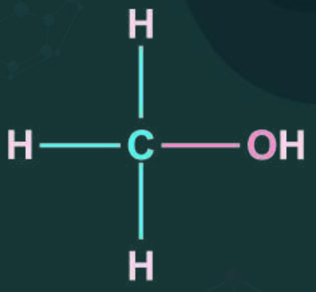
Trihydric

Classification of Alcohols and Phenols

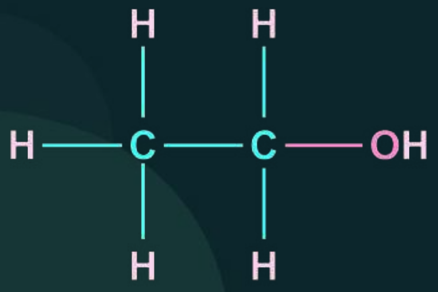
Monohydric alcohols

Number of -OH groups in alcohol = 1

Examples



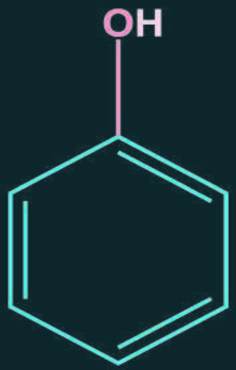
Methyl alcohol



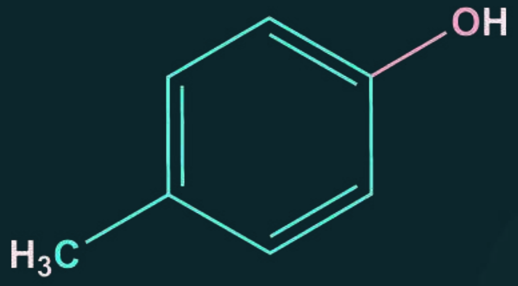
Ethyl alcohol

Monohydric phenols

Examples



Phenol



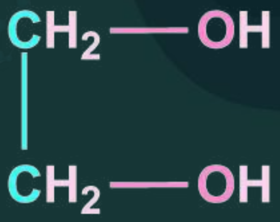
p-Methyl phenol

Classification of Alcohols and Phenols

Dihydric alcohols

Number of -OH groups in alcohol = 2

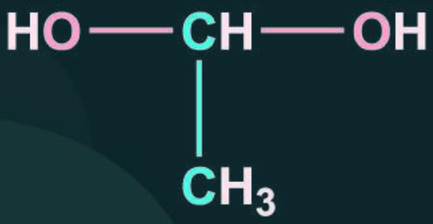
Examples



$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array}$$

Ethane-1,2-diol

Vicinal diol



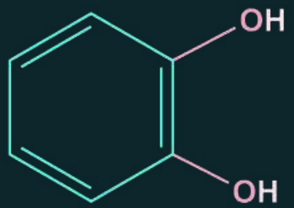
$$\begin{array}{c} HO-CH-OH \\ | \\ CH_3 \end{array}$$

Ethane-1,1-diol

Geminal diol

Dihydric phenols

Examples



Benzene-1,2-diol

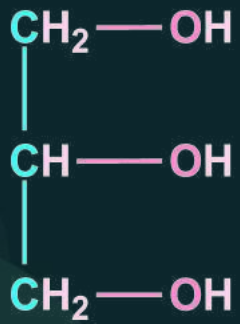
Benzene-1,4-diol

Classification of Alcohols and Phenols

Trihydric alcohols

Number of **-OH** groups in alcohol = **3**

Example

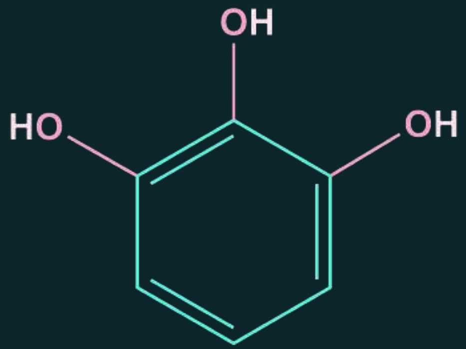


$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Propane-1,2,3-triol

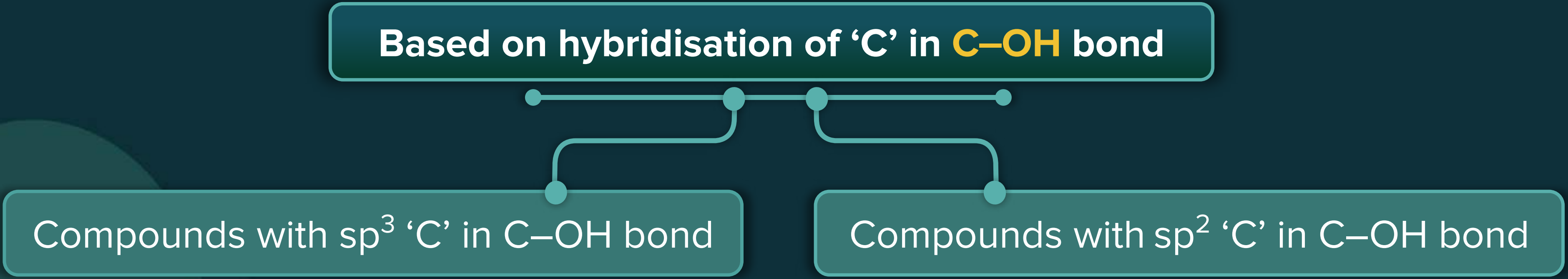
Trihydric phenols

Example



Benzene-1,2,3-triol

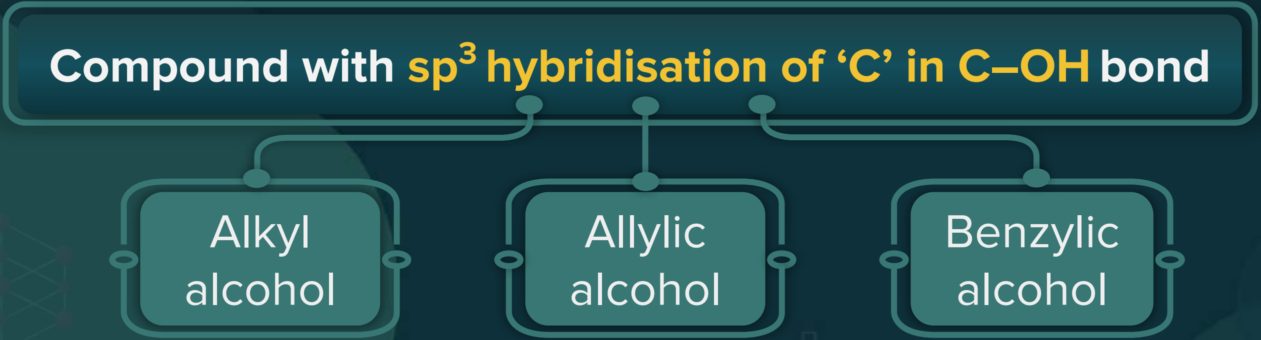
Classification of Alcohols and Phenols



Based on hybridisation of ‘C’ in C–OH bond

- Compounds with sp^3 ‘C’ in C–OH bond
- Compounds with sp^2 ‘C’ in C–OH bond

Compound with sp^3 ‘C’ in C-OH bond



Compound with sp^3 hybridisation of ‘C’ in C–OH bond

- Alkyl alcohol
- Allylic alcohol
- Benzylic alcohol

Classification of Alcohols and Phenols

Classification

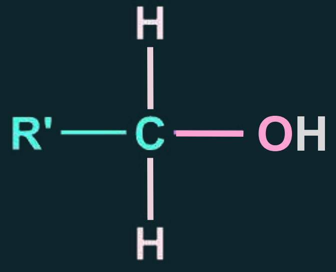
- Alkyl alcohol
  - 1°
  - 2°
  - 3°

Classification of Alcohols and Phenols

Alkyl alcohol

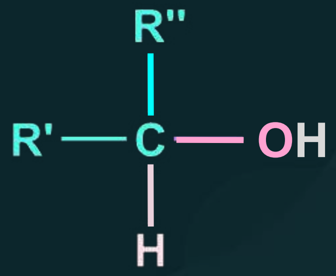
Primary alcohol

Number of carbons attached to the C-atom of sp^3 hybridisation in C–OH bond = 1



Secondary alcohol

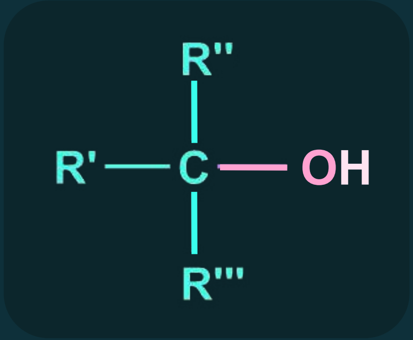
Number of carbons attached to the C-atom of sp^3 hybridisation in C–OH bond = 2



Classification of Alcohols and Phenols

Tertiary alcohol

Number of carbons attached to the C-atom of sp^3 hybridisation in C–OH bond = **3**

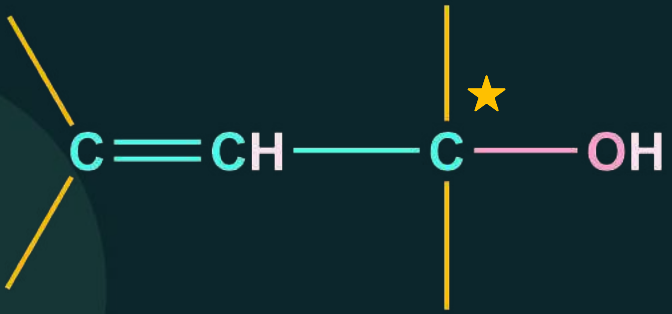


Classification of Alcohols and Phenols

Allylic alcohol

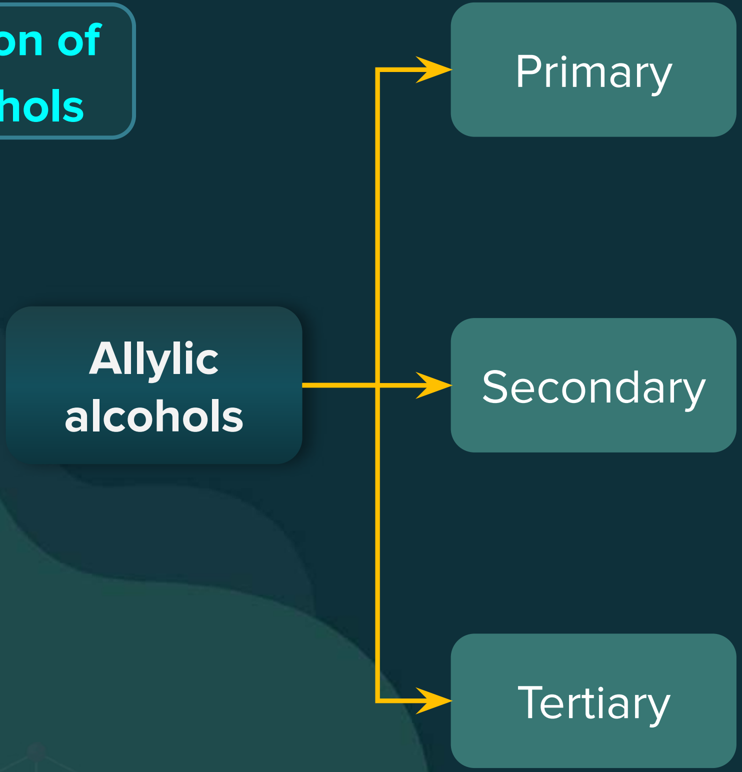
- Alcohols are referred to as allylic if the hydroxyl group is bonded to an allylic carbon atom.
- An allylic carbon is a carbon atom bonded to a carbon atom that in turn is doubly bonded to another carbon atom.

Example



Classification of Alcohols and Phenols

Classification of allylic alcohols



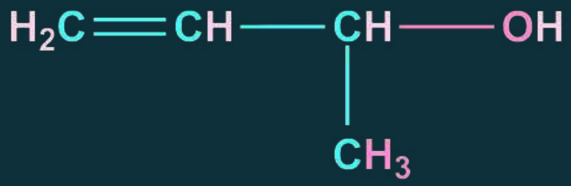
Allylic alcohols

Primary

$H_2C{=}CH{-}CH_2{-}OH$

Prop-2-en-1-ol

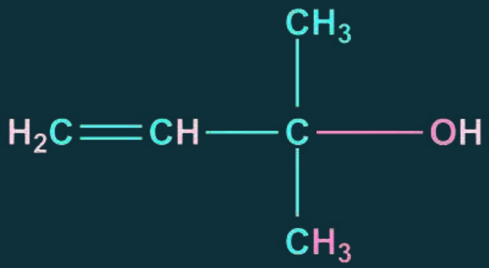
Secondary



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

But-3-en-2-ol

Tertiary



$H_2C{=}CH{-}\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}{-}OH$

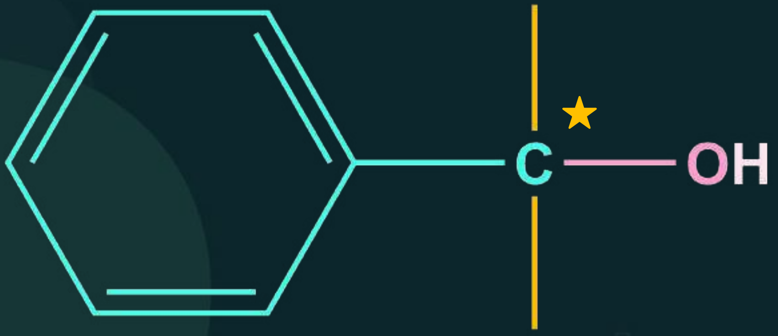
2-Methylbut-3-en-2-ol

Classification of Alcohols and Phenols

Benzylic alcohol

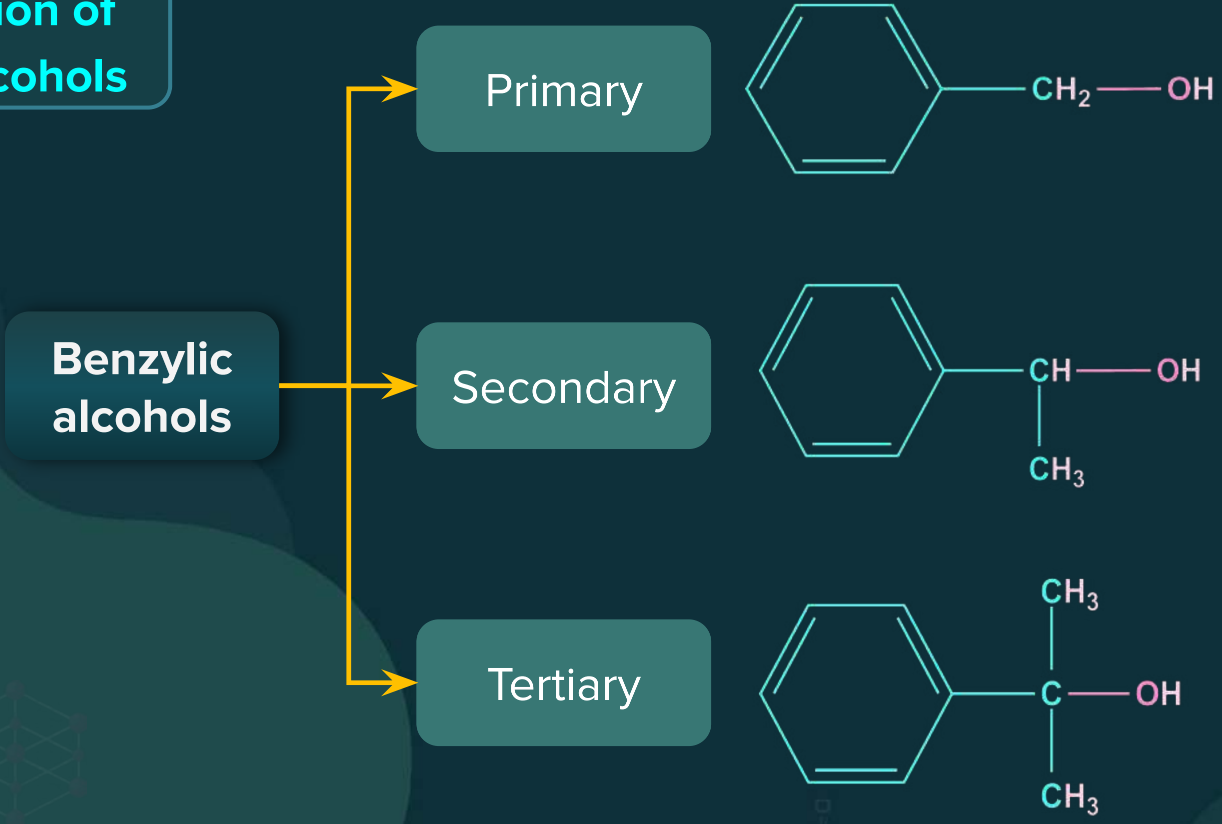
- Benzylic alcohol: Alcohols are referred to as benzylic if the hydroxyl group is bonded to a benzylic carbon.
- Benzylic carbon: Carbon next to the benzene ring.

Example



Classification of Alcohols and Phenols

Classification of benzylic alcohols

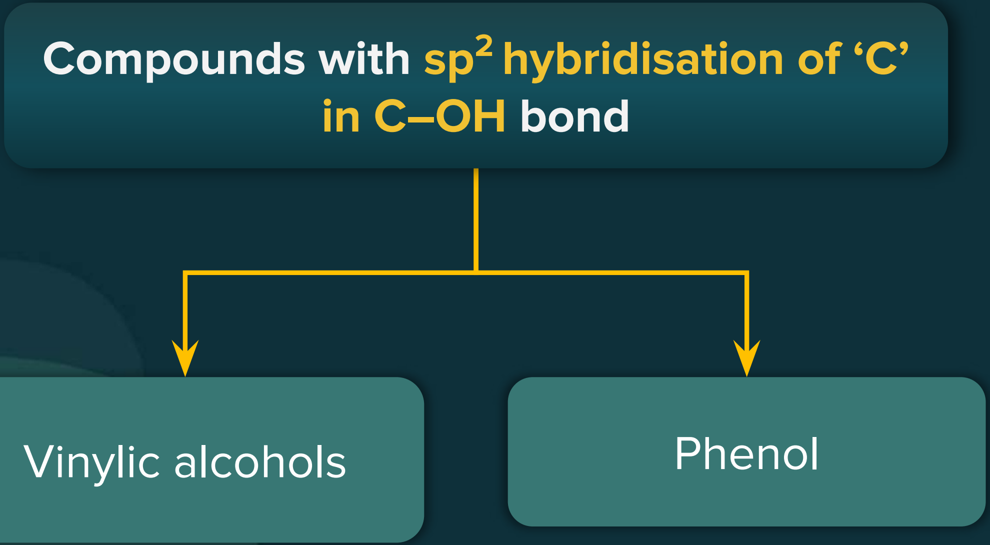


Benzylic alcohols

- Primary
- Secondary
- Tertiary

Classification of Alcohols and Phenols

Compound with sp^2 ‘C’ in C-OH bond



Compounds with sp^2 hybridisation of ‘C’ in C–OH bond

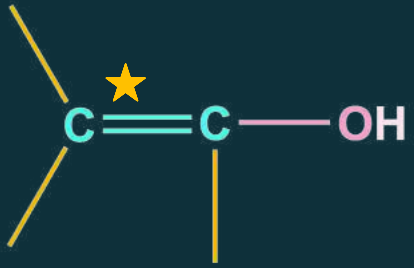
Vinylic alcohols

Phenol

Classification of Alcohols and Phenols

Vinylic alcohols

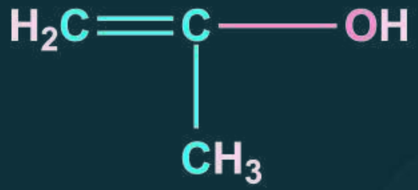
- Alcohol consisting of -OH group that is attached to vinylic carbon is known as vinylic alcohol.
- Vinylic carbon is a carbon that is involved in a double bond with another carbon.



Examples

$H_2C{=}CH{-}OH$

Ethenol



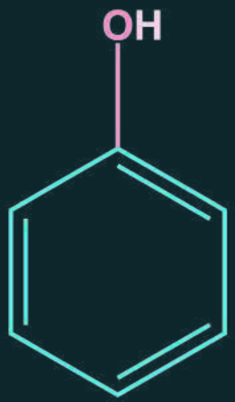
$$H_2C{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}OH$$

Prop-1-en-2-ol

Classification of Alcohols and Phenols

Phenol

- Phenols are organic aromatic compounds containing -OH functional group directly attached with the benzene ring.
- Disinfectant or antiseptic contains phenol compound.

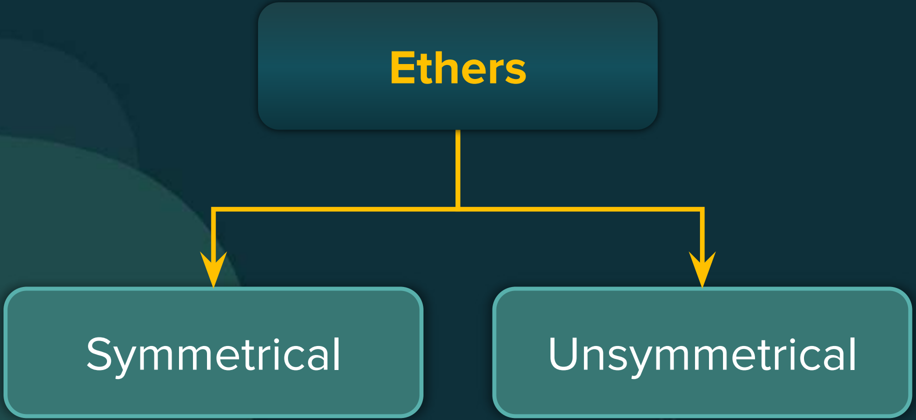


Ethers

Uses

i) Refrigerant contains the ether (i.e. dimethyl ether)
ii) Ether was used as an anesthetic

Classification


Ethers

Symmetrical

Unsymmetrical

Classification of Ethers

Symmetrical ethers

Alkyl or aryl group attached to either side of the oxygen atom are **same**.

Example: $C_2H_5OC_2H_5$

Unsymmetrical ethers

Alkyl or aryl group attached to either side of the oxygen atom are **different**.

Example: $C_2H_5OCH_3$

The IUPAC name of the compound is:

$H_2C{=}CH-CH_2-OH$

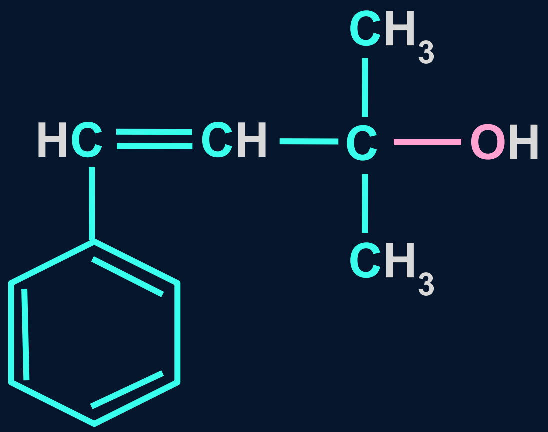
BOARDS

Solution

Step 1: Find the longest carbon chain containing the functional group.
Step 2: Start numbering from the carbon containing the highest priority group.
Hydroxyl group is the highest priority group and the number of carbon in the longest chain is three.

Hence, the IUPAC name is prop-2-en-1-ol.

The IUPAC name of the compound is:

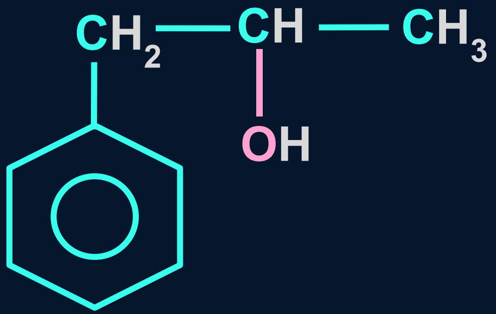


Solution

Step 1: Find the longest carbon chain containing the double bond.
Step 2: Start numbering in such a way to give lowest count to the carbon containing the highest priority group.
There are three groups attached to the longest four carbon chain i.e., hydroxyl, methyl, and phenyl. Hydroxyl group is the highest priority group.

Hence, the IUPAC name is 2-methyl-4-phenylbut-3-en-2-ol.

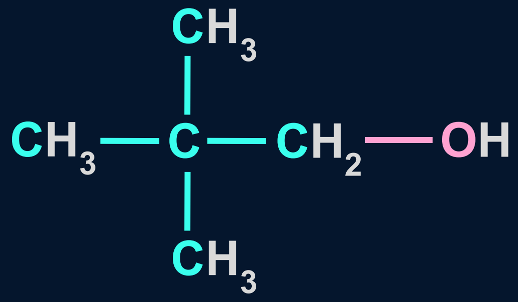
The IUPAC name of the compound is:



Solution

Step 1: Find the longest carbon chain.
Step 2: Start numbering in such a way to give lowest count to carbon containing the highest priority group.
There are two groups attached to the longest three carbon chain i.e., hydroxyl and phenyl group. Hydroxyl group is the highest priority group.
Hence, the IUPAC name is 1-phenylpropan-2-ol.

The IUPAC name of the compound is:



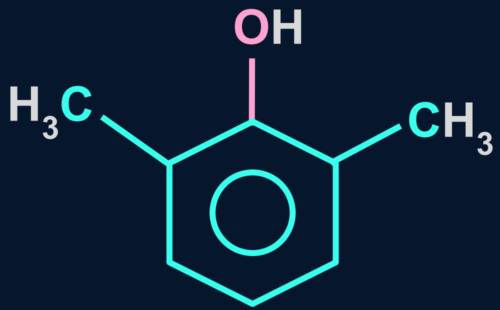
$CH_3-C(CH_3)_2-CH_2-OH$

Solution

Step 1: Find the longest carbon chain containing the functional group (here -OH).
Step 2: Start numbering from the carbon containing the highest priority group.
There are three groups attached to the longest three carbon chain i.e., hydroxyl and two methyl groups. Hydroxyl group is the highest priority group and methyl is the least priority group.

Hence, the IUPAC name is 2,2-Dimethylpropan-1-ol.

The IUPAC name of the compound is:



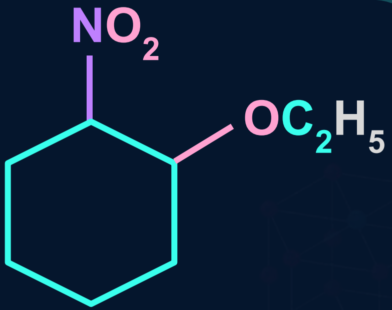
BOARDS

Solution

While naming a cyclic structure with -OH group, the -OH is assumed to be on the first carbon.
Hence, we start numbering from carbon containing -OH and we get one $-CH_3$ group at carbon-2 and another at carbon-6.

Hence, the IUPAC name is 2,6-Dimethylphenol.

The IUPAC name of the compound is:



BOARDS

Solution

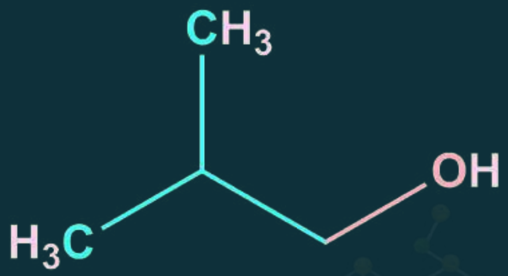
There are no suffixes for the nitro and ether groups, we only have prefixes for them.
All the substituents having only prefixes have the same priority order,
Prefix for ether (-OC_2H_5): Ethoxy
Prefix for nitro (-NO_2): Nitro
Here, we will number them as per alphabetical order.
Hence, we get ethoxy at carbon-1 and nitro at carbon-2.

Thus, the IUPAC name is 1-ethoxy-2-nitrocyclohexane.

The structure for 2-Methylpropan-1-ol is:

Solution

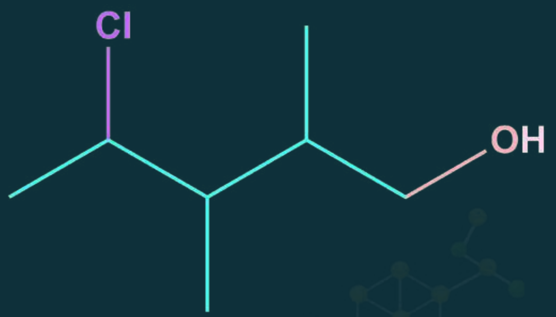
Here the parent chain is propane.
Then attach -OH (alcohol) to carbon-1 and methyl group to carbon-2.
Thus, the structure is given below:



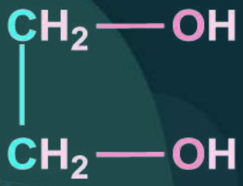
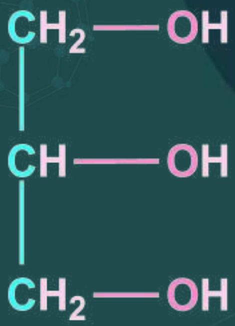
The structure for 4-Chloro-2,3-dimethylpentan-1-ol is:

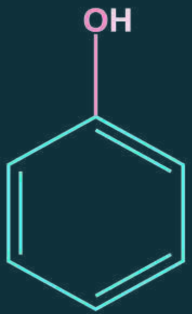
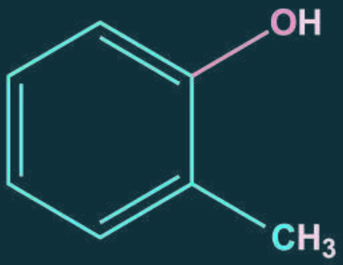
Solution

Here the parent alkane is pentane.
Attach -OH to carbon-1, one of the $-CH_3$ to carbon-2, other methyl to carbon-3 and chlorine to carbon-4 to get the required structure.

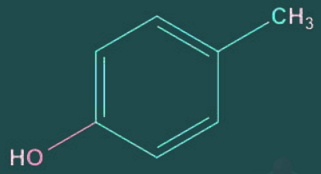


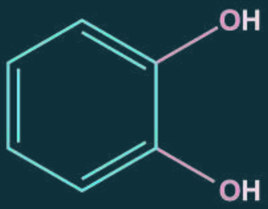
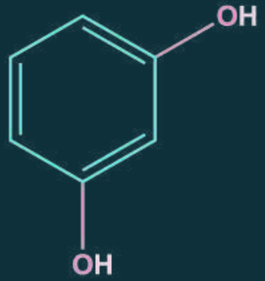
Common Names of Alcohols and Phenols

Structure	Common name
 $\begin{array}{l} CH_2-OH \\ \vert \\ CH_2-OH \end{array}$	Ethylene glycol
 $\begin{array}{l} CH_2-OH \\ \vert \\ CH-OH \\ \vert \\ CH_2-OH \end{array}$	Glycerol

Structure	Common name
	Phenol
	*o*-Cresol

Common Names of Alcohols and Phenols

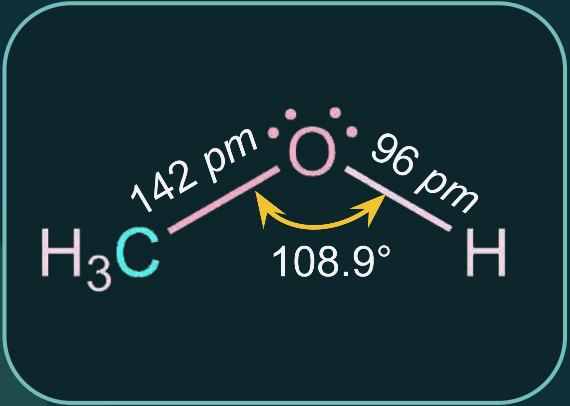
Structure	Common name
	*m*-Cresol
	*p*-Cresol

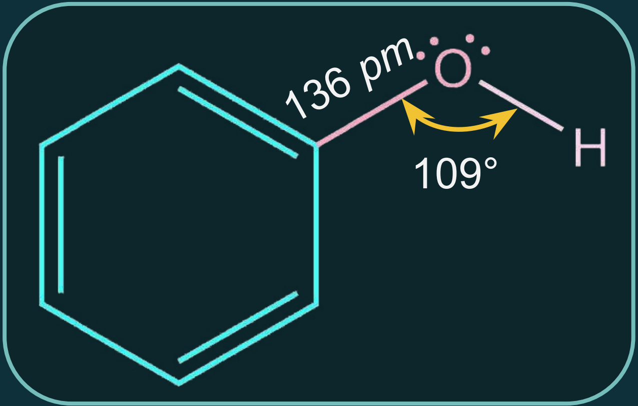
Structure	Common name
	Catechol
	Resorcinol

Common Names of Alcohols and Phenols

Structure	Common name
	Hydroquinone

Structure of Alcohol & Phenol





- The C-O-H bond angle in alcohols is **slightly less** than the tetrahedral angle (109° 28’).
- It is due to **repulsion** between the unshared electron pairs of oxygen.

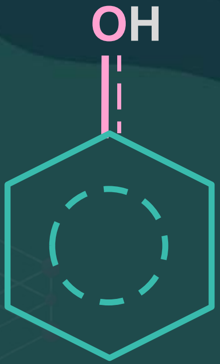
Structure of Phenol

The **C-O bond length** (136 *pm*) in phenol is slightly **less than that in methanol** (142 *pm*).

Reason

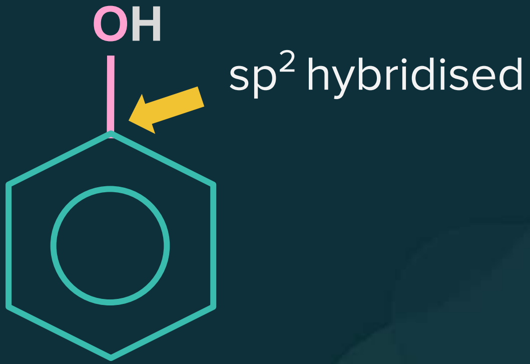
01

Partial double bond character (due to **conjugation** of lone pair of oxygen with the aromatic ring).

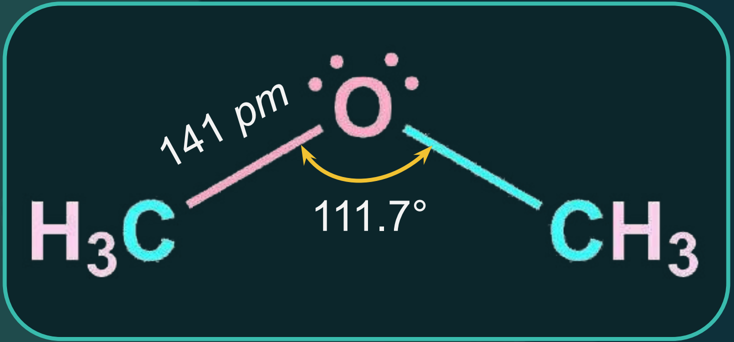


02

Due to **sp^2 hybridised carbon** to which oxygen is attached.



Structure of Ether



The bond angle is **slightly greater** than the tetrahedral angle (109° 28’) due to the repulsive interactions between two bulky (-R) groups.

The **C–O bond length** (**141 *pm***) is almost the **same** as in alcohols.

Physical Properties

Physical properties

- Solubility
- Boiling point

Solubility

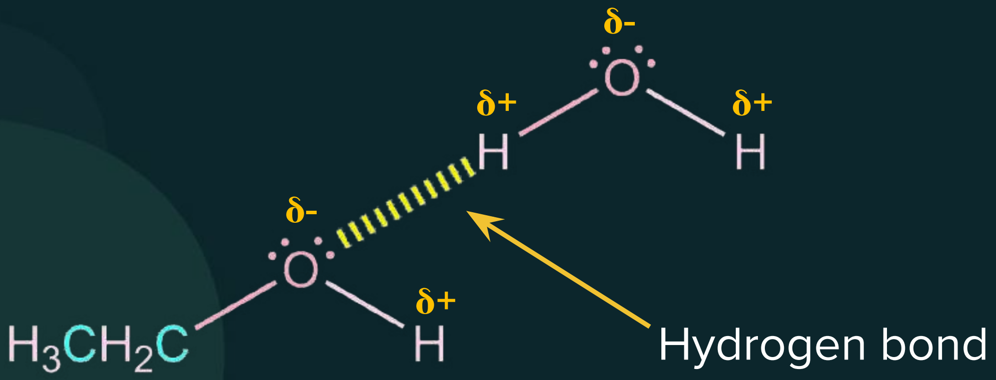
- **Miscible** in all proportions
  - Methanol and water
  - Ethanol and water
  - Propanol and water

Physical Properties

Reason

1 In these cases, the alkyl groups of the alcohols are **relatively small,** and the molecules therefore, **resemble water,** more than they do an alkane.

2 Molecules are capable of forming strong **hydrogen bonds** with each other.

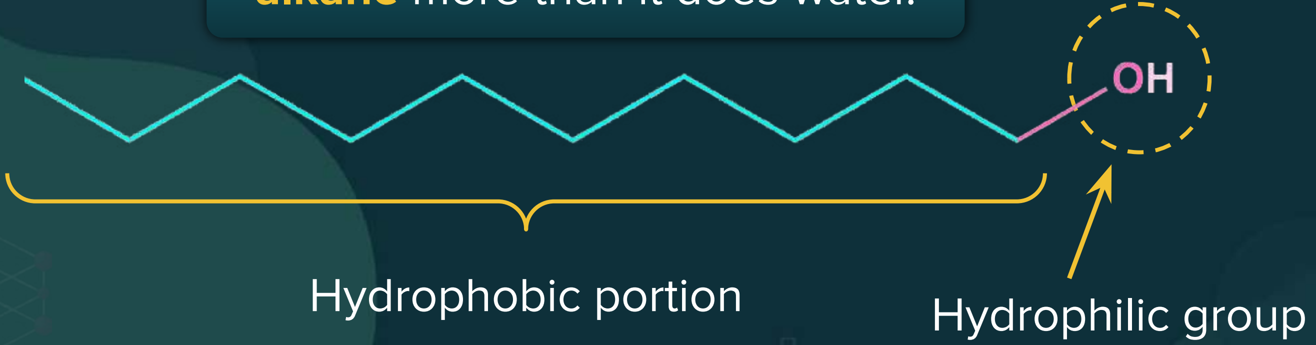


Physical Properties

If the carbon chain of an alcohol is **long**, alcohol is **much less soluble** in water.

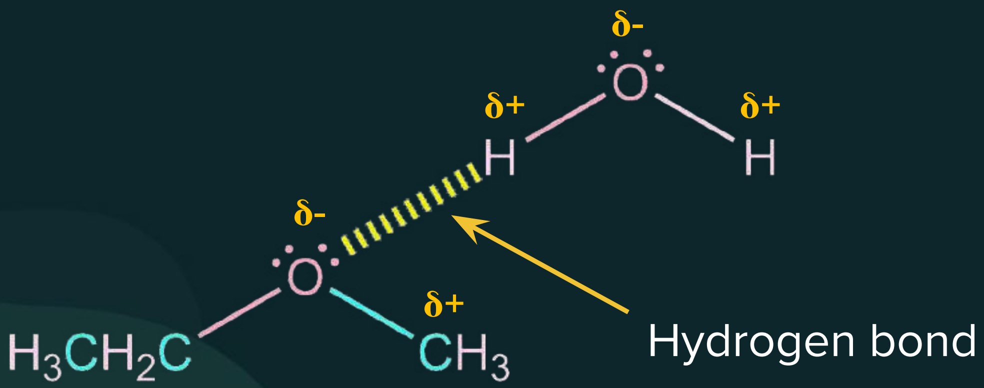
Decyl alcohol with a chain of 10 carbon atoms is only **very slightly soluble** in water.

Decyl alcohol **resembles an alkane** more than it does water.



Physical Properties

Ethers are **soluble in water** because they form **H-bond** and have solubilities **comparable to alcohols** of similar molar mass.



Ethers having more than 3 or 4 carbons are insoluble in water due to increase in length of hydrophobic part. Then, the extent of H-bonding will be less.

Arrange the following sets of compounds in order of their solubility:
n-Butane, Pentanol, and Butanol

BOARDS

Solution

- Alkanes are least soluble as they do not have any polar groups.
- More the number of carbons, less will be the solubility of alcohols. Hence, pentanol having 5 carbons will be less soluble than butanol having 4 carbons.

Hence, the order of solubility is as follows:

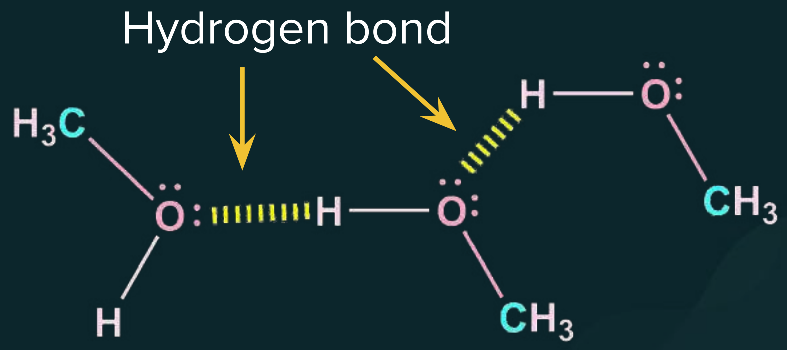
n-Butane < Pentanol < Butanol

Physical Properties

Boiling point

Alcohols have **much higher** boiling points than ethers, and hydrocarbons of comparable molar mass.

Alcohol molecules can associate with each other through **hydrogen bonding**, whereas those of **ethers and hydrocarbons cannot.**



Physical Properties

Ethers have B.P. that are roughly **comparable** with those of hydrocarbons of the **similar molar mass** (M.M.)

B.P. of Diethyl ether (M.M. = 74 $g\ mol^{-1}$) = 34.6 °C

B.P. of Pentane (M.M. = 72 $g\ mol^{-1}$) = 36 °C

The boiling point of alcohol increases with an increase in molecular weight.

Compound	**Boiling point (*K*)**
Methanol	337
Ethanol	351
Propanol	370
Phenol	455
Methoxymethane	248

Preparation of Alcohols

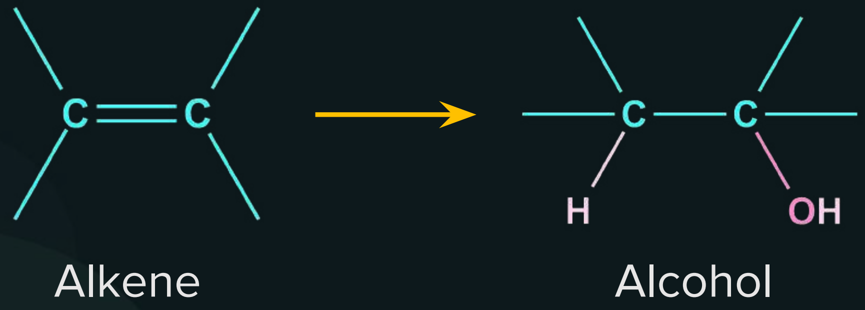
Preparation of alcohols

- From alkene
  - Acid-catalysed hydration
  - Hydroboration-oxidation
  - Using oxidising agents
- From carbonyl compound
- From Grignard reagent

Acid-Catalysed Hydration of Alkenes

Alkenes react with water in the presence of an acid catalyst to yield **alcohols**.

General reaction



Reagent used: dil. H_2SO_4

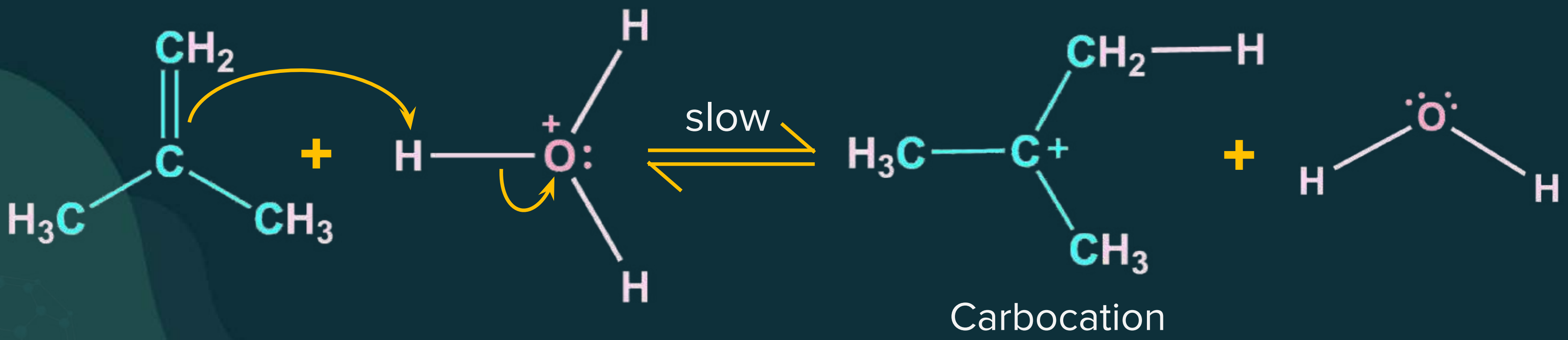
Acid-Catalysed Hydration of Alkenes

Steps involved in acid catalysed hydration

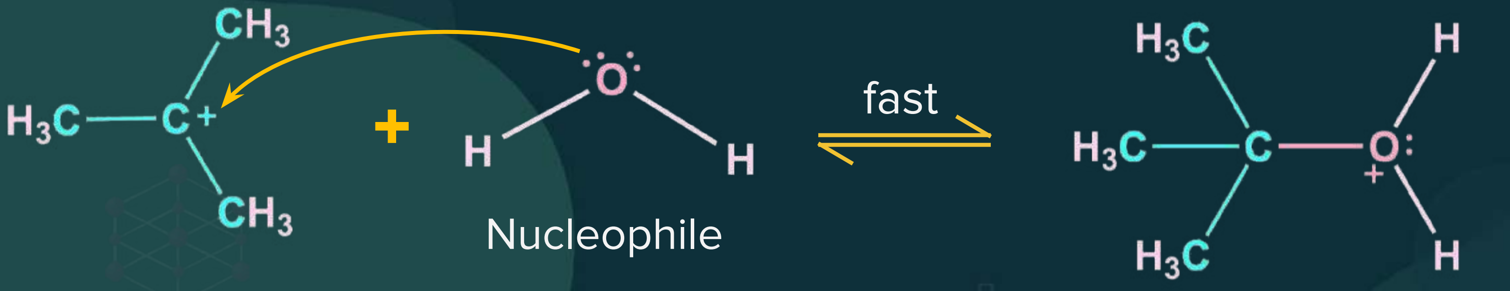
Step 1	Formation of carbocation
Step 2	Attack of nucleophile
Step 3	Deprotonation to form alcohol

Acid-Catalysed Hydration of Alkenes

Step 1: Formation of carbocation

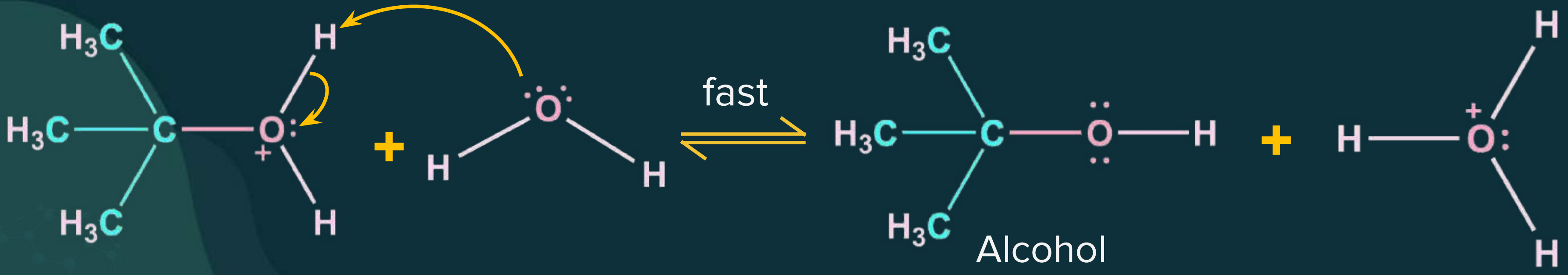


Step 2: Attack of nucleophile



Acid-Catalysed Hydration of Alkenes

Step 3: Deprotonation to form alcohol



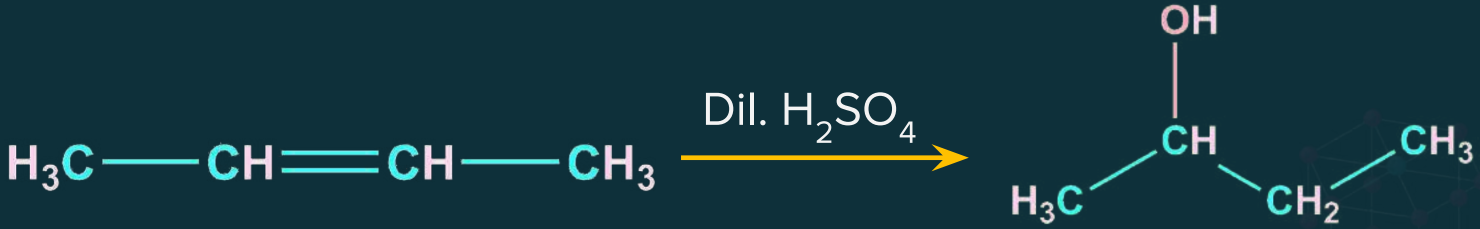
In case of unsymmetrical alkenes, the addition of water takes place in accordance with **Markovnikov's rule**.

Give the major products of the following reactions.

$$H_3C-CH=CH-CH_3 \xrightarrow{\text{Dil. } H_2SO_4}$$

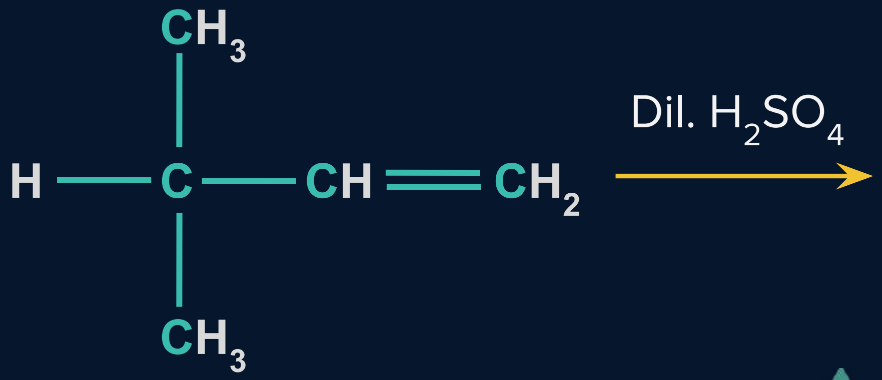
Solution

a) But-2-ene on reaction with dil.H_2SO_4 gives butan-2-ol. Here, H^+ adds on one side of double bond and OH^- adds on another side of double bond.



b) Here, there will be formation of secondary benzylic carbocation which gains extra stability due to resonance. Hence the OH^- adds at secondary benzylic position and the H^+ will add at the next carbon atom.

Give the major products of the following reaction.



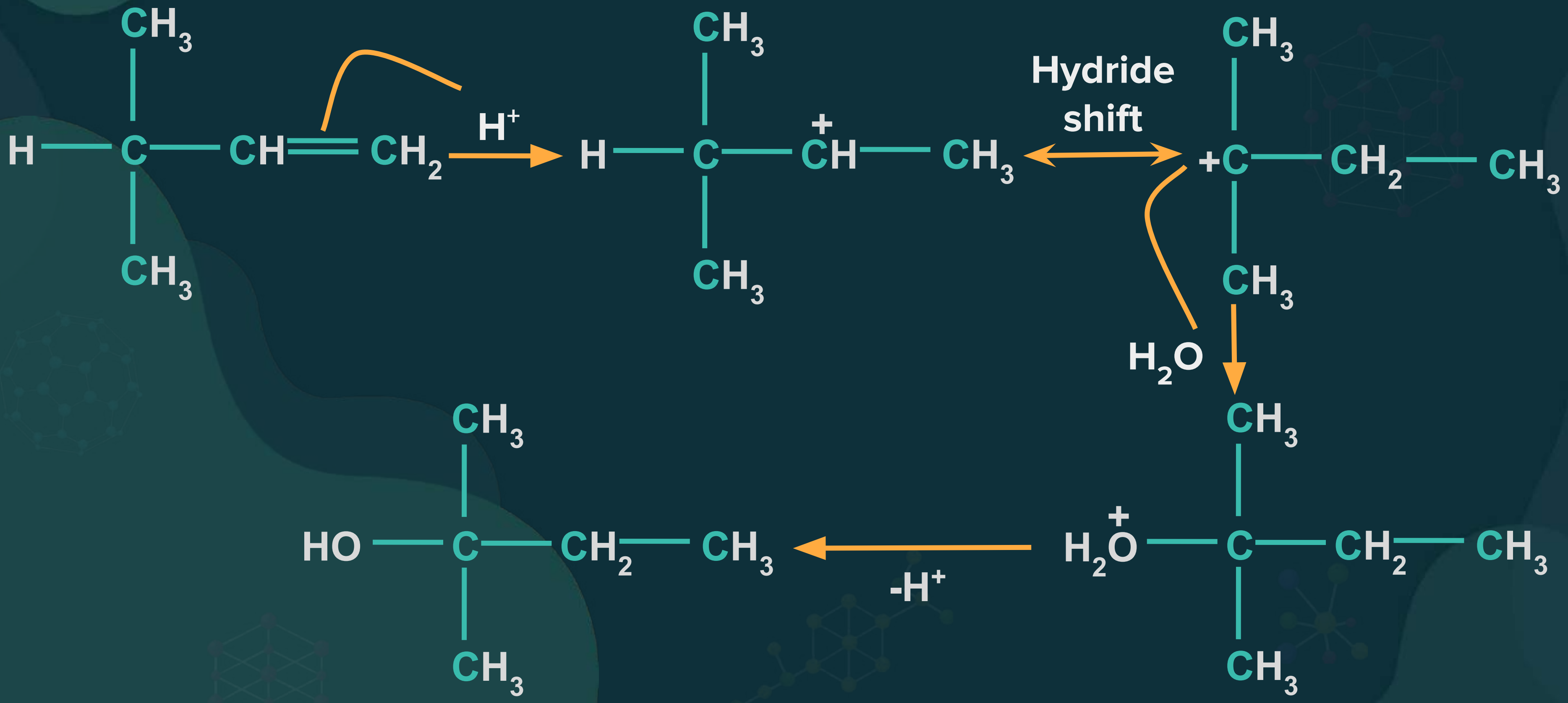
$$H-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2 \xrightarrow{\text{Dil. } H_2SO_4}$$

Solution

Step 1: Formation of a secondary carbocation which is more stable than the primary carbocation.

Step 2: Hydride shift occurs to form a tertiary carbocation which is more stable than secondary one.

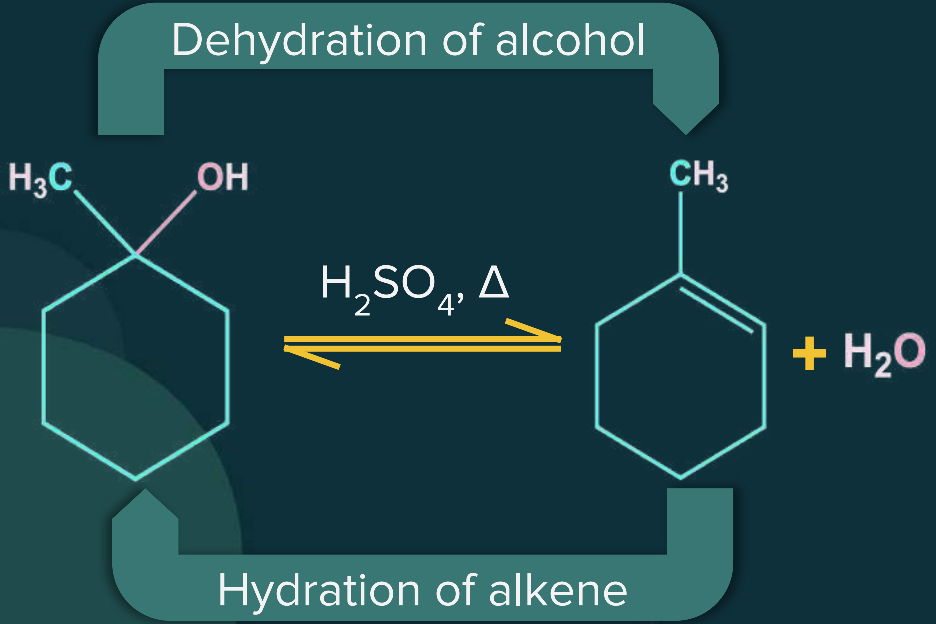
Step 3: Attack of water occurs at the carbocation position.
Step 4: Deprotonation occurs to form an alcohol i.e., 2-methylbutan-2-ol.



2-Methylbutan-2-ol

Acid-Catalysed Hydration of Alkenes

Acid-catalysed hydration of alkenes is **reversible** & the mechanism for the acid-catalysed hydration of an alkene is simply the reverse of that for the dehydration of an alcohol.



The major product obtained on acid–catalysed hydration of 2-Phenylpropene is:

BOARDS

a) 2-Phenylpropan-2-ol

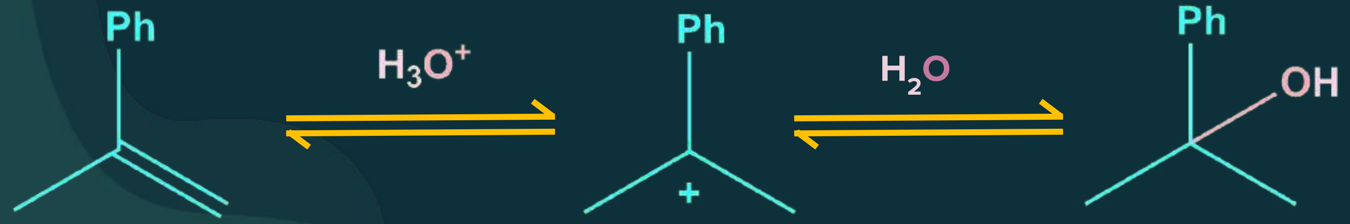
b) 2-Phenylpropan-1-ol

c) 3-Phenylpropan-2-ol

d) 1-Phenylpropan-1-ol

Solution

Step 1: Formation of a secondary benzylic carbocation.
Step 2: Attack of water occurs at the secondary benzylic carbocation position.
Step 3: Deprotonation occurs to form an alcohol i.e. **2-Phenylpropan-2-ol.**



2-Phenylpropene

Secondary benzylic carbocation

2-Phenylpropan-2-ol

Hence, option (a) is the correct answer.

Preparation of Alcohol from Alkene

Preparation of Alcohols

From alkene

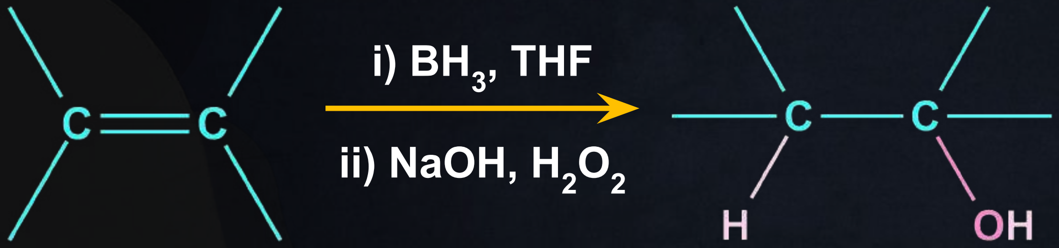
From carbonyl compound

From Grignard reagent

Alcohols can be prepared by reduction of alkenes.

Preparation of Alcohol from Alkene

Hydroboration-oxidation



If the reaction involves **unsymmetrical** alkenes.

Anti-Markovnikov's Rule

Example

$$CH_3-CH=CH_2 \xrightarrow[\text{ii) NaOH, } H_2O_2]{\text{i) } BH_3\text{, THF}} CH_3-CH_2-CH_2-OH$$

Preparation of Alcohol from Alkene

Mechanism

$$CH_3-CH=CH_2 + BH_3 \longrightarrow CH_3-CH_2-CH_2-BH_2$$

Alkylborane

$$\Big\downarrow \; CH_3-CH=CH_2$$

$$(CH_3-CH_2-CH_2)_2-BH$$

Dialkylborane

Preparation of Alcohol from Alkene

$$(CH_3-CH_2-CH_2)_2-BH$$

Dialkylborane

$$CH_3-CH=CH_2$$

$$\big\downarrow$$

$$(CH_3-CH_2-CH_2)_3-B$$

Trialkylborane

$$(CH_3-CH_2-CH_2)_3-B$$

$$H_2O_2/\,OH^- \Big\downarrow \text{ Oxidation}$$

$$3\,CH_3-CH_2-CH_2-OH + BO_3^{3-}$$

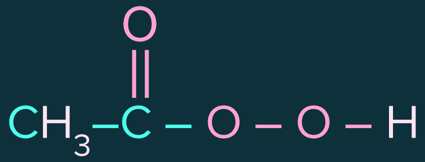
Propan-1-ol may be prepared by the reaction of propene with:

BOARDS

a) H_3BO_3

b) H_2SO_4/H_2O

c) B_2H_6, NaOH, H_2O_2

d) 

$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-H$

Solution

- Hydroboration-oxidation reaction of propene will give propan-1-ol as the major product. The alcohol formed as a result of hydroboration-oxidation looks as if it has been formed by the addition of water to the alkene in according to anti-Markovnikov's rule.

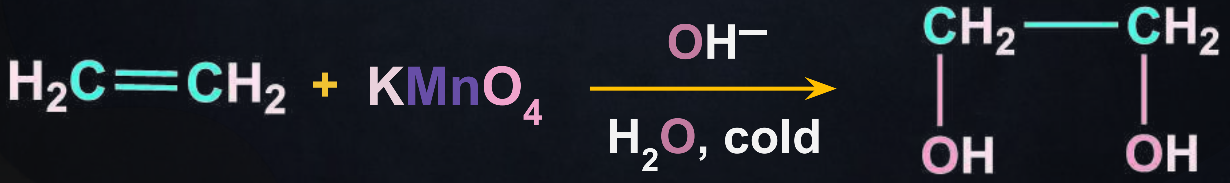
$$3\ CH_3-CH=CH_2 \xrightarrow[\text{ii) NaOH, } H_2O_2]{\text{i) } BH_3\text{, THF}} 3\ H_3C-CH_2-CH_2-OH + B(OH)_3$$

- Hence, the reagent used to convert propene to propan-1-ol is B_2H_6, NaOH-H_2O_2.
- By addition of H_2SO_4/ H_2O, it gives Markovnikov’s product i.e., 2-propanol.
- Peracid given is option (d) is an oxidising agent. But here reduction is needed.

Thus, option (c) is the correct answer.

Preparation of Alcohols from Alkenes

Diol can be prepared from oxidation of alkene by using $KMnO_4$ in presence of alkaline medium and low temperature.



$$H_2C{=}CH_2 + KMnO_4 \xrightarrow[H_2O,\ cold]{OH^-} \underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}}$$

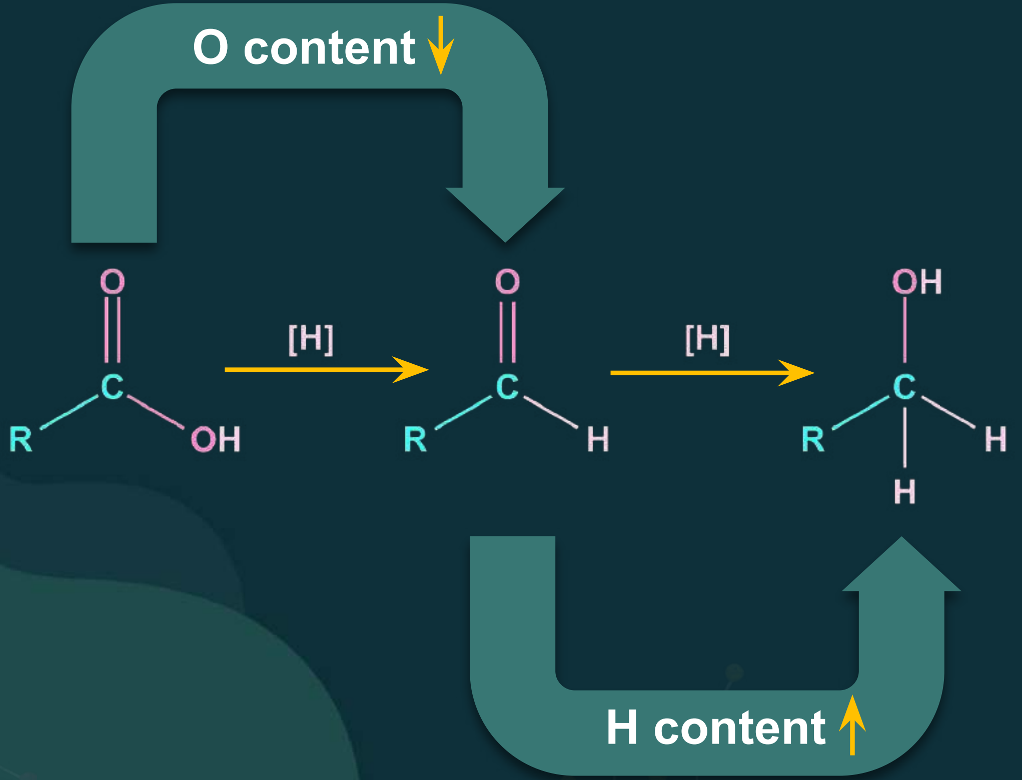
Preparation of Alcohols from Carbonyl Compounds

Preparation of Alcohols

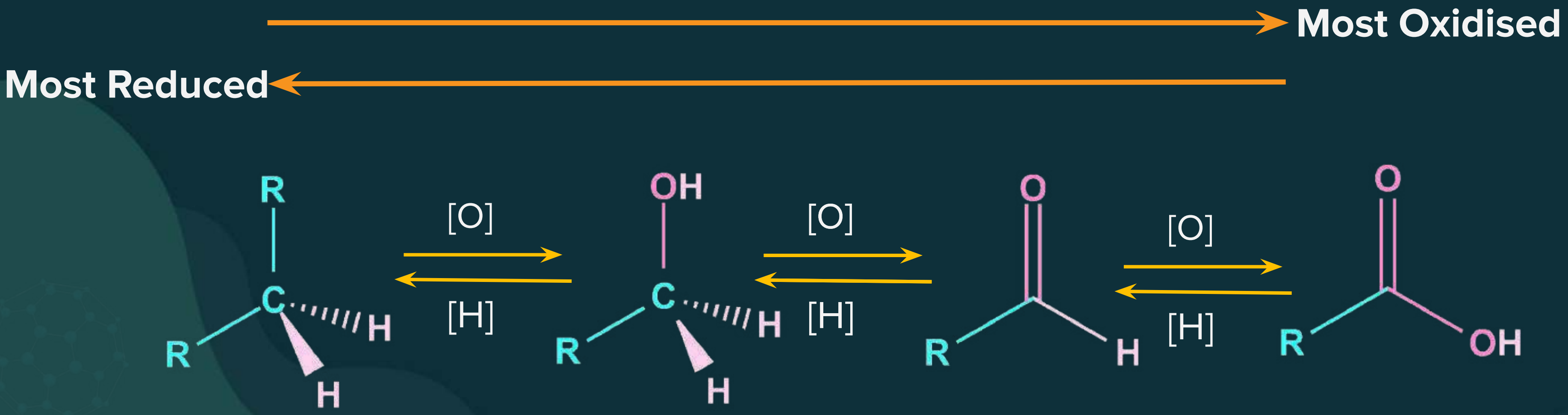
- From alkene
- From carbonyl compound
- From Grignard reagent

Alcohols can be prepared by reduction of carbonyl compounds.

Preparation of Alcohol from Carbonyl Compounds



Preparation of Alcohol from Carbonyl Compounds



This explains, on going from left to right, there involves increase in O atom (generally) or decrease in H atom which takes us to most oxidized molecule while on going from right to left there occurs increase in H atom which led to most reduced molecule among given set of molecules.

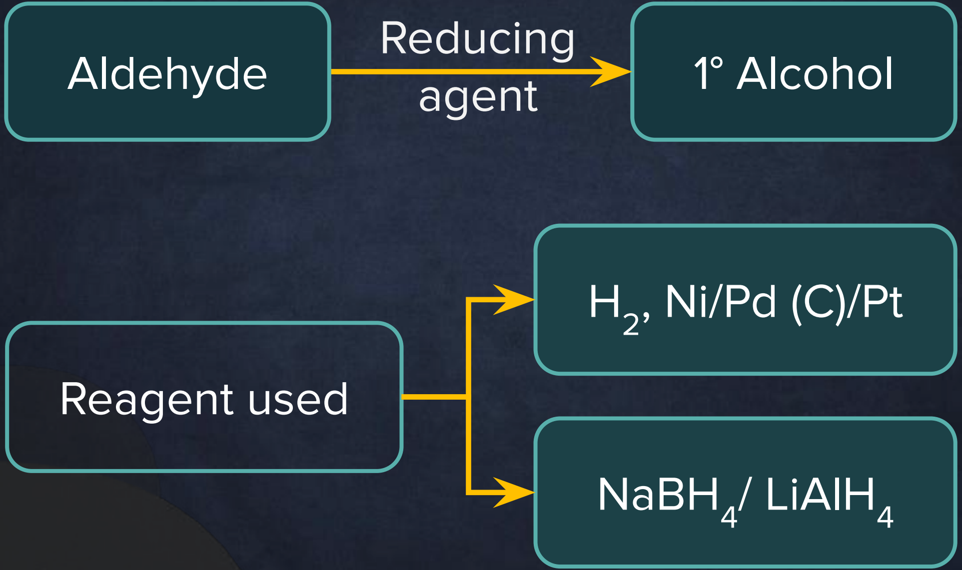
Preparation of Alcohol from Carbonyl Compounds

Preparation of alcohols from carbonyl compounds

- From aldehyde
- From ketone
- From carboxylic acid
- From ester

Preparation of Alcohol from Carbonyl Compounds

Reduction of aldehyde

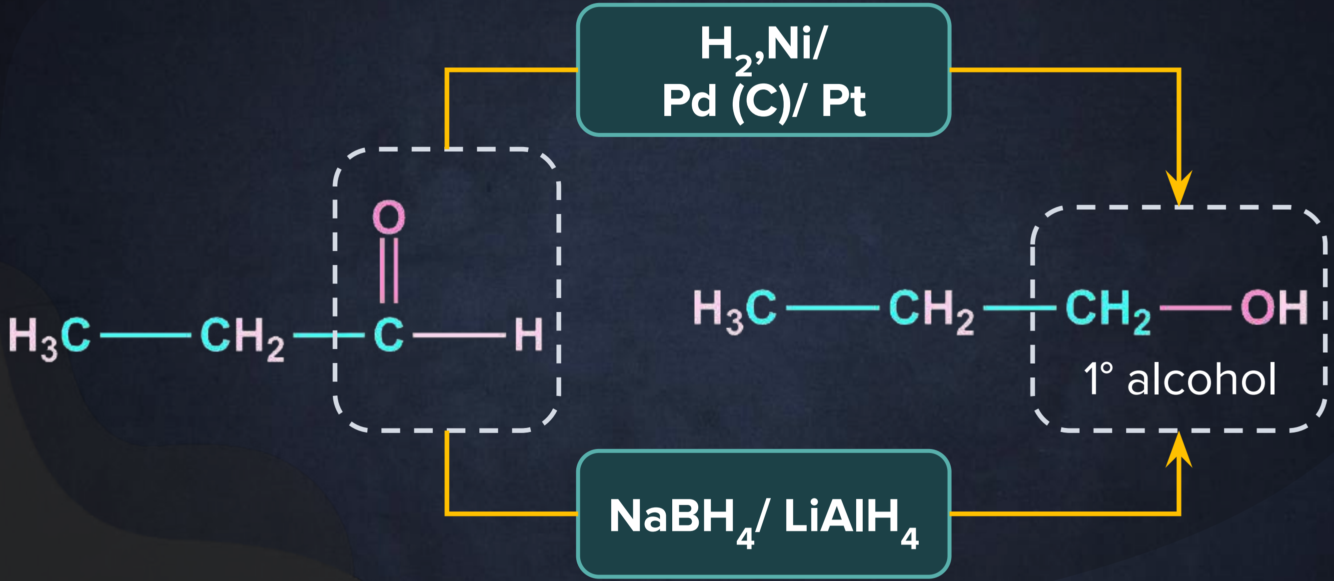


Aldehyde $\xrightarrow{\text{Reducing agent}}$ 1° Alcohol

Reagent used

- H_2, Ni/Pd (C)/Pt
- $NaBH_4$/ $LiAlH_4$

Preparation of Alcohol from Carbonyl Compounds



H_2,Ni/
Pd (C)/ Pt

$H_3C-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$

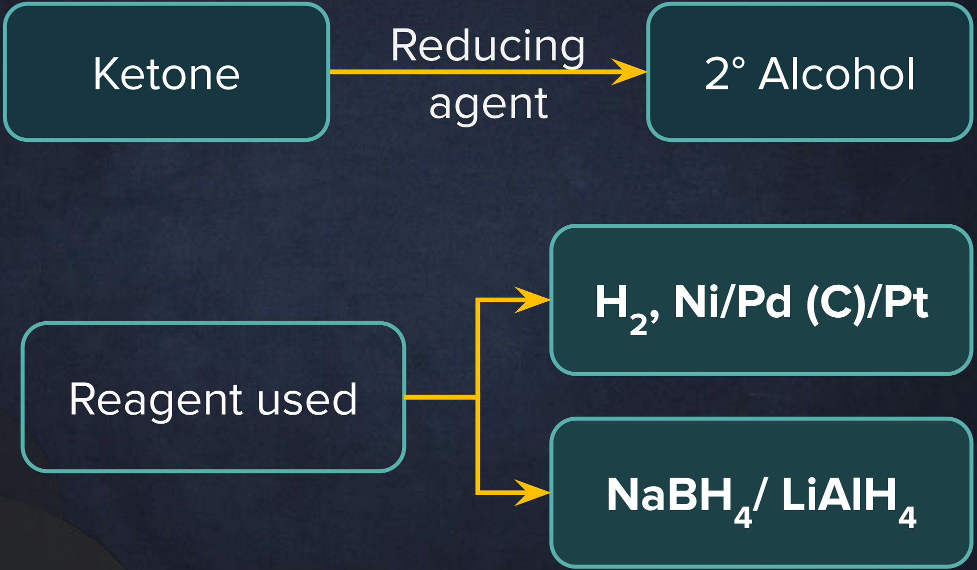
$H_3C-CH_2-CH_2-OH$

1° alcohol

$NaBH_4$/ $LiAlH_4$

Preparation of Alcohol from Carbonyl Compounds

Reduction of ketone



Ketone

Reducing agent

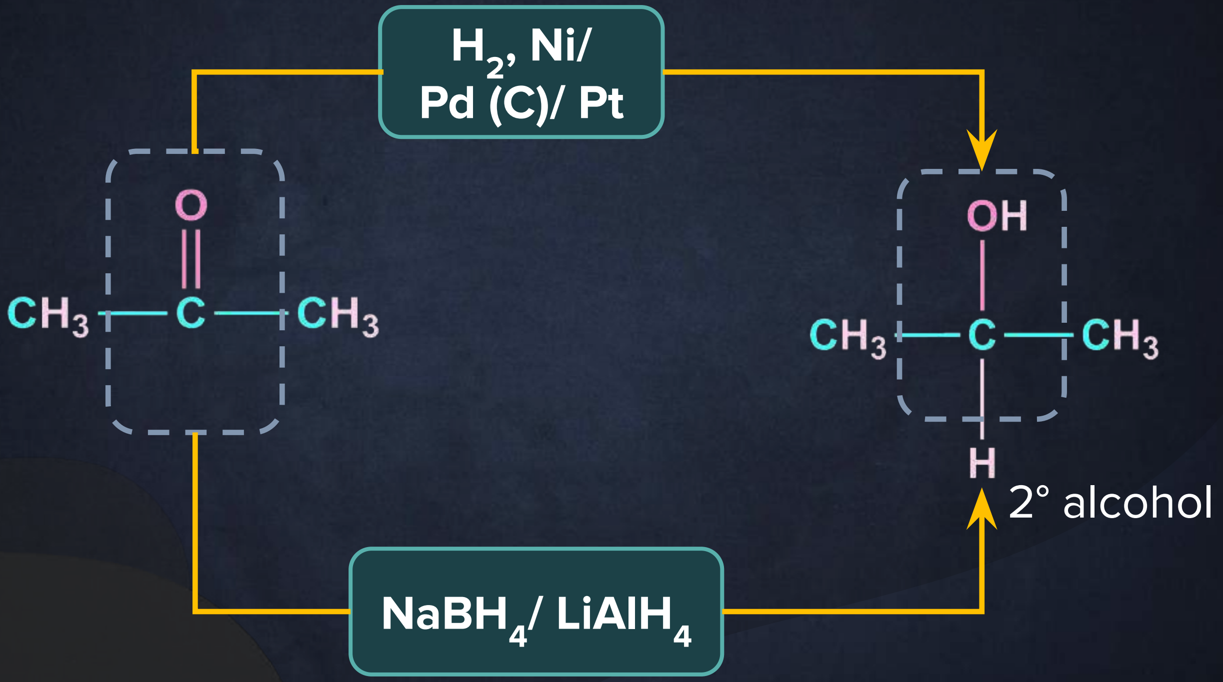
2° Alcohol

Reagent used

H_2, Ni/Pd (C)/Pt

$NaBH_4$/ $LiAlH_4$

Preparation of Alcohol from Carbonyl Compounds

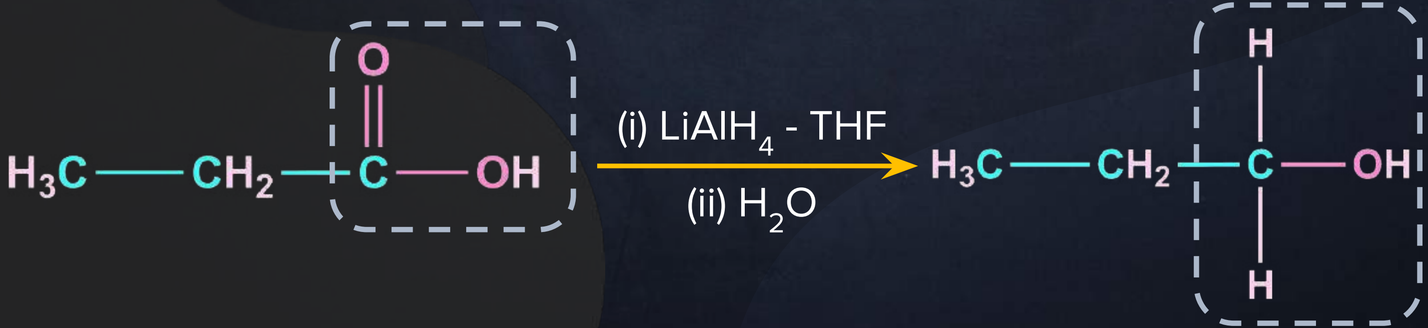


Preparation of Alcohol from Carbonyl Compounds

Reduction of carboxylic acid

Carboxylic acid $\xrightarrow[\text{agent}]{\text{Reducing}}$ 1° Alcohol

Reagent used → (i) $LiAlH_4$ - THF
(ii) H_2O



$$H_3C-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4 \text{ - THF}} H_3C-CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-OH$$

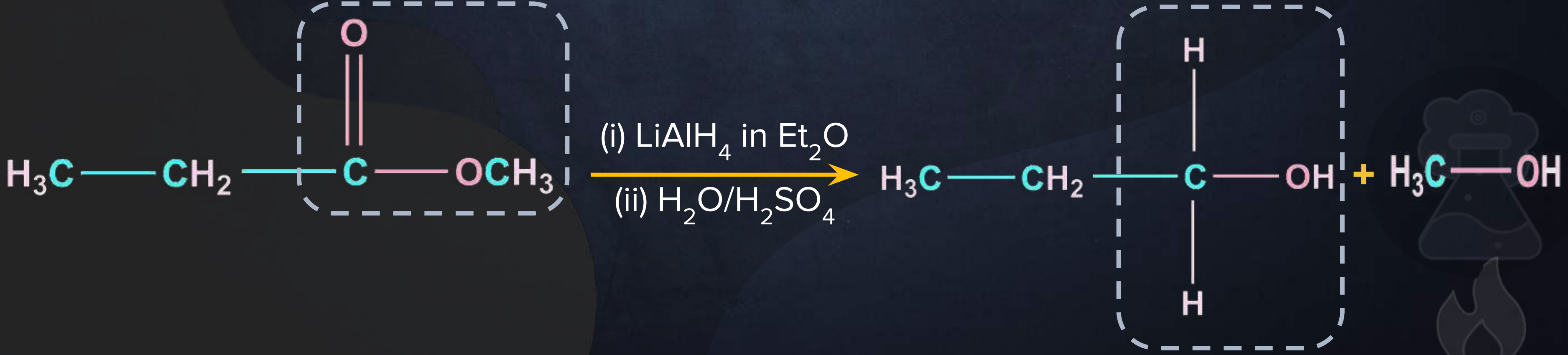
1° alcohol

Preparation of Alcohol from Carbonyl Compounds

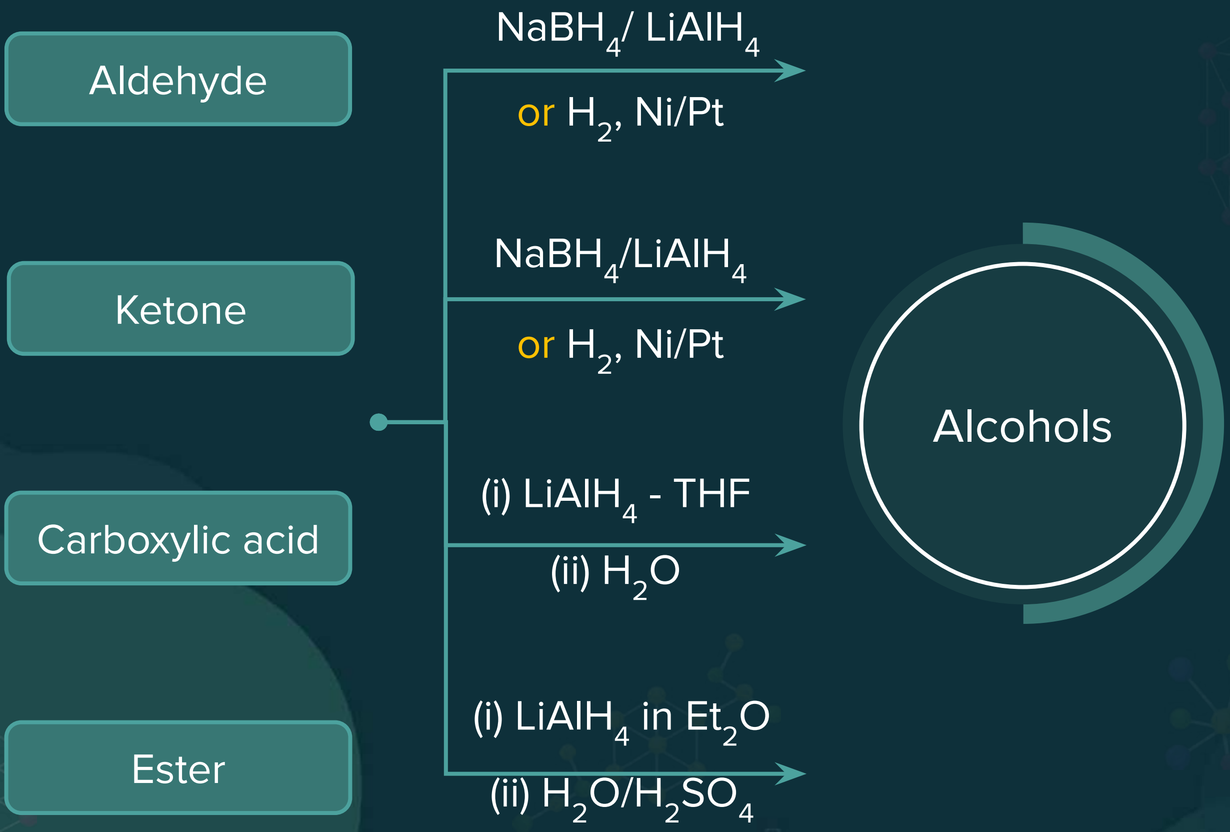
Reduction of ester

Ester → Alcohol

Reagent used → (i) $LiAlH_4$ in Et_2O
(ii) H_2O/H_2SO_4



Preparation of Alcohol from Carbonyl Compounds



Aldehyde

$NaBH_4$/ $LiAlH_4$

or H_2, Ni/Pt

Ketone

$NaBH_4$/$LiAlH_4$

or H_2, Ni/Pt

Carboxylic acid

(i) $LiAlH_4$ - THF

(ii) H_2O

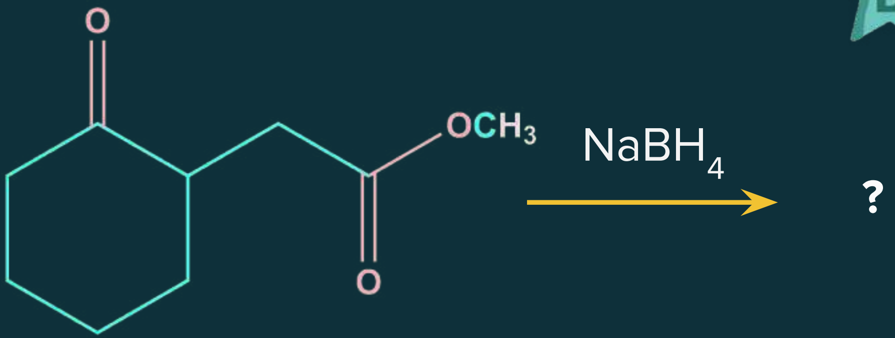
Ester

(i) $LiAlH_4$ in Et_2O

(ii) H_2O/H_2SO_4

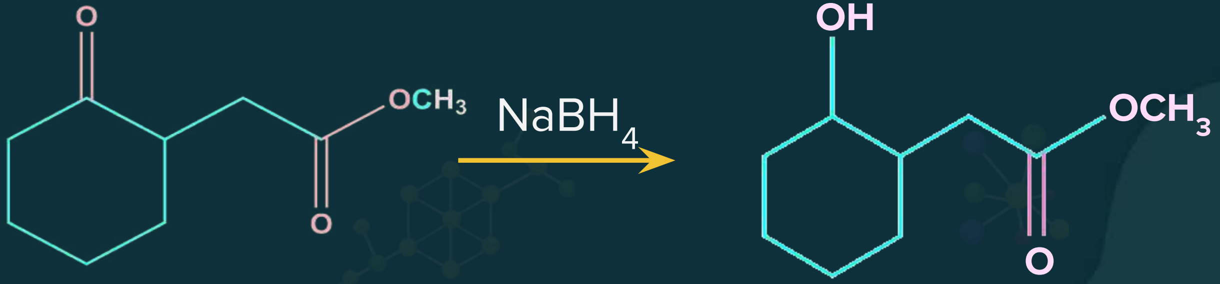
Alcohols

Write structures of the products of the following reaction:

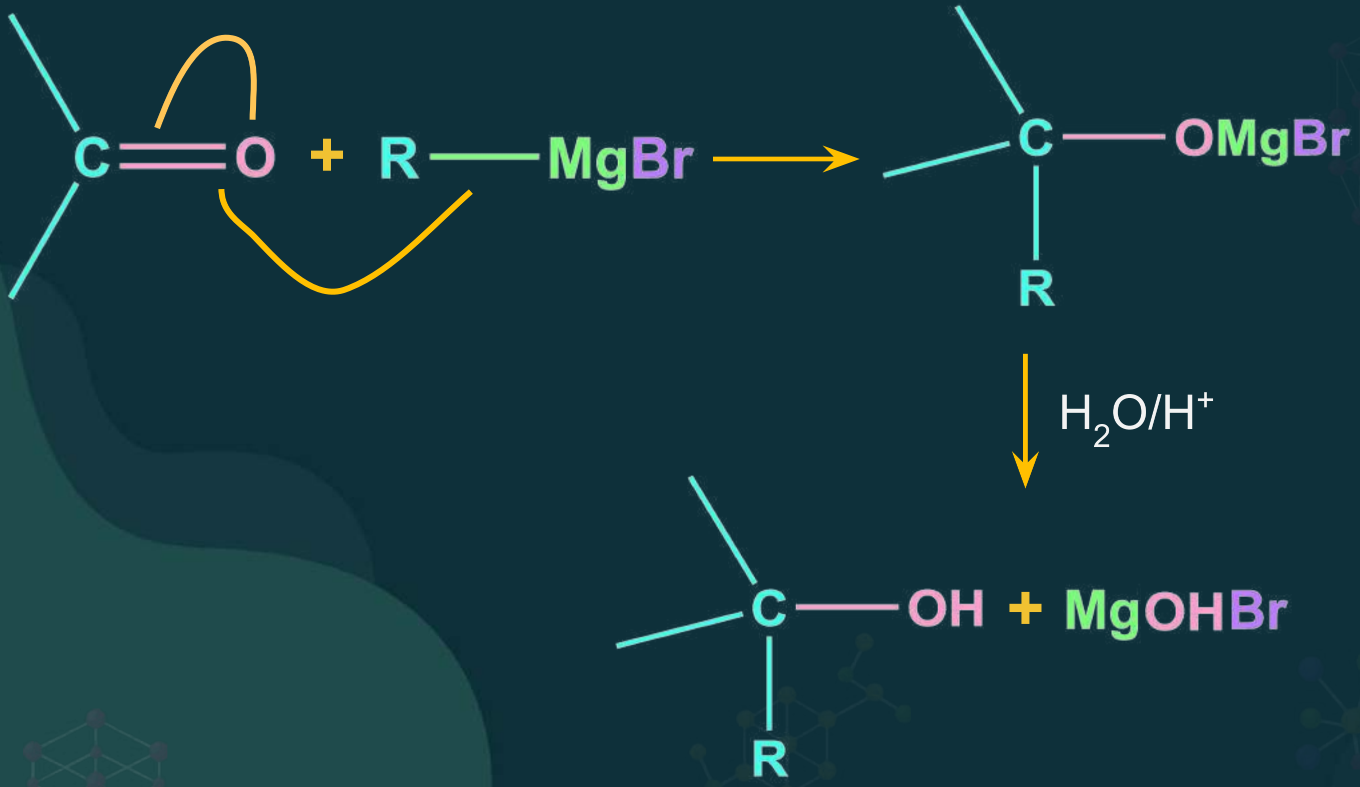


Solution

The NaBH$_4$ will not reduce carboxylic acids and esters. It can only help in the reduction of aldehydes or ketones.

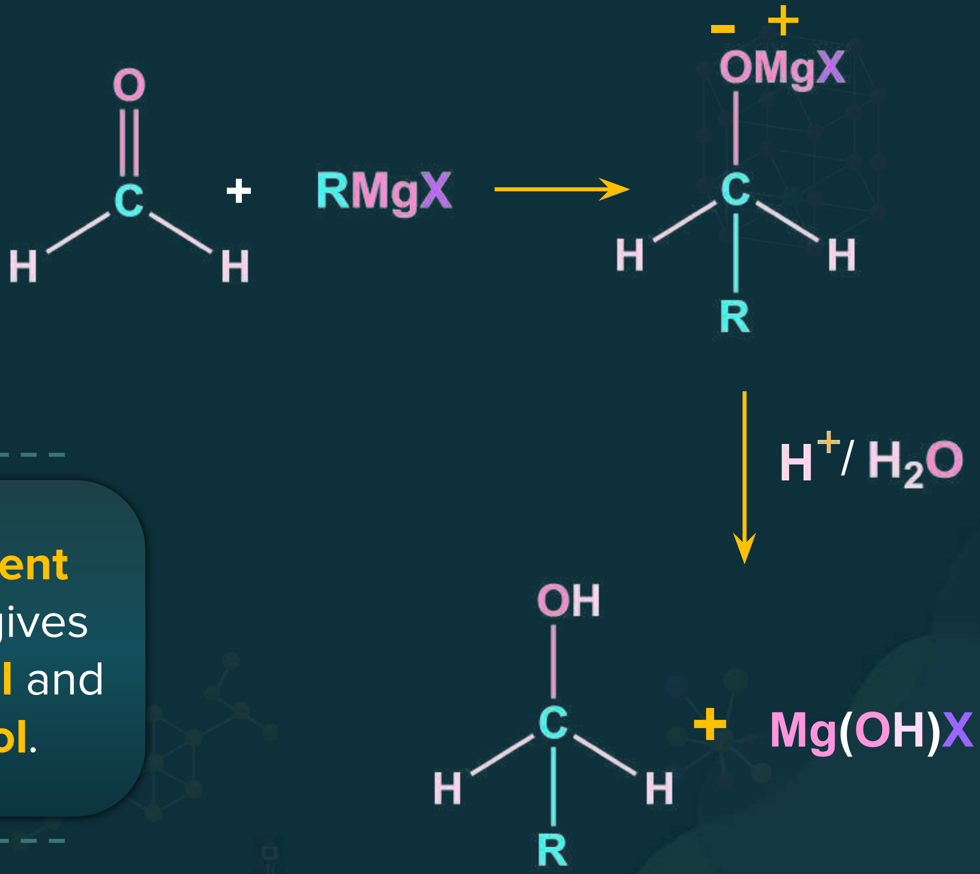


Addition of Grignard Reagent



Addition of Grignard Reagent

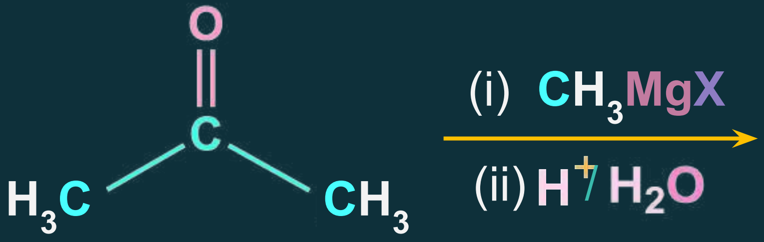
Reaction of Grignard reagent with formaldehyde



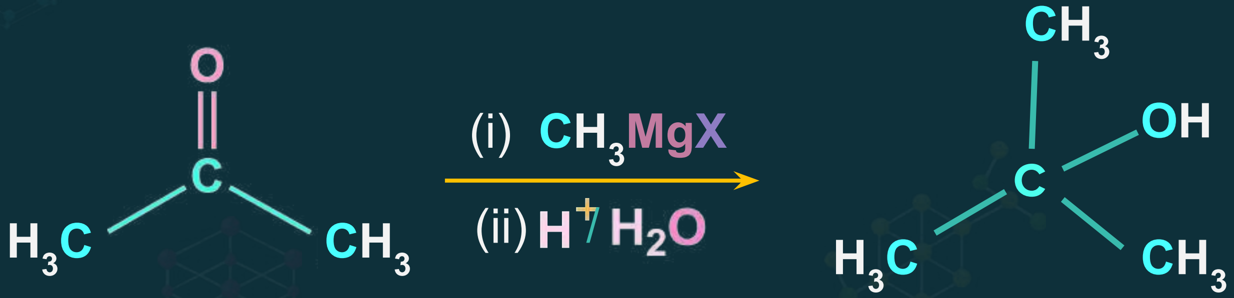
Upon treatment with **Grignard reagent** and followed by hydrolysis, **ketone** gives **3^0 alcohol**, **aldehyde** gives **2^0 alcohol** and only **formaldehyde** gives **1^0 alcohol**.

The product of the following reaction is:

BOARDS



Solution



Which of the following products is formed when benzaldehyde is treated with CH_3MgBr and the addition product so obtained is subjected to acid hydrolysis?

BOARDS

a) A secondary alcohol

b) A primary alcohol

c) Phenol

d) tert-Butyl alcohol

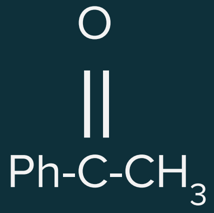
Solution

$$C_6H_5CHO + CH_3MgBr \longrightarrow C_6H_5CH(CH_3)OH$$

When benzaldehyde reacts with the Grignard reagent then we get a secondary alcohol.

Thus, option (a) is the correct answer.

How many compounds out of the following will give secondary alcohol on treatment with Grignard reagent?

(1) 

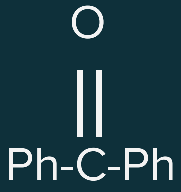
$Ph-\overset{\overset{O}{\|}}{C}-CH_3$

(2) $Ph-CHO$

(3) $HCHO$

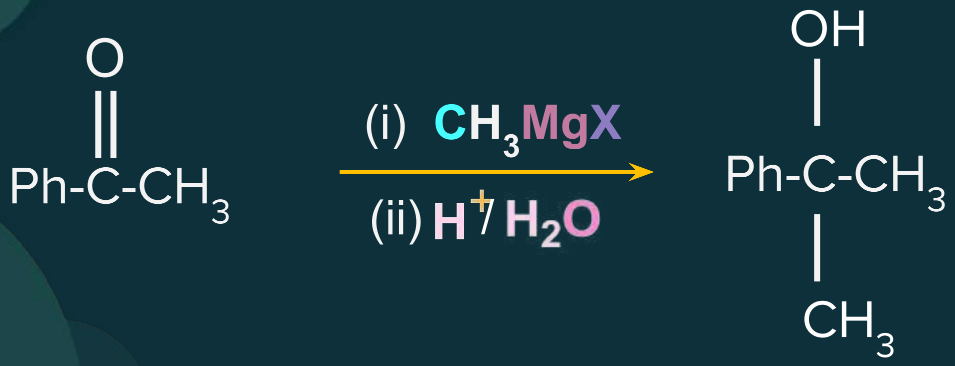
(4) CH_3CH_2CHO

(5) CH_3CHO

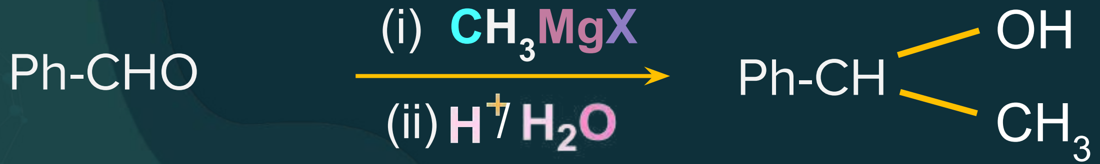
(6) 

$Ph-\overset{\overset{O}{\|}}{C}-Ph$

Solution

(1) 

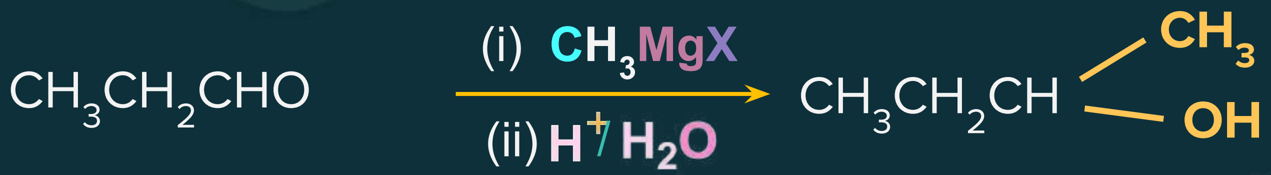
$$\mathrm{Ph\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3} \xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) } CH_3MgX} \mathrm{Ph\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}CH_3}$$

(2) 

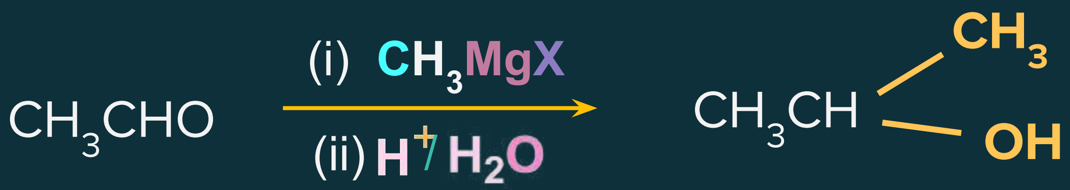
$$\mathrm{Ph\text{-}CHO} \xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) } CH_3MgX} \mathrm{Ph\text{-}CH}\begin{matrix} \diagup \mathrm{OH} \\ \diagdown \mathrm{CH_3} \end{matrix}$$

(3) $$\mathrm{HCHO} \xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) } CH_3MgX} \mathrm{CH_3CHOH}$$

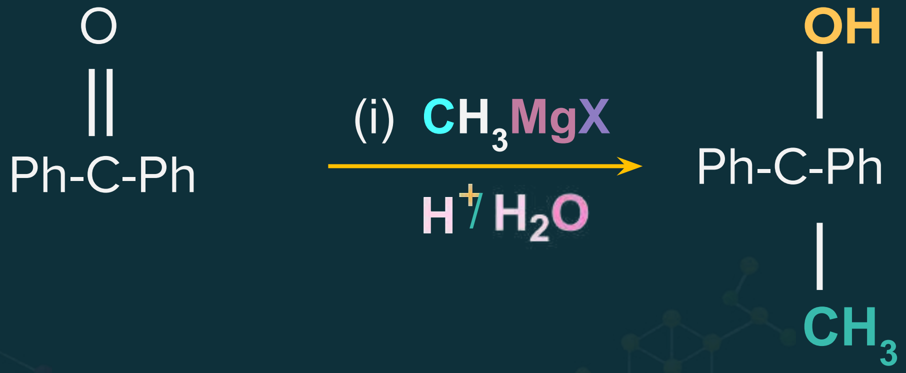
(4)



(5)



(6)



Thus, three compounds will give secondary aldehyde.

The product of the following reaction is:

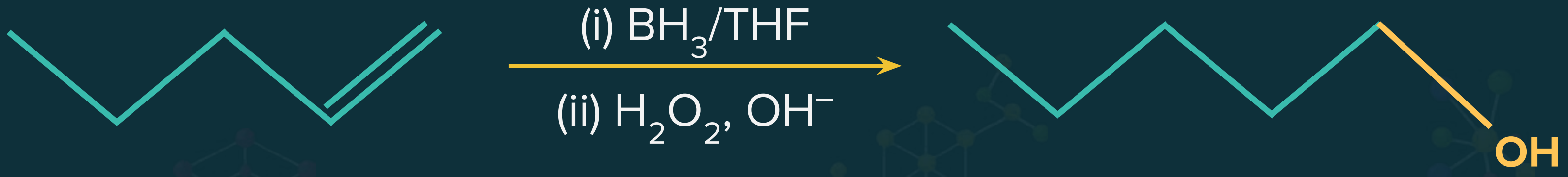
a) Pentan-1-ol

b) Pentan-2-ol

c) Pentane

d) 1,2-Pentanediol

Solution



Thus, option (a) is the correct answer.

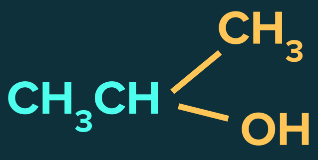
Give product A and B of the following reaction.

BOARDS

$$HC\equiv CH \xrightarrow[20\%\ H_2SO_4]{1\%\ HgSO_4} A \xrightarrow[H_2O]{CH_3MgX} B$$

Solution

$$HC\equiv CH \xrightarrow[20\%\ H_2SO_4]{1\%\ HgSO_4} \underset{A}{CH_3CHO} \xrightarrow[H_2O]{CH_3MgX}$$



$CH_3CH(CH_3)OH$

B

Preparation of Phenol

Preparation of Phenol

- From haloarenes
- From benzene via benzenesulphonic acid
- From aniline via diazonium salts
- From cumene

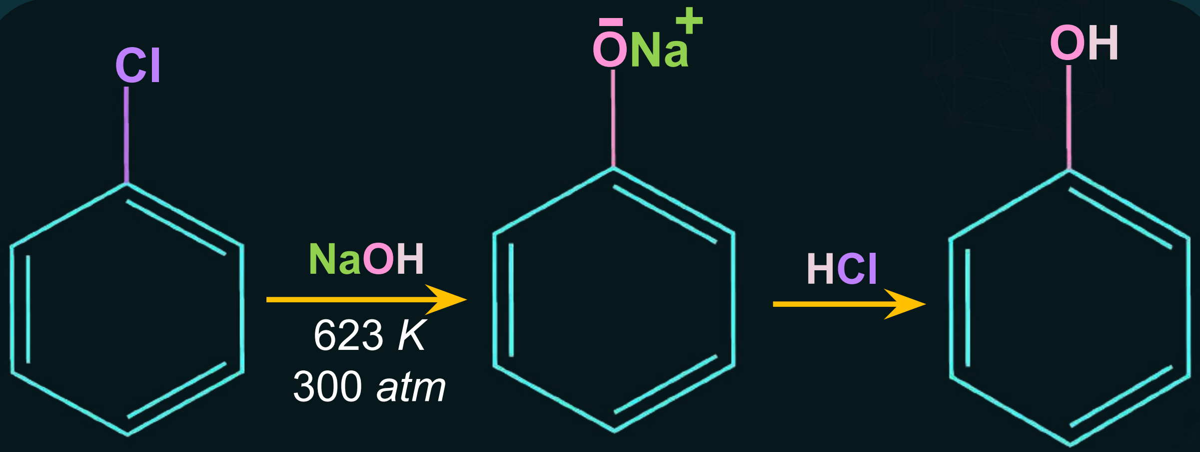
Recall

Dow Process

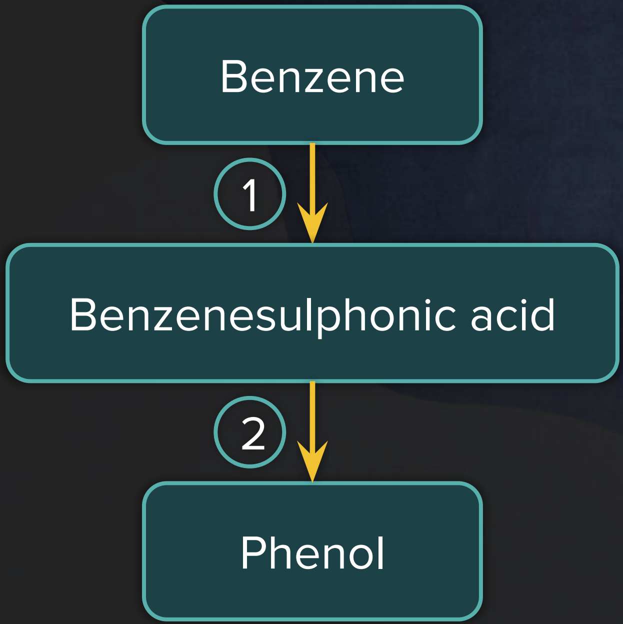
Reagent and reaction conditions:

1 NaOH
623 *K*, 300 *atm*

2 HCl (aq)



Phenol from Benzene via Benzenesulfonic Acid



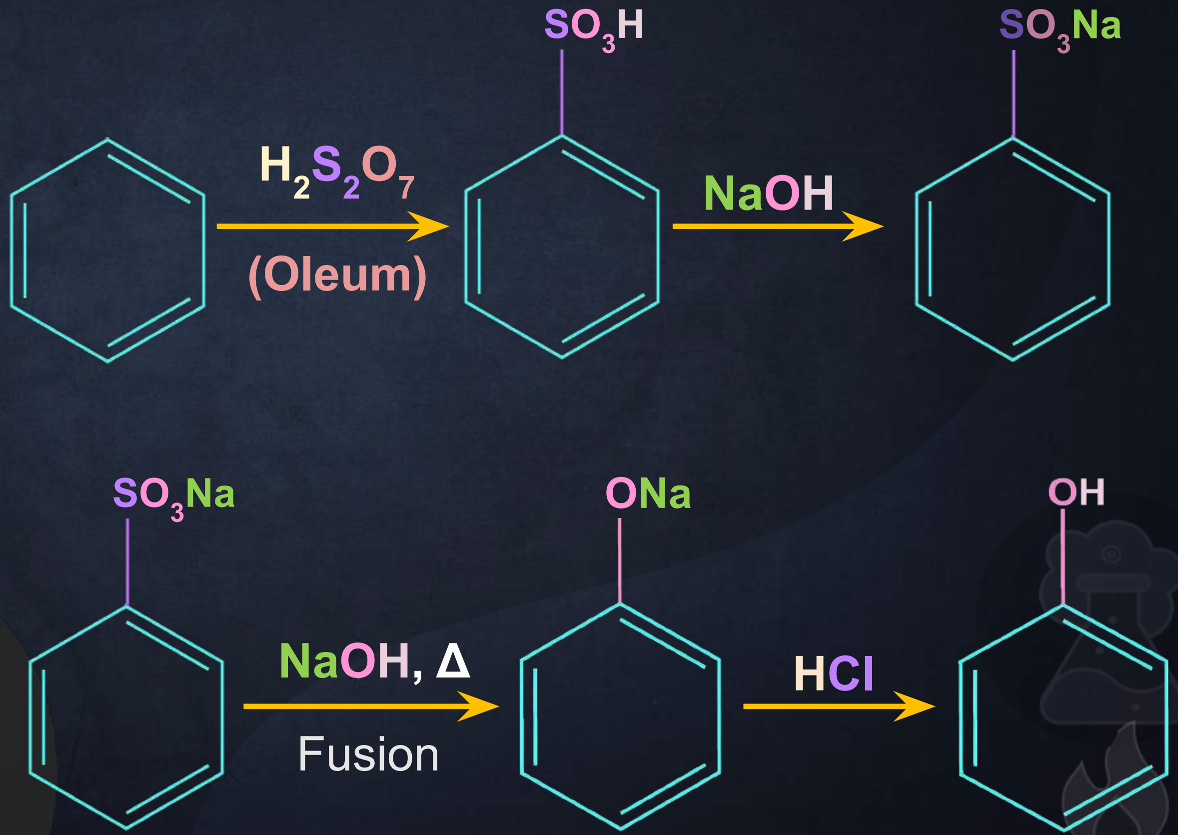
Benzene

1

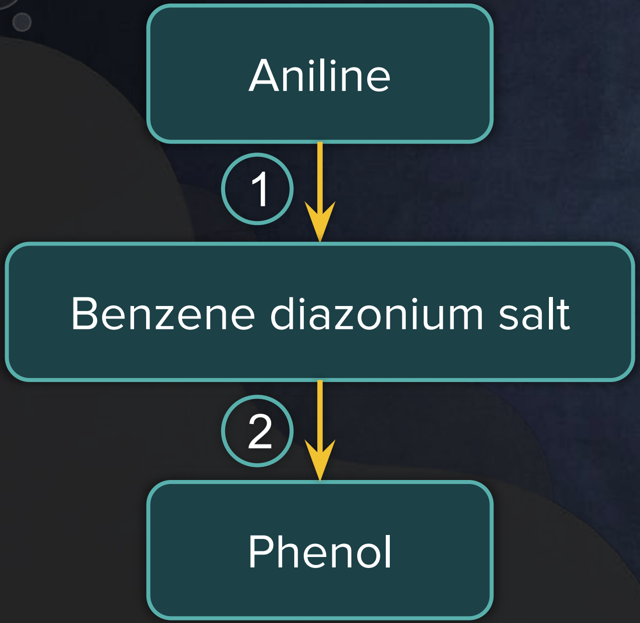
Benzenesulphonic acid

2

Phenol



Phenols from Aniline via Diazonium Salt

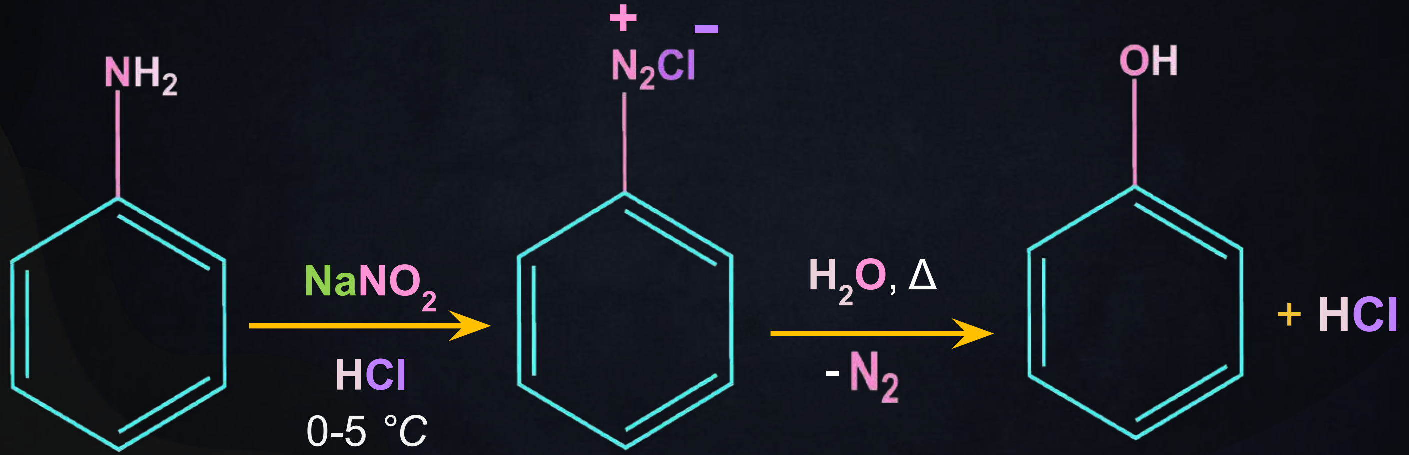


Reagent and reaction conditions:

1 $NaNO_2$ + HCl at 0-5 °C

2 H_2O warm

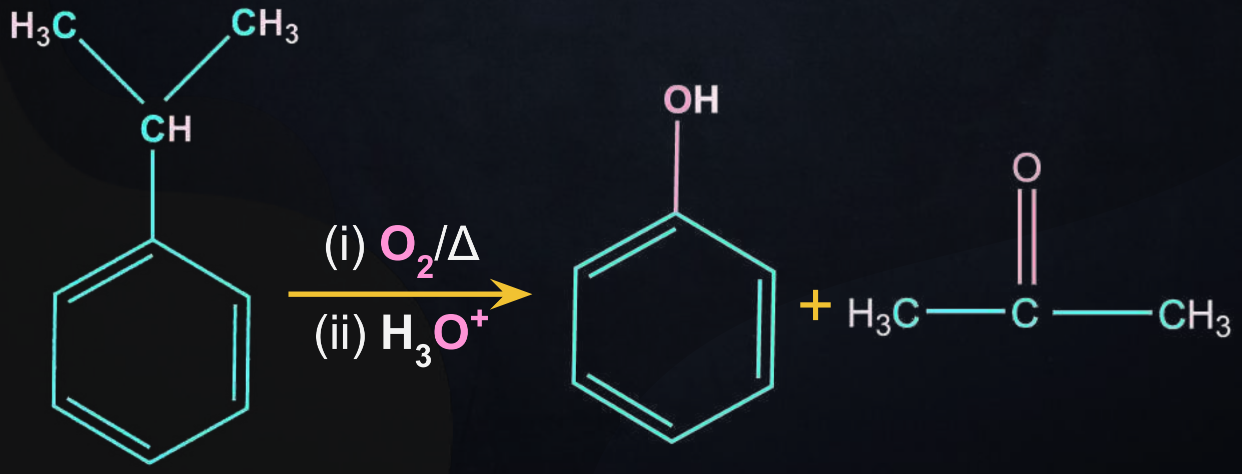
Phenols from Aniline via Diazonium Salt



Phenols from Cumene

Cumene + O_2
followed by
acidic hydrolysis

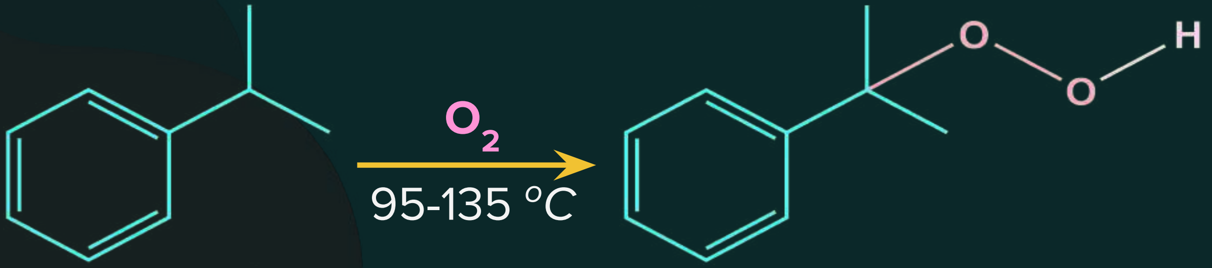
Phenol + Acetone



Phenols from Cumene

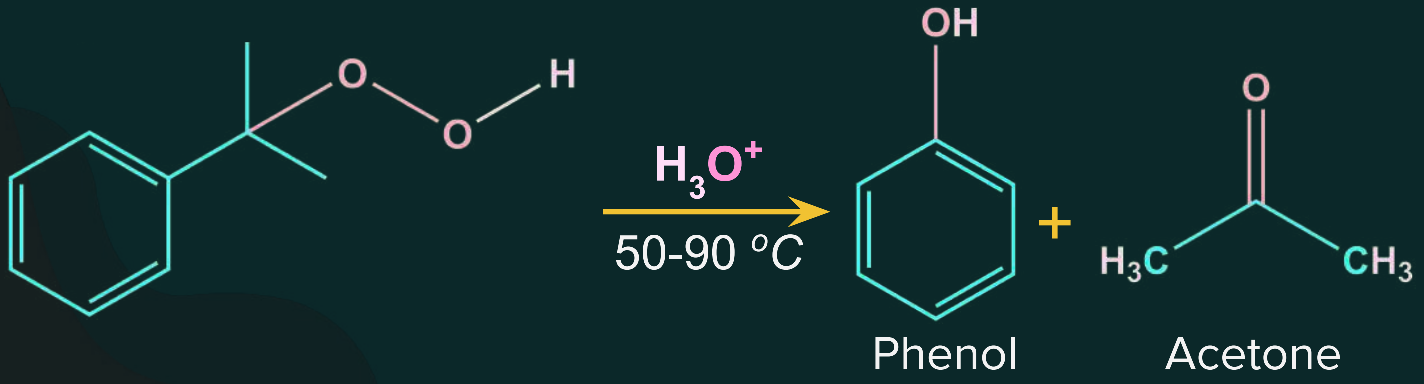
Step 1 Formation of Cumene hydroperoxide

Step 2 Treatment with acid



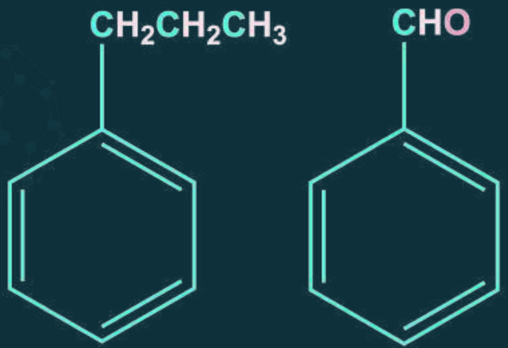
Cumene hydroperoxide

Phenols from Cumene



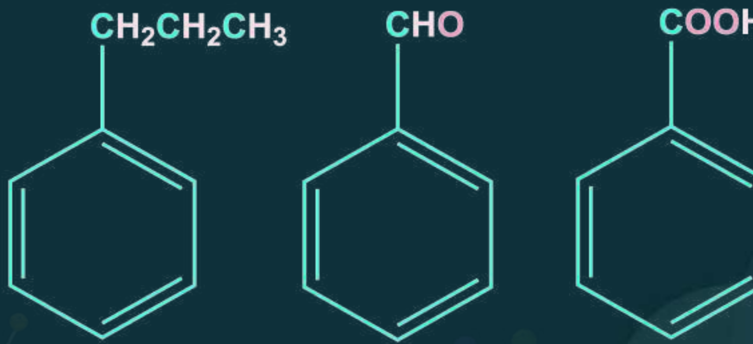
Identify the major products P, Q, and R in the following sequence of a reaction.

a)

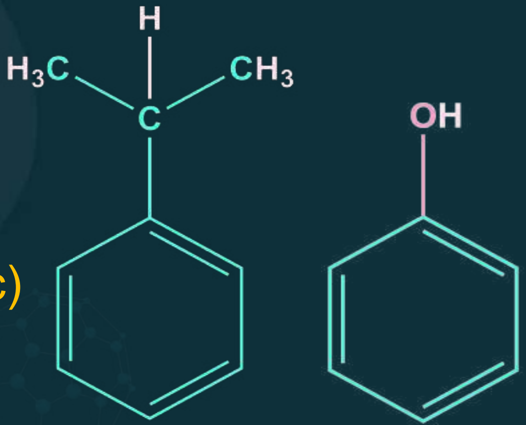


CH_3CH_2OH

b)

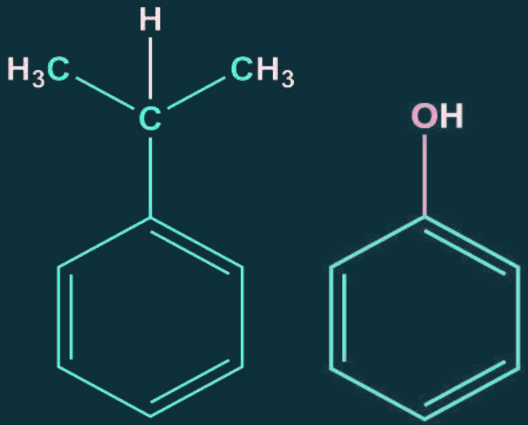


c)



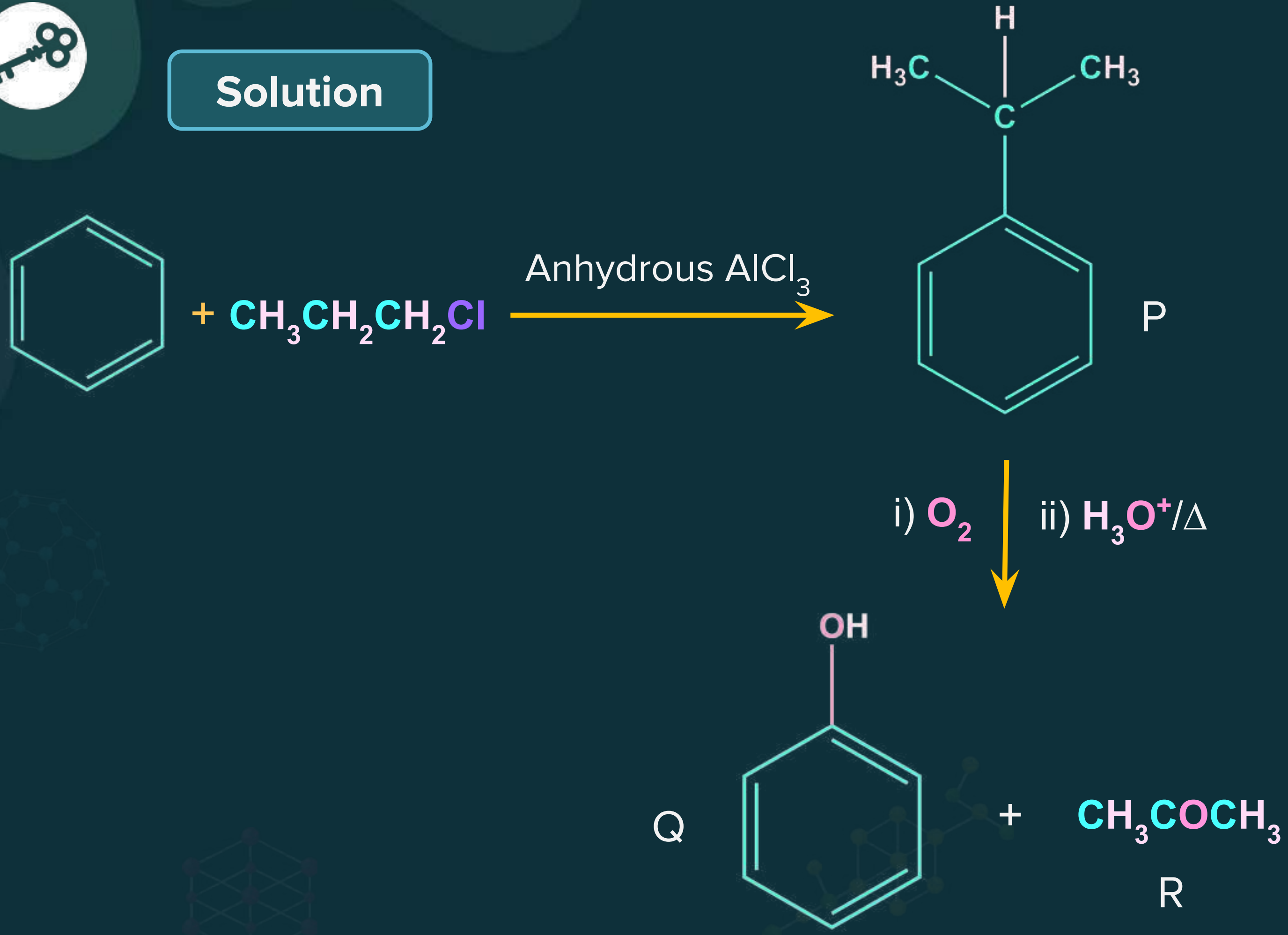
CH_3COCH_3

d)

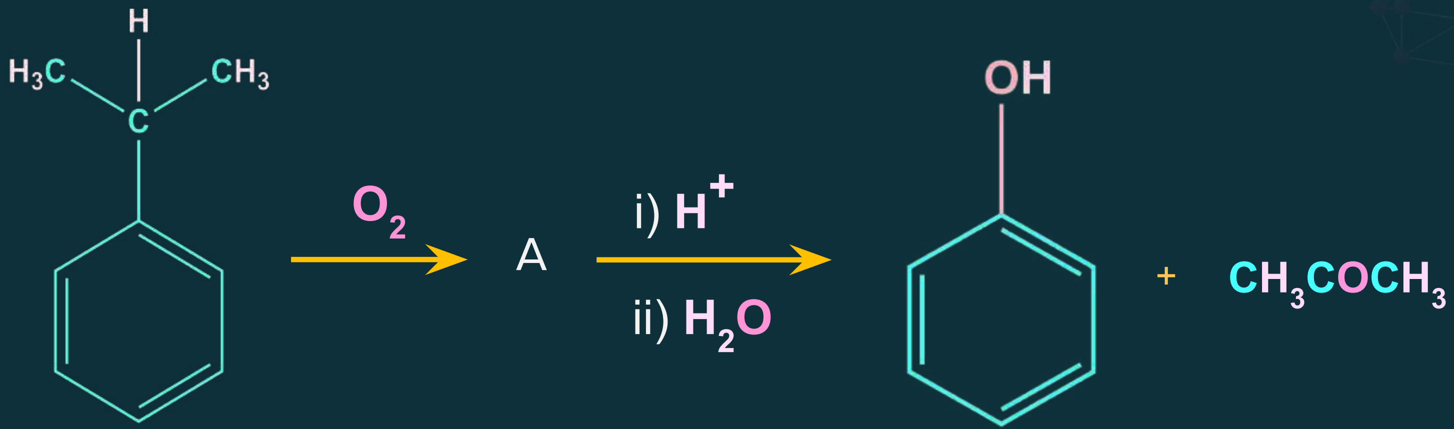


$CH_3CH(OH)CH_3$

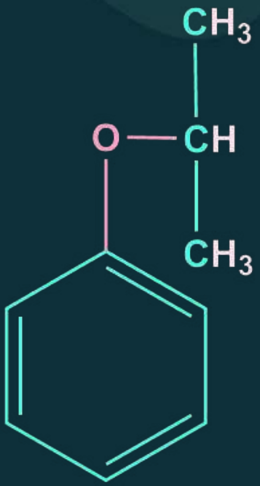
Solution


+ $CH_3CH_2CH_2Cl$
Anhydrous $AlCl_3$
H
H_3C
C
CH_3
P
i) O_2
ii) H_3O^+/Δ
OH
Q
+
CH_3COCH_3
R

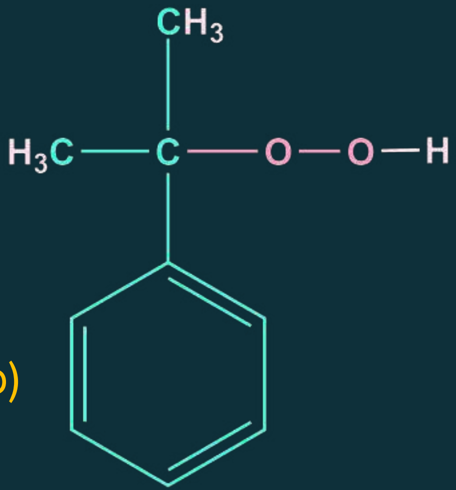
The structure of intermediate A in the following reaction is:



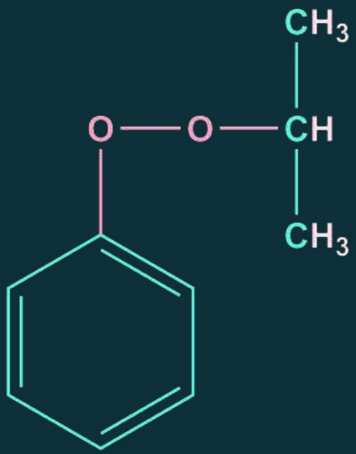
a)



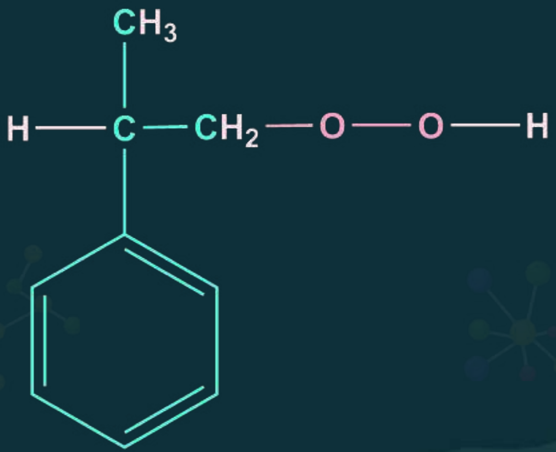
b)



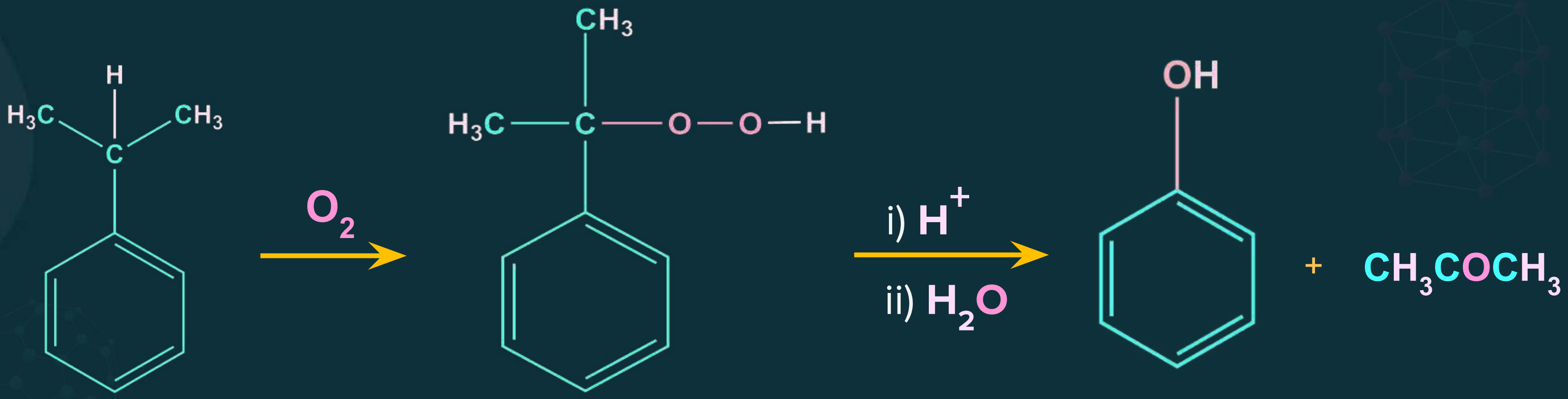
c)



d)



Solution



Cumene reacts with O_2 to form cumene hydroperoxide. Cumene hydroperoxide reacts with H_3O^+ to form phenol and acetone.

Thus, option (b) is the correct answer.

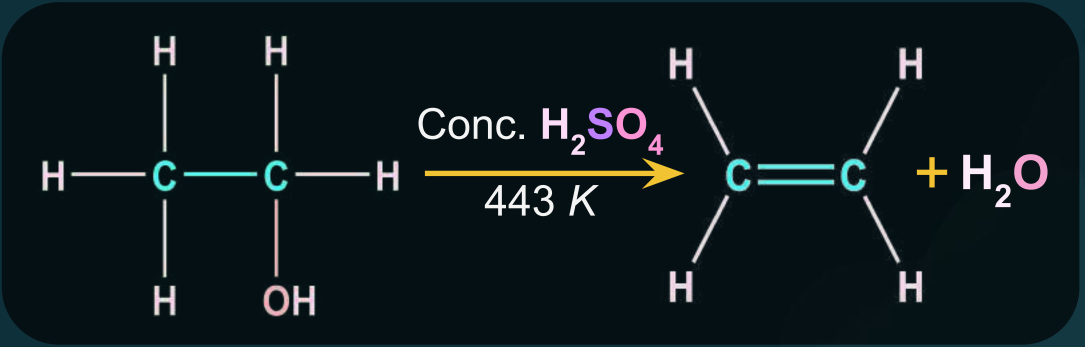
Preparation of Ethers

Preparation of Ethers

- Dehydration of alcohols
- Williamson synthesis

Recall

Alcohols can **dehydrate** to form **alkenes**.



$$CH_3CH_2OH \xrightarrow[443\ K]{\text{Conc. } H_2SO_4} CH_2{=}CH_2 + H_2O$$

Preparation of Ethers

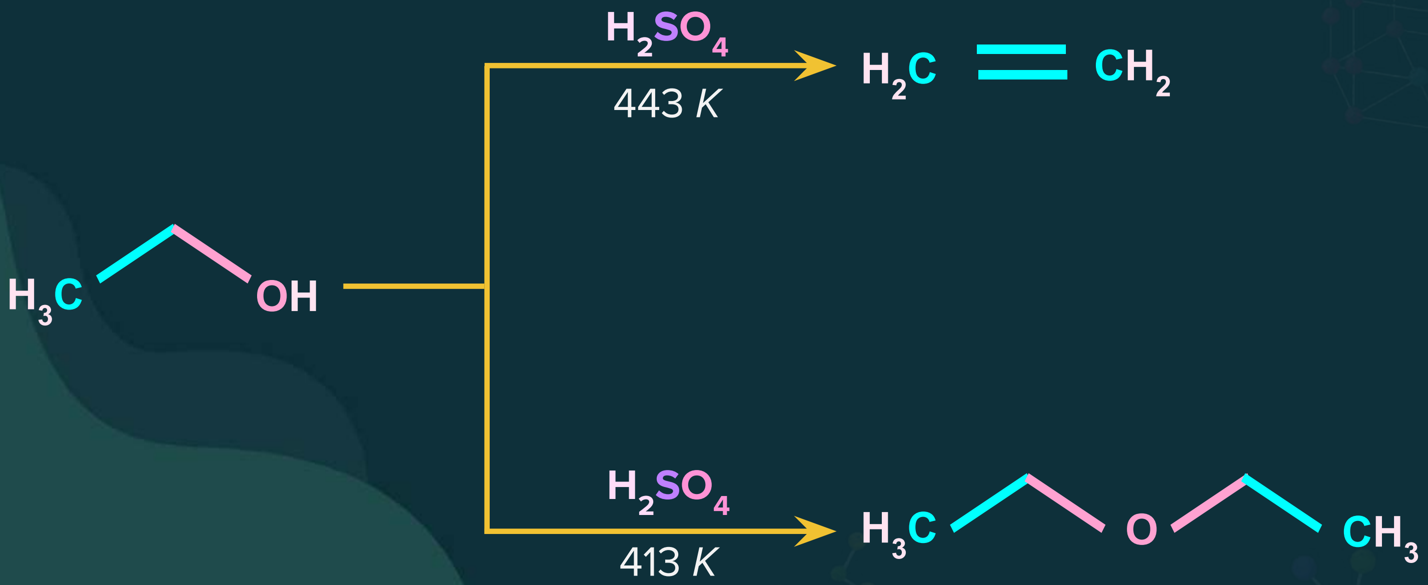
Dehydration of Alcohols

Primary alcohols can also dehydrate to form ethers.

$$R-OH + HO-R \xrightarrow[-H_2O]{HA/\Delta} R-O-R$$

Dehydration to form an ether usually takes place at a **lower temperature** than dehydration to the alkene.

Preparation of Ethers



Preparation of Ethers

Mechanism

The formation of the ether by intermolecular dehydration of alcohols occurs by an **S_N2 mechanism.**

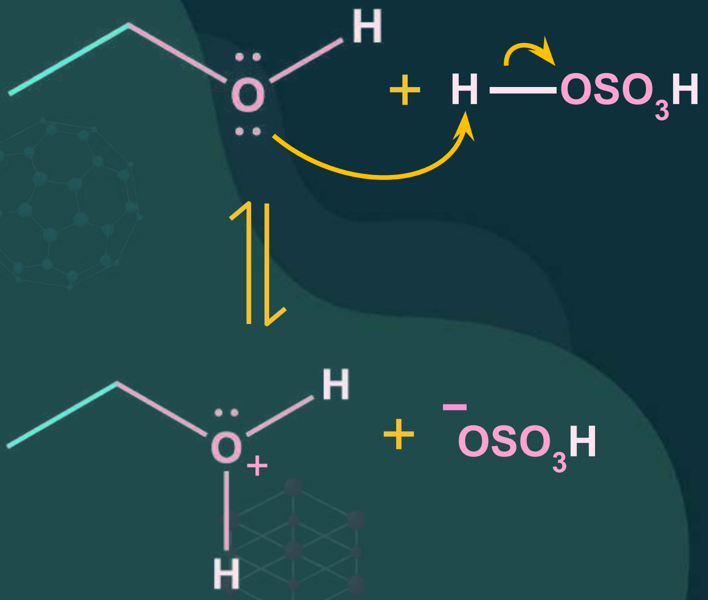
Step 1 Protonation of alcohol

Step 2 Attack of nucleophile

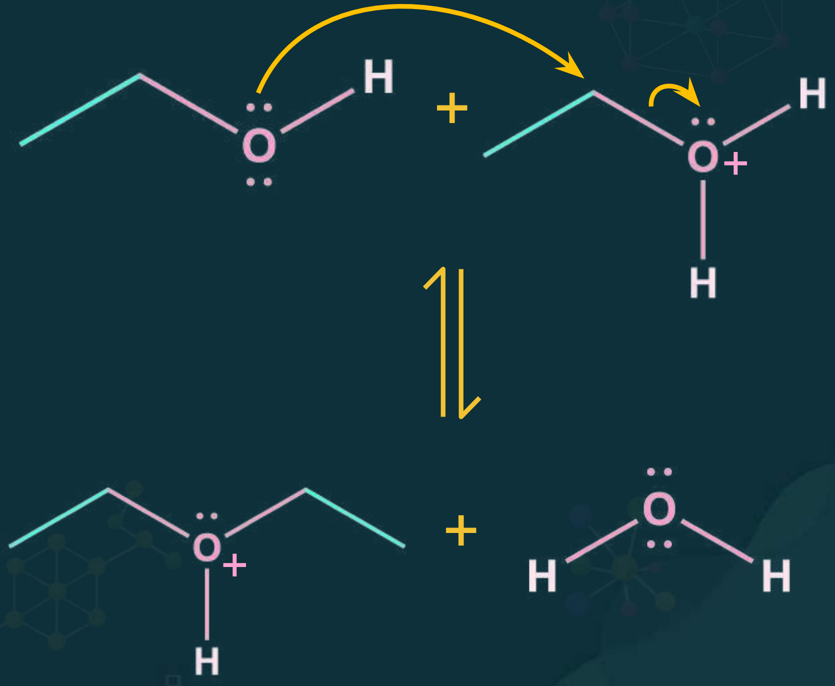
Step 3 Deprotonation

Preparation of Ethers

Protonation of alcohol



Attack of nucleophile



Preparation of Ethers

Deprotonation

Limitations of Intermolecular Dehydrations

01

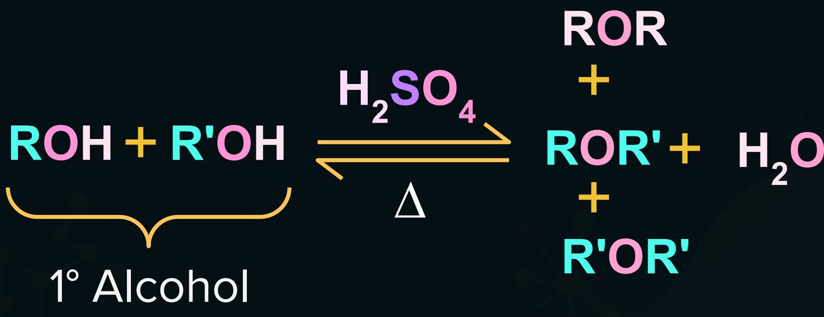
Synthesising ethers using **secondary alcohol** is usually unsuccessful because **alkenes form too easily**.

02

Synthesis of ethers with **tertiary alkyl** groups lead **exclusively to the alkenes.**

03

Not useful for the preparation of **unsymmetrical ethers** from primary alcohols because the reaction leads to a mixture of products.



$$\underbrace{ROH + R'OH}_{1^\circ\ \text{Alcohol}} \underset{\Delta}{\overset{H_2SO_4}{\rightleftharpoons}} \begin{matrix} ROR \\ + \\ ROR' \\ + \\ R'OR' \end{matrix} + H_2O$$

In the given reaction,

$$R - OH + ROH \xrightarrow[\Delta]{\text{conc. } H_2SO_4} R - OR + HOH$$

alcohol is:

a) Primary alcohol

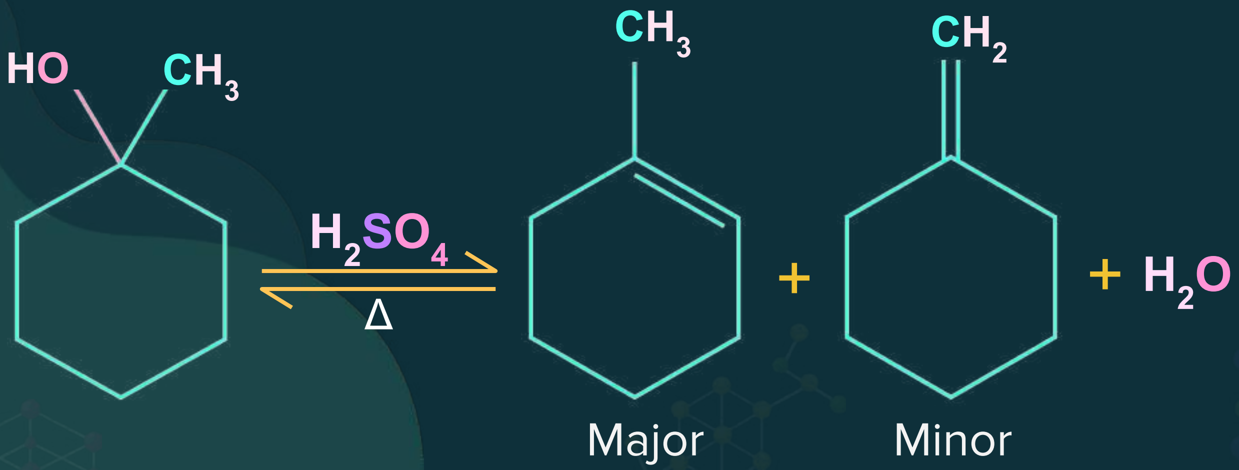
b) Secondary alcohol

c) Tertiary alcohol

d) All of these

Solution

Synthesising ethers using secondary alcohol is usually unsuccessful because alkenes form too easily and synthesis of ethers with tertiary alkyl groups lead exclusively to the alkenes. Therefore only primary alcohols are used in the reaction.



Thus, option (a) is the correct answer.

Which of the following alcohols gives the **best yield of dialkyl ether** on being heated with a trace of sulphuric acid?

BOARDS

a) Pentan-2-ol

b) 2-Methyl-2-butanol

c) Cyclopentanol

d) Pentan-1-ol

Solution

Synthesising ethers using secondary alcohol is usually unsuccessful because alkenes form too easily and synthesis of ethers with tertiary alkyl groups lead exclusively to the alkenes. Therefore only primary alcohols are used in the reaction. Pentan-2-ol and cyclopentanol are secondary alcohols, 2-methyl-2-butanol is tertiary alcohol and pentan-1-ol is primary alcohol.

Thus, option (d) is the correct answer.

Preparation of Ethers

Williamson synthesis

Synthesis of symmetrical & unsymmetrical ethers by a **nucleophilic substitution** reaction.

General reaction

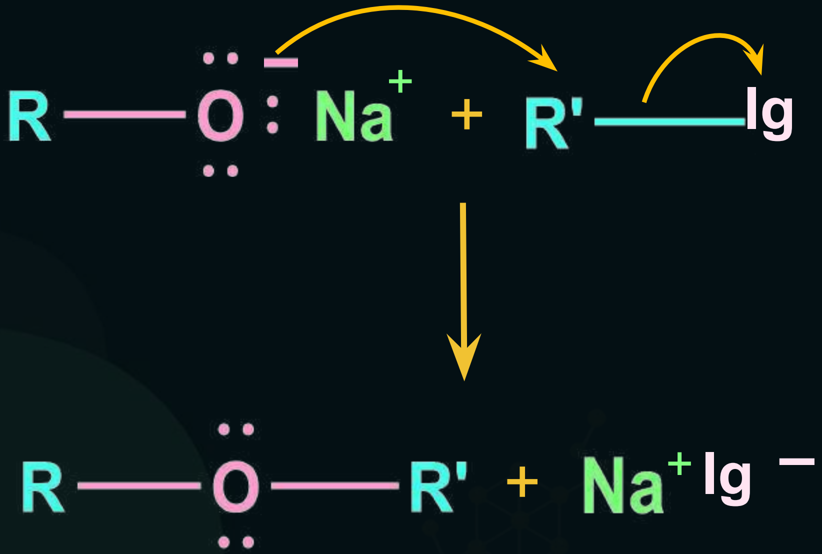
$$R'\text{—}ONa + R\text{—}X \longrightarrow R'\text{—}O\text{—}R + NaX$$

The **alkoxide ion** reacts with the substrate via **S_N2 mechanism.**

The substrate must be **unhindered** (**1° or 2° alkyl halides**) & bear a **good leaving group**.

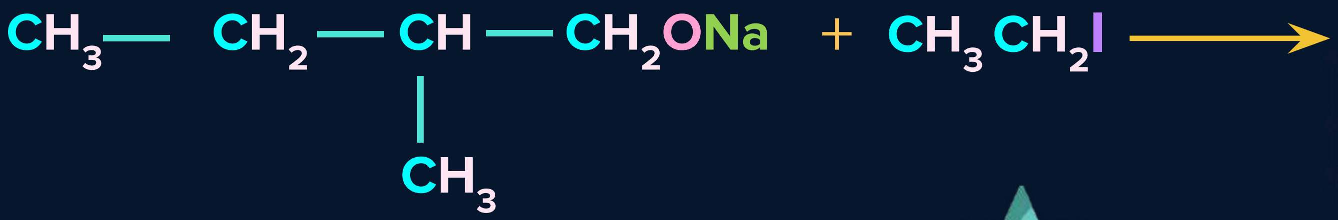
Preparation of Ethers

Mechanism



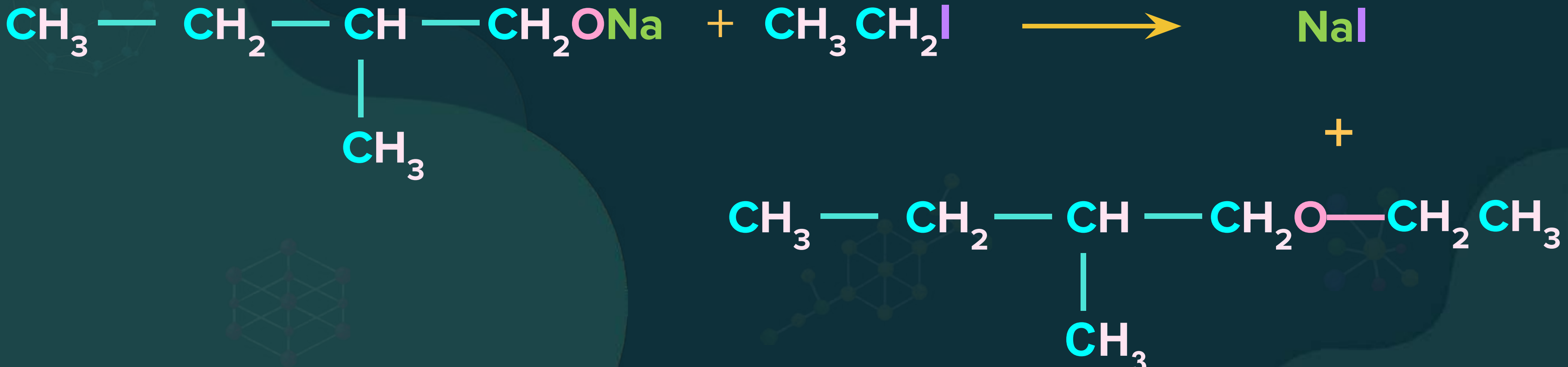
$$R-\ddot{\underset{..}{O}}\!:^{-}\ Na^{+} + R'-Ig \longrightarrow R-\ddot{\underset{..}{O}}-R' + Na^{+}Ig^{-}$$

What is the major **product** of the following reaction?



$$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2ONa + CH_3CH_2I \longrightarrow$$

Solution



$$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2ONa + CH_3CH_2I \longrightarrow NaI + CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2O-CH_2CH_3$$

Preparation of Ethers

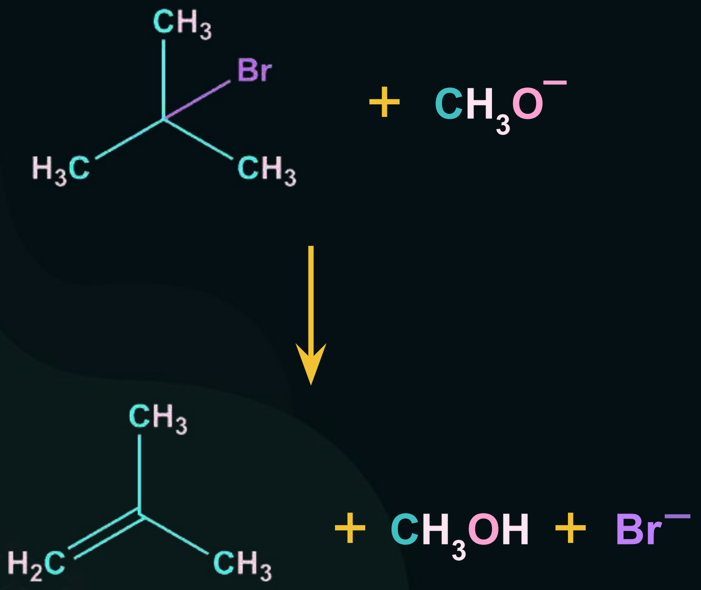
To synthesise tert-butylmethyl ether, can we take the **starting materials** as tert-Butyl halide and methoxide ion?

If a **tert-butyl halide** and **methoxide ion** is used as reactants, it would result in an **elimination product** and little amount or **no ether.**

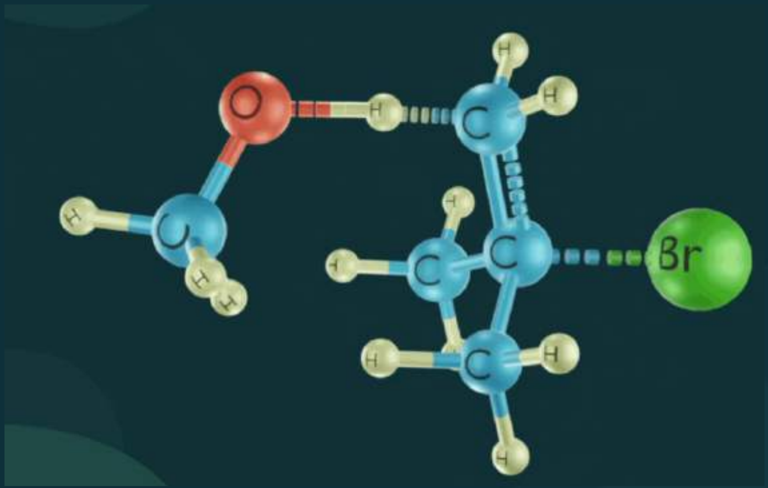
Because reaction of a **tertiary alkyl halide** under S_N2/ E2 condition forms primarily the **elimination product.**

Preparation of Ethers

Mechanism



Via transition state

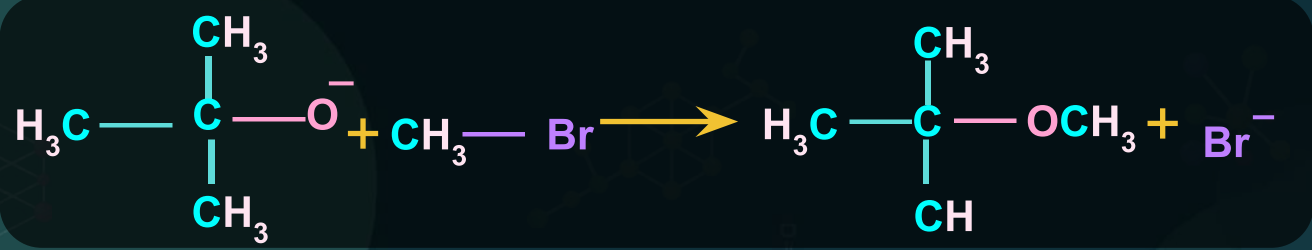


Preparation of Ethers

In carrying out a Williamson synthesis of ether, **less hindered** alkyl group should be provided by the **alkyl halide.**

More hindered alkyl group should come from the **alkoxide.**

To synthesise tert-butyl methyl ether, the starting materials **should** be a **methyl halide** and **tert-butoxide ion**.

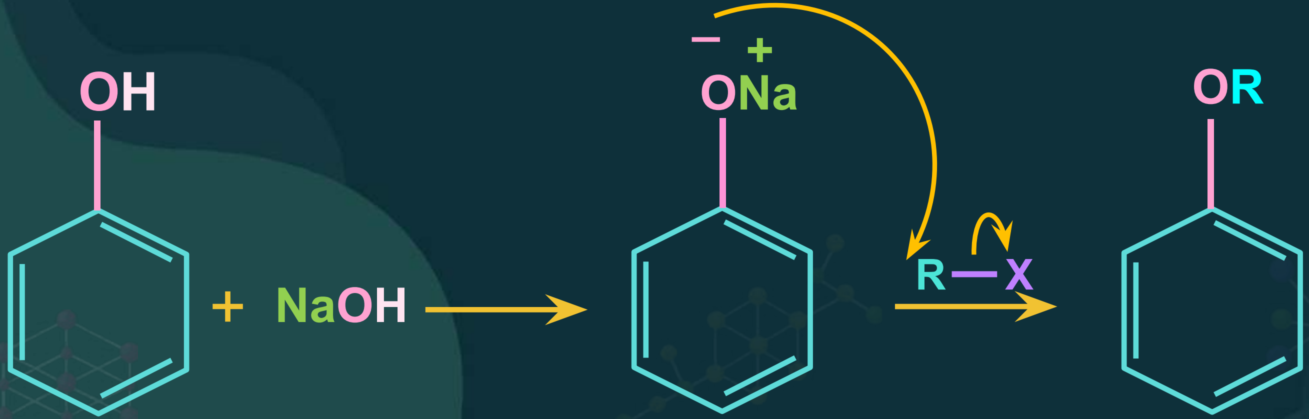


$$H_3C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}O^- + CH_3{-}Br \longrightarrow H_3C{-}\overset{CH_3}{\underset{CH}{C}}{-}OCH_3 + Br^-$$

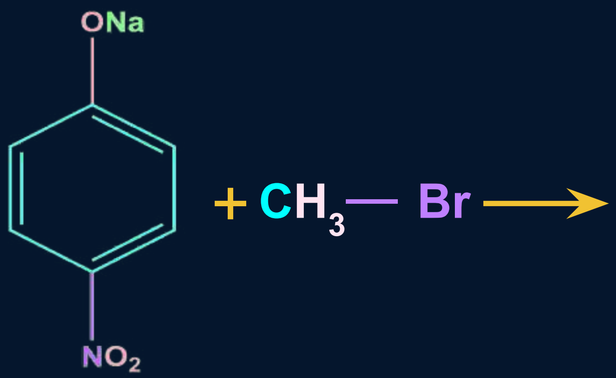
Preparation of Ethers

To prepare alkyl phenyl ether

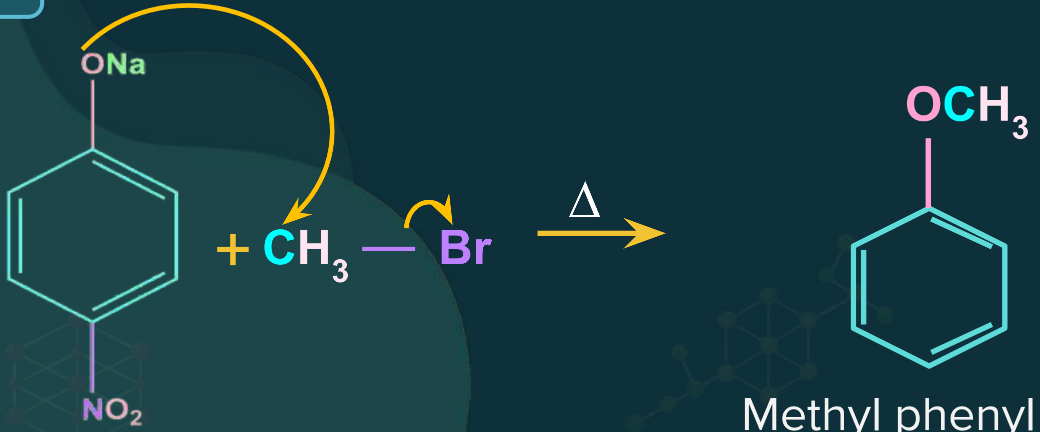
Phenoxide ion is treated with alkyl halide



Predict the product:



Solution



Methyl phenyl ether

Williamson synthesis of ether is an example of:

BOARDS

a) Nucleophilic addition

b) Electrophilic addition

c) Electrophilic substitution

d) Nucleophilic substitution

Solution

Williamson synthesis is a synthesis of symmetrical and asymmetrical ethers by a **nucleophilic substitution** reaction.

Thus, option (d) is the correct answer.

$(CH_3)_3C\text{-}O\text{-}CH_2\text{-}C_6H_5$ can be best prepared from Williamson synthesis, using:

a) $(CH_3)_3C\text{-}Cl$ and C_6H_5ONa

b) $C_6H_5CH_2Cl$ and $(CH_3)_3C\text{-}ONa$

c) $(CH_3)_3C\text{-}O\text{-}CH_2\text{-}Cl$ and C_6H_5ONa

d) None of these

Solution

There can be two way of breaking the ether bond in the compound:

Case I

$$(CH_3)_3C{-}Cl + NaO{-}CH_2{-}C_6H_5$$

$$\downarrow$$

$$(CH_3)_3C{-}O{-}CH_2{-}C_6H_5$$

Case II

$$(CH_3)_3C{-}ONa + Cl{-}CH_2{-}C_6H_5$$

$$\downarrow$$

$$(CH_3)_3C{-}O{-}CH_2{-}C_6H_5$$

But halogen should attached with primary carbon therefore second possibility is used to form the product.

Thus, option (b) is the correct answer.

Which one is formed when **sodium phenoxide** is heated with ethyl iodide?

a) Ethyl phenyl ether

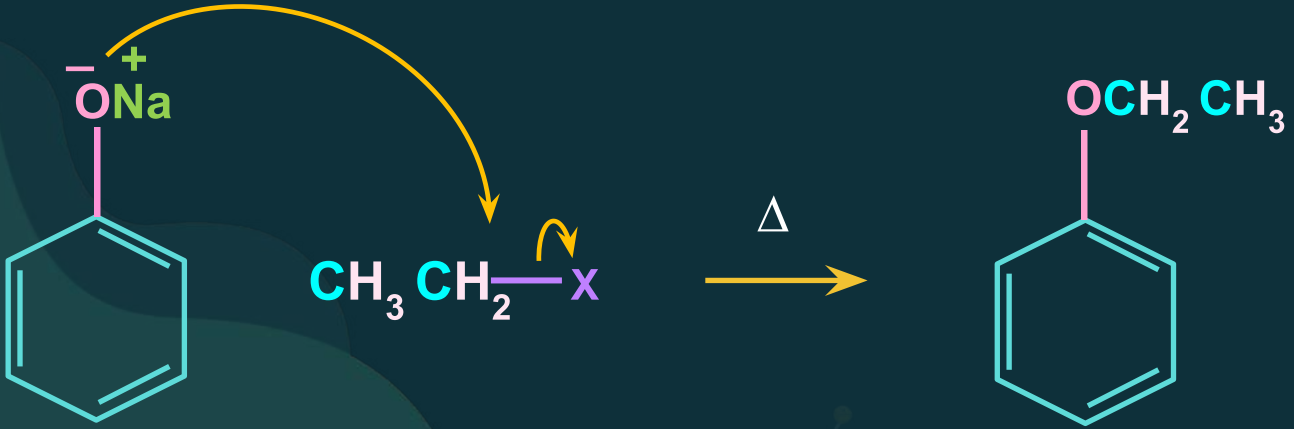
b) Ethyl phenyl alcohol

c) Phenol

d) None of these

Solution

The reaction is given as follow:



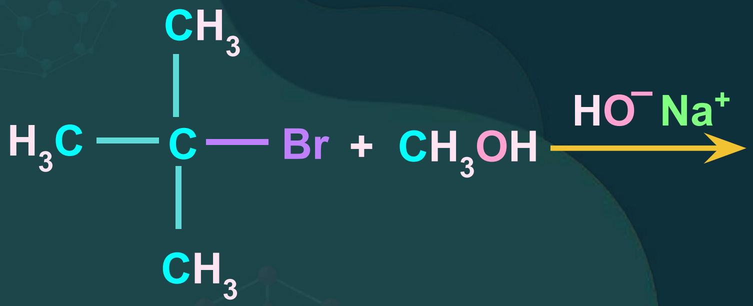
Ethyl phenyl ether

Thus, option (a) is the correct answer.

In which of the following reactions the product obtained is **t-butyl methyl ether**?

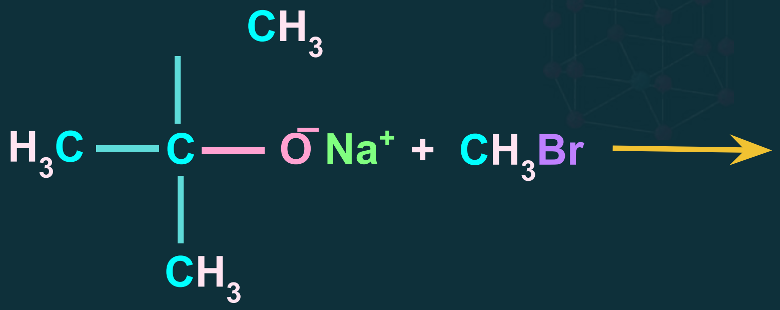
a) $CH_3OH + HO-CH_2-CH_3 \xrightarrow{\text{Conc. } H_2SO_4}$

b)



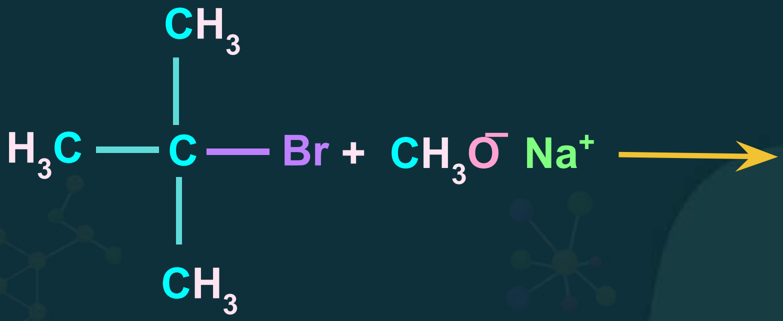
$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-Br + CH_3OH \xrightarrow{HO^{-}Na^{+}}$

c)



$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-\overset{-}{O}Na^{+} + CH_3Br \longrightarrow$

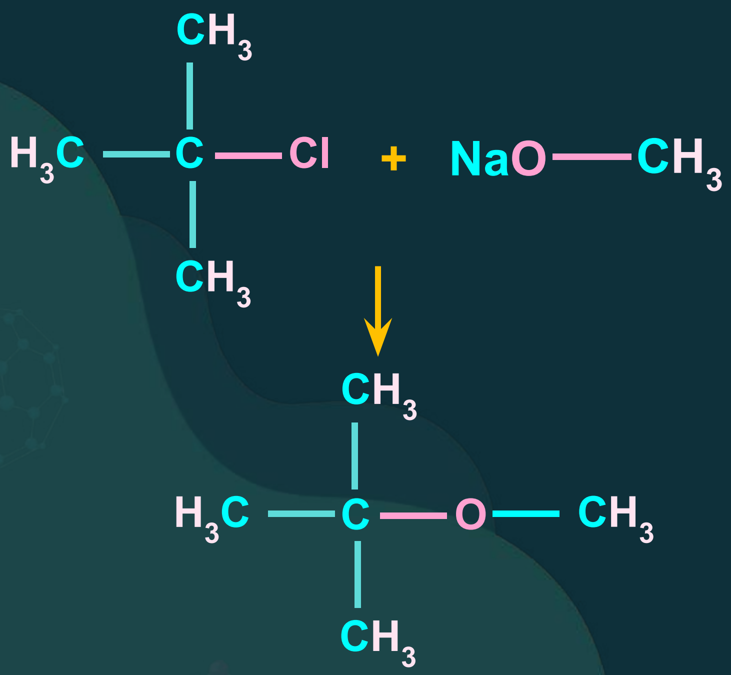
d)



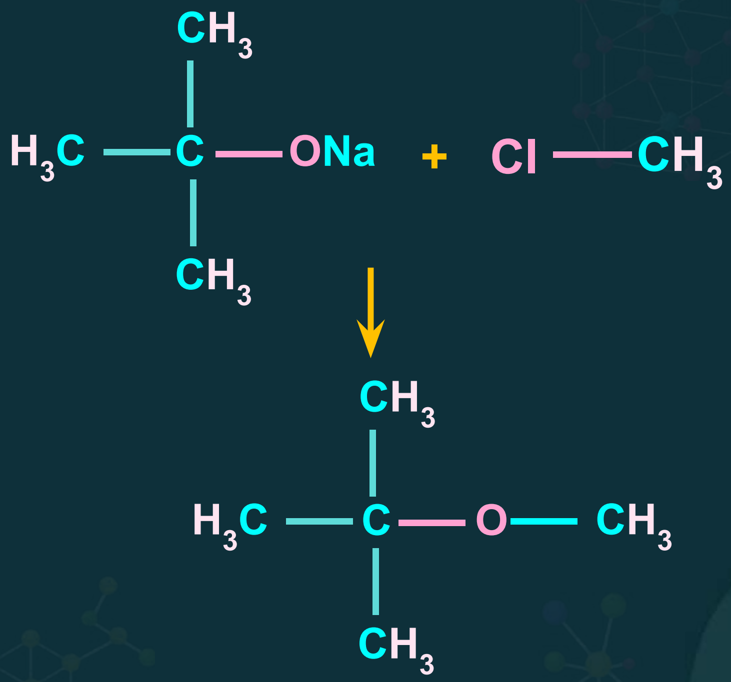
$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-Br + CH_3\overset{-}{O}Na^{+} \longrightarrow$

Solution

Case I



Case II



But halogen should attached with primary carbon therefore second possibility is used to form the product. **Thus, option (c) is the correct answer.**

The formation of diethyl ether from ethanol is based on:

a) Dehydrogenation reaction

b) Hydrogenation reaction

c) Dehydration reaction

d) Heterolytic fission reaction

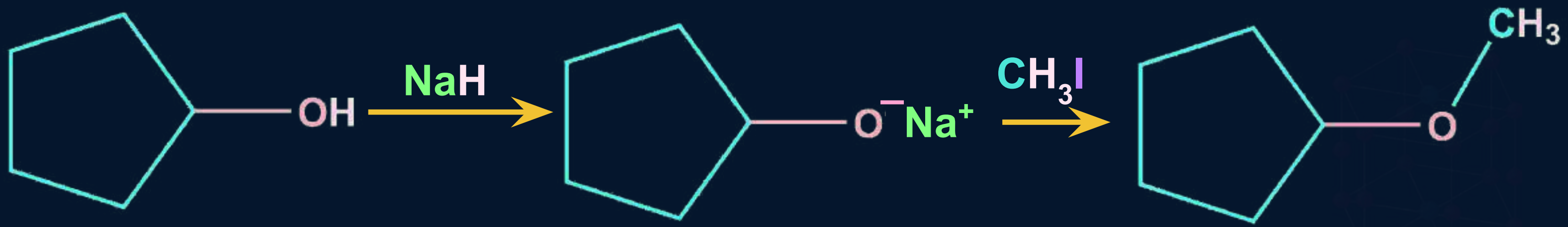
Solution

When ethanol is heated in presence of acid at 140 °C then formation of ether take place by releasing the water molecules and when water molecule is release in any reaction then this reaction is known as dehydration reaction.

$$C_2H_5\text{—}OH + HO\text{—}C_2H_5 \xrightarrow{140\ ^\circ C} C_2H_5\text{—}O\text{—}C_2H_5 + H_2O$$

Thus, option (c) is the correct answer.

The following reaction can be **classified** as:



Solution

In the reaction first alcohol react with sodium hydride and formation of sodium alkoxide take place and the sodium alkoxide react with alkyl halide and gives ether. These reaction happens in williamson synthesis.

Hence, this reaction is williamson synthesis of ether.

Chemical properties of Alcohols

- **Chemical Properties**
  - Reactions of alcohols
  - Reactions of phenol
  - Reactions of ether

Chemical properties of Alcohols

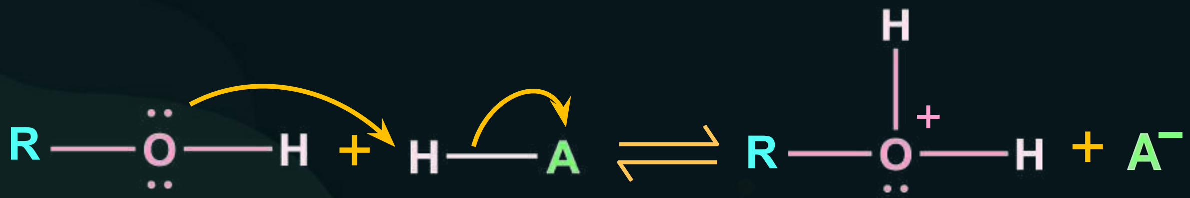
Alcohols can react both as

- Nucleophile
- Electrophile

Chemical properties of Alcohols

Alcohol as a Nucleophile

The **oxygen** atom of the hydroxyl group is **nucleophilic** in nature.



$$R-\ddot{\underset{\cdot\cdot}{O}}-H + H-A \rightleftharpoons R-\overset{\overset{H}{|}}{\underset{\cdot\cdot}{O}}{}^{+}-H + A^{-}$$

Chemical properties of Alcohols

Alcohol as an electrophile

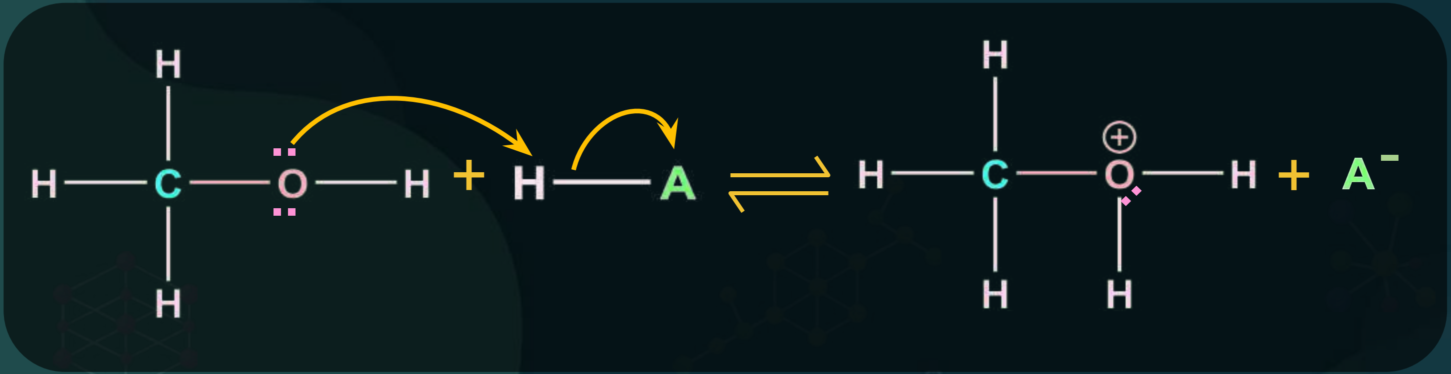
Polarisation of the C —O bond makes the carbon atom partially positive, and if it were not for the fact that OH^- is a poor leaving group, this **carbon** would be susceptible to **nucleophilic** attack.

The **hydroxyl** group can be converted to a good **leaving group,** so as to allow **substitution** or **elimination** reactions.

Chemical properties of Alcohols

Protonated alcohol as an electrophile

Protonation of the alcohol converts a poor leaving group (**OH^-**) into a good leaving group (**H_2O**).

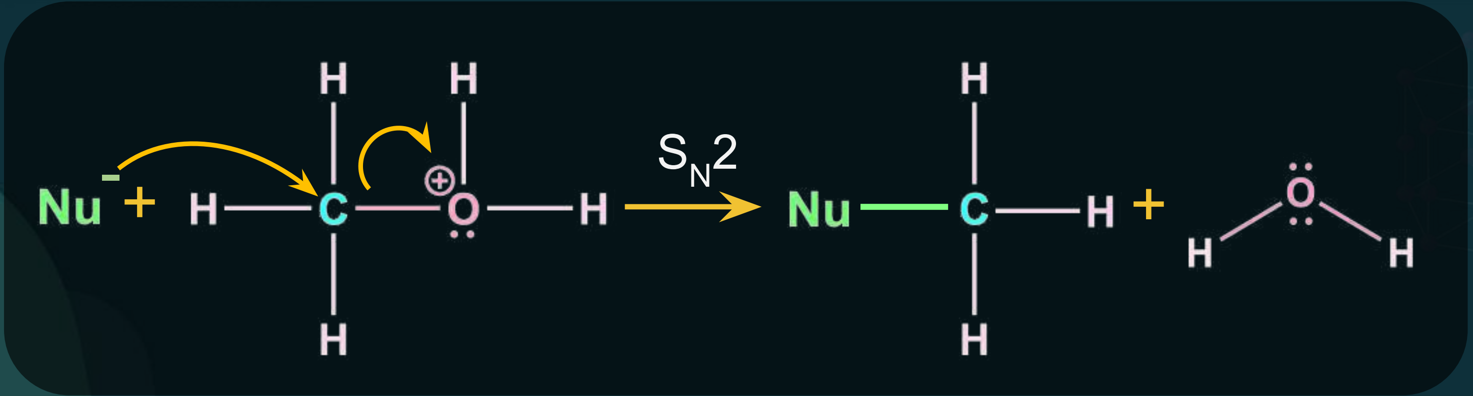


Chemical properties of Alcohols

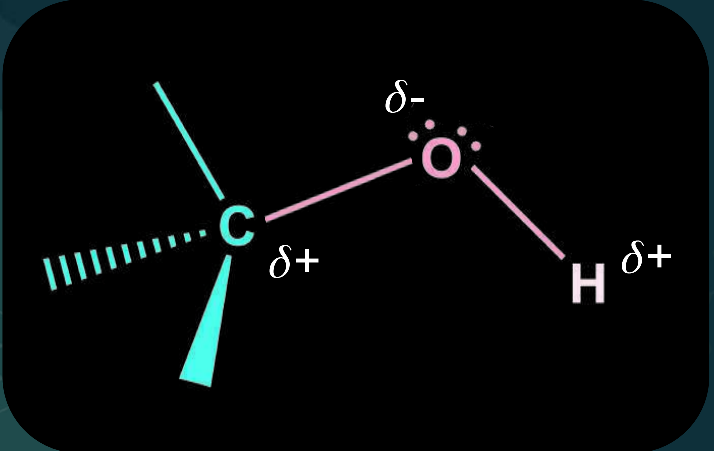
Protonation also makes the carbon atom even more positive (because **-$\overset{+}{O}H_2$** is more electron withdrawing than **-OH** making it more susceptible to **nucleophilic attack.**

Once the alcohol is protonated, **substitution reactions** become possible (S_N2 or S_N1, depending on the class of alcohol).

Chemical properties of Alcohols



Recall



The C-O and O-H bonds of an alcohol are **polarised.**

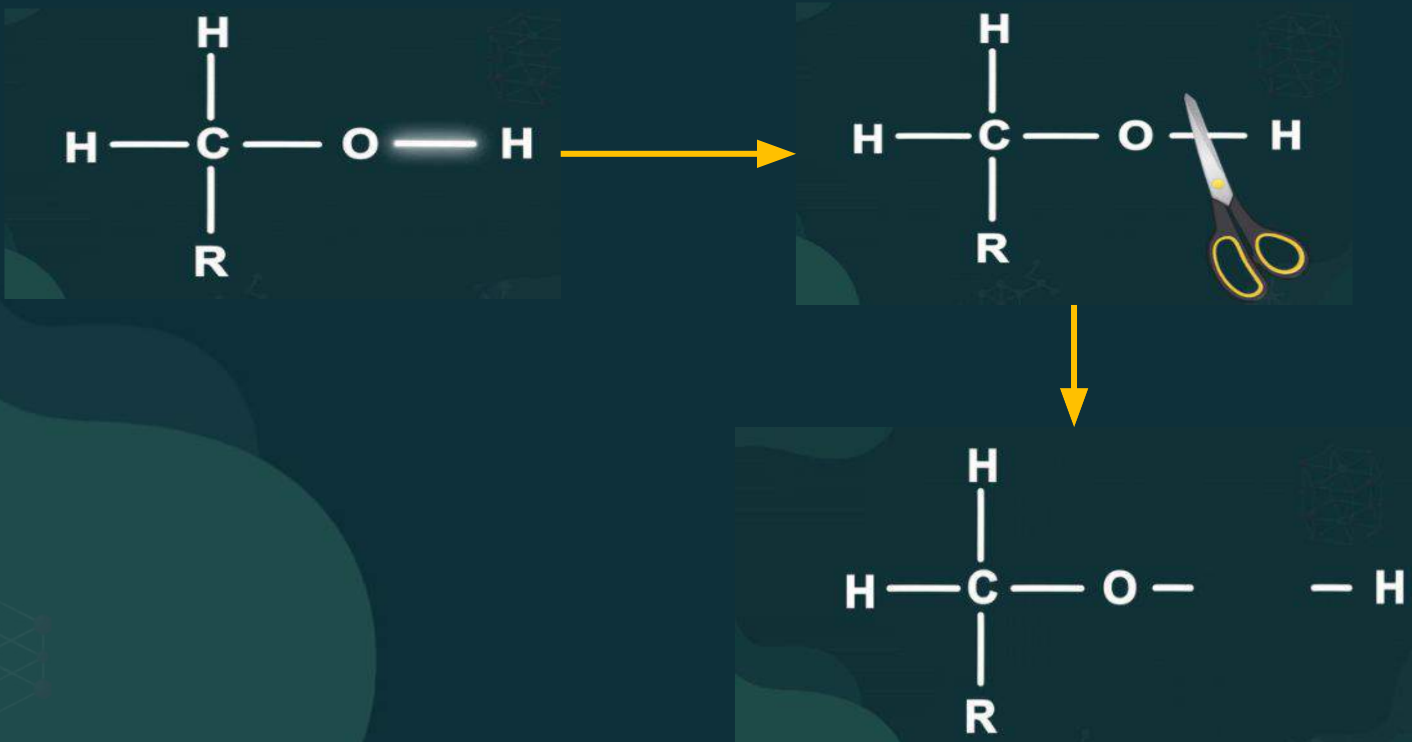
Chemical properties of Alcohols

Chemical Reactions of Alcohols

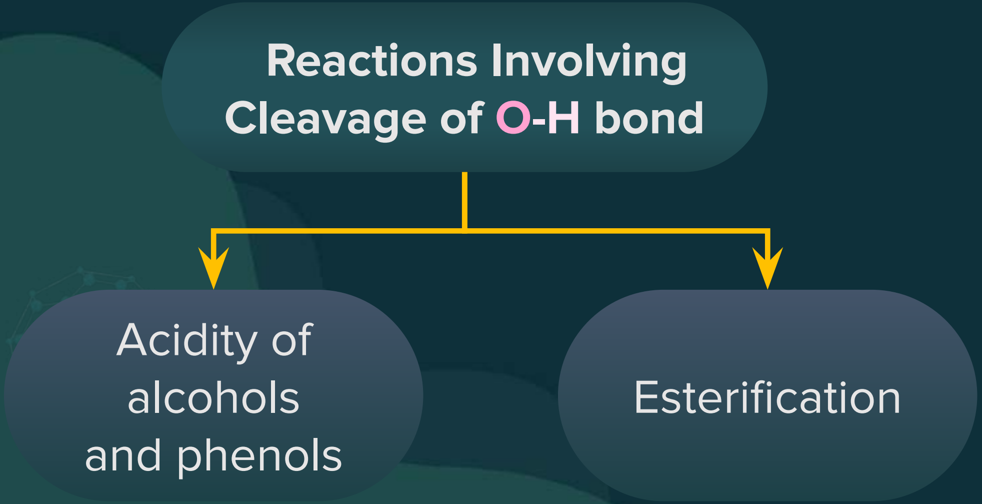
- Based on cleavage of O-H bond
- Based on cleavage of C-O bond

Chemical properties of Alcohols

Reactions Involving Cleavage of O-H Bond



Chemical properties of Alcohols



Reactions Involving Cleavage of O-H bond

Acidity of alcohols and phenols

Esterification

Acidity of alcohols and phenols

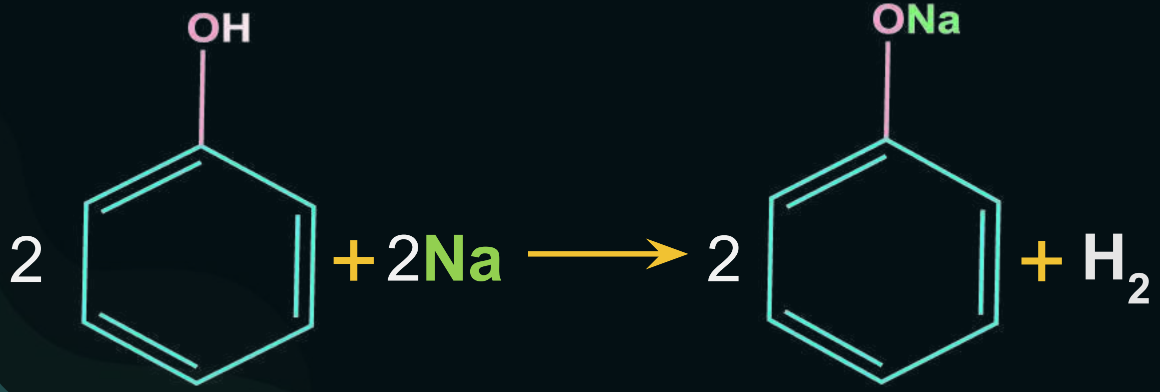
Reaction with **metals**

Alcohols & phenol release **H_2** gas on reaction with sodium or potassium or other alkali metals.

This reflects the **presence** of **acidic** hydrogen.

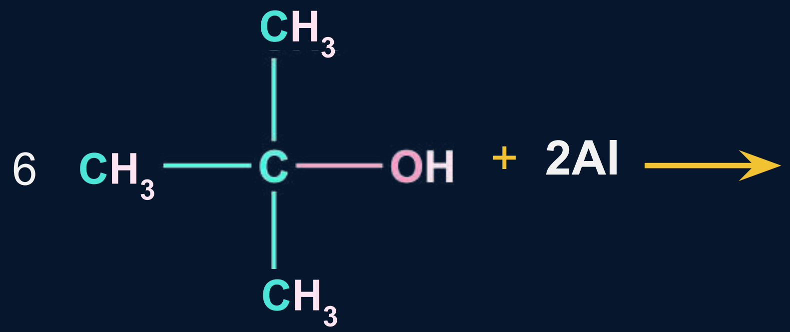
Chemical properties of Alcohols

$$2R\text{-}OH + 2Na \longrightarrow 2RONa + H_2$$



Polarisation of the O-H bond makes the hydrogen partially positive and makes them weak acid.

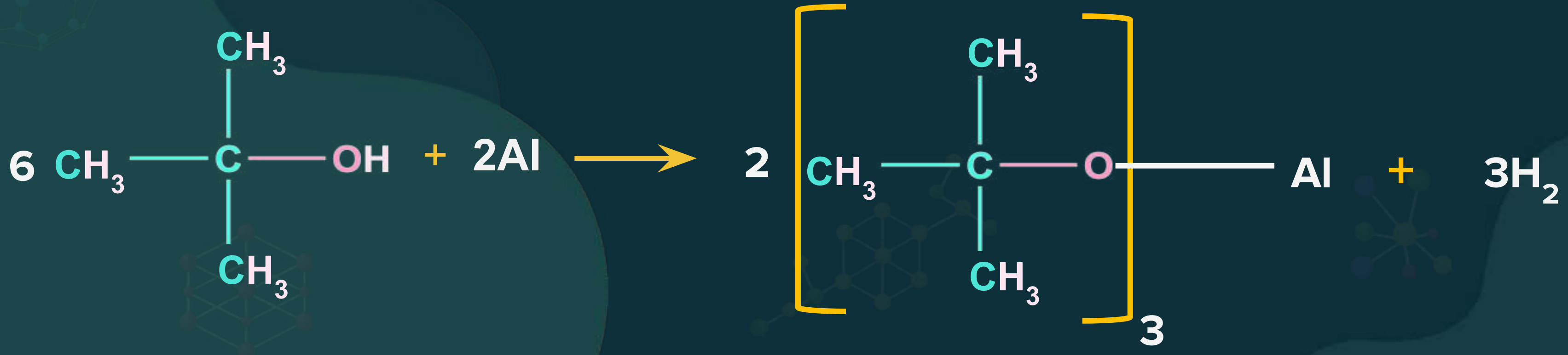
The **major product** formed in the following reaction is:



$$6\ CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + 2Al \longrightarrow$$

Solution

The reaction of given alcohol with Al is given as follow:



$$6\ CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + 2Al \longrightarrow 2\left[CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O\right]_3-Al + 3H_2$$

Acidity of Alcohols and Phenols

$$R-OH \longrightarrow RO^- + H^+$$

Stability of alkoxide ion ↑

Acidity of phenol ↑

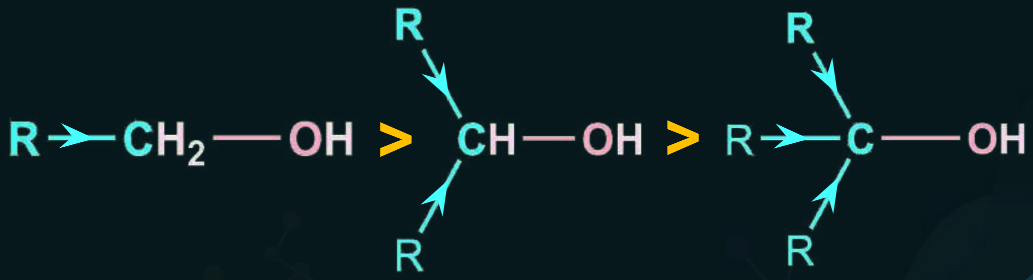
Sterically hindered alcohols, such as tert-butyl alcohol, are **less acidic** than unhindered alcohols such as ethanol or methanol.

Acidity of Alcohols and Phenols

With an **unhindered** alcohol, water molecules can **easily solvate** the alkoxide anion, hence making it stable.

Formation of the alcohol's conjugate base is easier, and therefore its **acidity is increased.**

Alkyl groups are **electron donating in nature,** making formation of alkoxide anion of tertiary alcohol more difficult than other alcohols.



$$R \rightarrow CH_2 - OH > \overset{R}{\underset{R}{CH}} - OH > R \rightarrow \overset{R}{\underset{R}{C}} - OH$$

Acidity of Alcohols and Phenols

Comparison of Acidity

Alcohols have acidities **similar** to that of water.

Methanol is a **slightly stronger** acid than water.

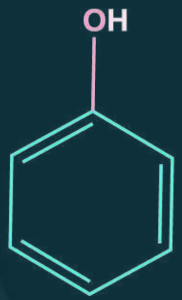
Acid	pK_a
CH_3OH	15.5
H_2O	15.74
CH_3CH_2OH	15.9
$(CH_3)_3COH$	18.0

As pK_a value decreases, then acidity strength increases.

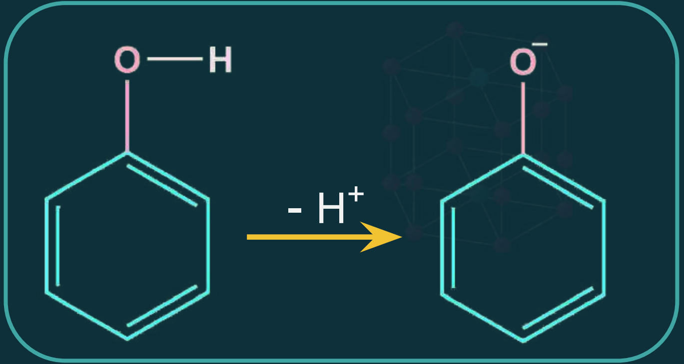
Acidity of Phenol and Alcohols

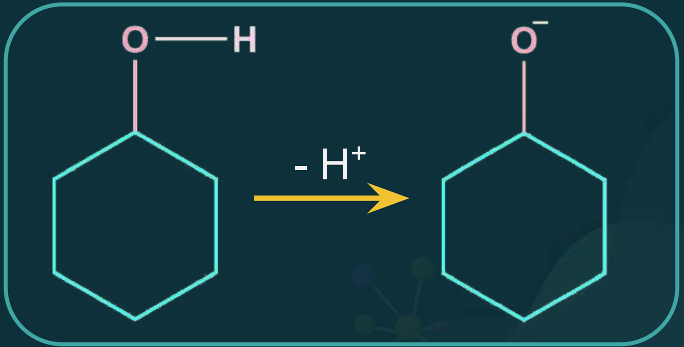
Although phenols are **structurally similar** to alcohols, they are much **stronger acids**.

Cyclohexanol
$pK_a = 18$

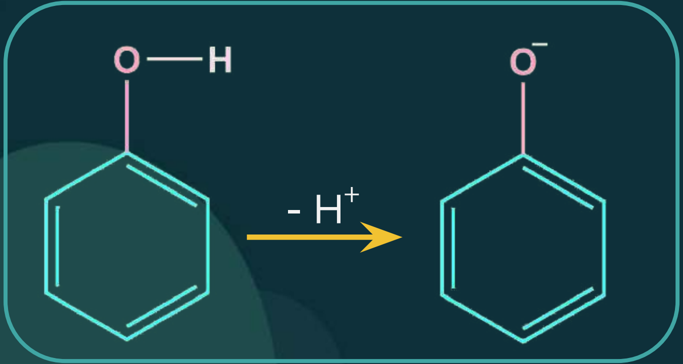


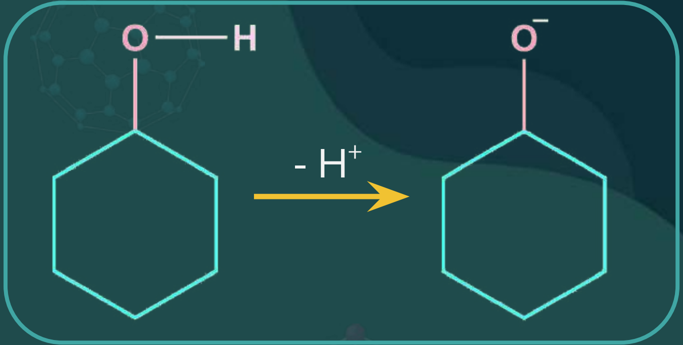
Phenol
$pK_a = 9.89$





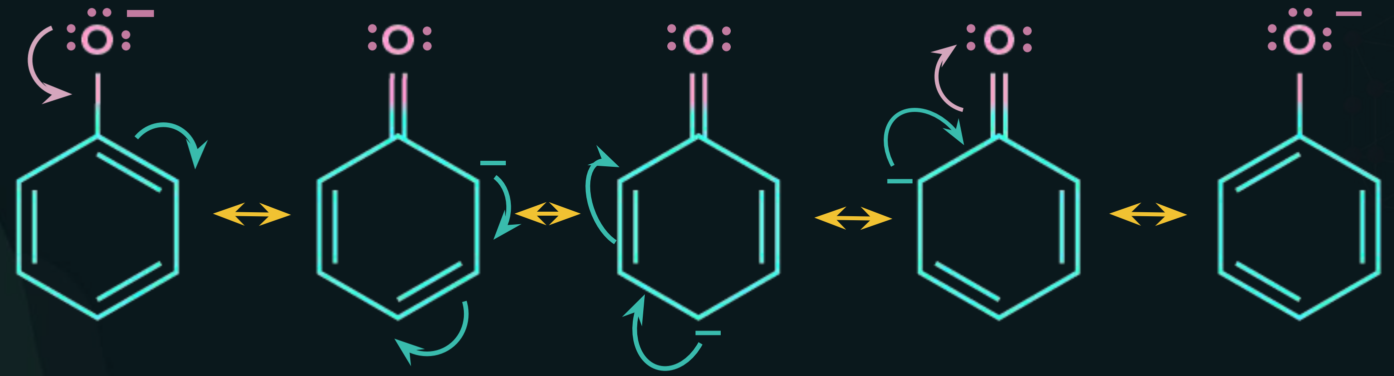
Acidity of Phenol and Alcohols





The hydroxyl group in phenol is directly attached to the **sp^2 hybridised carbon** of benzene ring, that acts as an **electron withdrawing** group because of more 's' character in it and thus, **stabilising** the negative charge of **oxygen** atom.

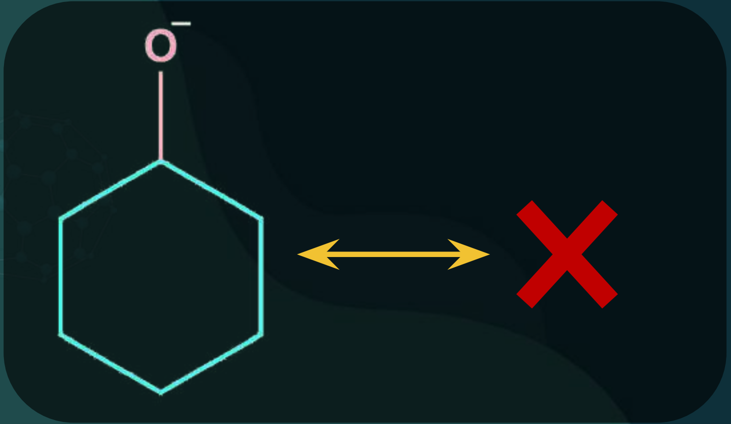
Acidity of Phenol and Alcohols



Phenoxide ion (conjugate base of phenol) is **resonance stabilised**

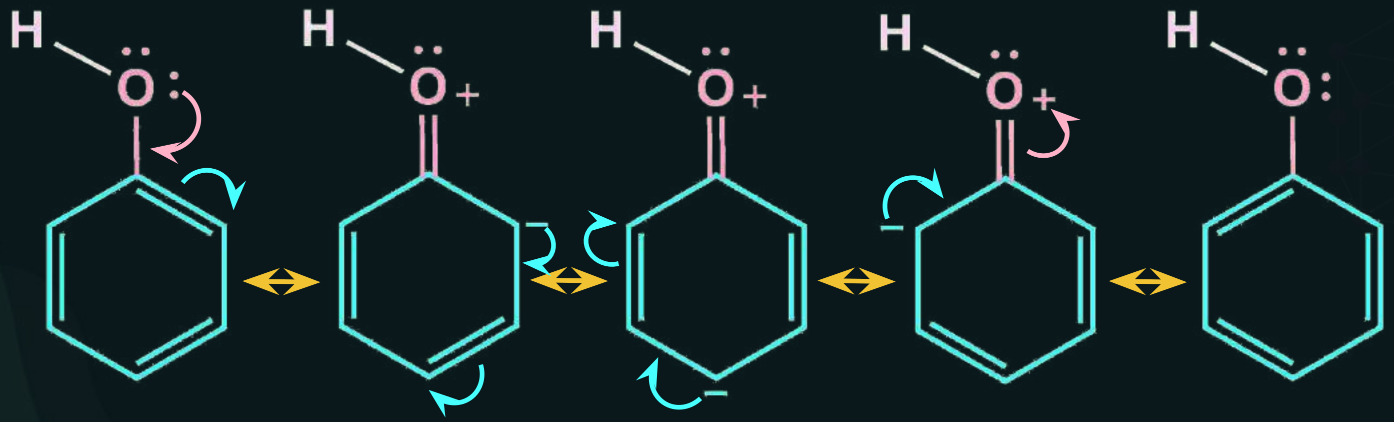
Acidity of Phenol and Alcohols

No stabilisation by resonance



Unlike the structures for phenol, resonance structures for the phenoxide ion **do not involve charge separation**.

Resonance Structures of Phenol



Greater stabilisation of the phenoxide ion (the conjugate base) than of phenol (the acid) has an **acid-strengthening effect**.

Acidity of Phenols

-I, -M groups

Increase acidity of phenol

They effectively **disperse** the -ve charge on phenoxide ion.

+I, +M groups

Decrease acidity of phenol

The order of pK_a values for the following compounds is:

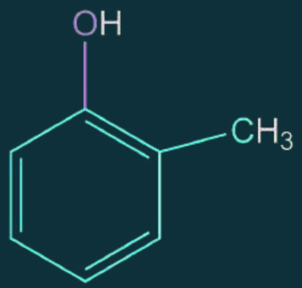
BOARDS

o-Cresol ☐ m-Cresol ☐ Phenol

Solution

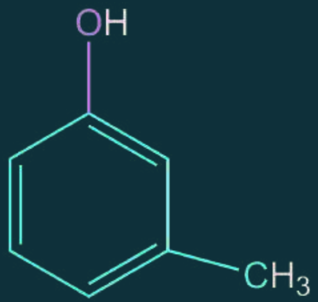
Higher the pK_a lesser the acidic strength of the substance.

$-CH_3$ is an electron donating group (EDG) and exerts an +I and +H effect . In case of o – cresol –OH group is closest to $–CH_3$ group attached to phenol than $–CH_3$ group attached to meta position in m – cresol. So acidity of m – cresol is greater than o – cresol and among the given compounds phenol is the most acidic as no +I or +H group is attached to effect the acidity of phenol.



o - cresol

<



m - cresol

<

Phenol

Order of acidic strength

Therefore order of pK_a is given as :

o-Cresol > m-Cresol > Phenol

The order of pK_a values for the following compounds is:

Ethanol ☐ p-Cresol ☐ m-Cresol

Solution

Higher the pK_a lesser the acidic strength of the substance.

CH_3 is an electron donating group (EDG) and exerts a +I and +H effect . In case of p – cresol $–CH_3$ group exerts +I and +H to $–OH$ group attached to benzene and $–CH_3$ group attached to meta position in m – cresol exerts only +I effect and is more acidic than p - cresol. Ethanol is the least acidic as ethanol has no electron withdrawing benzyl group attached to it.

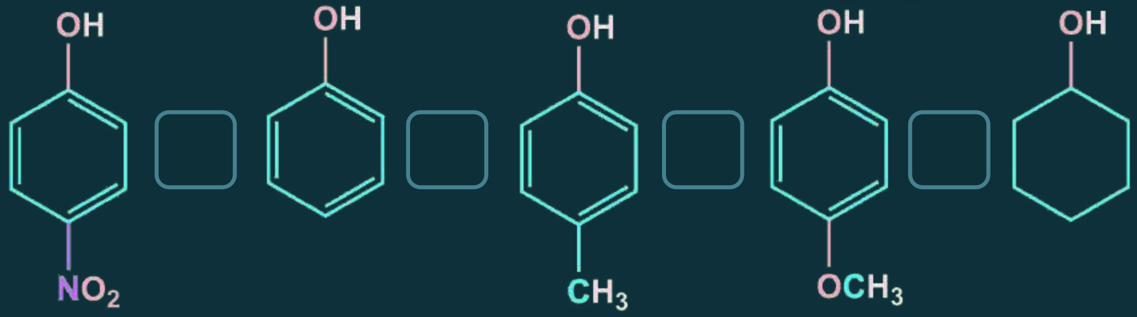
So, order of acidic strength is

Ethanol < p-Cresol < m-Cresol

Therefore, order of pK_a is :

Ethanol > p-Cresol > m-Cresol

The **order of pK_a** values for the following compounds is:

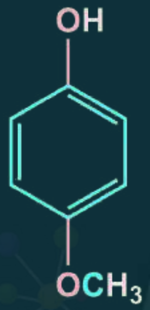


Solution

p – nitrophenol has a $-NO_2$ group which exerts both –I and –R effect on phenol and decreases electron density on –OH group and increases acidic strength of the compound.

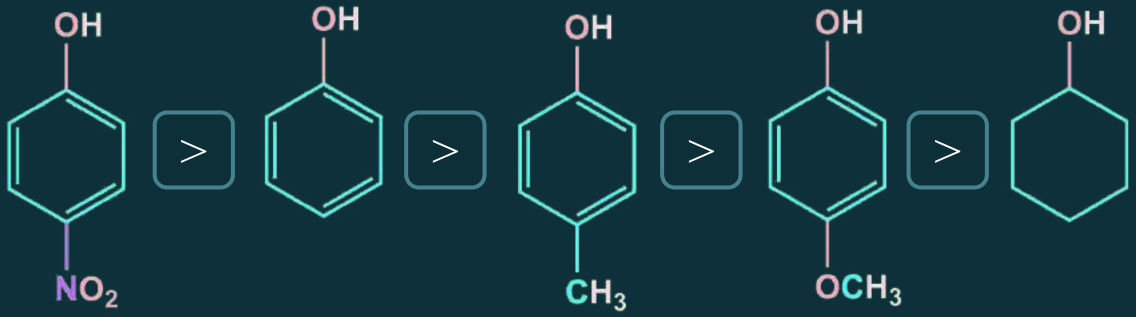
CH_3 is an electron donating group (EDG) and exerts a +I and +H effect . In case of p – cresol –CH_3 group exerts +I and +H to –OH group attached to phenol and decreases acidic strength of phenol.

OCH_3 is an electron donating group (EDG) and exerts a +I and +R effect . In this case –OCH_3 group exerts +I and +R to –OH group more than -CH_3 group attached to phenol and decreases acidic strength of phenol more than -CH_3 group.

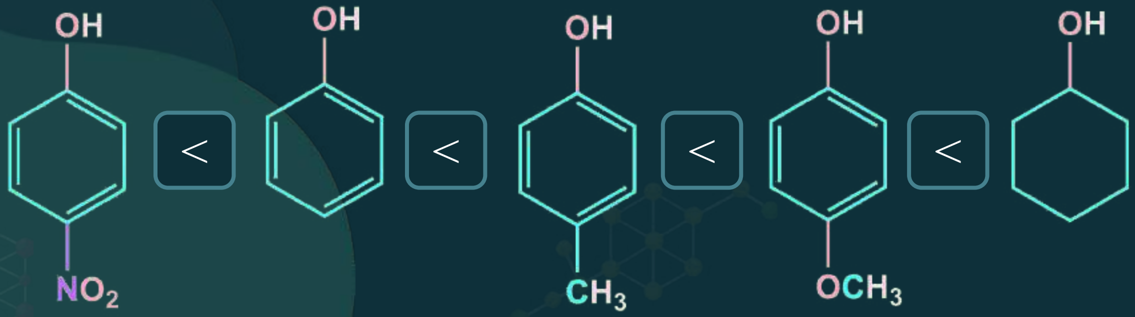


Cyclohexanol is least acidic as there is no benzyl group to decrease electron density on –OH group.

Order of acidic strength:



Therefore, order of pK_a is:

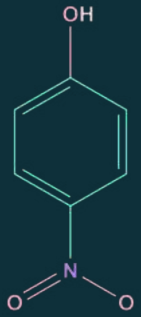


Which one is the **most acidic** compound?

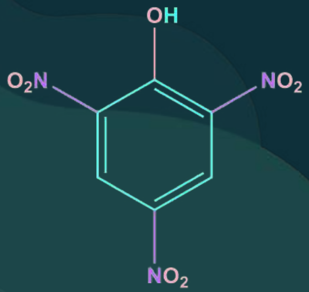
BOARDS

a)

b)



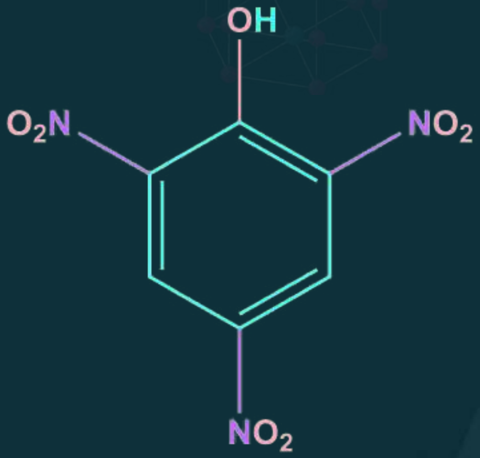
c)



d)

Solution

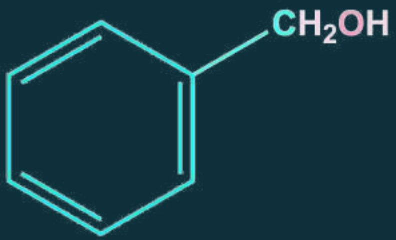
In 2,4,6–trinitrophenol has the highest acidic strength as electron withdrawing group (EDG) is attached on ortho and para positions, so –NO_2 group at 2 , 4 and 6 positions exerts –R and –I effect as well which in turn reduces the electron density on –OH group and has the highest acidic strength among the given compounds.



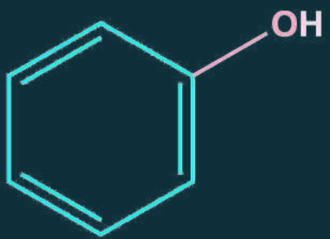
Hence, option (c) is the correct answer.

Which of the following compounds has the **most acidic nature**?

a)

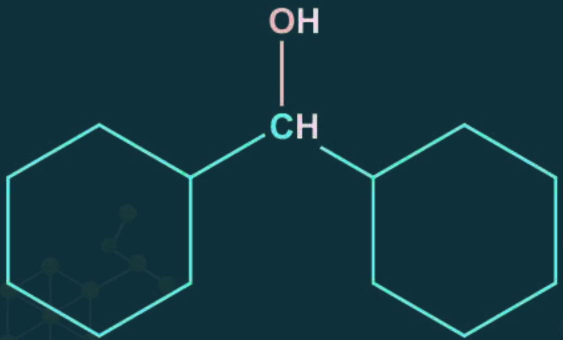


b)

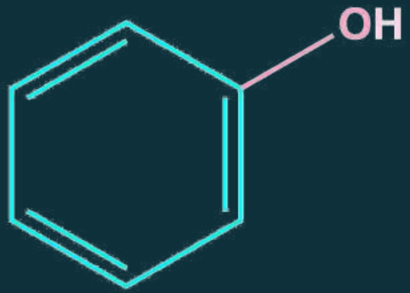


c)

d)



Solution



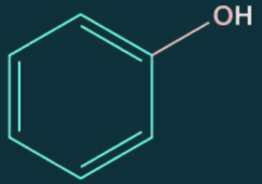
Phenols are more acidic than alcohol as electron withdrawing benzyl group is directly attached to –OH group which stabilizes the phenoxide ion which is a conjugate base formed by release of H^+ ion from phenol.

Hence, option (b) is the correct answer.

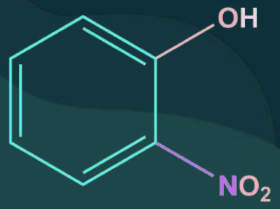
Which one of the following compounds is the **most acidic**?

a) $Cl-H_2C-CH_2-OH$

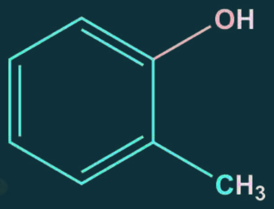
b)



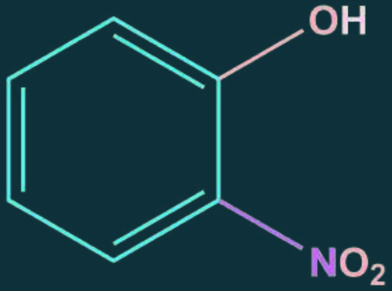
c)



d)



Solution



o–Nitrophenol has the highest acidic strength as electron withdrawing group (EDG) $-NO_2$ is attached at ortho position, so $-NO_2$ group exerts –R and –I effect as well which in turn reduces the electron density on –OH group and has the highest acidic strength among the given compounds.

Hence, option (c) is the correct answer.

Amongst the following four compounds, the **acidity order** is:

BOARDS

(i) Phenol

(ii) Methyl phenol

(iii) m-Nitrophenol

(iv) p-Nitrophenol

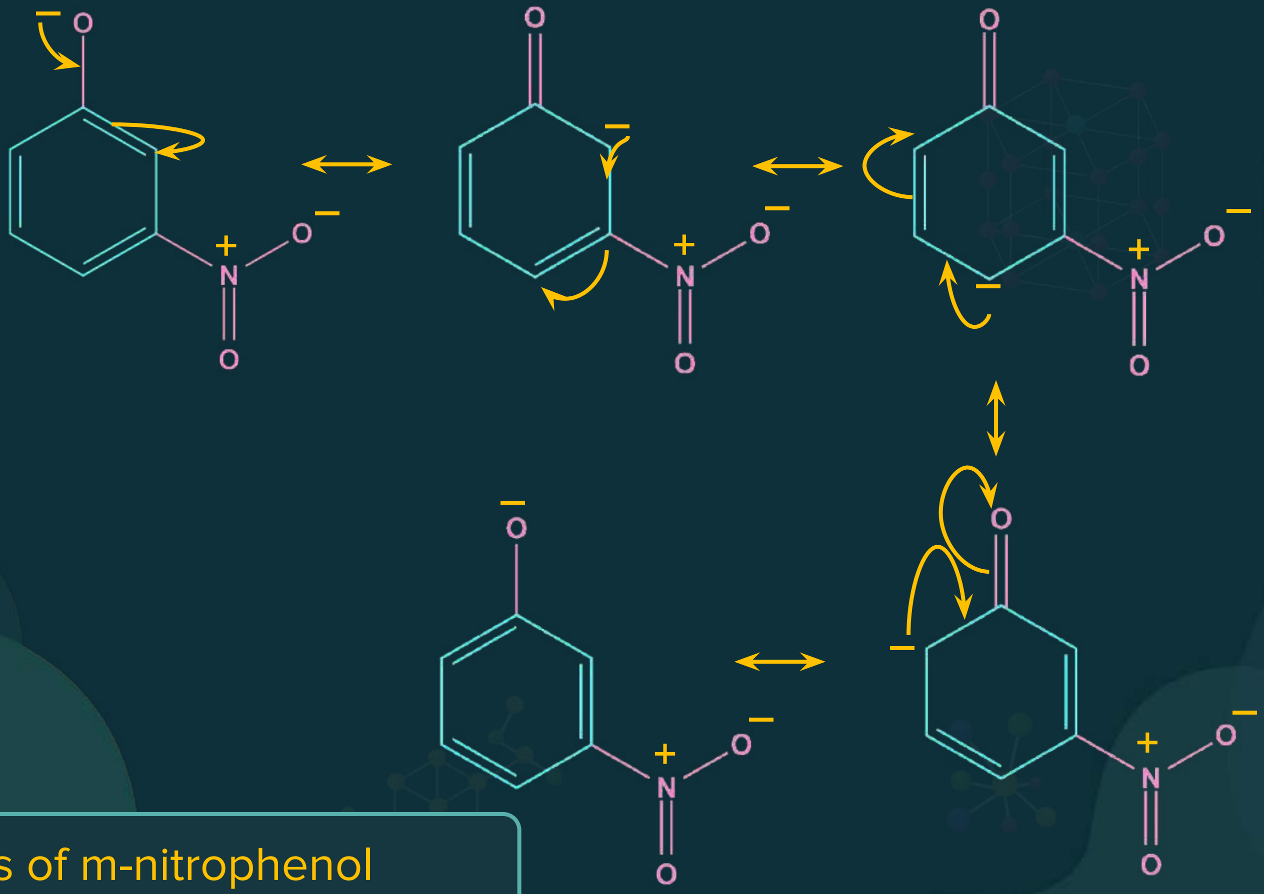
a) (iv) > (iii) > (i) > (ii)

b) (iii) > (iv) > (i) > (ii)

c) (i) > (iv) > (iii) > (ii)

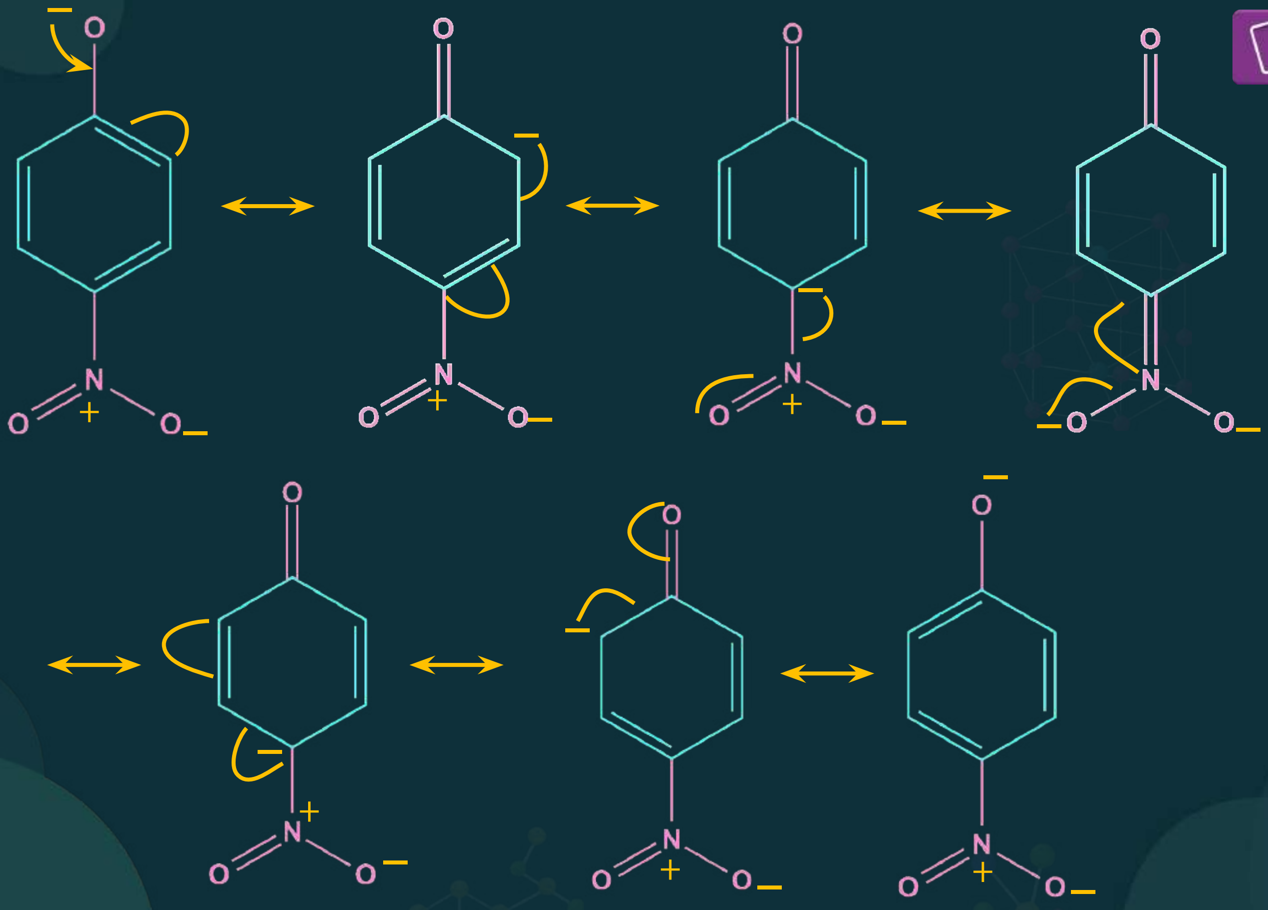
d) (ii) > (i) > (iii) > (iv)

Solution



Resonating structures of m-nitrophenol

In case of m–nitrophenol negative charge is slightly stabilised by –I effect of nitro group but not stabilised by –M effect of nitro group but in p–nitrophenol negative charge is stabilized by –M as well as –I effect of nitro group. So, p–nitrophenol is more acidic than m–nitrophenol.



Resonating structures of p-Nitrophenol

Methyl phenol which is an alcohol is less acidic than phenol, So

Order of acidic strength is:

p–nitrophenol > **m–nitrophenol** > **phenol** > **methyl phenol**

Hence, option (a) is the correct answer.

Which of the following fact(s) explain(s) as to why p-nitrophenol is more acidic than phenol?

BOARDS

(i) –I Effect of nitro group

(ii) Greater resonance effect of p-nitrophenoxy group

(iii) Steric effect of bulky nitro group

a) (i) and (ii)

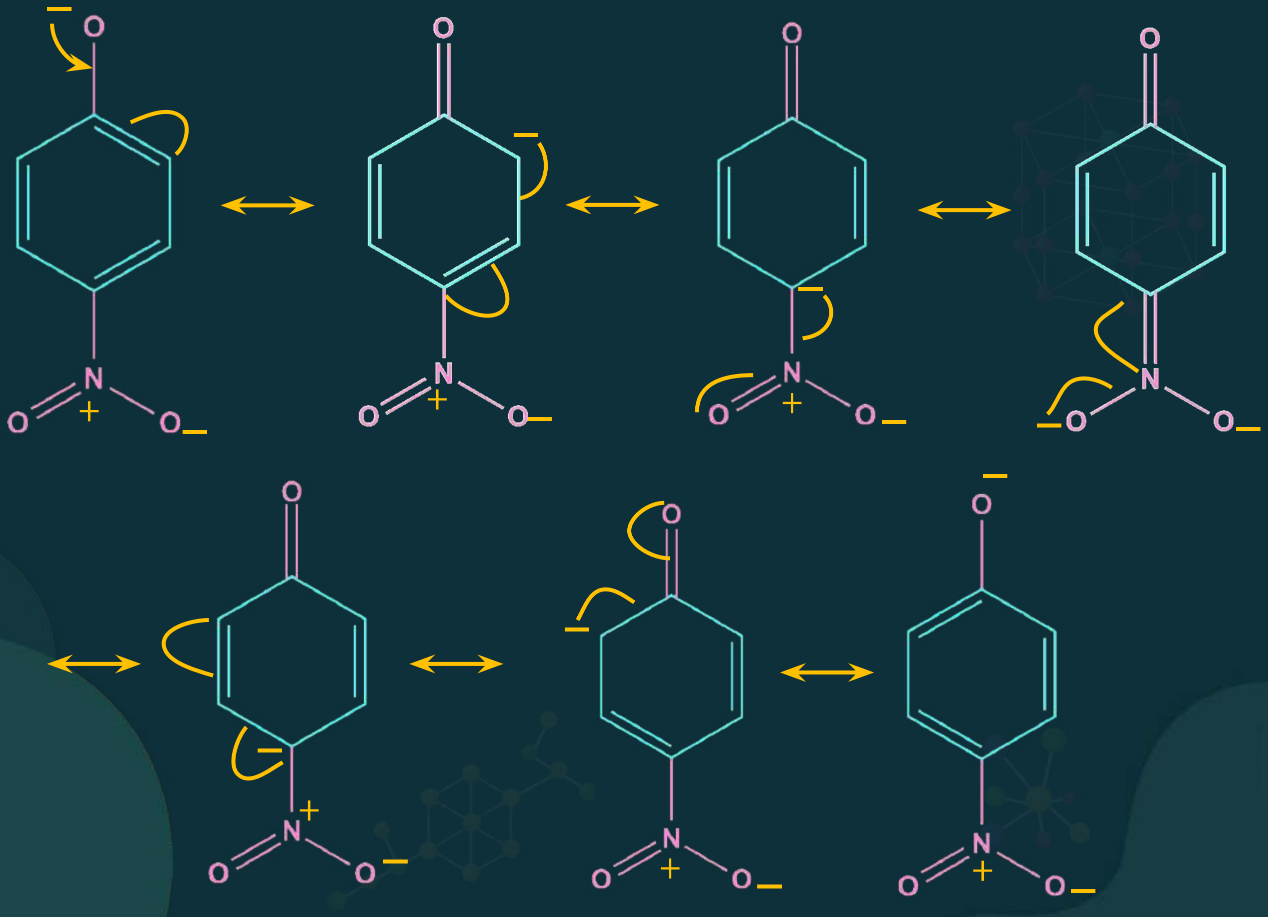
b) (i) and (iii)

c) (ii) and (iii)

d) (ii) alone

Solution

Resonating structures
of p - nitrophenol.



Solution

p–Nitrophenol is more acidic due to –I effect of nitro group and greater resonance effect of p-nitrophenoxy group.
But there is no steric hindrance in the molecule as molecule is symmetric and OH and NO_2 groups are located opposite to each other

Hence, option (a) is the correct answer.

Given are cyclohexanol (I), acetic acid (II), 2,4,6-trinitrophenol (III) and phenol (IV). In these, the order of **decreasing acidic character** will be:

BOARDS

a) III > II > IV > I

c) II > III > IV > I

b) II > III > I > IV

d) III > IV > II > I

Solution

Cyclohexanol is least acidic as alcohols are weaker acids than phenols and carboxylic acid. 2,4,6-trinitrophenol is more acidic than acetic acid and phenols because phenoxide ion conjugate base is stabilized by delocalization of electrons by three –M groups attached to it as $-NO_2$ group. So, order of acidic strength is :

III > II > IV > I

Therefore, option (a) is the correct answer.

$ClCH_2CH_2OH$ is stronger acid than CH_3CH_2OH because of:

BOARDS

a) -I effect of Cl increases negative charge on O atom of alcohol.

b) -I effect of Cl disperses negative charge on O atom of alcohol to produce more stable cation.

c) -I effect of Cl disperses negative charge on O atom of alcohol to produce more stable anion.

d) None of these

Solution

$ClCH_2CH_2OH$ is more stronger acid than CH_3CH_2OH as Cl stabilizes the alkoxide ion formed as a conjugate base by the removal of H^+ ion from the alcohol.

-I effect of Cl disperses negative charge on O atom of alcohol to produce more stable anion.

Therefore, option (c) is the correct answer.

Assertion: Phenol is a strong acid than ethanol.
Reason: Groups with +M effect decreases acidity at p-position.

BOARDS

a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

c) If the Assertion is correct but Reason is incorrect.

d) If both the Assertion and Reason are incorrect

Solution

For assertion phenols are more acidic than alcohols as in phenols OH group is attached to benzyl group which is electron withdrawing in nature and stabilizes the conjugate base formed.

Reason is also correct that groups with +M effect decreases acidity at para position but for alcohols this is not the correct as alcohols do not show conjugation.

Both assertion and reason are correct but reason is not a correct explanation of the assertion.

Therefore, option (b) is the correct answer.

Increasing order of acid strength among p-methoxyphenol, p-methylphenol and p-nitrophenol is:

BOARDS

a) p-Nitrophenol, p-Methoxyphenol, p-Methylphenol

b) p-Methylphenol, p-Methoxyphenol, p-Nitrophenol

c) p-Nitrophenol, p-Methylphenol, p-Methoxyphenol

d) p-Methoxyphenol, p-Methylphenol, p-Nitrophenol

Solution

Methoxy group is more electron releasing than methyl group and hence destabilizes negatively charged phenoxide ion more than methyl group, so p–methylphenol is more acidic than p–methoxyphenol.

In case of p–nitrophenol –M group NO_2 stabilizes the phenoxide ion and increases the acidic strength of p–nitrophenol.

Therefore, option (d) is the correct answer.

The **order of pK_a** values for the following compounds is:

BOARDS

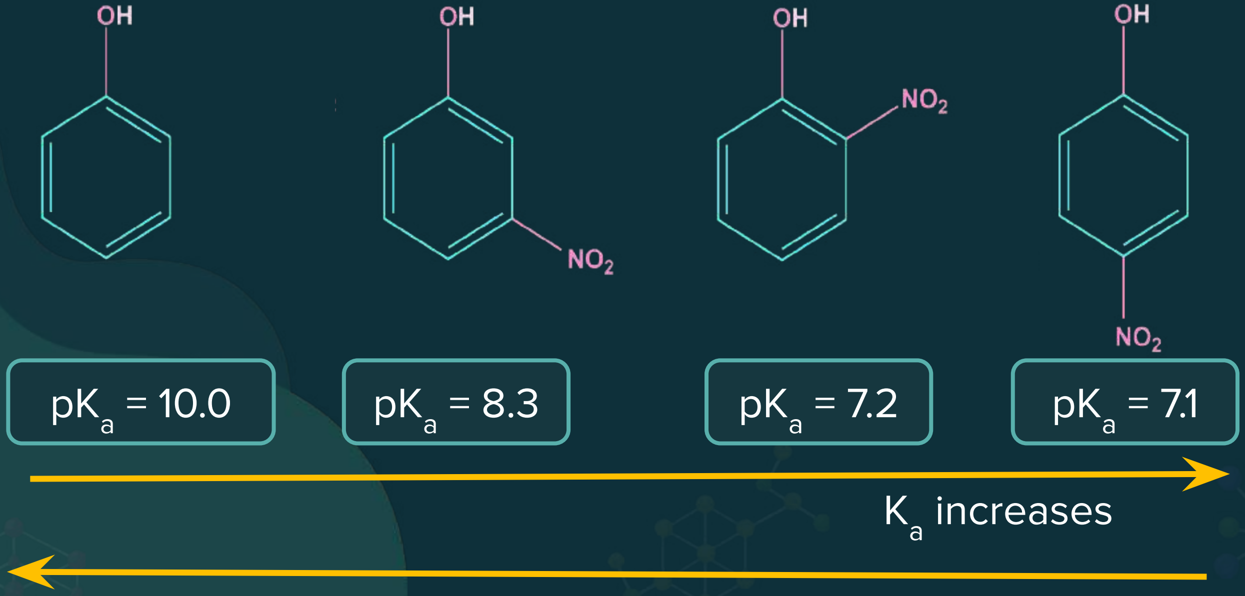
m-Nitrophenol ☐ o-Nitrophenol ☐ p-Nitrophenol

Solution

Electron withdrawing groups, NO_2 stabilizes the phenoxide ion more by dispersing the negative charge relative to phenol (i.e., proton release become easy) and thus increases the acidic strength of phenols. **Higher the pK_a lesser the acidic strength of the substance.**

But still o-nitrophenol is less acidic than p-nitrophenol as there exists **intramolecular hydrogen bonding** in o-nitrophenol this hinders the cleavage of OH bond in o-nitrophenol and consequently decreases the acidic strength.

So, the order is:



pK_a = 10.0

pK_a = 8.3

pK_a = 7.2

pK_a = 7.1

K_a increases

pK_a increases

Esterification

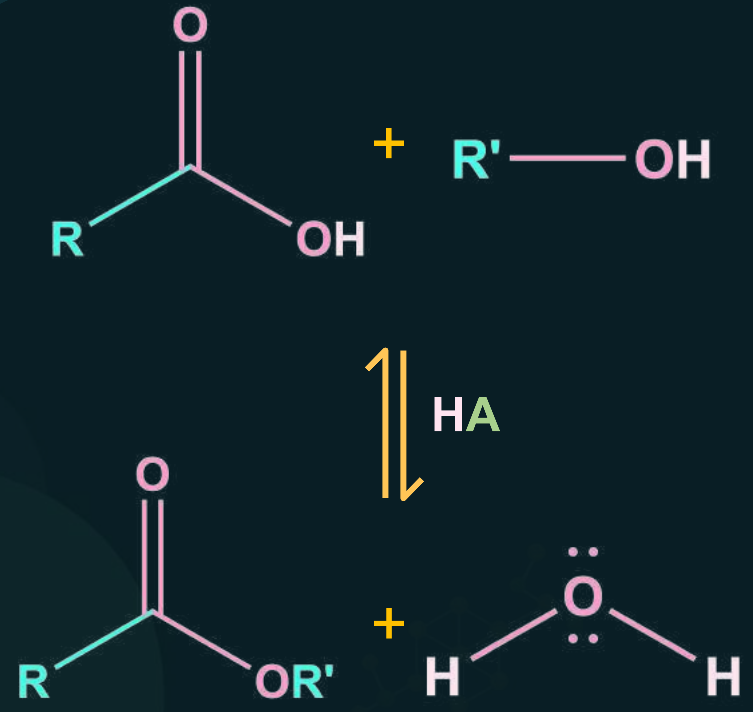
Esterification

- From carboxylic acid
- From acyl chloride
- From carboxylic acid anhydride

Carboxylic acid reacts with alcohols to form esters through a **condensation reaction** known as **esterification.**

Esterification

General reaction



Acid-catalysed Esterification

Esterification proceeds **very slowly** in the absence of strong acids.

When an acid and an alcohol are reacted with a small amount of **conc. H_2SO_4 or HCl,** they reach equilibrium within few hours.

The position of equilibrium controls the **amount** of the ester formed.

The use of an **excess** of either the carboxylic acid or the alcohol **increases the yield** based on the limiting reagent.

Acid-catalysed Esterification

The **yield** of an esterification reaction can also be **increased** by **removing water** from the reaction mixture as it is formed.

Esters from Acyl Chlorides

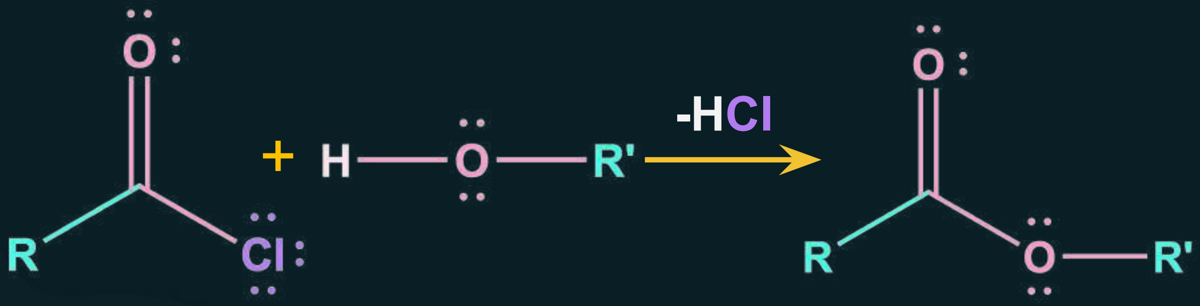
The **yield** of an esterification reaction can also be **increased** by **removing water** from the reaction mixture as it is formed.

The reaction of **acyl chlorides with alcohols** is one of the best ways to synthesise an ester.

This reaction does **not** require an **acid catalyst.**

Esters from Acyl Chlorides

General reaction

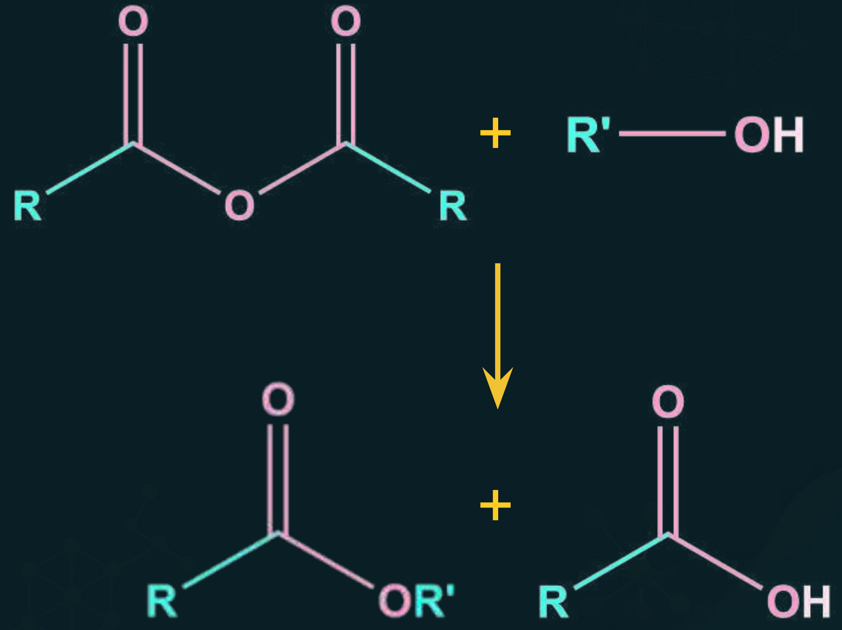


Pyridine is often added to the reaction mixture to react with the HCl that forms.

Esters from Carboxylic Acid Anhydride

Carboxylic acid anhydride reacts with **alcohols** to form esters in the absence of an acid catalyst.

General reaction



Esters from Acyl Chloride or Anhydride

Ester synthesis is often accomplished **best** by the reaction of an alcohol with an **acyl chloride** or **acid anhydride**.

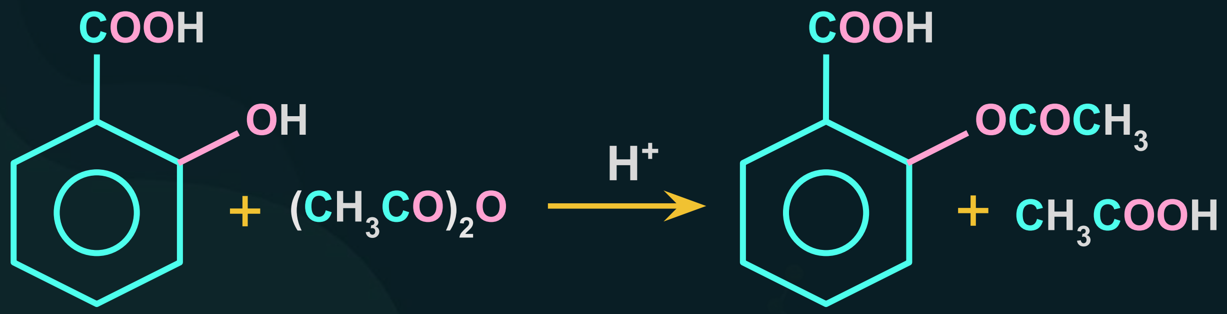
These reagents **avoid** the use of a strong acid, as is needed for acid-catalysed esterification.

↓

A strong acid may cause **side reactions** depending on what other functional groups are present.

Application

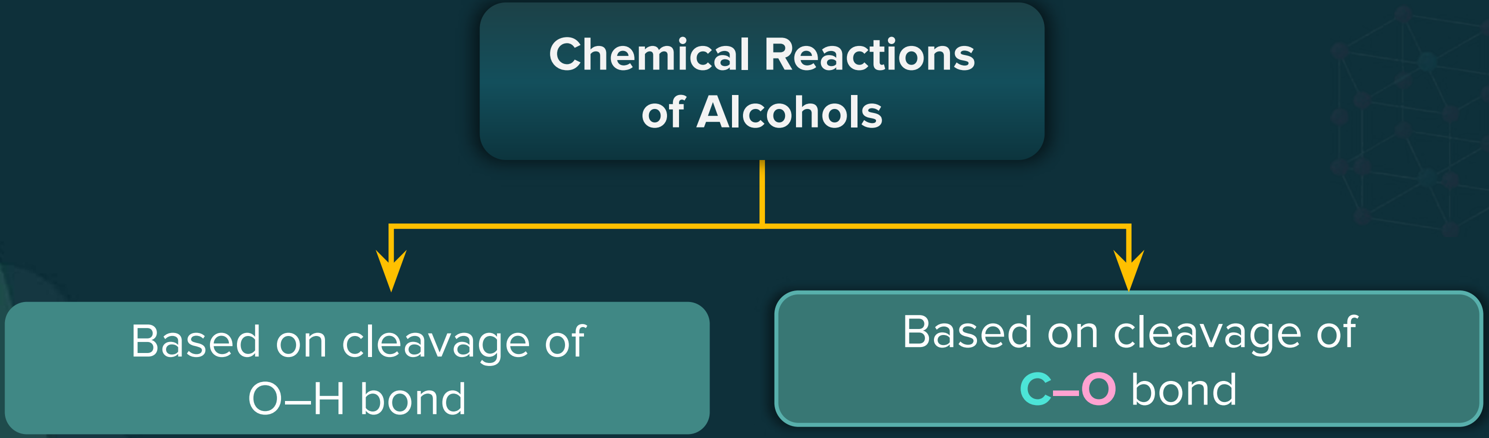
Reaction of salicylic acid with acetic anhydride yields the widely used **pain reliever aspirin.**



Salicylic acid

Acetylsalicylic acid (Aspirin)

Chemical Reactions of Alcohols



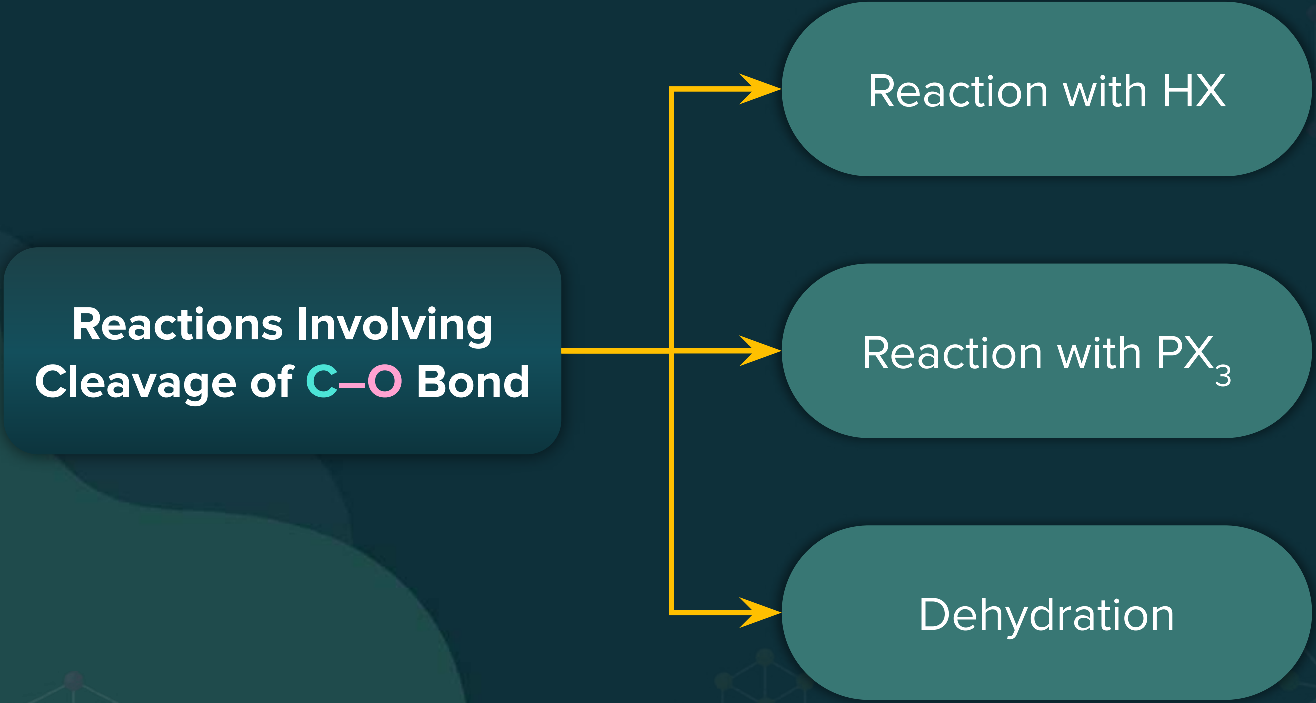
Chemical Reactions of Alcohols

Based on cleavage of O–H bond

Based on cleavage of C–O bond

$$H-\underset{R}{\overset{H}{C}}-O-H \longrightarrow H-\underset{R}{\overset{H}{C}}- \; + \; -O-H$$

Reactions Involving Cleavage of C-O Bond



Reactions Involving Cleavage of C–O Bond

- Reaction with HX
- Reaction with PX_3
- Dehydration

Reactions Involving Cleavage of C-O Bond

Reaction with hydrogen halide

When alcohols react with a hydrogen halide, a **substitution** takes place producing an alkyl halide and water.

$$R{-}OH + HX \longrightarrow R{-}X + H_2O$$

Order of reactivity of alcohols

3° Alcohol > 2° Alcohol > 1° Alcohol

Reactions Involving Cleavage of C-O Bond

Order of reactivity of HX

HI > HBr > HCl

HF is generally **unreactive**.

The **reactivity of halogen acid (HX)** can be explained on the basis of bond dissociation energy which is least for HI.

Test for Alcohols

Lucas Test

Primary, secondary, or tertiary alcohol can be determined by taking advantage of the **relative rates** at which the three classes of alcohols react with conc. HCl/ $ZnCl_2$.

Lucas reagent **Conc. HCl/ Any. $ZnCl_2$**

The Lucas reagent gives **white turbidity** or cloudiness with alcohols (-OH groups attached with **sp^3** hybridised carbon).

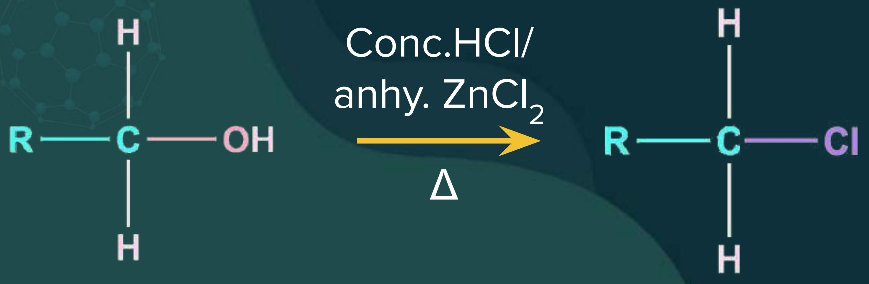
- If alcohol reacts with concentrated HCl in the presence of anhydrous $ZnCl_2$, alkyl halide and water is formed. The general chemical reaction is given as;

$$\textbf{R-OH + Conc. HCl/ ZnCl}_2 \rightarrow \textbf{R-X + H}_2\textbf{O}$$

Lucas Test

1° alcohol

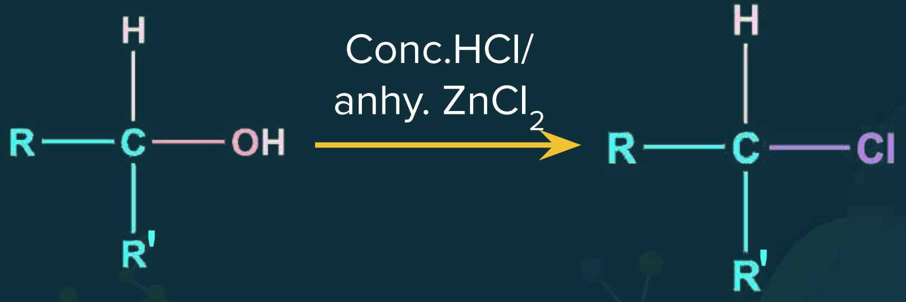
- At room temperature, Primary alcohol does not turbid or cloudy solution with Lucas reagent but on heating the chemical reaction will proceeds as:



$$R-\underset{H}{\overset{H}{C}}-OH \xrightarrow[\Delta]{\text{Conc.HCl/ anhy. }ZnCl_2} R-\underset{H}{\overset{H}{C}}-Cl$$

2° alcohol

- At room temperature, secondary alcohol gives turbidity or cloudy solution with Lucas reagent after 5 minutes.

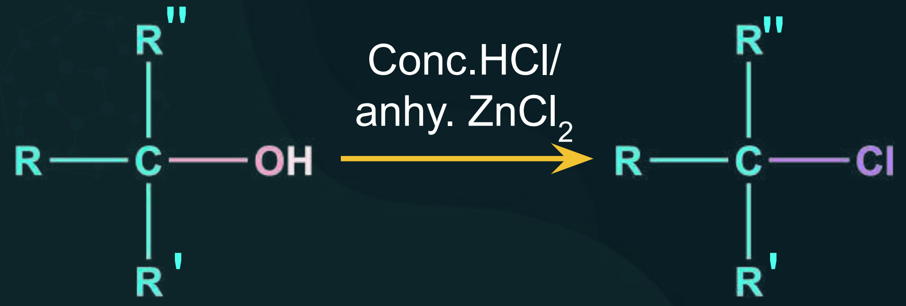


$$R-\underset{R'}{\overset{H}{C}}-OH \xrightarrow{\text{Conc.HCl/ anhy. }ZnCl_2} R-\underset{R'}{\overset{H}{C}}-Cl$$

Lucas Test

3° alcohol

Gives turbidity immediately



$$R-\underset{R'}{\overset{R''}{C}}-OH \xrightarrow[\text{anhy. }ZnCl_2]{\text{Conc.}HCl/} R-\underset{R'}{\overset{R''}{C}}-Cl$$

If the hydroxyl carbon only has a single R group, it is known as primary alcohol. If it has two R groups, it is a secondary alcohol, and if it has three R groups, it is a tertiary alcohol.

Phenols do not give Lucas test.

Reactions Involving Cleavage of C-O Bond

Reaction with Phosphorus Trihalide

Alcohols are converted into **alkyl halides** by reaction with phosphorus trihalides.

$$3R\text{—}OH + PX_3 \longrightarrow 3R\text{—}X + H_3PO_3$$

$PX_3 = PCl_3, PBr_3, PI_3$

Example:

$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$

Reactions Involving Cleavage of C-O Bond

Dehydration of alcohol

Dehydration requires an **acid catalyst** to protonate the hydroxyl group of the alcohol and convert it to a **good leaving group.**

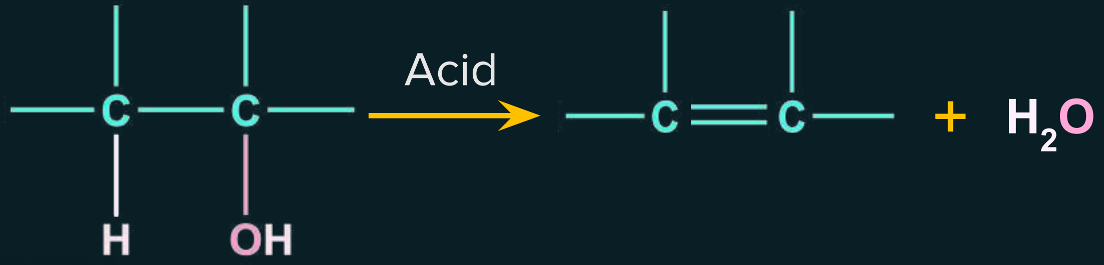
Loss of water, followed by loss of proton, gives **alkene**.

Reagents

1. H_3PO_4 / Δ
2. Conc. H_2SO_4 / Δ

Dehydration reaction of alcohol

General reaction



$$-\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{OH}{|}}{\overset{|}{C}}- \xrightarrow{\text{Acid}} -\overset{|}{C}=\overset{|}{C}- + H_2O$$

Dehydration of alcohol preferably involves the formation of trans alkene.

Dehydration reaction of alcohol

Mechanism

Dehydration of alcohol to form alkene follows **E1 mechanism.**

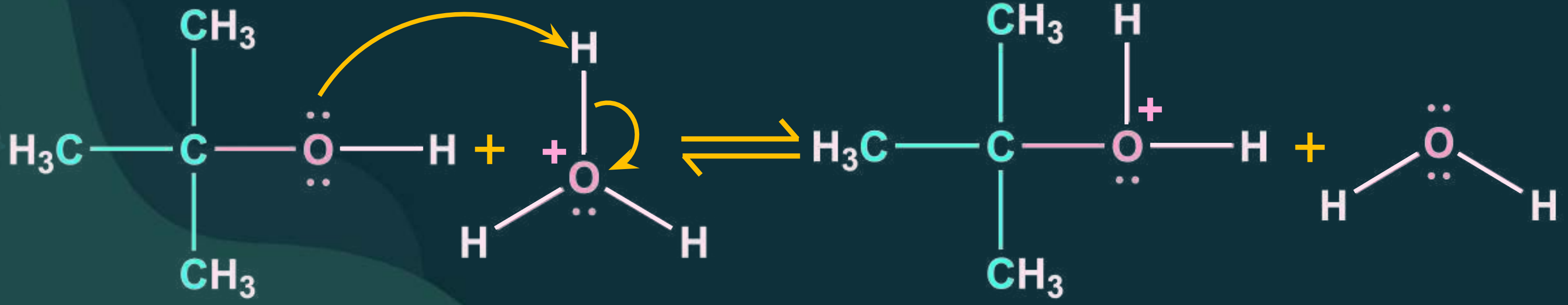
Step 1 Protonation of alcohol

Step 2 Formation of carbocation

Step 3 Deprotonation

Dehydration reaction of alcohol

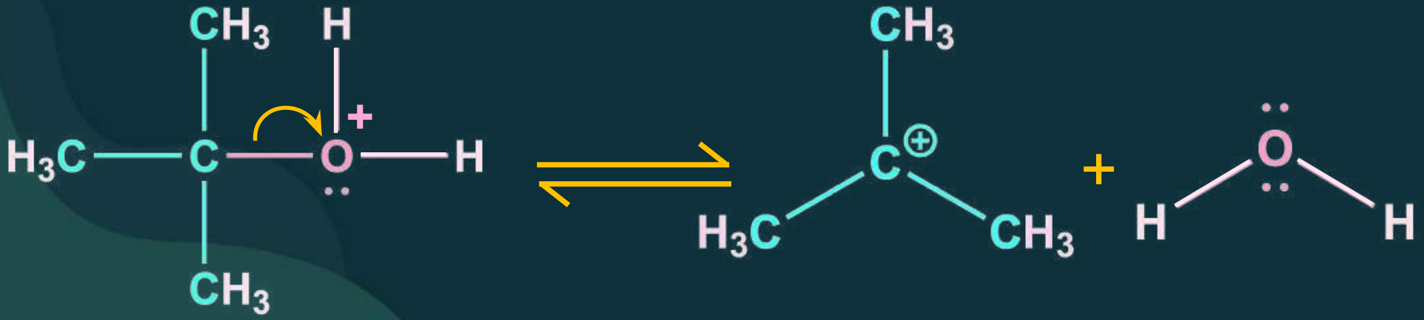
Step 1 Protonation of alcohol



Dehydration reaction of alcohol

Step 2

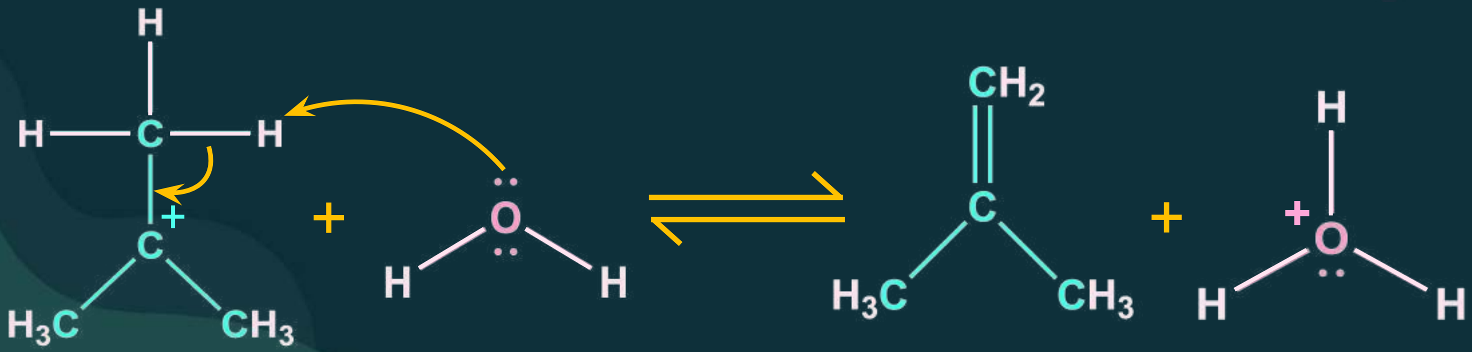
Formation of carbocation



Dehydration reaction of alcohol

Step 3

Deprotonation



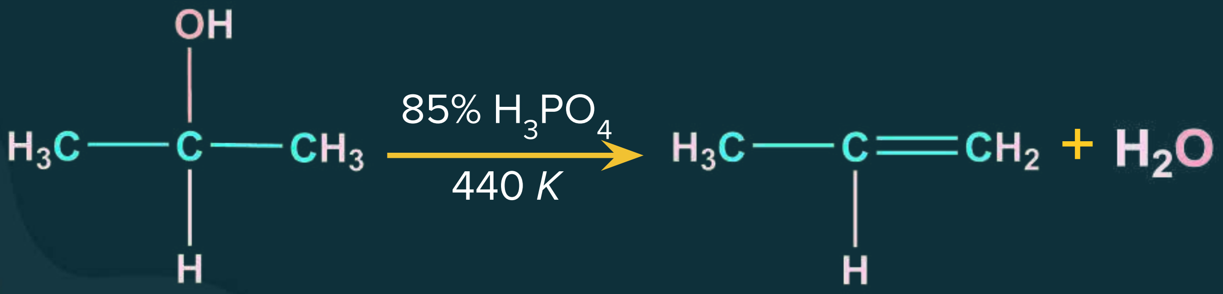
Order of reactivity of alcohols

3° Alcohol > 2° Alcohol > 1° Alcohol

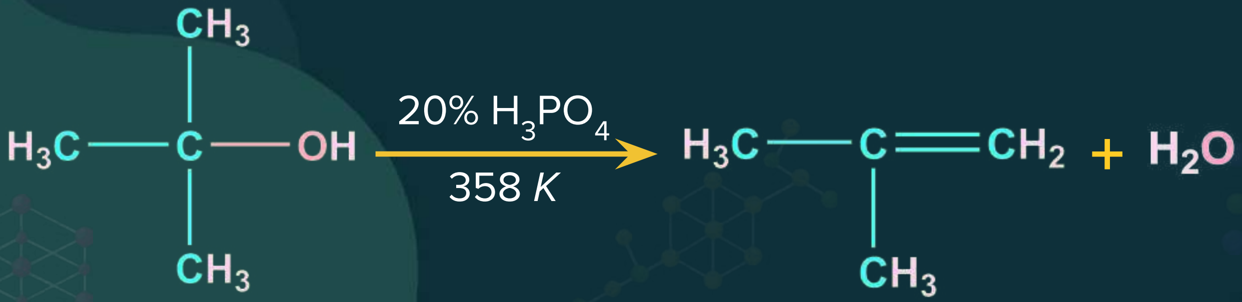
Dehydration reaction of alcohol

Examples:

$$C_2H_5OH \xrightarrow[443\ K]{\text{Conc. } H_2SO_4} H_2C{=}CH_2 + H_2O$$



$$H_3C-\overset{OH}{\underset{H}{C}}-CH_3 \xrightarrow[440\ K]{85\%\ H_3PO_4} H_3C-\underset{H}{C}{=}CH_2 + H_2O$$

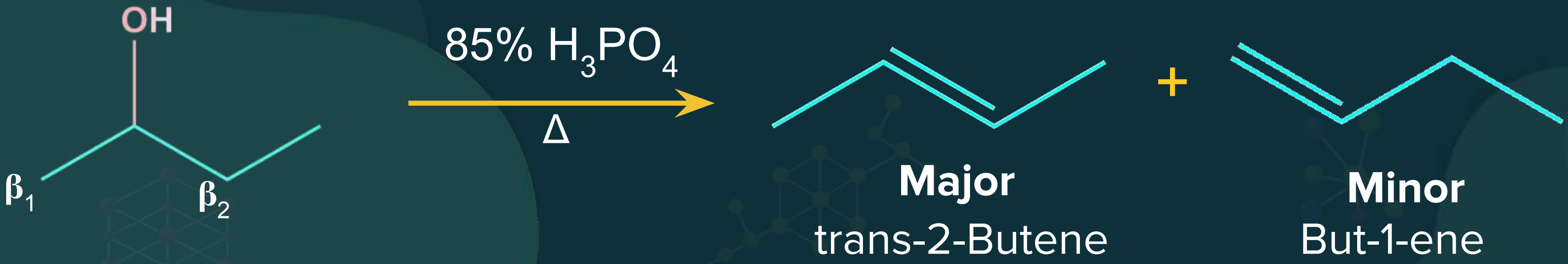


$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow[358\ K]{20\%\ H_3PO_4} H_3C-\underset{CH_3}{C}{=}CH_2 + H_2O$$

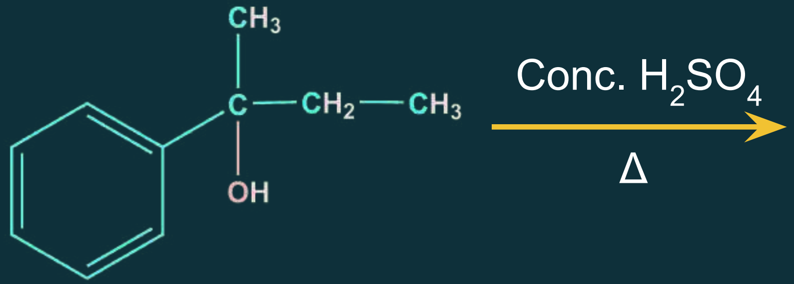
Identify the products in the given reaction.

Solution

This reaction involves the removal of $\boldsymbol{\beta}_2$ hydrogen to give trans-2-butene as a major product and removal of $\boldsymbol{\beta}_1$ hydrogen to give but-1-ene as minor product.

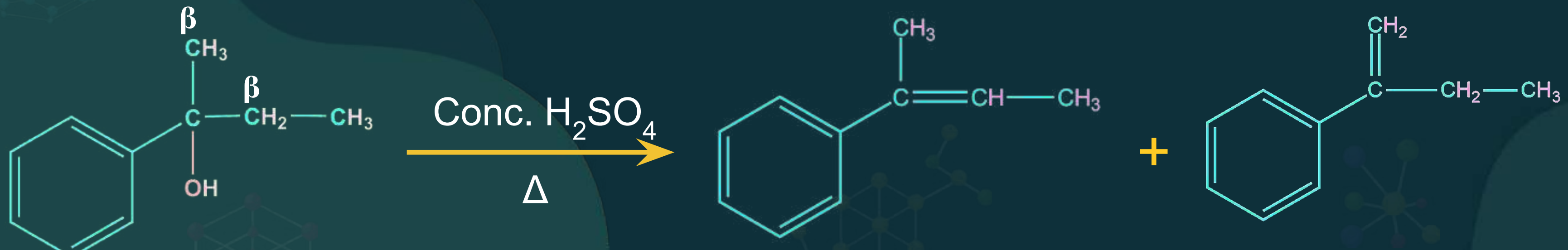


Identify the products in the given reaction.



Solution

Since there are two types of beta hydrogen, hence 2 alkenes are possible.



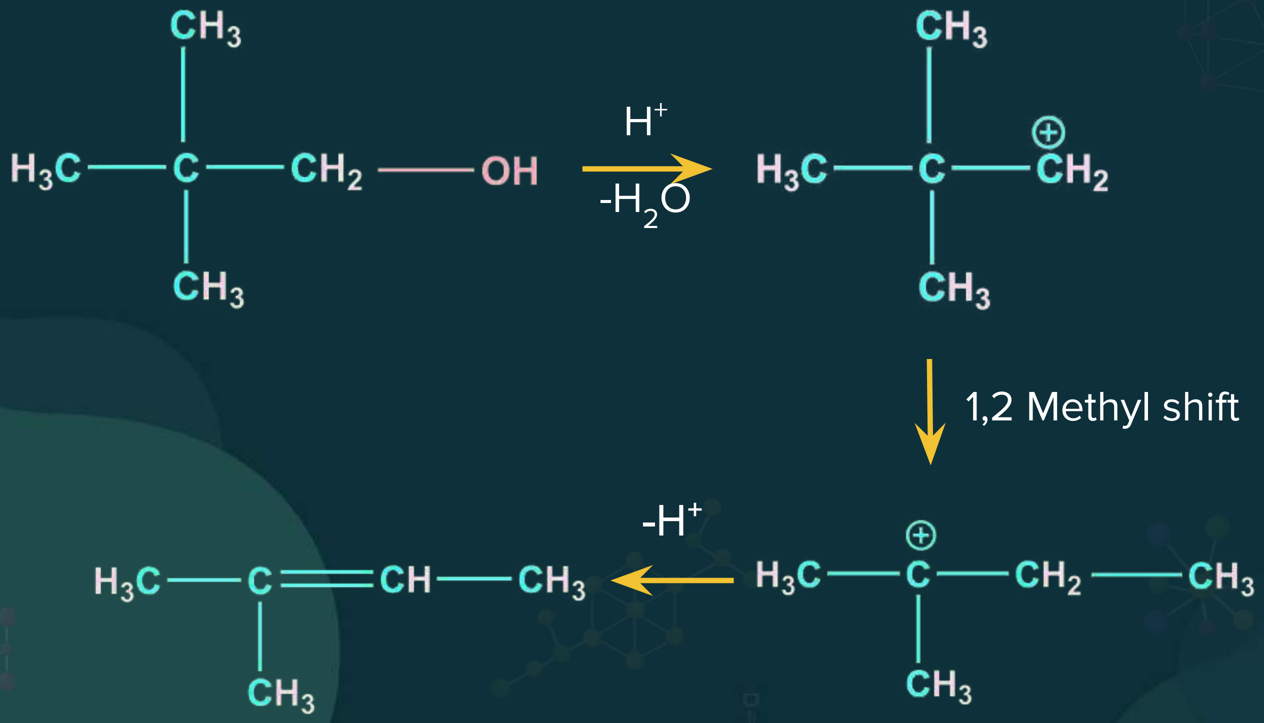
Major product

Minor product

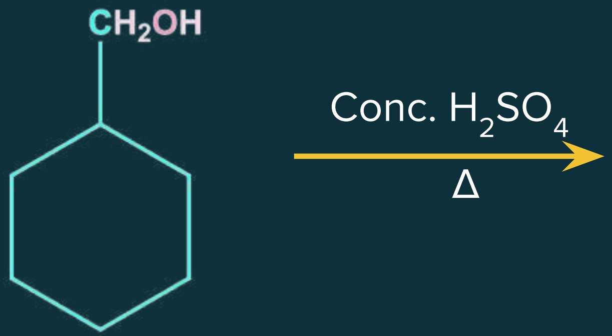
Dehydration reaction of alcohol

Is **rearrangement** also possible for the carbocation formed?

Examples:

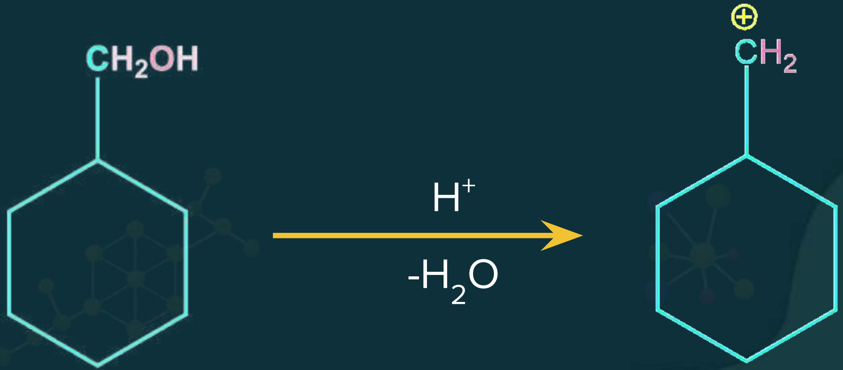


Major product formed in the following reaction is:

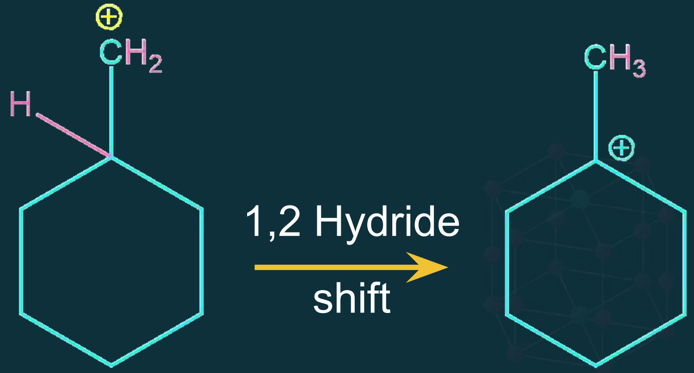


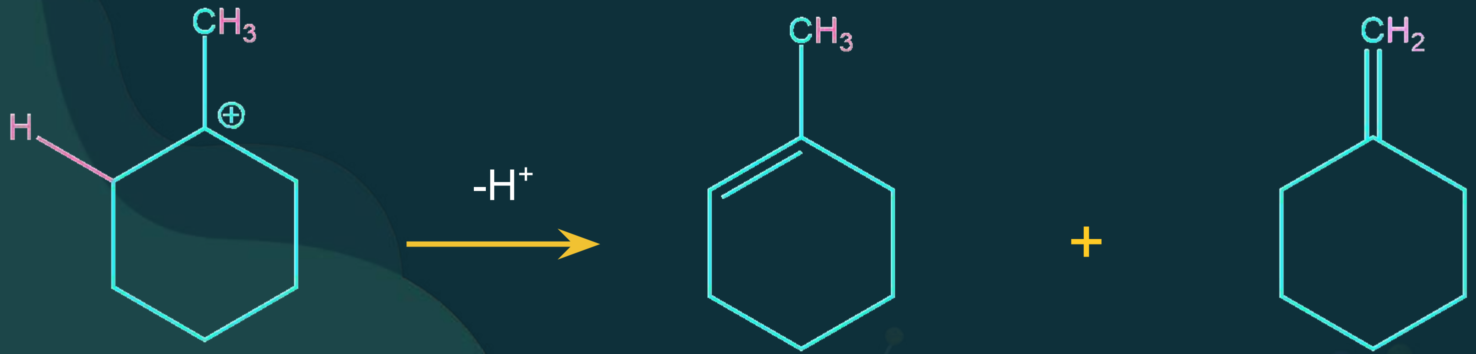
Solution

Here the first step involves the formation of carbocation Cyclohexylmethylium.



Since the carbocation form is primary, a hydride shift takes place and formation of methylcyclohexan-1-ylium takes place. Now methylcyclohexan-1-ylium has two beta carbon hence 2 alkenes can be formed.

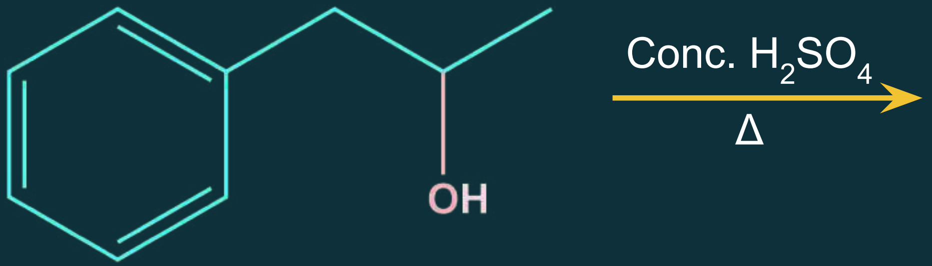




Methylene cyclohexane Methylenecyclohex-1-ene

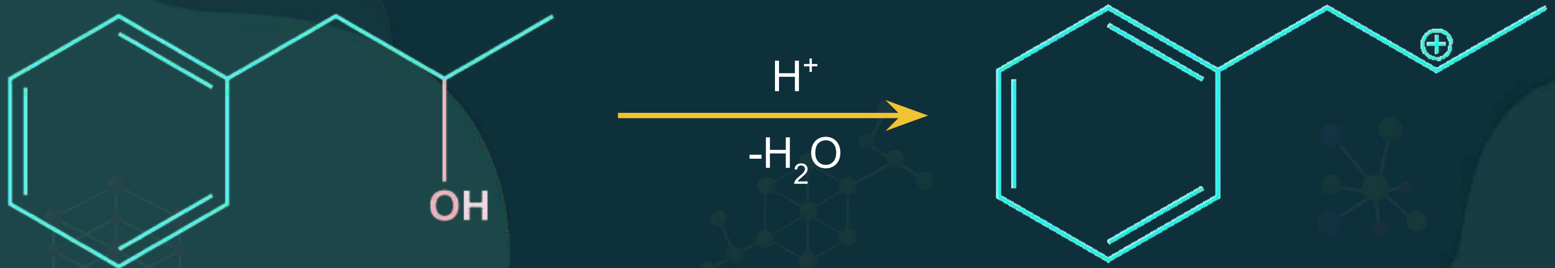
Since, Methylcyclohex-1-ene is more substituted alkene hence the major product.

Major product formed in the following reaction is:

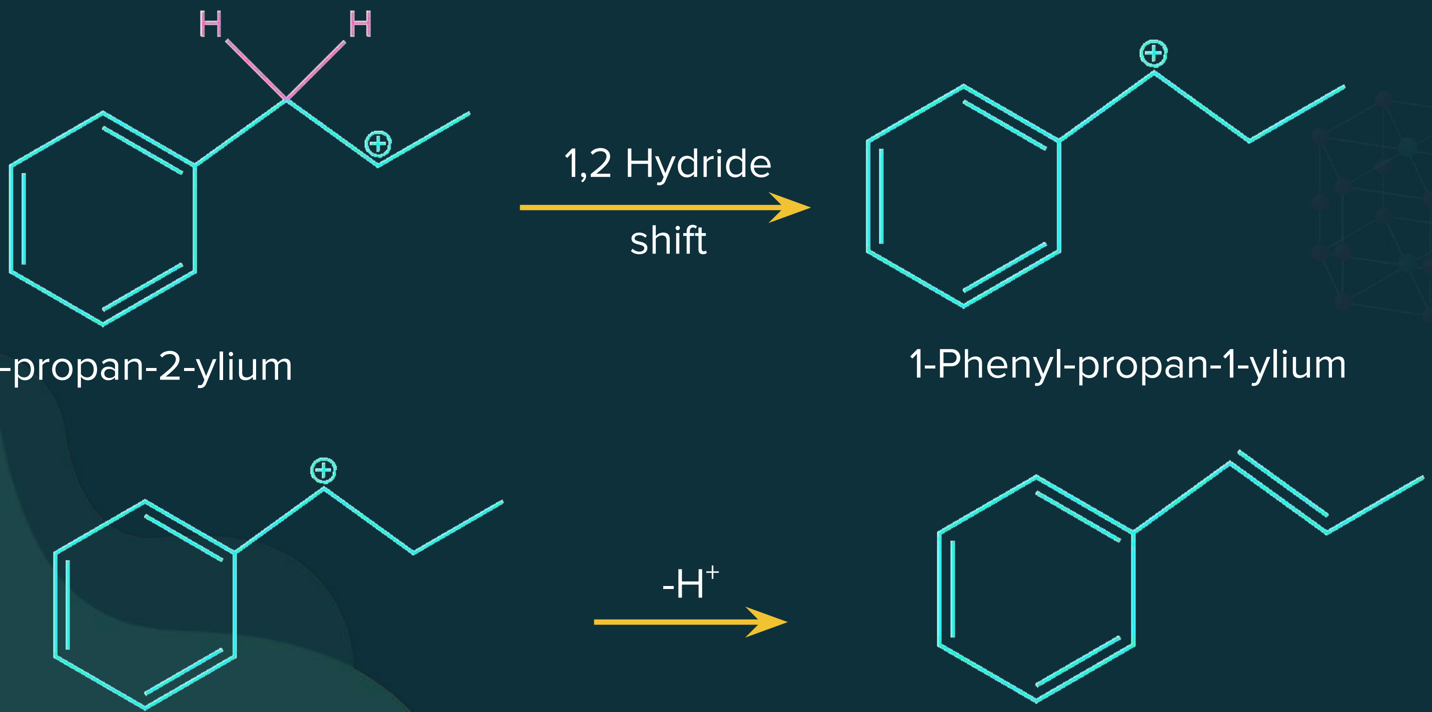


Solution

Here the first step involves the formation of carbocation; 1-phenyl-propan-2-ylium.



1-Phenyl-propan-2-ylium.



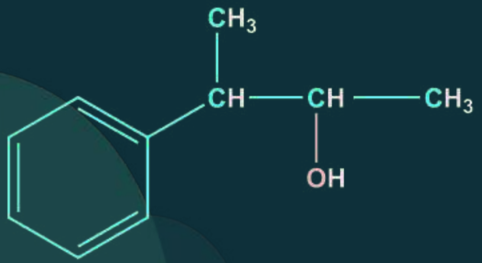
1-Phenyl-propan-2-ylium

1-Phenyl-propan-1-ylium

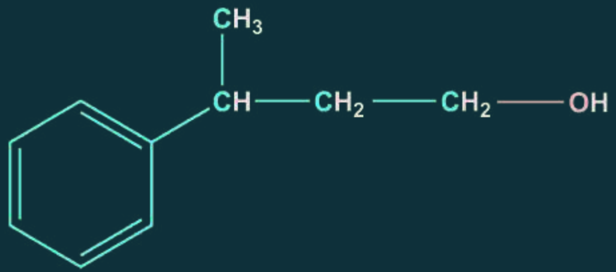
1-Phenyl-propan-1-ylium

Prop-1-en-1-ylbenzene

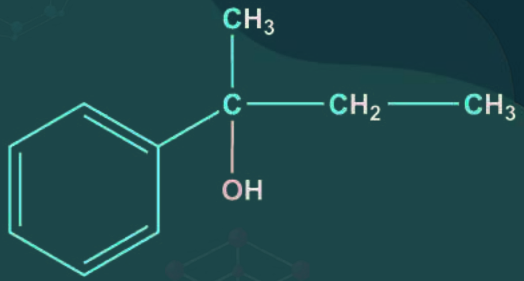
The relative rate of acid catalysed dehydration of following alcohols would be:



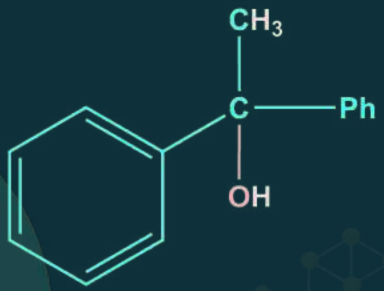
I



II



III



IV

a) III > I > IV > II

b) III > IV > I > II

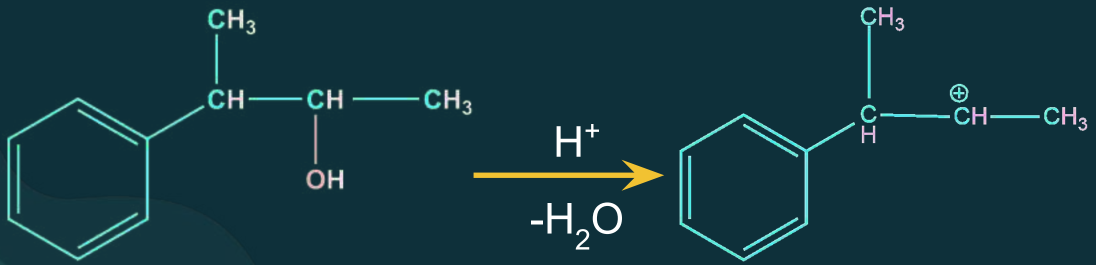
c) I > III > IV > II

d) IV > III > I > II

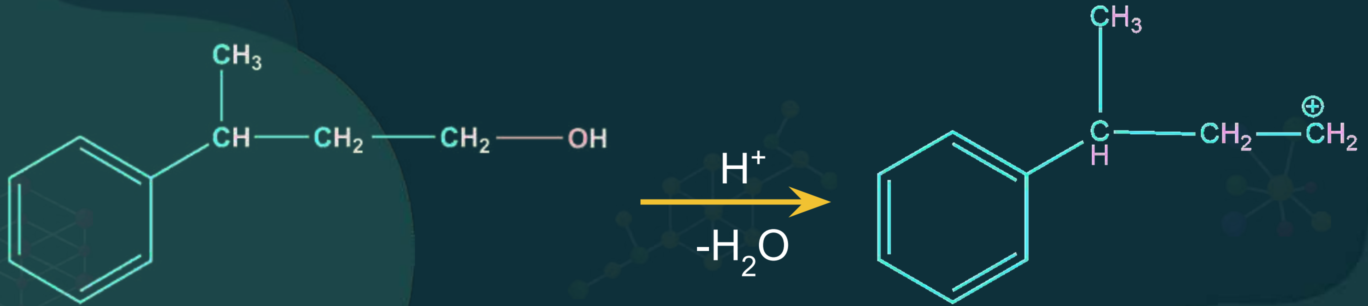
Solution

Rate of acid catalysed dehydration of alcohols depends upon stability of carbocation formed during the reaction. So stable the carbocation formed, higher will be rate.

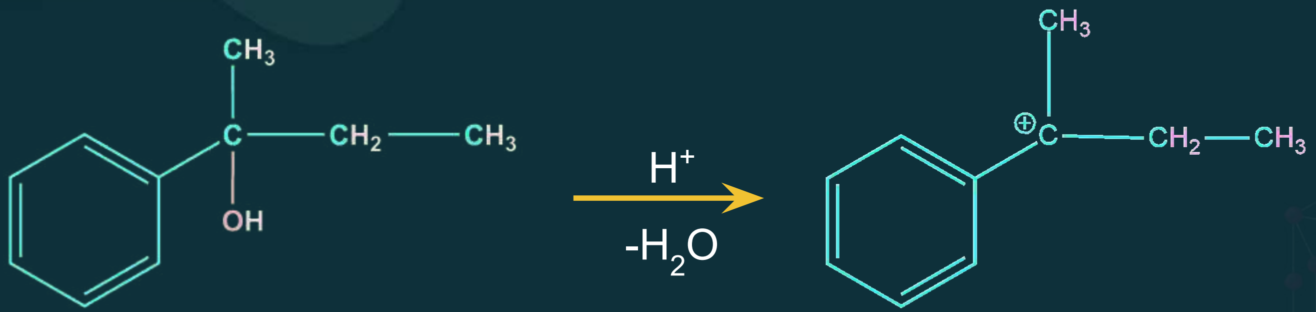
(I)



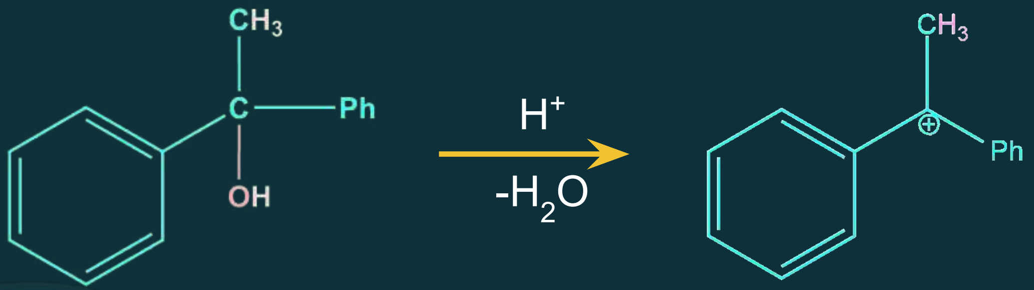
(II)



(III)



(IV)



In case (I), secondary carbocation will be formed. In case (II) primary carbocation will be formed. In case (III) tertiary carbocation will be formed. In case (IV) there will be also tertiary carbocation formed. Since tertiary carbocation is most stable hence acid catalysed dehydration will be more in tertiary. Since there are two benzyl group in case (iv), hence the order of rate will be IV > III > I > II.

Hence, option (d) is the correct answer.

During dehydration of alcohols to alkenes by heating with concentrated H_2SO_4 the initiation step is:

a) Protonation of alcohol molecule

b) Formation of carbocation

c) Elimination of water

d) Formation of an ester

Solution

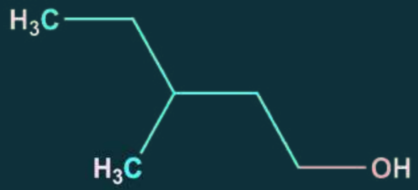
During dehydration of alcohols to alkenes by heating with concentrated H_2SO_4 the initiation step is protonation of alcohol molecule.

Hence, option (a) is the correct answer.

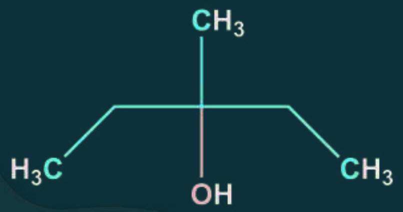
Among the following compounds which can be dehydrated very easily?

a)

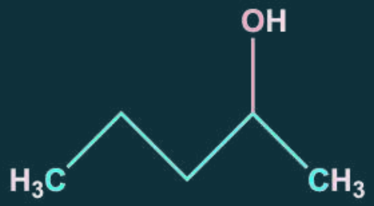
b)



c)



d)



Solution

The ease of dehydration of alcohols is $3^\circ > 2^\circ > 1^\circ$. Here option (a) and (b) are the primary alcohol and option (d) is secondary alcohol, and option (c) is tertiary alcohol. As we know tertiary carbocation is most stable hence acid catalysed dehydration will be more in tertiary.

Hence, option (c) will be the correct answer.

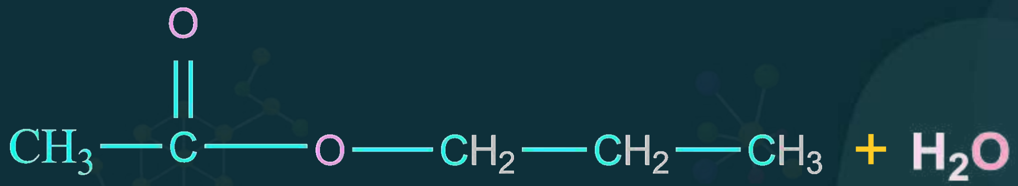
Major product formed in the following reaction is:

$$H_3C{-}COOH + H_3C{-}CH_2{-}CH_2{-}OH \xrightarrow{\text{Acid}}$$

Solution

This is an example of esterification reaction.

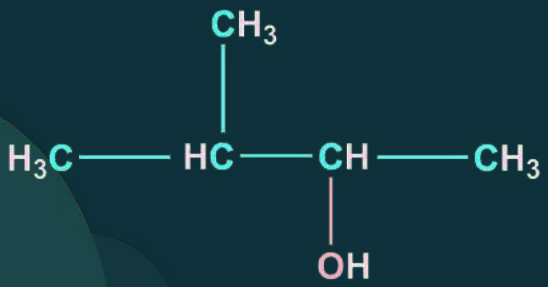
$$\underset{\textbf{Acetic acid}}{H_3C{-}COOH} + \underset{\textbf{Propanol}}{HO{-}CH_2{-}CH_2{-}CH_3} \xrightarrow{\text{Acid}}$$



$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}CH_3 + H_2O$$

Propyl acetate

Consider the following reactions,

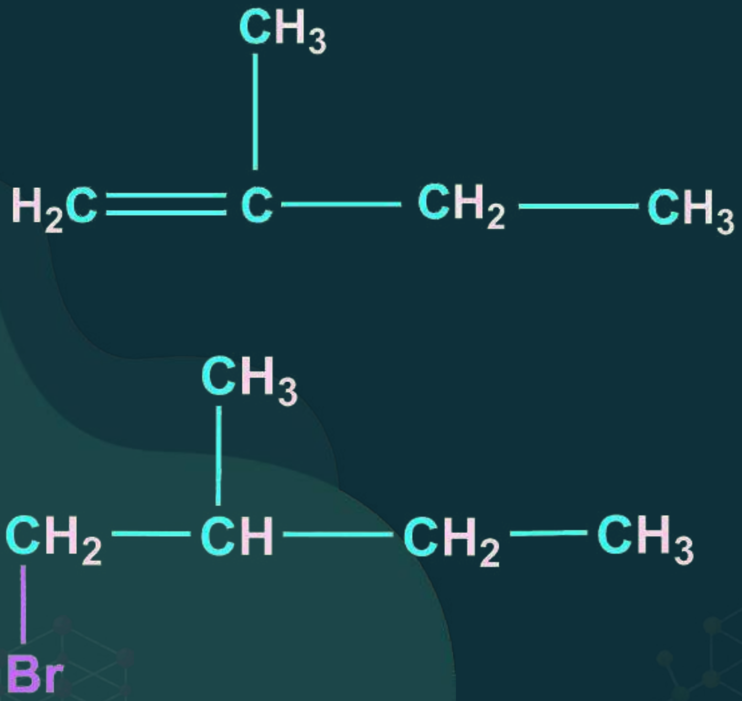


$$H_3C-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[\Delta]{H^+,\ \text{Heat}} \underset{\text{(Major product)}}{A} + \underset{\text{(Minor product)}}{B}$$

$$A \xrightarrow[\text{in absence of peroxide}]{\text{HBr, dark}} \underset{\text{(Major product)}}{C} + \underset{\text{(Minor product)}}{D}$$

In the following **major products (A) and (C)** are respectively.

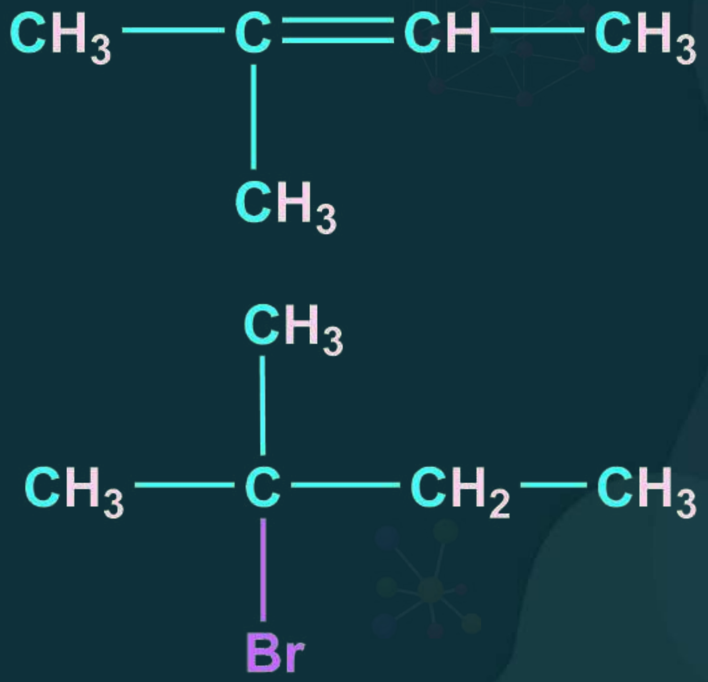
(a)



$$H_2C=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3$$

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

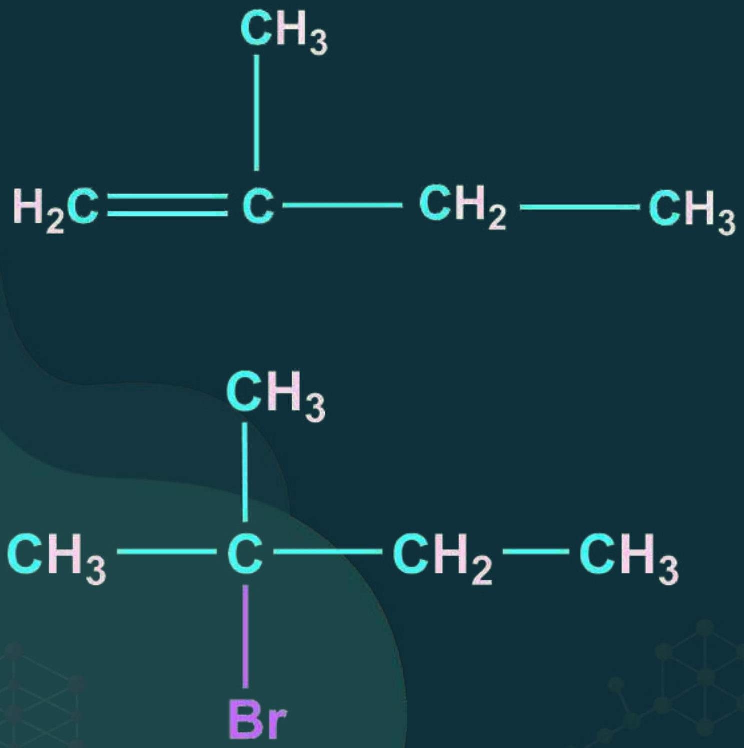
(b)



$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$$

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

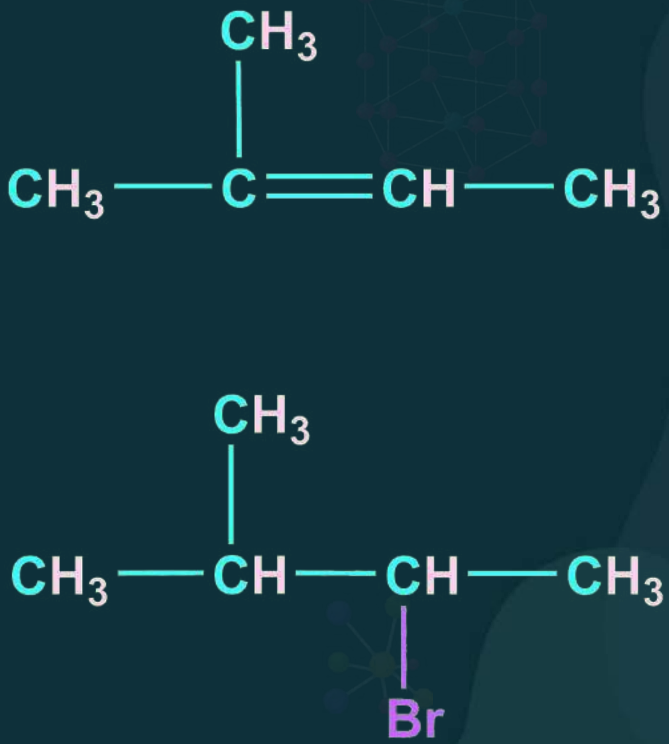
(c)



$$H_2C=C(CH_3)-CH_2-CH_3$$

$$CH_3-C(CH_3)(Br)-CH_2-CH_3$$

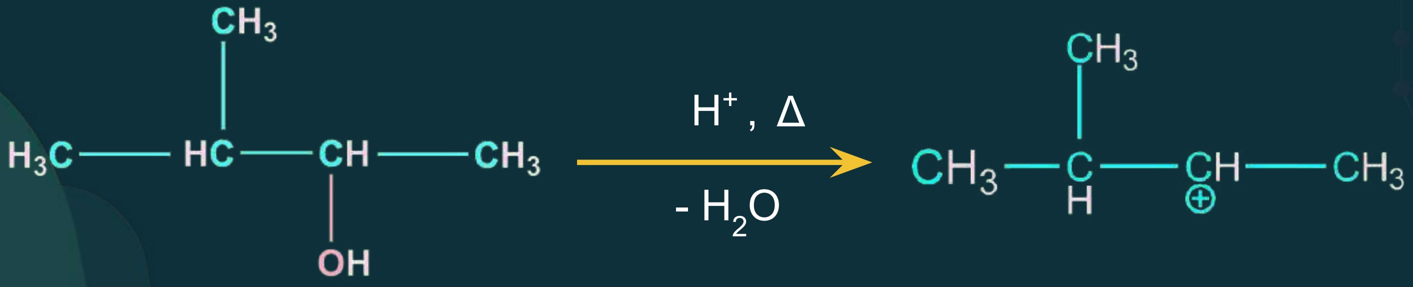
(d)



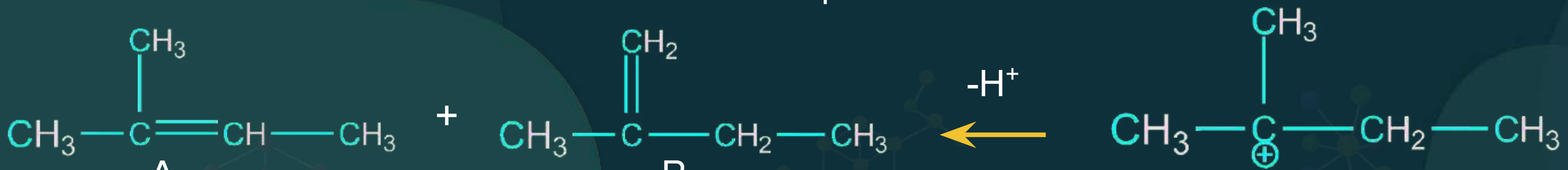
$$CH_3-C(CH_3)=CH-CH_3$$

$$CH_3-CH(CH_3)-CH(Br)-CH_3$$

Solution

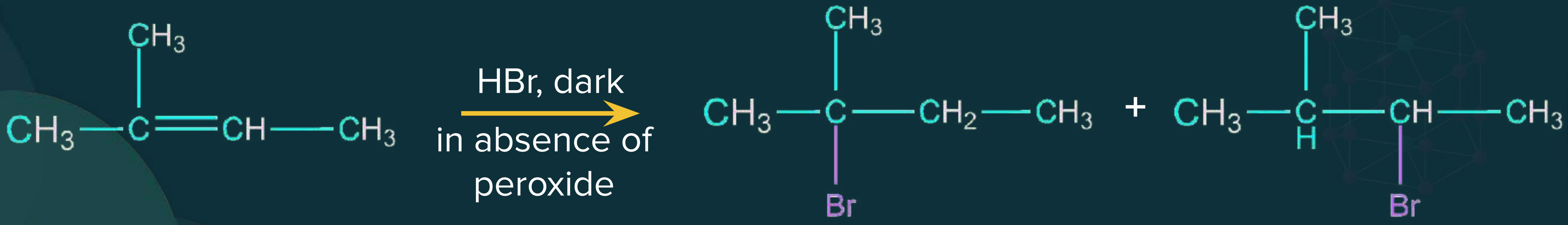


When an alcohol has two or three different β-carbons, dehydration is regioselective and follow Saytzeff or Zaitsev rule. The more substituted alkene is the major product when a mixture of constitutional isomers are possible.



A
(Major product)

B
(Minor product)



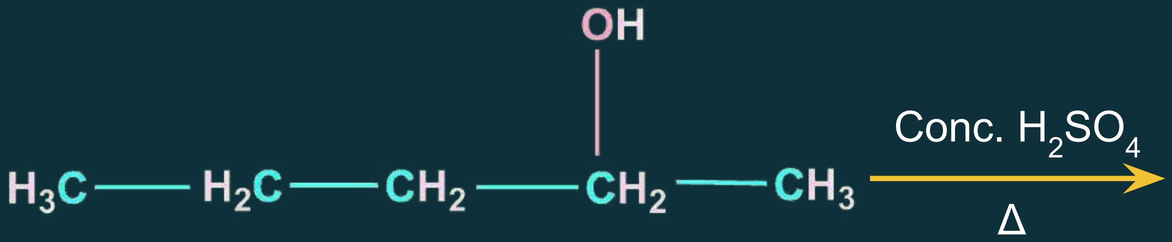
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_3 \xrightarrow[\text{in absence of peroxide}]{\text{HBr, dark}} CH_3-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_3 + CH_3-\underset{H}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3$$

C
(Major product)

D
(Minor product)

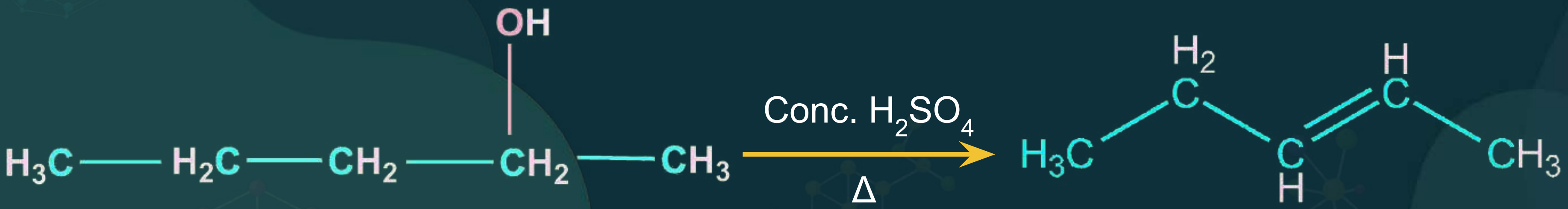
Hence, option (b) is the correct answer.

Predict the major product of the acid catalysed dehydration of the following alcohol:



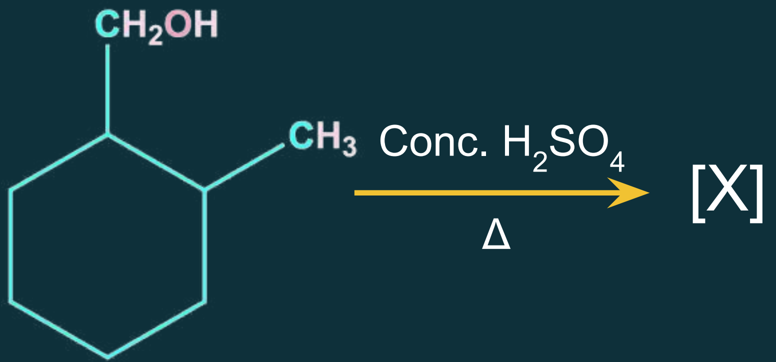
$$H_3C-H_2C-CH_2-\overset{\displaystyle OH}{\overset{|}{CH_2}}-CH_3 \xrightarrow[\Delta]{\text{Conc. } H_2SO_4}$$

Solution

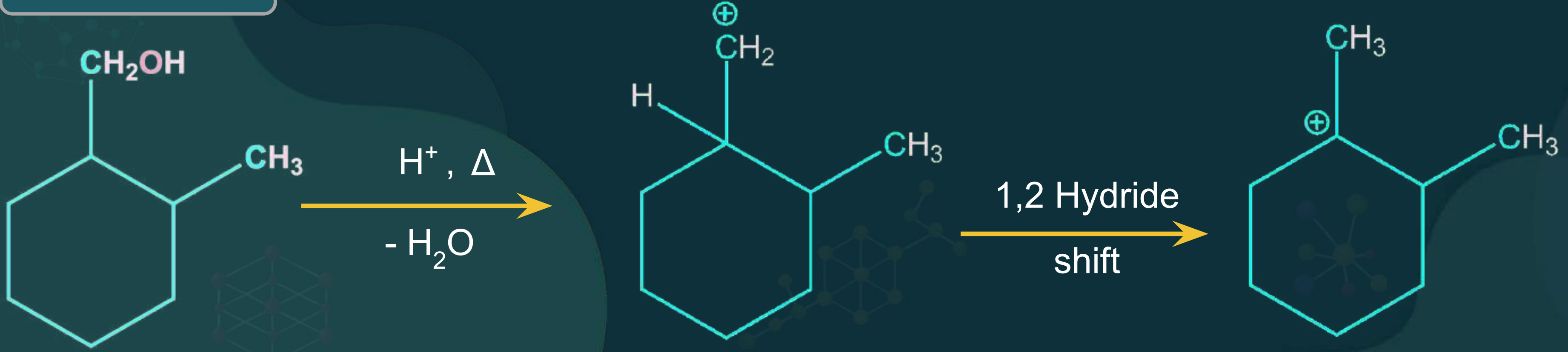


(Major product)

In the give reaction: Identify X.



Solution



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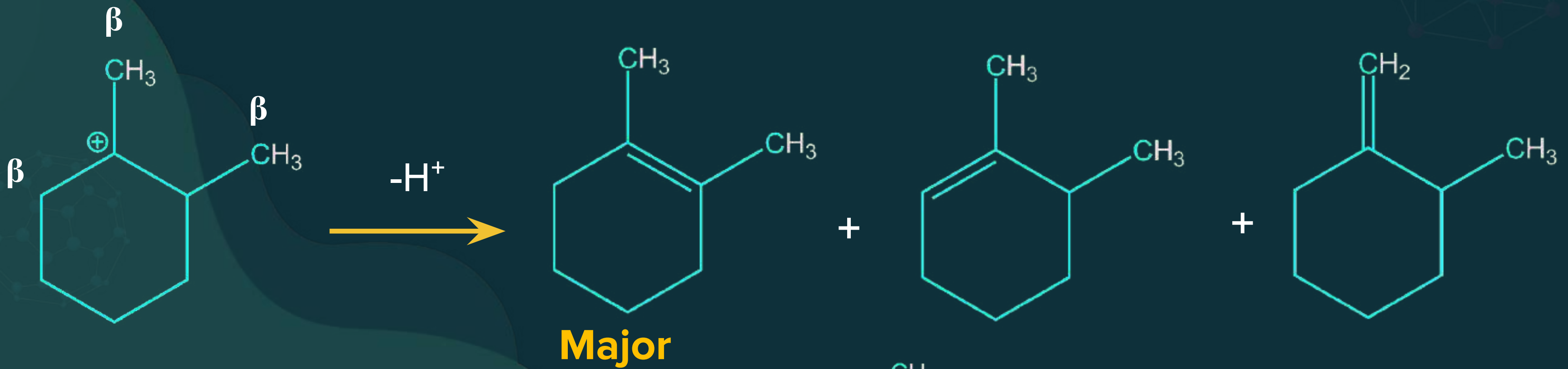
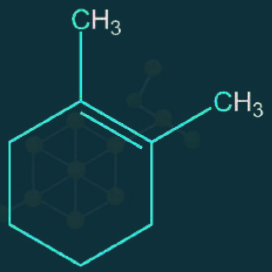
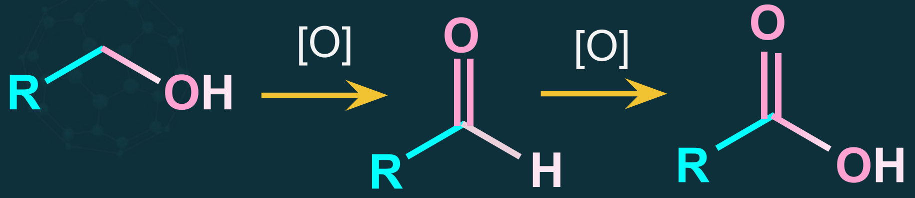


[X]



Oxidation of alcohol

Primary alcohols can be **oxidized** to aldehydes and carboxylic acids.



1° Alcohol Aldehyde Carboxylic acid

The oxidation of aldehydes to carboxylic acids in aqueous solutions is **easier** than oxidation of primary alcohols to aldehydes.

↓

It is **difficult to stop** the oxidation of a primary alcohol at the aldehyde stage, unless **specialised reagents** are used.

Oxidation of alcohol

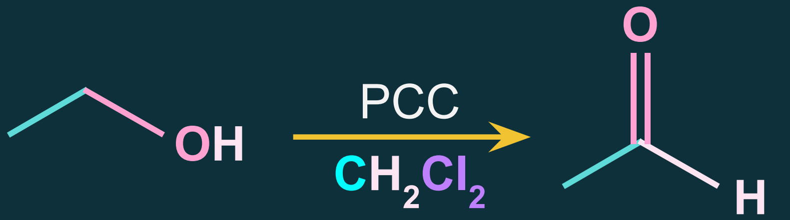
PCC

- An excellent reagent for converting a primary alcohol to an aldehyde is **pyridinium chlorochromate (PCC)**.
- **PCC** is formed when **CrO_3 is dissolved in HCl** and then treated with **pyridine**.
- PCC **does not** attack double bonds.

Pyridinium chlorochromate
(PCC)

Oxidation of alcohol

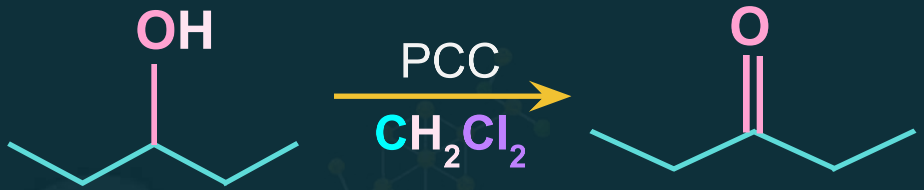
- **PCC**, when dissolved in methylene chloride (CH_2Cl_2), will oxidise a primary alcohol to an **aldehyde** and stop at that stage.



Primary alcohol

Aldehyde

- PCC will also oxidise a secondary alcohol to a **ketone**.



Secondary alcohol

Ketone

What is the **product** of the following reaction?

$$CH_3 - CH = CH - CH_2 - \underset{\cdot\cdot}{\ddot{O}}H \xrightarrow{PCC}$$

Solution

$$CH_3 - CH = CH - CH_2 - \underset{\cdot\cdot}{\ddot{O}}H$$

$$\Big\downarrow \text{PCC}$$

$$CH_3 - CH = CH - HC = \underset{\cdot\cdot}{\ddot{O}}$$

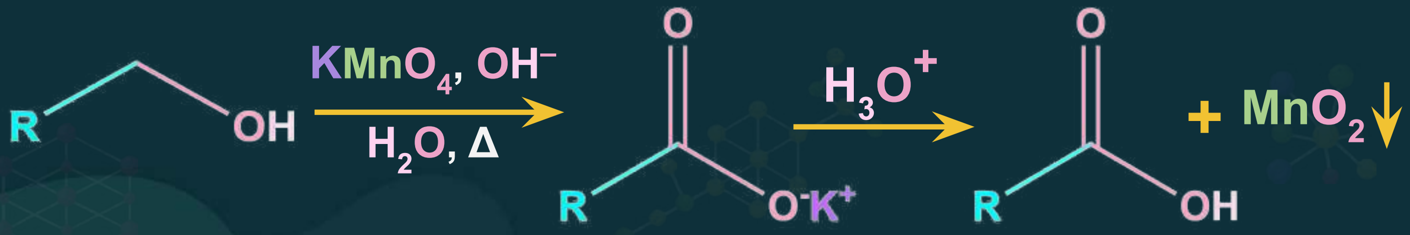
Oxidation of alcohol

Oxidation of 1° Alcohols to Carboxylic Acids

- **Primary alcohols** can be oxidised to **carboxylic acids** by potassium permanganate **($KMnO_4$)**, or chromic acid **(H_2CrO_4)**.

$$RCH_2OH \xrightarrow{KMnO_4 \text{ or } H_2CrO_4} RCOOH$$

- The reaction with **$KMnO_4$** is usually carried out in **basic** aqueous solution, from which **MnO_2 precipitates** as the oxidation takes place.



On oxidising ethanal using a strong oxidising agent, carboxylic acid is obtained. Which of the following statements is correct regarding the formed carboxylic acid?

(a) Number of C-atoms in formed carboxylic acid will be one greater than that of aldehyde taken.

(b) Number of C-atoms in formed carboxylic acid will be one less than that of aldehyde taken.

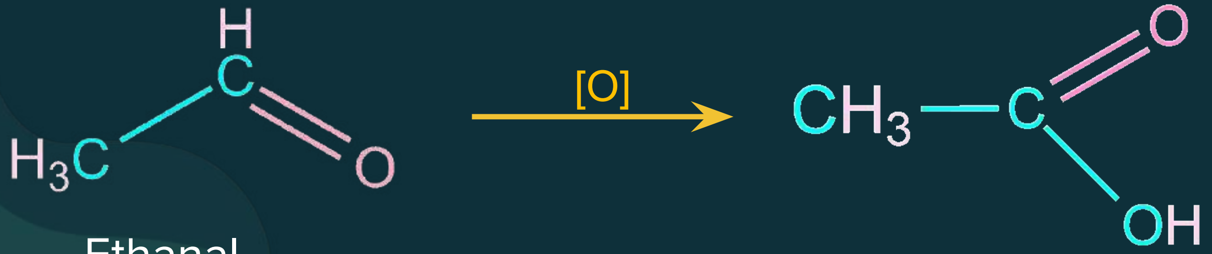
(c) Number of C-atoms in formed carboxylic acid will be same as that of aldehyde taken.

(d) None of these

Solution

Ethanal on oxidation will give ethanoic acid.

So, the number of carbon atom will be same as that of aldehyde.



Ethanal

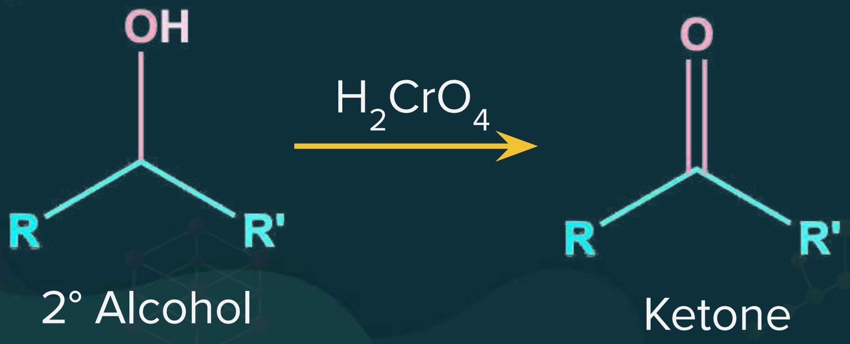
Ethanoic acid

Hence, option (c) is the correct answer.

Oxidation of Alcohol

Oxidation of 2° Alcohols to Ketone

Both **$KMnO_4$** and **H_2CrO_4** can also be used to oxidise a **secondary alcohol** to a **ketone.**



2° Alcohol

Ketone

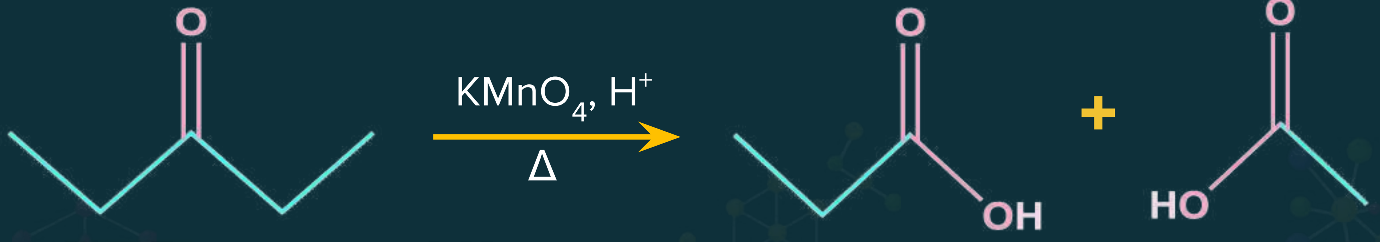
Can **ketone** also be converted into **carboxylic acid**?

Oxidation of 2° alcohols usually **stops at the ketone stage** because further oxidation requires the breaking of a **C–C** bond and occurs only under drastic condition.

Oxidation of Alcohol

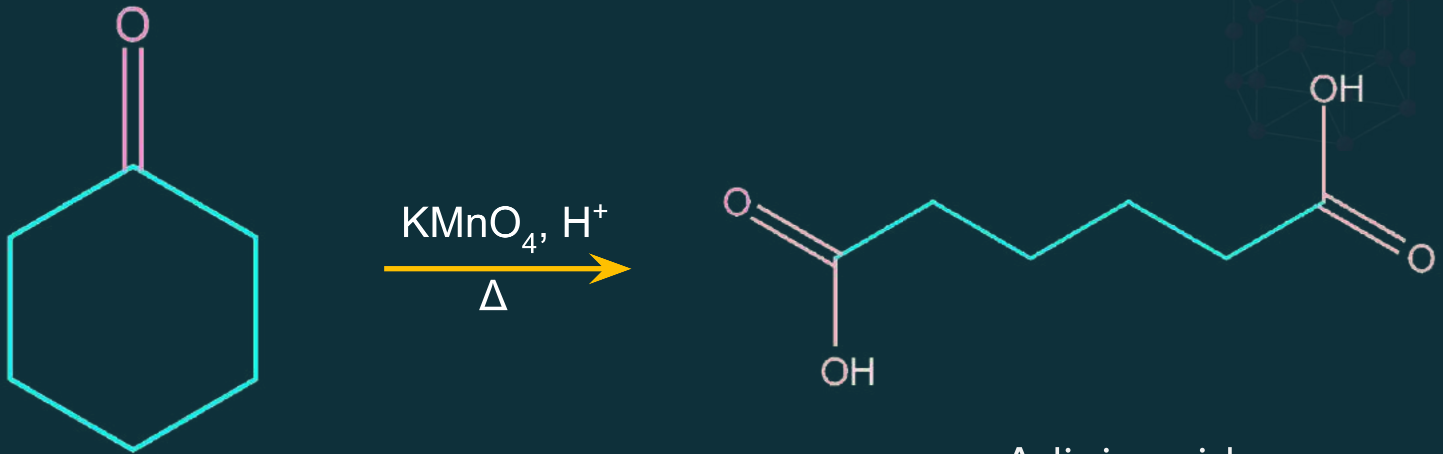
Acidic $KMnO_4$ & $K_2Cr_2O_7$ as Oxidising Agents

- Ketones are oxidised with difficulty. They are oxidised only on heating with a **strong oxidising agent**.
- Cleavage of C-C bonds takes place and a mixture of **carboxylic acids** containing **lesser number** of carbon atoms are formed.



Oxidation of Alcohol

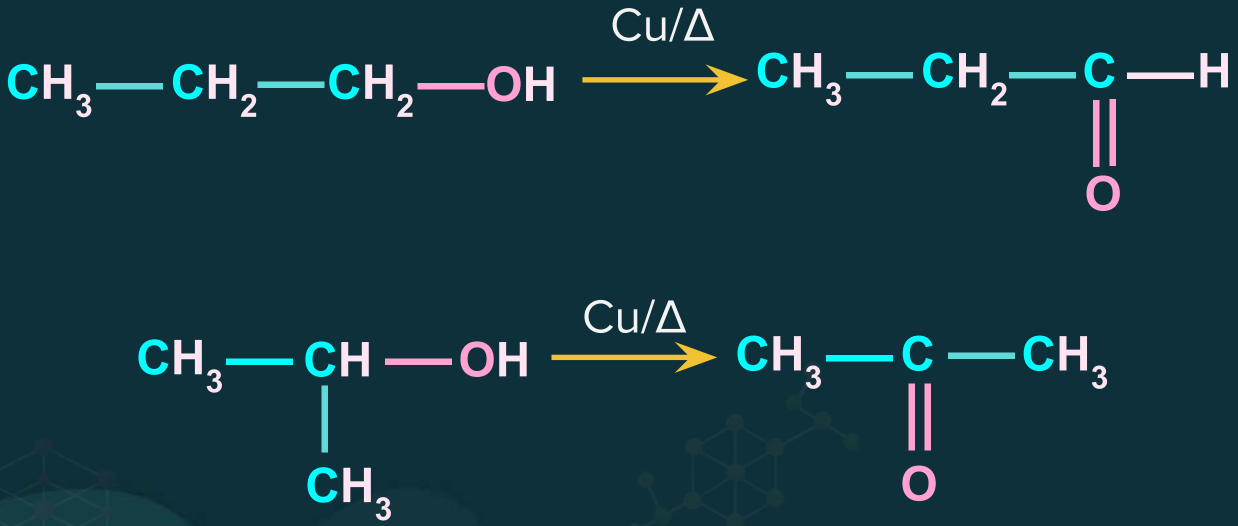
Example:



Adipic acid

Oxidation of Alcohol

- When the vapours of a primary or a secondary alcohol are passed over **heated copper** at 573 *K*, dehydrogenation takes place and an **aldehyde or a ketone is formed.** while tertiary alcohols undergo **dehydration to give alkene**.

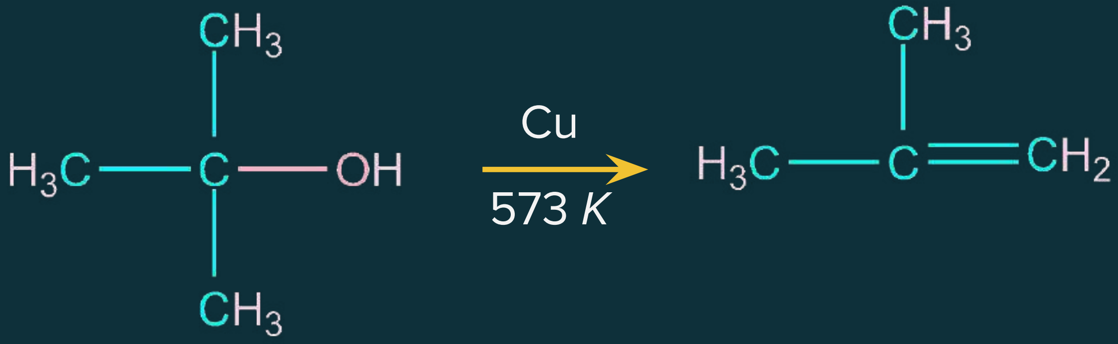


$$CH_3-CH_2-CH_2-OH \xrightarrow{Cu/\Delta} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-H$$

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-OH \xrightarrow{Cu/\Delta} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

Oxidation of Alcohol

- Tertiary alcohols undergo **dehydration to give alkene**.



$$(CH_3)_3C-OH \xrightarrow[573\,K]{Cu} (CH_3)_2C=CH_2$$

Oxidation of Alcohol

Summary of Oxidation

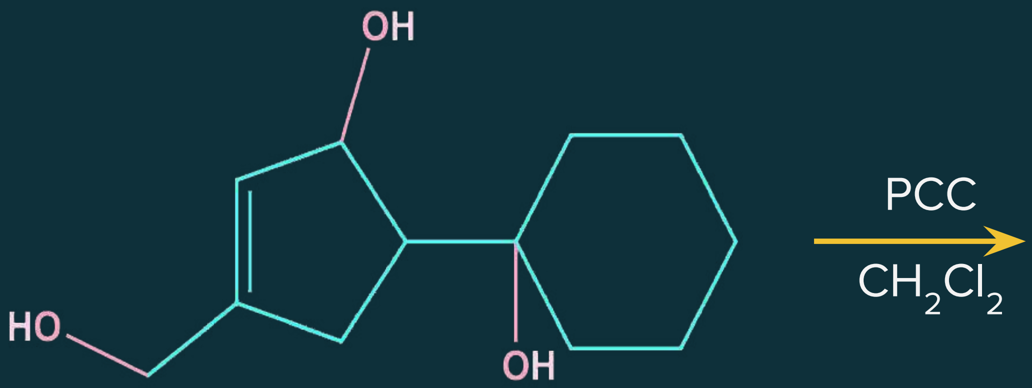
Alcohol	Weak oxidising agent	
	PCC	**CrO_3/Inert medium**
1° alcohol	Aldehyde	
2° alcohol	Ketone	
3° alcohol	Not oxidised	

Alcohol	Strong oxidising agent	
	CrO_3 in water or H_2CrO_4	**$KMnO_4/H^+$**
1° alcohol	Carboxylic acid	
2° alcohol	Ketone	
3° alcohol	Not oxidised	

Oxidation of Alcohol

Alcohol	Very strong oxidising agent **$KMnO_4/H^+$/heat**	**Copper & heat** as oxidising agent
1° alcohol	Carboxylic acid	Aldehyde
2° alcohol	Mixture of carboxylic acid	Ketone
3° alcohol	___	Dehydrate to alkene

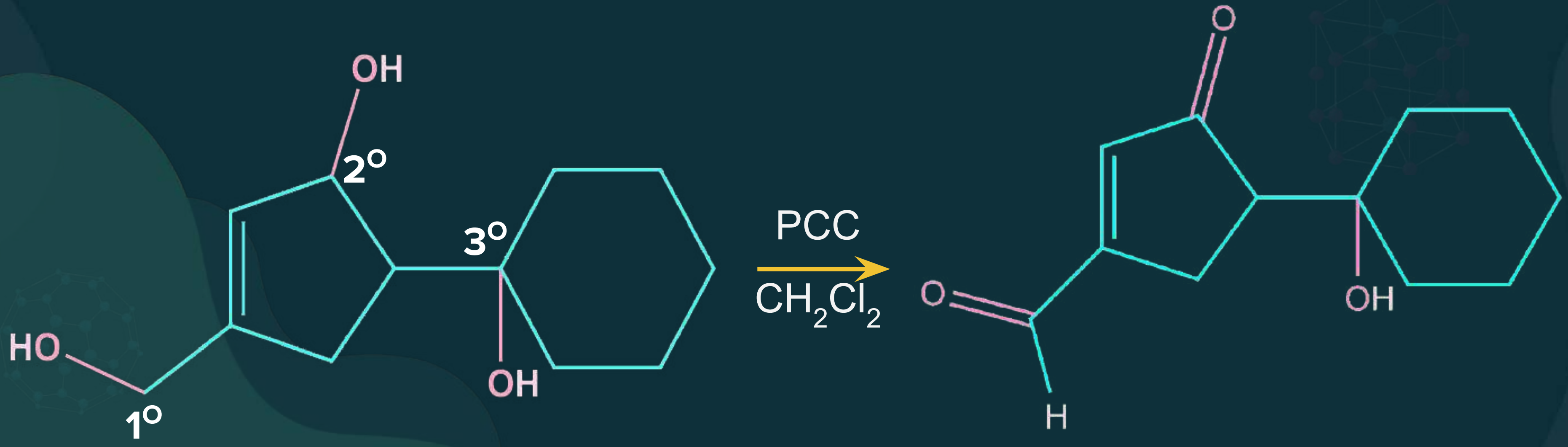
The major product formed in the following reaction is:



Solution

Alkene and tertiary alcohol will not react with PCC. So, it will remain unchanged.

Primary and secondary will be converted to aldehyde and ketone respectively.


OH
2°
3°
HO
1°
OH
PCC
CH_2Cl_2
O
O
H
OH

Which one of the following on oxidation gives a ketone?

a) Primary alcohol

b) Secondary alcohol

c) Tertiary alcohol

d) All of these

Solution

(a) Primary alcohols on oxidation give aldehyde.

(b) Secondary alcohols on oxidation gives ketone.

(c) Oxidation of tertiary alcohol gives alkene.

Hence, option (b) is correct answer.

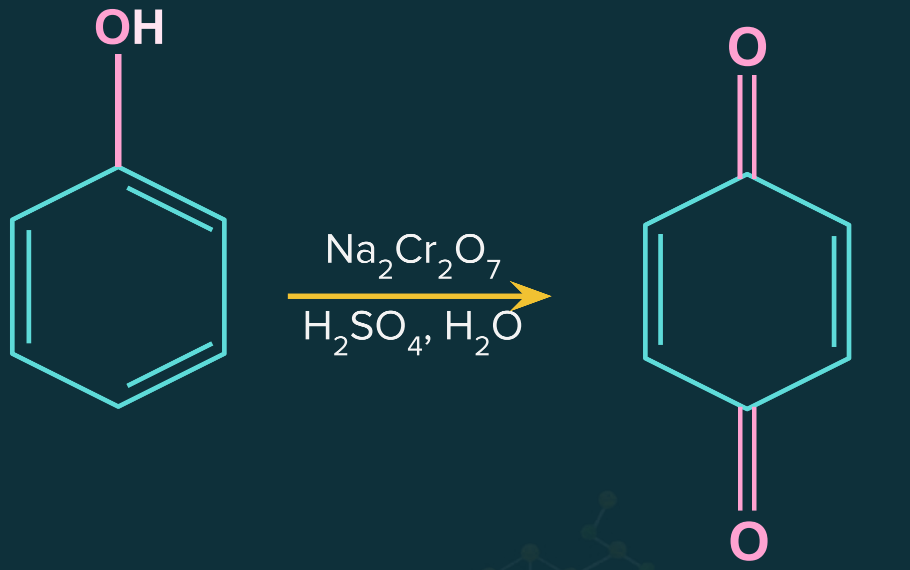
Reaction of Phenol

Reactions of phenol

1. Oxidation
2. Electrophilic aromatic substitution
3. Kolbe reaction
4. Reimer-Tiemann reaction
5. Reaction of phenol with zinc dust

Reaction of Phenol

Oxidation of Phenol



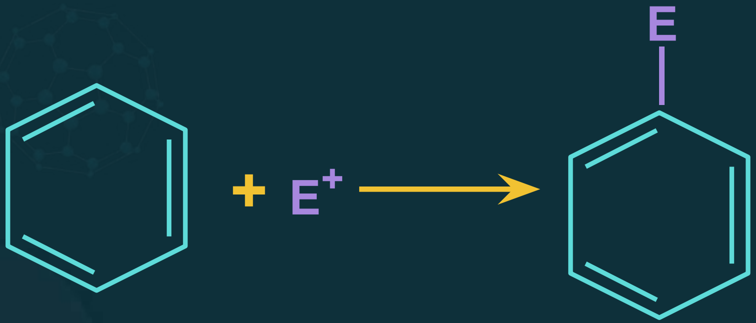
$\xrightarrow[H_2SO_4,\ H_2O]{Na_2Cr_2O_7}$

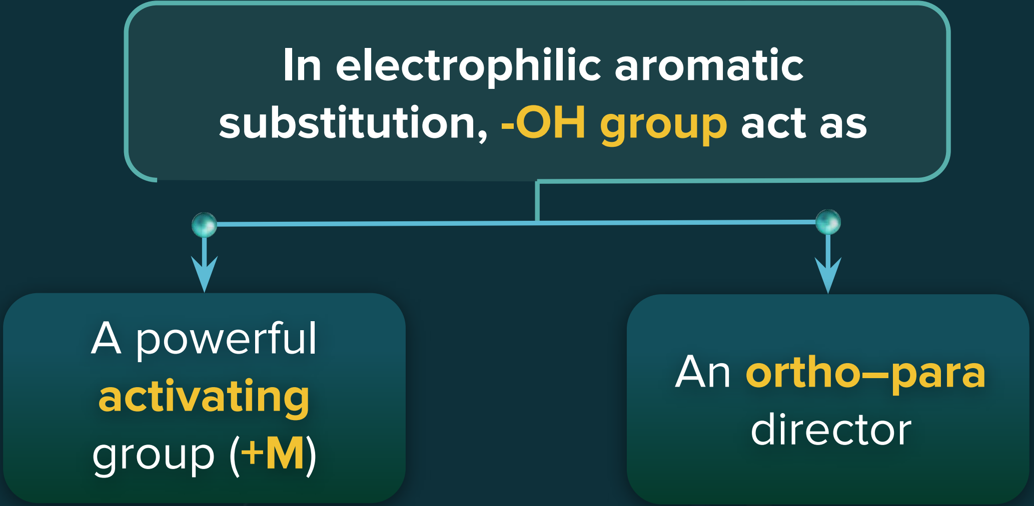
Benzoquinone

Reaction of Phenol

Electrophilic aromatic substitution

General reaction





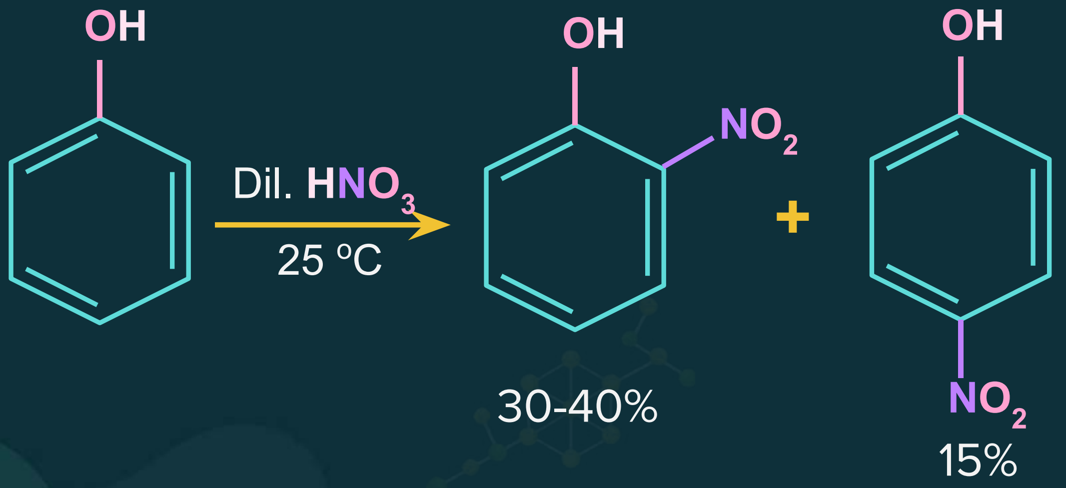
In electrophilic aromatic substitution, -OH group act as

- A powerful **activating** group (**+M**)
- An **ortho–para** director

Reaction of Phenol

Nitration

- Phenol reacts with dilute nitric acid to yield a mixture of o- and p-Nitrophenol.
- Probability of attack at ortho position is more than on para, because of double the number of ortho positions in benzene ring.



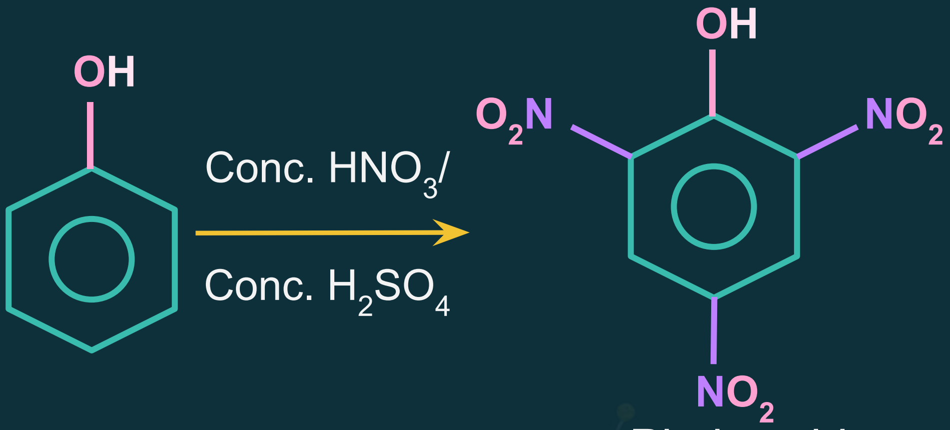
Reaction of Phenol

1. Yield is relatively **low** (because of oxidation of the ring).
2. Ortho & para isomers can be **separated by steam distillation**.

o-Nitrophenol	**p**-Nitrophenol
Intramolecular H-bonding	**Intermolecular** H-bonding
More volatile	**Less** volatile
Passes over with the steam	**Remains** in the distillation flask

Reaction of Phenol

Phenol with conc. nitric acid gives picric acid in **low yield** (because of oxidation of ring).

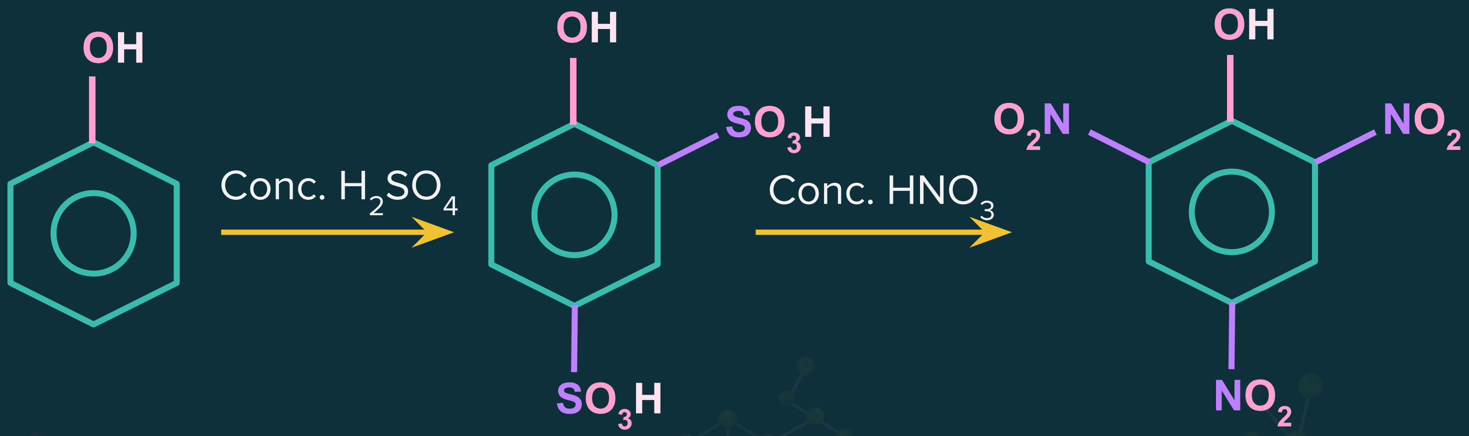


Picric acid

- Nitration of phenol to give picric acid is highly exothermic.

Reaction of Phenol

Is there any **other** convenient method for preparing **picric acid**?



Picric acid

Reaction of Phenol

Pikros
(Greek word)

Bitter

Picric acid:

(a) It is yellow colored substance which is used to dye the silk material.

(b) It can be used to make explosives.

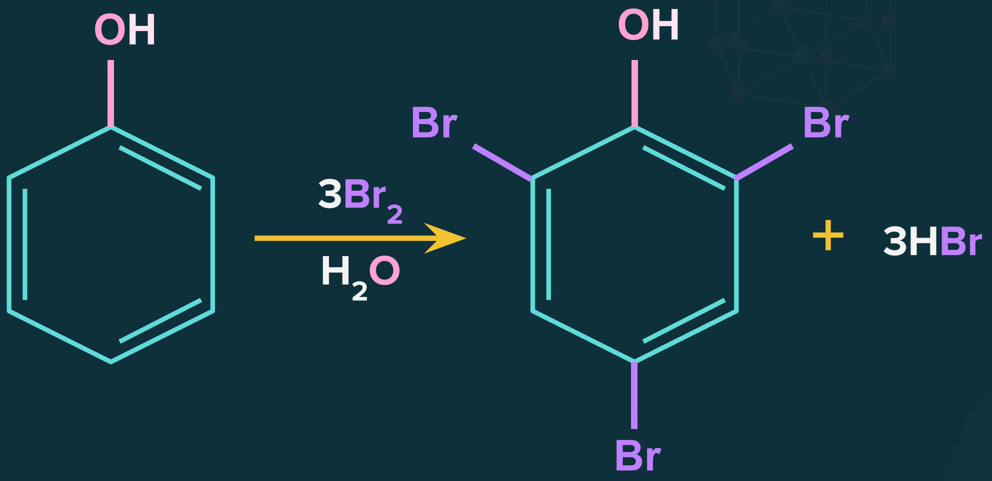
(c) Acidic strength of picric acid is more than carboxylic acid.

Reaction of Phenols

Bromination

When phenol is treated with bromine water, white precipitate of 2,4,6-tribromophenol is formed.

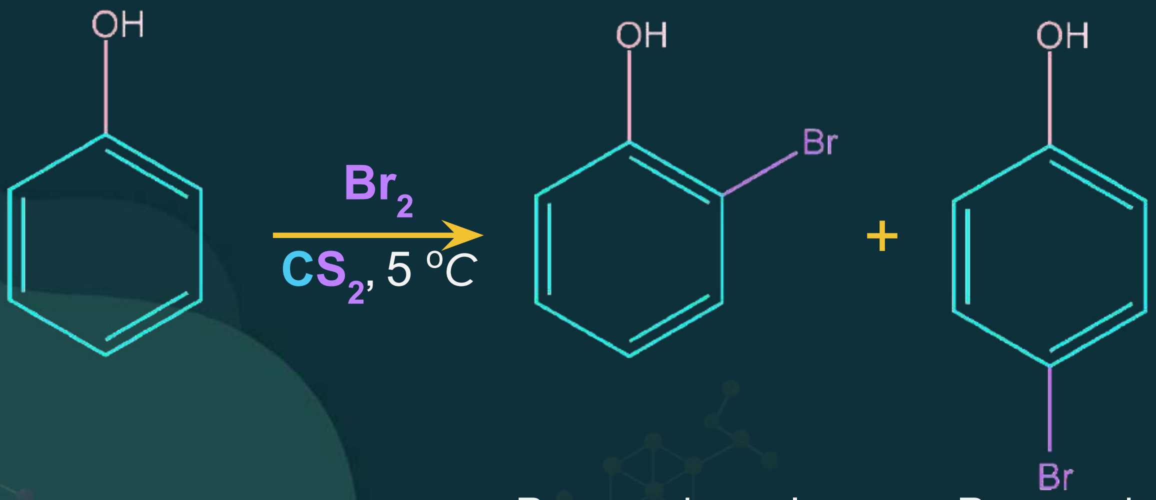
A Lewis acid is **not required** for the bromination of phenol due to highly activating effect of -OH group attached to the benzene ring.



2,4,6-Tribromophenol
(≈ 100%)

Reaction of Phenols

- **Monobromination** of phenol can be achieved by carrying out the reaction in solvents such as CS_2 or $CHCl_3$ at a low temperature, conditions that **reduce** the **electrophilic reactivity** of bromine.
- The **major product** is the **para isomer**.

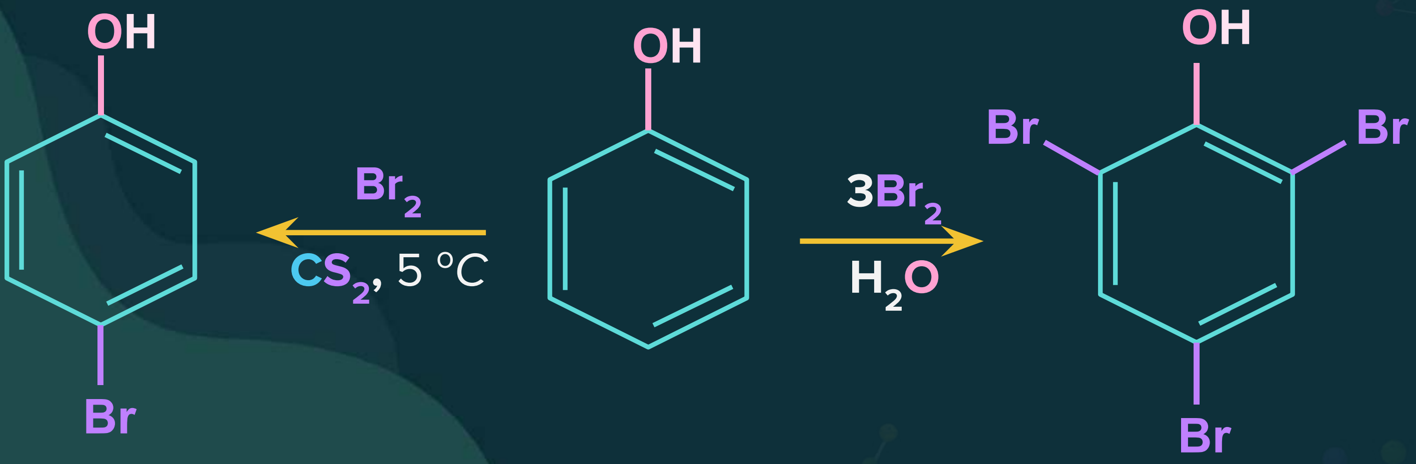


o-Bromophenol
(Minor)

p-Bromophenol
(Major)

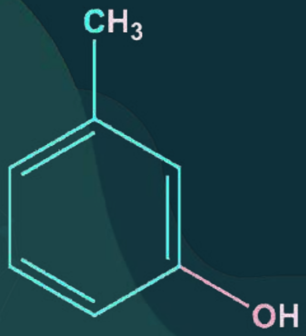
Reaction of Phenols

Bromination

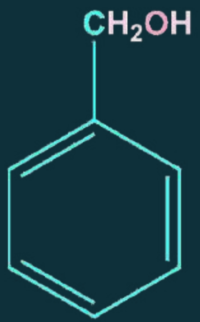


The structure of the compound that gives a tribromo derivative on treatment with bromine water is:

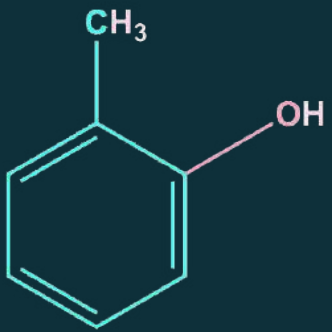
(a)



(b)



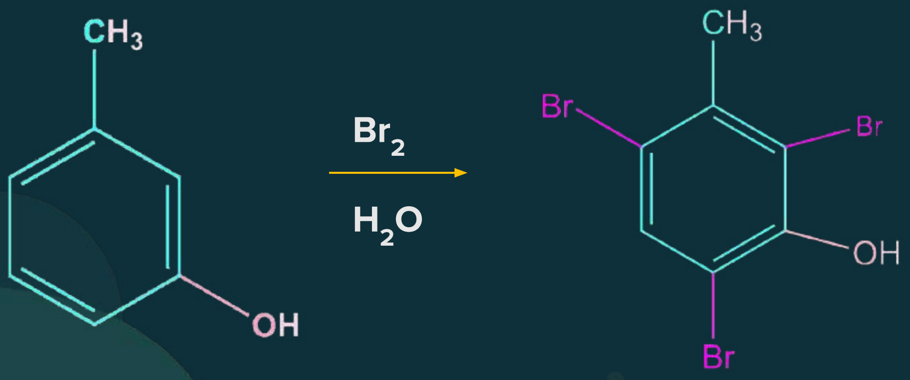
(c)



(d)

Solution

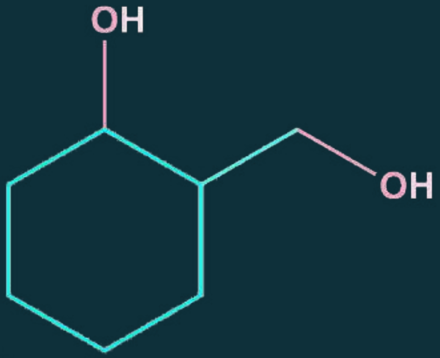
In option (a) $-CH_3$ is attached on meta position w. r. t. $-OH$ group. So, it will not affect the attachment of bromine on two ortho and one para position w. r. t. $-OH$ group and forms a tribromo derivative in aqueous solution of bromine.



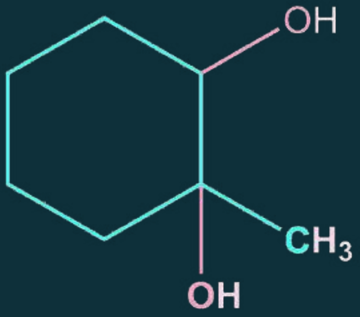
Therefore, option (a) is the correct answer.

The alcohol refusing to generate a carbonyl compound on oxidation with acidified $KMnO_4$ is:

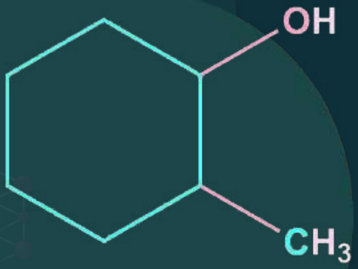
(a)



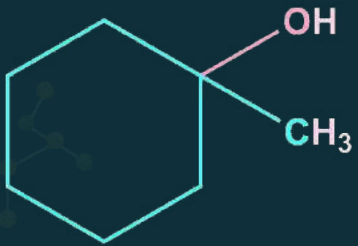
(b)



(c)



(d)



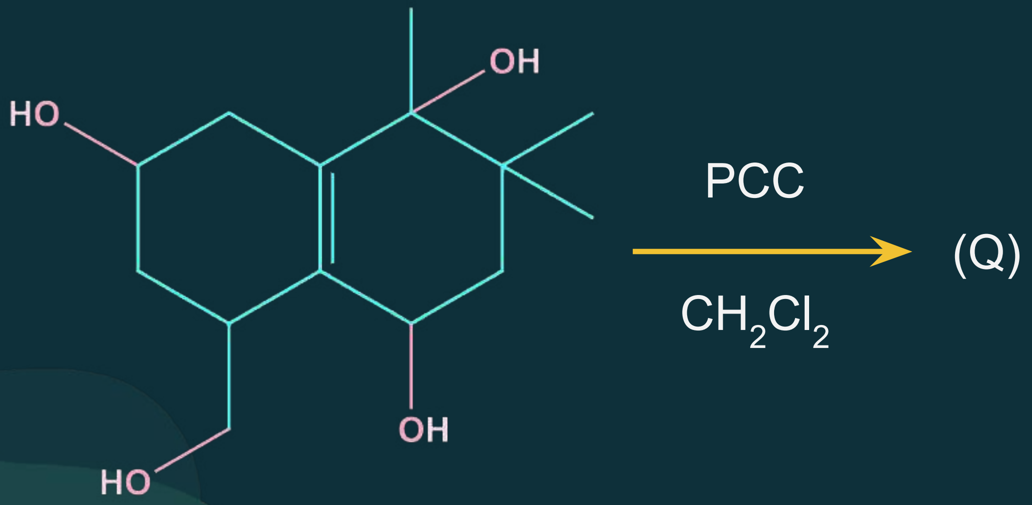
Solution

- Primary alcohols can oxidise in presence of acidified $KMnO_4$ to give carboxylic acids.
- Secondary alcohols can oxidise to give ketones in presence of acidified $KMnO_4$.
- Tertiary alcohols does not undergo oxidation reaction as carbon atom carrying –OH group does not have a hydrogen atom attached and instead bonded to a carbon atom.

Tertiary alcohol

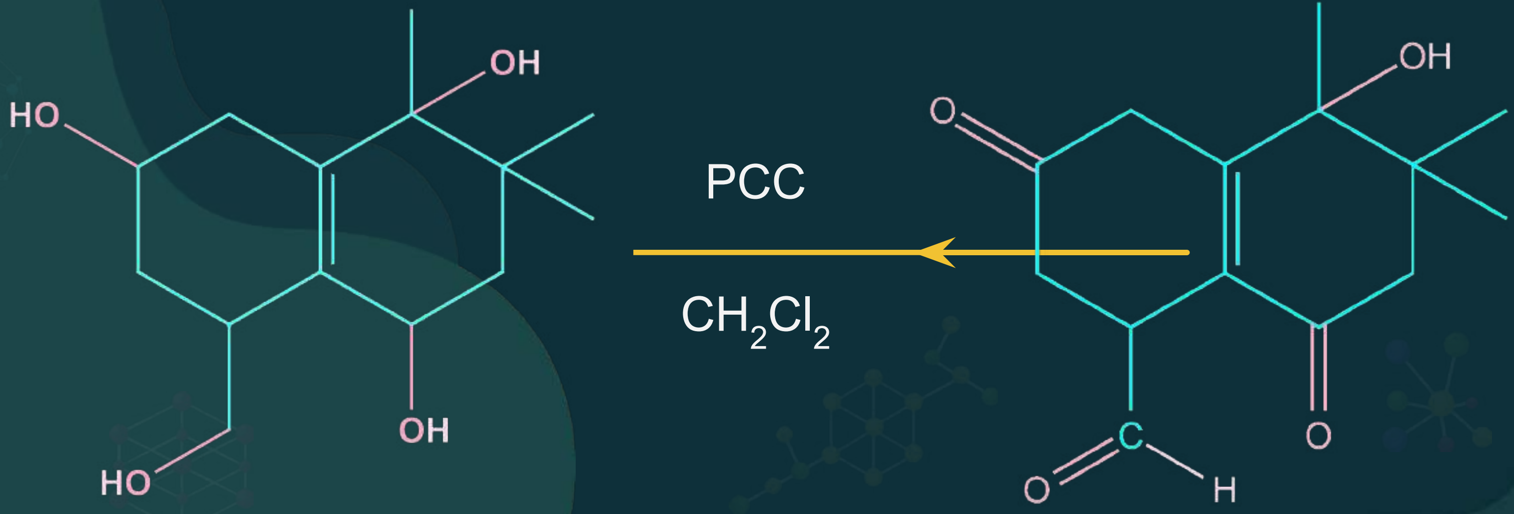
Therefore option (d) is the correct answer.

Identify product (Q) in the given reaction.



Solution

PCC is a mild oxidizing agent which can oxidize primary and secondary alcohols to aldehydes and ketones but cannot oxidize tertiary alcohol and alkenes. The product formed is shown below:



Secondary alcohols on heating with copper at 300 °C give:

BOARDS

(a) Alkenes (b) Aldehydes (c) Ketones (d) tert-Alcohol

Solution

- Alcohols undergo **dehydrogenation** i.e., loss of hydrogen or oxidation, when vapours of alcohol are passed over catalytic Cu at 300 °C.
- Primary alcohols upon dehydrogenation give corresponding aldehydes.
- Secondary alcohols upon dehydrogenation give corresponding ketones.

Therefore, option (c) is the correct answer.

The most suitable reagent for the conversion of

$RCH_2OH \longrightarrow RCHO$ is:

BOARDS

(a) $KMnO_4$ (b) $K_2Cr_2O_7$ (c) CrO_3 (d) PCC

Solution

- $KMnO_4$, $K_2Cr_2O_7$ and CrO_3 are all powerful oxidising agents. They convert primary alcohols to carboxylic acid directly.
- PCC (Pyridinium chlorochromate) is a mild oxidising agent. It oxidises primary alcohols to aldehydes and secondary alcohols to ketones.

Therefore, option (d) is the correct answer.

Picric acid is:

BOARDS

(a) Trinitrophenol

(b) Trinitrotoluene

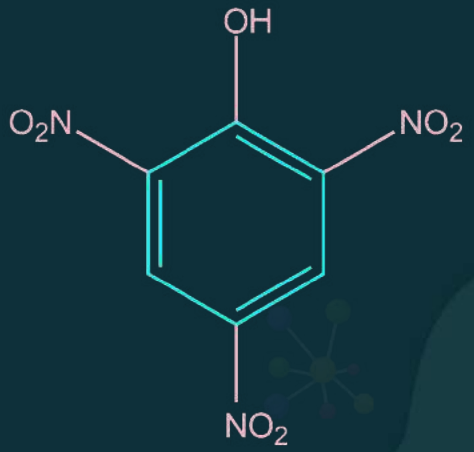
(c) Trinitrobenzene

(d) Tribromobenzene

Solution

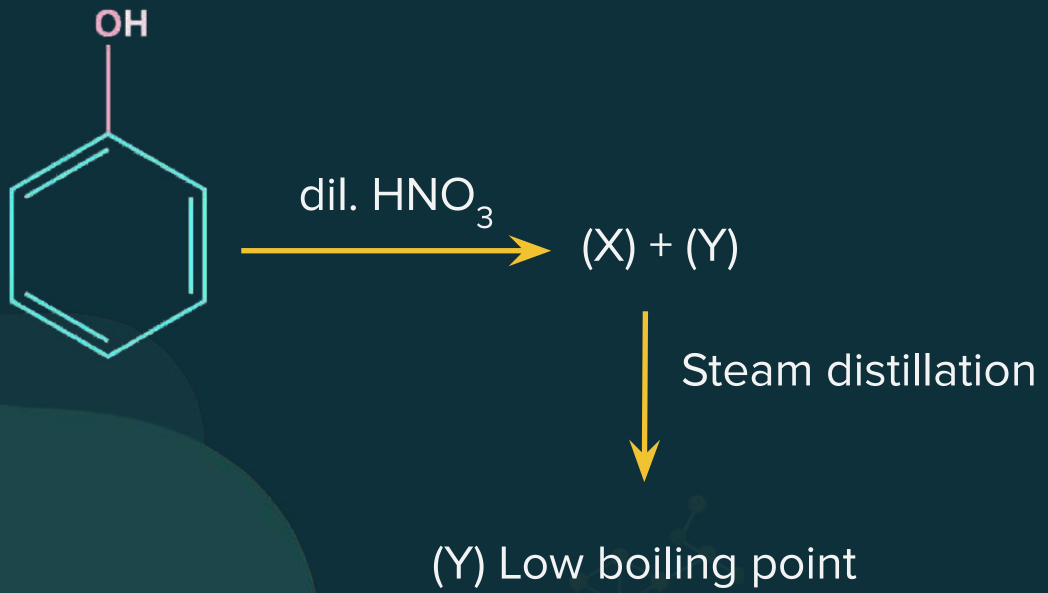
Picric acid is the common name for 2,4,6-trinitrophenol.

Therefore, option (a) is the correct answer.



Picric acid

Observe the following reaction.
Y is:



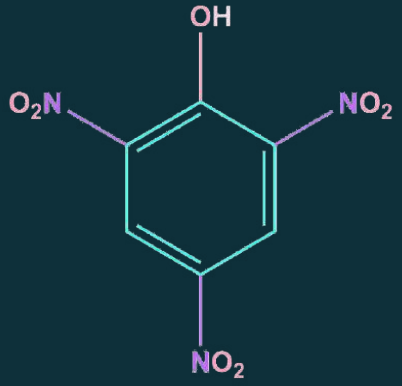
dil. HNO_3

(X) + (Y)

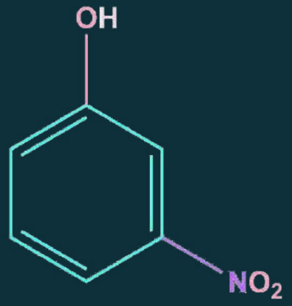
Steam distillation

(Y) Low boiling point

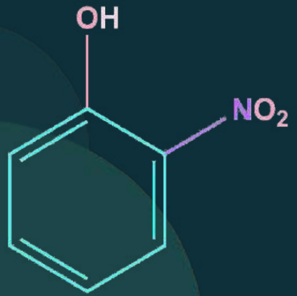
(a)



(b)



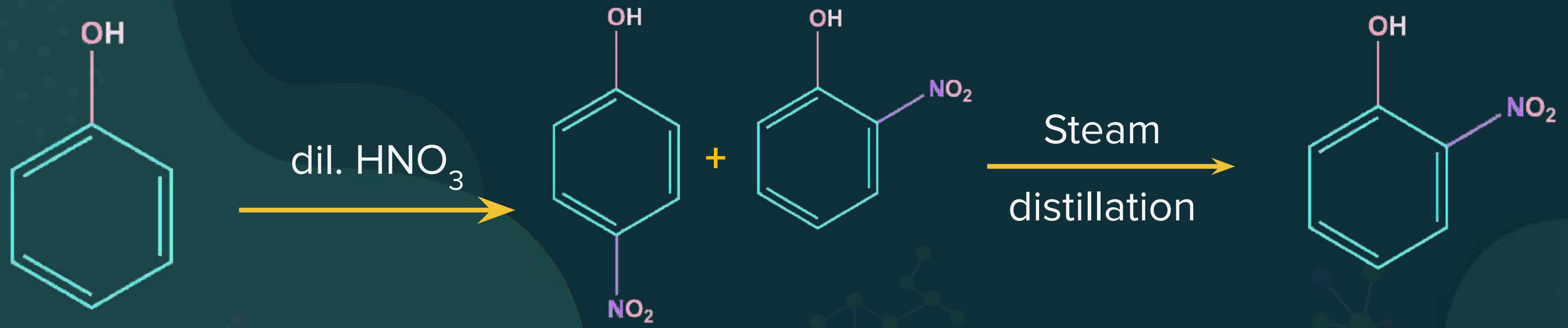
(c)



(d)

Solution

Phenol on reaction with dil. HNO_3 forms ortho and para nitrophenol and on steam distillation separates the para product as it has higher boiling point due to presence of intermolecular hydrogen bonding. So, Y is ortho nitrophenol, as it has lower boiling point due to intramolecular interactions.



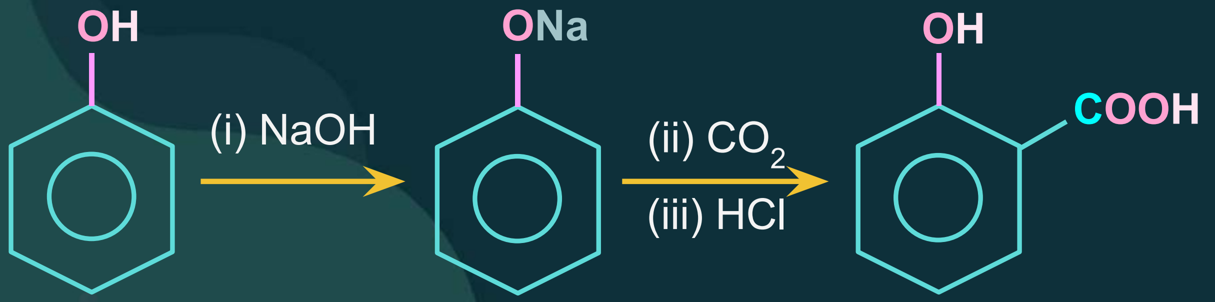
(X) **(Y)** **(Y) Low boiling point**

Therefore, option (c) is the correct answer.

Reaction of Phenols

Kolbe's reaction

Phenol in the presence of base NaOH, reacts with CO_2 at high temperature and pressure to yield sodium salicylate which on acidification yield o-hydroxybenzoic acid. This reaction is electrophilic aromatic substitution in which CO_2 behave as an electrophile.

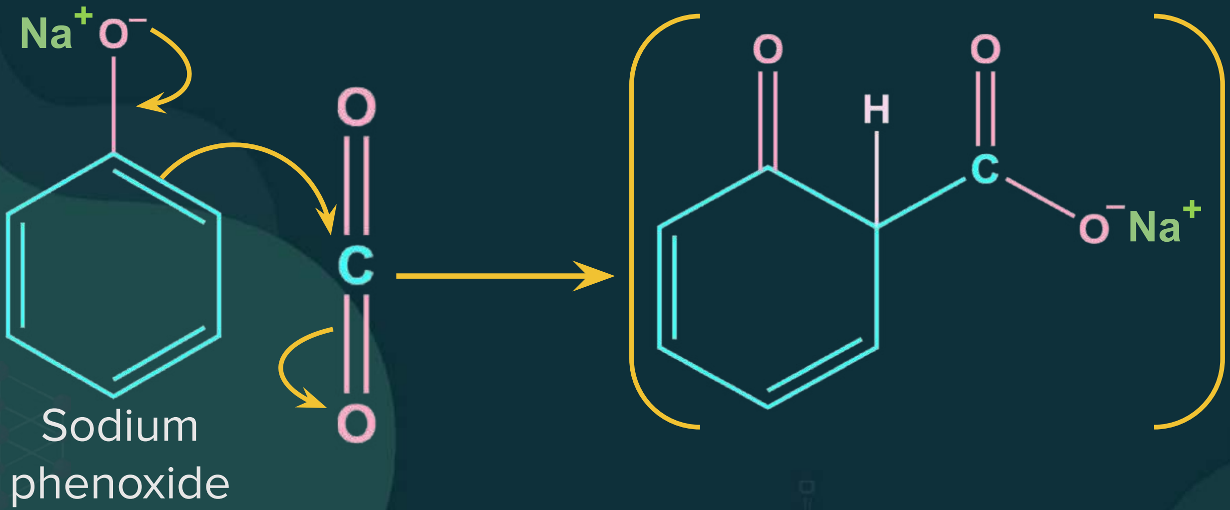


o-Hydroxybenzoic acid
(Salicylic acid)

Reaction of Phenols

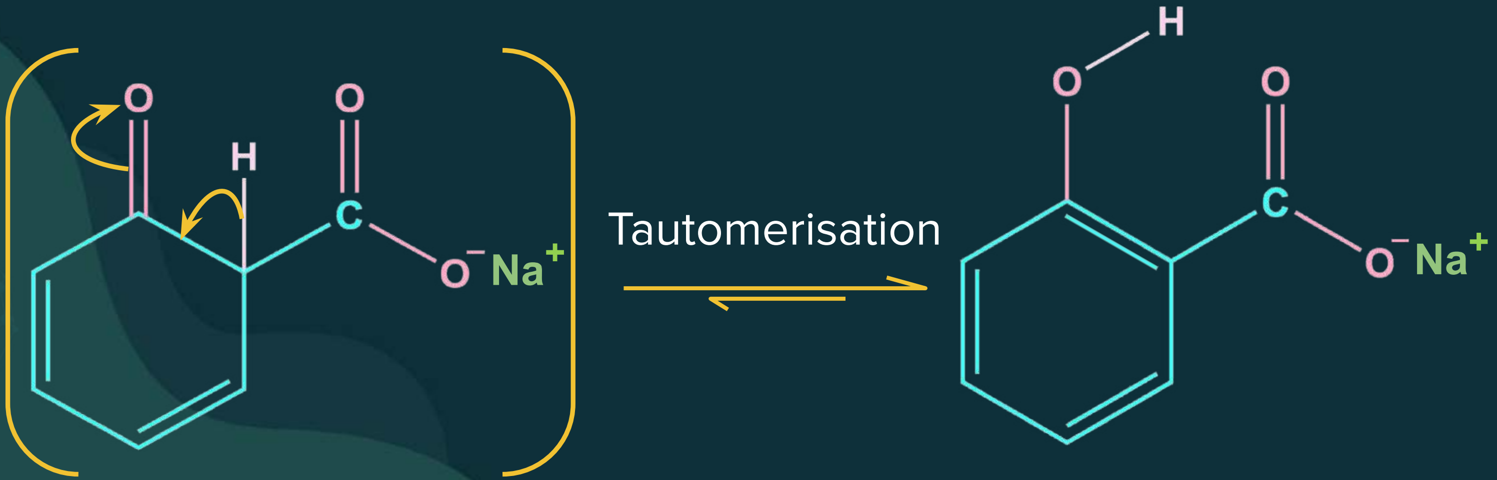
Mechanism

- NaOH is a base which abstracts the acidic hydrogen of phenol and gives phenoxide ion or sodium phenoxide. This makes the benzene ring more electron rich.
- Since, phenoxide ion is even more reactive than phenol, it undergoes electrophilic attack even by CO_2, a weak electrophile.



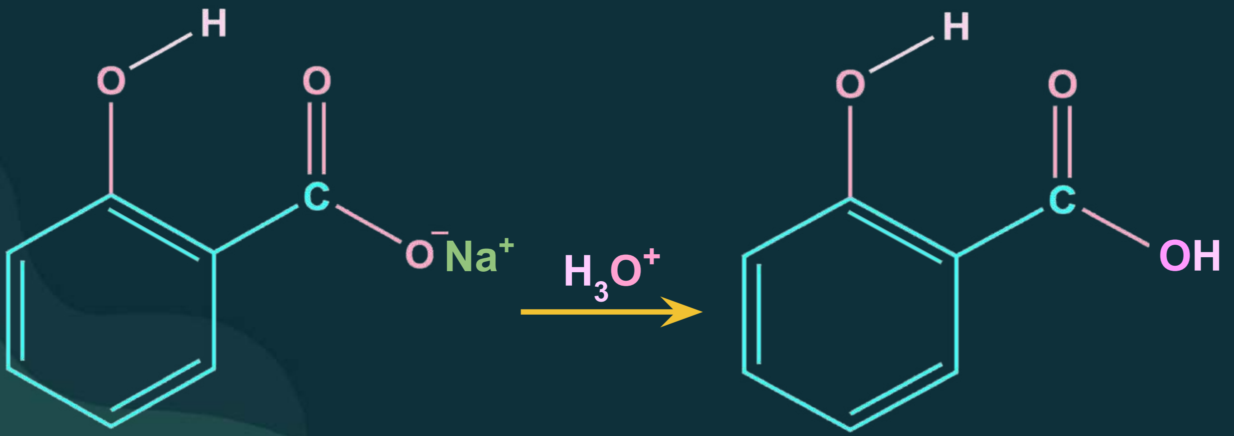
Sodium phenoxide

Reaction of Phenols



Sodium salicylate

Reaction of Phenols

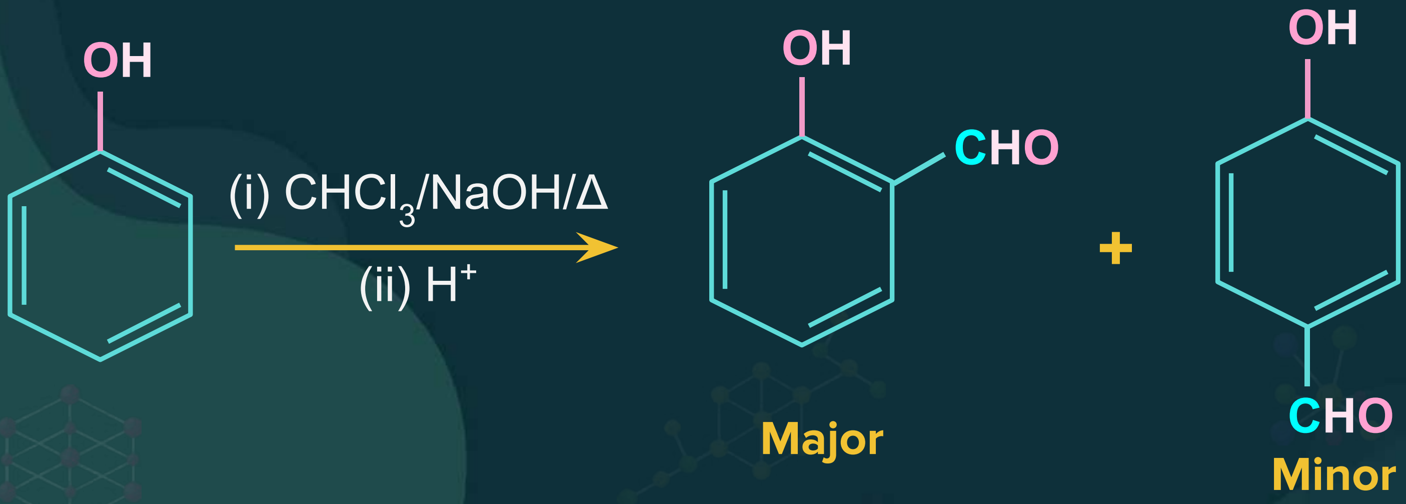


o-Hydroxybenzoic acid
(Salicylic acid)

Reaction of Phenols

Reimer-Tiemann reaction

- When phenol is refluxed with chloroform and NaOH at 340 *K*, followed by hydrolysis give salicylaldehyde.



Reaction of Phenols

Reimer-Tiemann reaction

Mechanism

Step 1 Generation of electrophile

Step 2 Attack of phenoxide ion on electrophile

Reaction of Phenols

Reimer-Tiemann reaction

Step 1 Generation of electrophile

$$CHCl_3 + NaOH \longrightarrow \bar{C}Cl_3 \longrightarrow :CCl_2$$

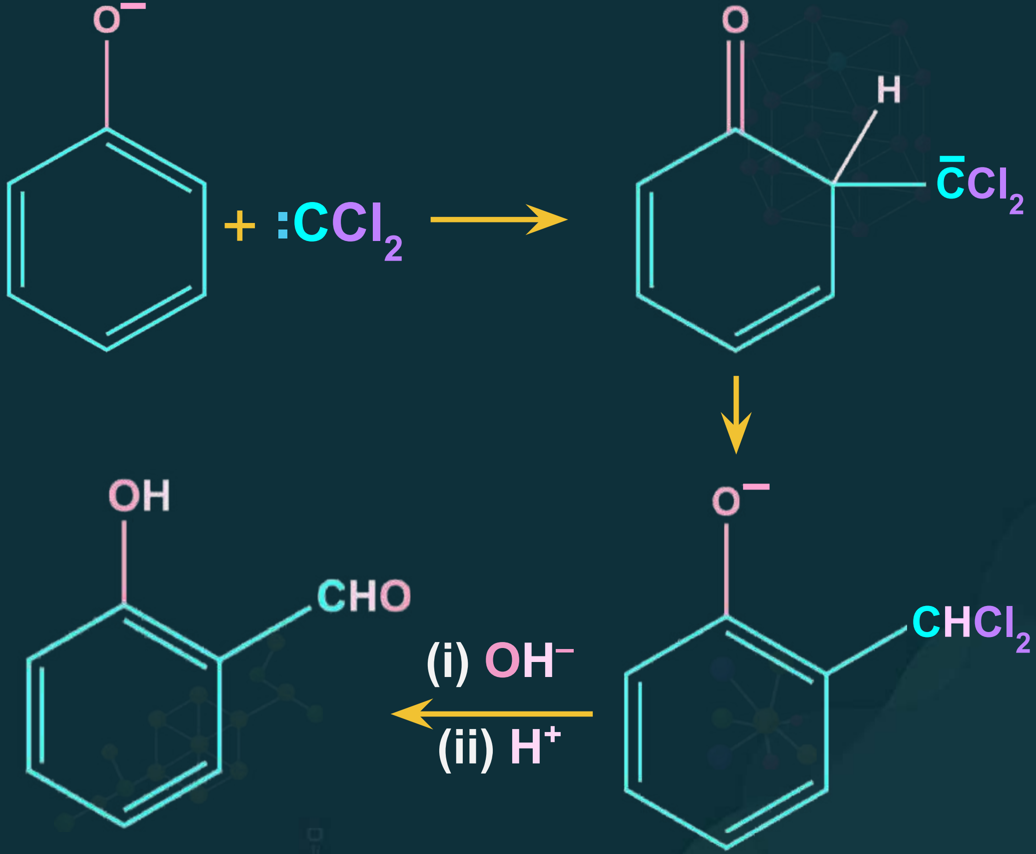
Electrophile

Reaction of Phenols

Reimer-Tiemann reaction

Step 2

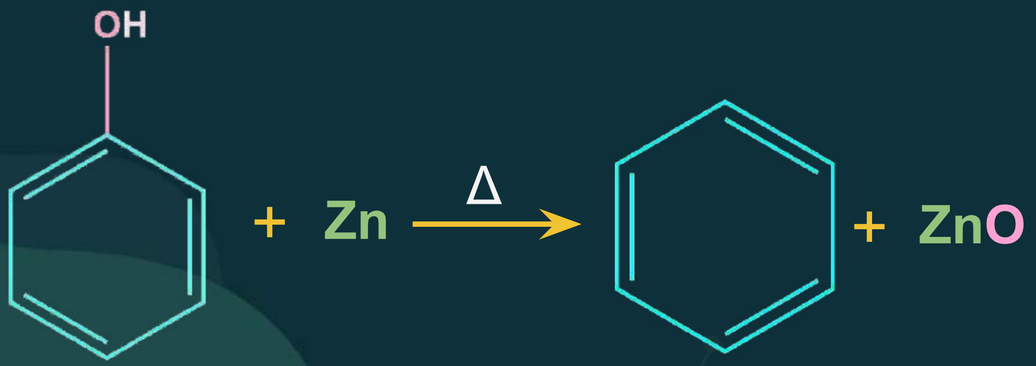
Attack of phenoxide ion on electrophile



Reaction of Phenols

Reaction of alcohol with zinc dust

- Phenol is converted to benzene on heating with zinc dust.



Which of following statements is correct?

BOARDS

(a) In Reimer-Tiemann reaction, dichlorocarbene intermediate is produced.

(b) Reimer-Tiemann reaction is an example of electrophilic substitution reaction.

(c) Highly reactive ring like aniline and highly deactivated ring like nitrobenzene, cyanobenzene do not give Friedel-Crafts reaction.

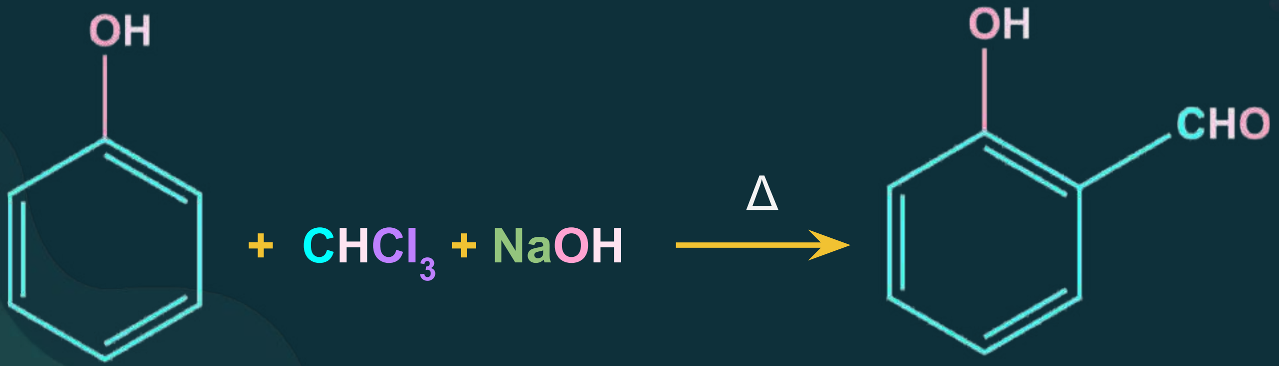
(d) All of these

Solution

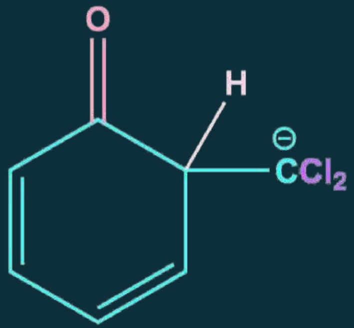
- In Reimer-Tiemann reaction, dichlorocarbene intermediate is produced and is an example of electrophilic substitution reaction.
- Highly reactive ring like aniline and highly deactivated ring like nitrobenzene, cyanobenzene do not give Friedel-Crafts reaction.

Therefore, option (d) is the correct answer.

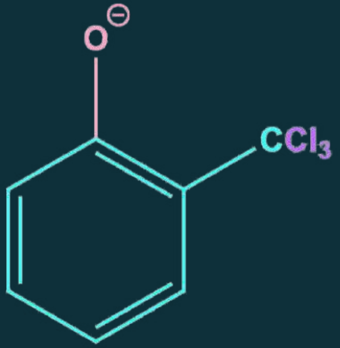
Identify the intermediates of the following reaction.



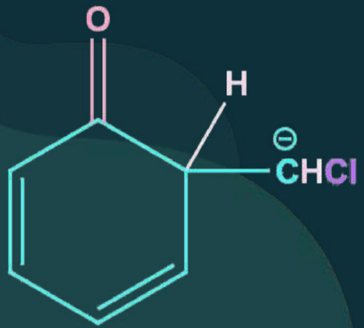
(a)



(b)



(c)



(d) All of these

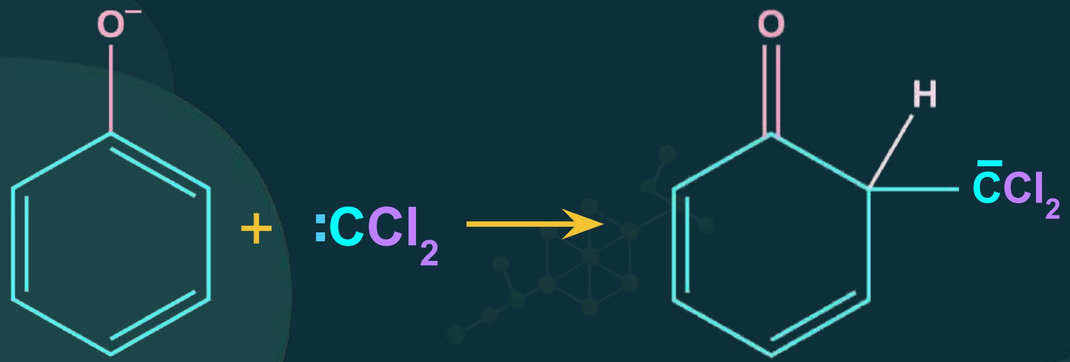
Solution

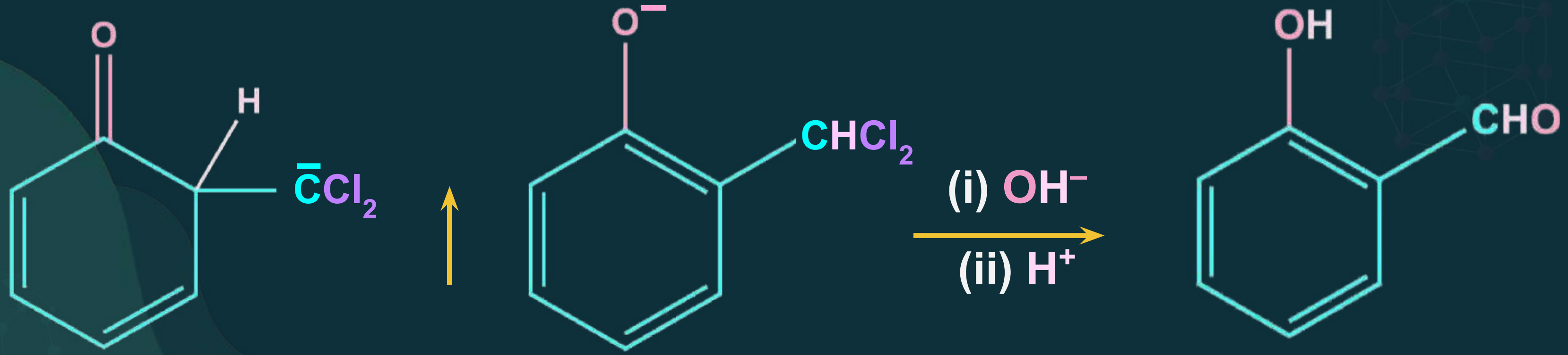
The given reaction is Reimer-Tiemann reaction.
Mechanism of reaction:

Step 1: Generation of electrophile

$$CHCl_3 + NaOH \longrightarrow \bar{C}Cl_3 \longrightarrow \underset{\text{Electrophile}}{:CCl_2}$$

Step 2: Attack of phenoxide ion on electrophile





Therefore, option (a) is the correct answer.

Commercially Important Alcohols

Important alcohols

- Methanol (CH_3OH)
- Ethanol (C_2H_5OH)

Methanol

Earlier, methanol was produced by the **destructive distillation of wood** (i.e., heating wood to a high temperature in the absence of air).

Hence, it was also known as **wood alcohol**.

Preparation and Properties of Methanol

Now, most methanol is prepared by the **catalytic hydrogenation of CO.**

$$CO + 2H_2 \xrightarrow[\substack{300\text{-}400\ ^\circ C \\ 200\text{-}300\ atm}]{ZnO\text{-}Cr_2O_3} CH_3OH$$

Preparation and Properties of Methanol

Harmful effects of methanol

- Methanol is **toxic. Ingestion** of even small quantities of methanol can cause **blindness** and large quantities cause death.
- Methanol poisoning can also occur by **inhalation** of the vapours or by prolonged exposure to the skin.

Uses of methanol

- It is used for making formaldehyde.
- It is used as solvent in paints.
- Methanol is converted into formaldehyde by catalytic vapour phase oxidation over a metal oxide catalyst.

Preparation and Properties of Methanol

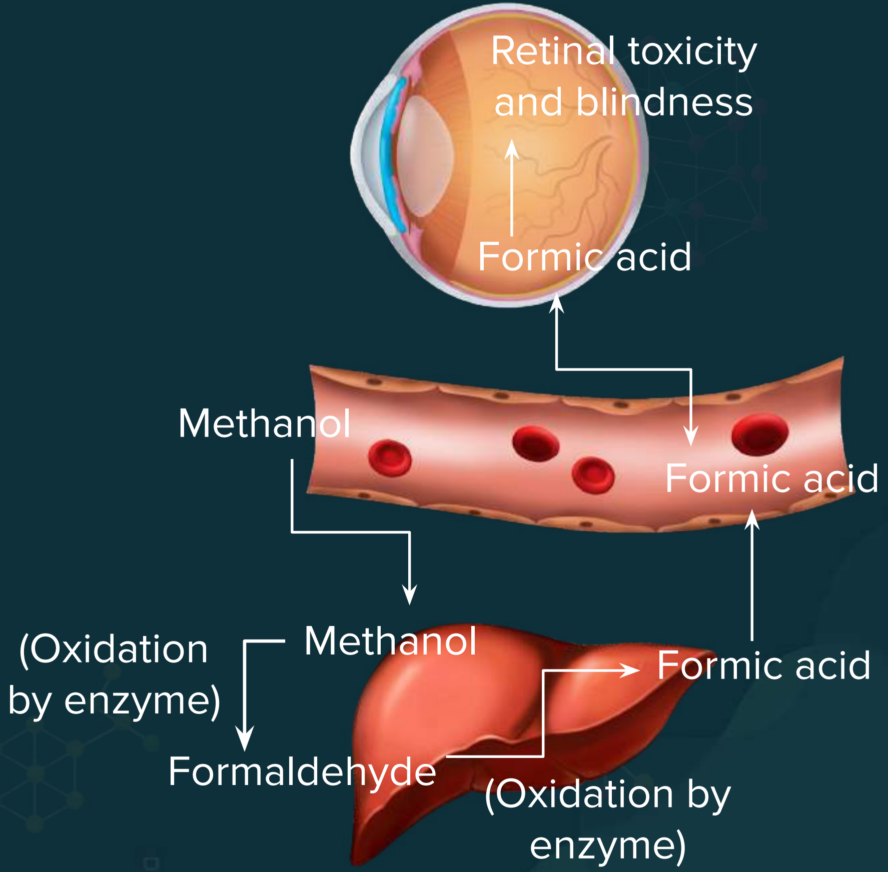
In one variation of the process methanol is vapourized, mixed with air and then passed over the catalyst at 300–600 °C. The formaldehyde produced is absorbed in water and then fed to a fractionating column.

Toxicity of methanol

Methanol is toxic in nature. When methanol enters in the body it gets oxidised to formaldehyde and on further oxidation it forms formic acid. Both behave as poison and travel to other parts of the body with blood and affect the nervous system and retina and cause permanent blindness.

Preparation and Properties of Methanol

It can also cause death. If someone consumes methanol then we should give ethanol to reduce the harmful effects of the methanol as it limits the oxidation of methanol in the human body.



Preparation and Properties of Ethanol

Ethanol

Ethanol can be made by the **fermentation** of sugars.

Synthesis of ethanol in the form of wine by the fermentation of the sugars of fruit juices was probably the **first accomplishment** in the field of organic synthesis.

Preparation and Properties of Methanol

Ethanol

Sugars from a wide variety of sources can be used in the preparation of alcoholic beverages.

Often, these sugars are from grains, and it is this derivation that accounts for ethanol having the synonym “**grain alcohol**”.

$$C_6H_{12}O_6 \xrightarrow[3O_2]{\text{Zymase}} C_2H_5OH + 4CO_2\uparrow + 3H_2O$$

Glucose/
Fructose

Ethanol

Carbon
dioxide

It shows after the whole fermentation and purification process, alcohol is stored in final tank and ready to pack in bottles and for shipping to sale.

Preparation and Properties of Ethanol

Preparation of ethanol

- Fermentation is usually carried out by **adding yeast** to a mixture of sugars and water.
- Yeast contains **enzymes** that promote a long series of reactions that ultimately **convert a simple sugar** ($C_6H_{12}O_6$) to ethanol and carbon dioxide.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Preparation and Properties of Ethanol

Fermentation **does not** produce beverages with an ethanol content greater than **12–15%**.

Enzymes of the yeast are **deactivated** at higher concentrations

To produce beverages of **higher alcohol content**, the aqueous solution must be **distilled**.

Preparation and Properties of Ethanol

Industrial preparation of ethanol

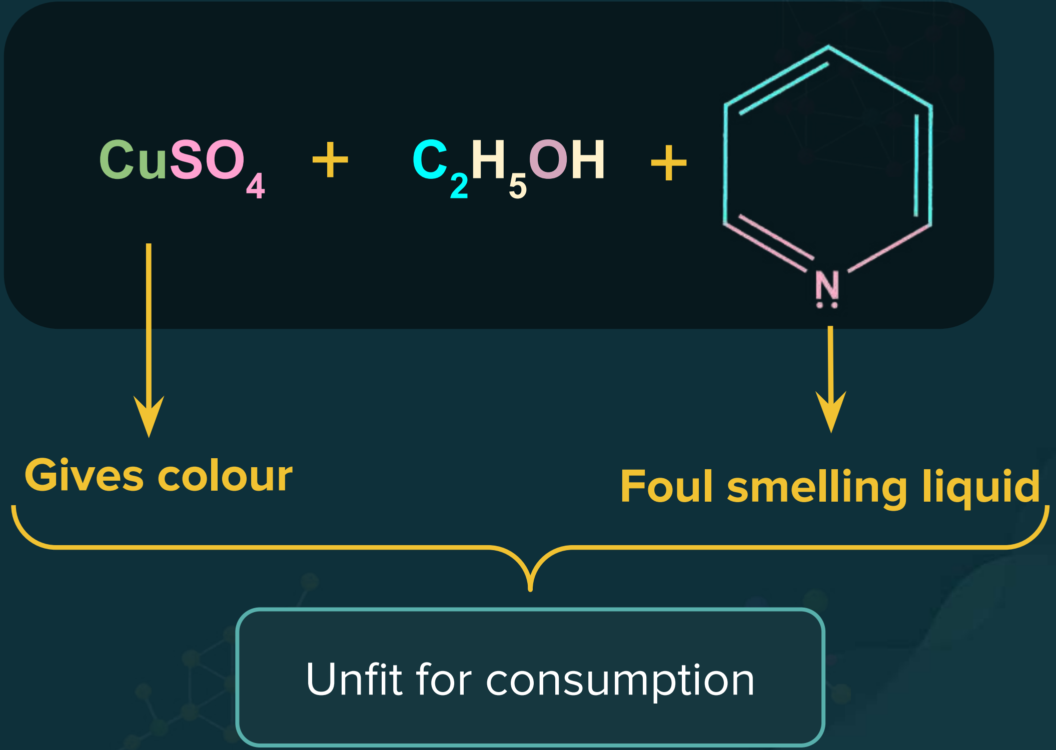
$$H_2C \mid CH_2 + H_2O \xrightarrow{\text{Acid}} CH_3{-}CH_2{-}OH$$

About **5%** of the world's ethanol supply is produced this way.

Preparation and Properties of Ethanol

Denaturation of ethanol

Mixing **toxic** and/or **bad tasting** additives is used to make commercial alcohol unfit for drinking.



$CuSO_4 + C_2H_5OH +$

Gives colour

Foul smelling liquid

Unfit for consumption

Preparation and Properties of Ethanol

Example:

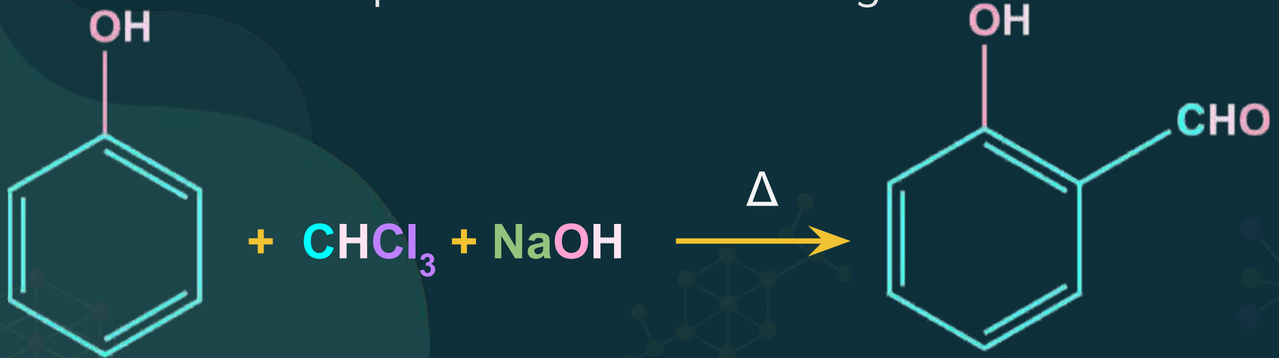
Denaturing of alcohol (pyridine is used for foul smelling), is done to make it unfit for human consumption.

Reaction of phenol with chloroform in presence of dilute sodium hydroxide, finally introduces which one of the following functional group?

(a) $-CH_2Cl$ (b) $-COOH$ (c) $-CHCl_2$ (d) $-CHO$

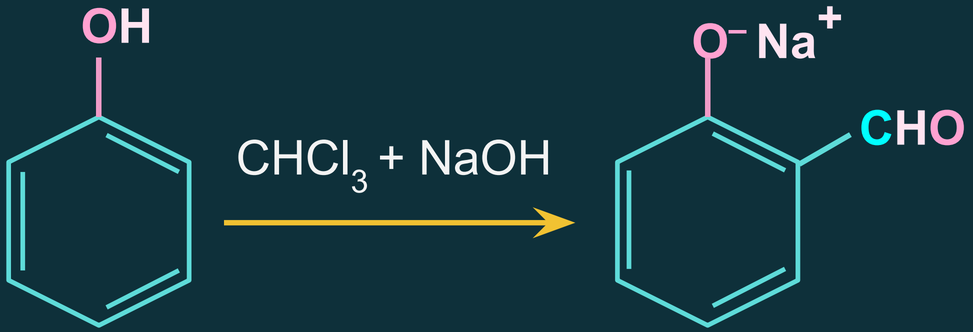
Solution

On treating phenol with chloroform in the presence of sodium hydroxide, a –CHO group is introduced at ortho position of benzene ring.



Therefore, option (d) is the correct answer.

In this reaction, the electrophile involved is:



(a) $CHCl_2^+$ (b) HCO^+ (c) $:CCl_2$ (d) CCl_3

Solution

The given reaction is Reimer-Tiemann reaction. Electrophile involved in this reaction is dichlorocarbene ($:CCl_2$).

$$CHCl_3 + NaOH \longrightarrow \bar{C}Cl_3 \longrightarrow \underset{\text{Electrophile}}{:CCl_2}$$

Therefore, option (c) is the correct answer.

When phenol is treated with $CHCl_3$ and NaOH, the product formed is:

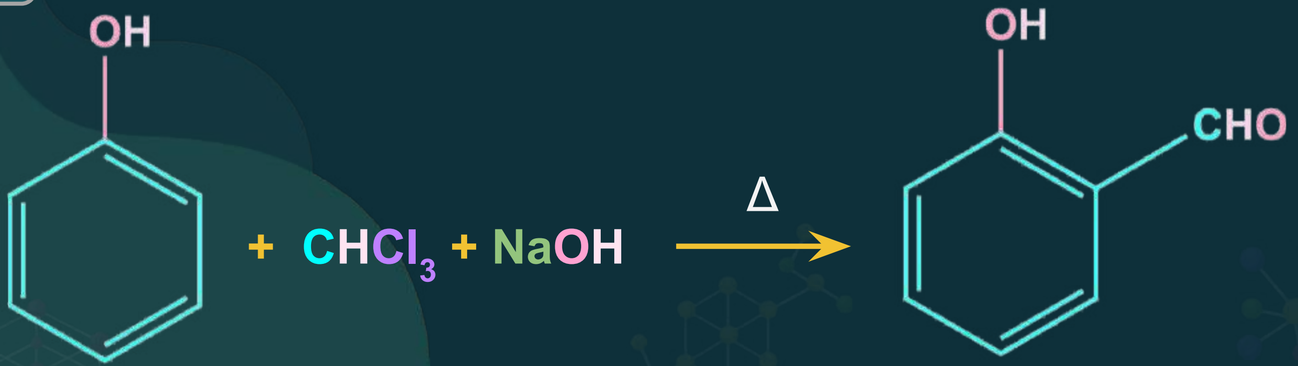
(a) Benzaldehyde

(b) Salicylaldehyde

(c) Salicylic acid

(d) Benzoic acid

Solution



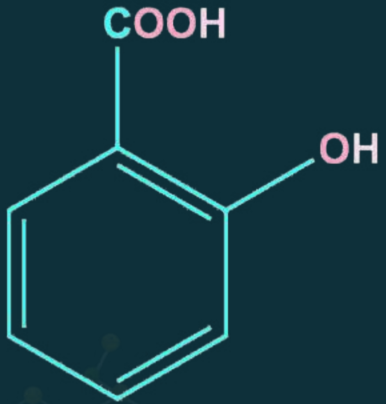
Salicylaldehyde

Therefore, option (b) is the correct answer.

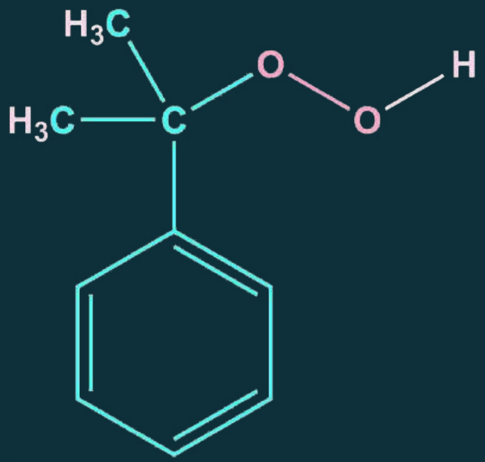
Phenol is distilled with Zn dust followed by Friedel-Crafts alkylation with propyl chloride in presence of $AlCl_3$ to give a compound (B). B is oxidised in presence of air to form compound C. The structural formula of C is:

(a)

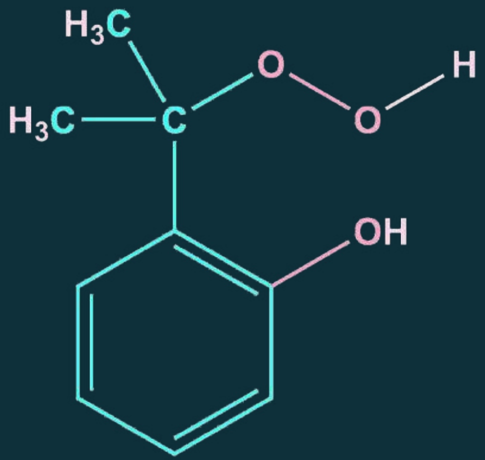
(b)



(c)

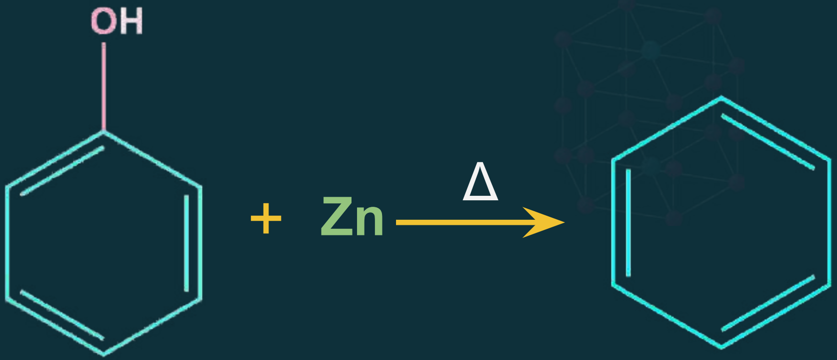


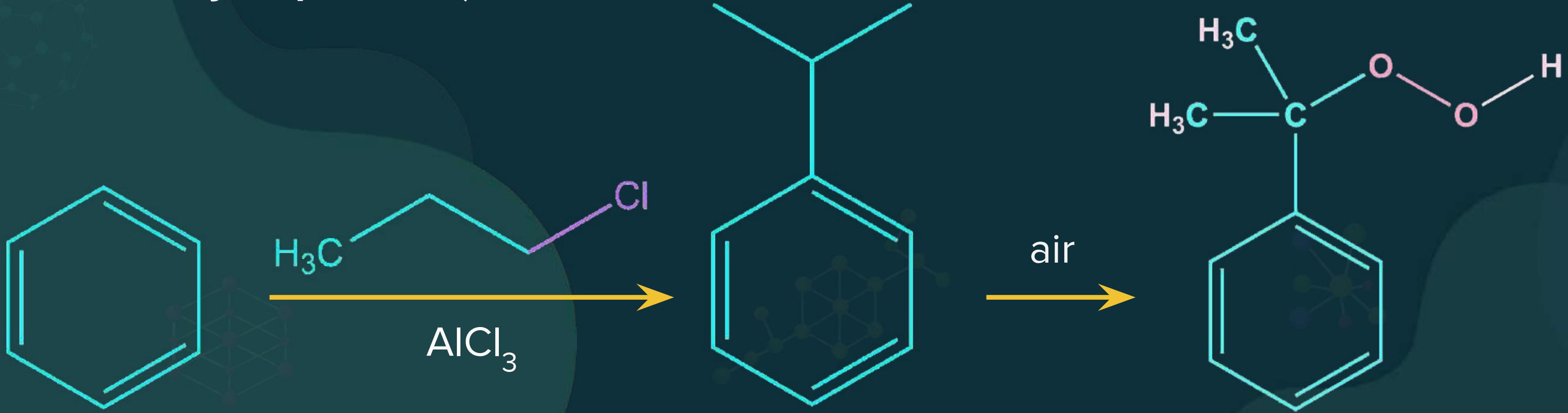
(d)



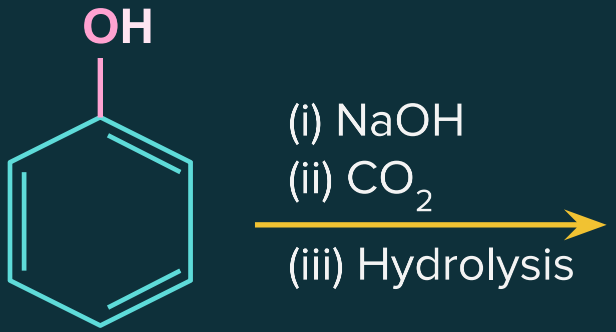
Solution

Phenol on reaction with Zn dust gives benzene which on further reaction with propyl chloride in presence of $AlCl_3$ undergoes Friedel Crafts alkylation involves formation of carbocation and hydride shift to give isopropyl benzene (Cummene) which on oxidation in the presence of air gives **(2-hydroperoxypropan-2-yl)benzene or (Cummene hydroperoxide)**





The product obtained from the reaction is:



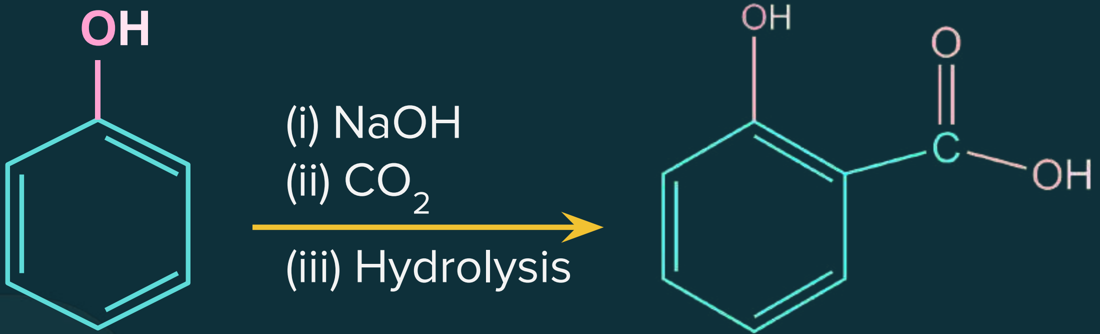
(a) Benzene

(b) Toluene

(c) Salicylic acid

(d) Benzoic acid

Solution



Clearly from the reaction above salicylic acid is formed upon Kolbe’s reaction.

Therefore, option (c) is the correct answer.

Assertion: Phenol undergo Kolbe’s reaction, ethanol does not.
Reason: Phenoxide ion is more basic than ethoxide ion.

BOARDS

(a) If both assertion and reason are correct and the reason is a correct explanation of the assertion.

(b) If both assertion and reason are correct but reason is not a correct explanation of the assertion.

(c) If the assertion is correct but reason is incorrect.

(d) If both the assertion and reason are incorrect.

Solution

Since in phenol and alcohol, phenol is more acidic than ethanol. Therefore, ethoxide ion is more basic than phenoxide ion.

Therefore, assertion is correct but reason is incorrect.

Hence, option (c) is the correct answer.

Methanol is industrially prepared by:

BOARDS

(a) Oxidation of CH_4 by steam at 900 °C

(b) Reduction of HCHO using $LiAlH_4$

(c) Reaction HCHO with a solution of NaOH

(d) Reduction of CO using H_2 and $ZnO\text{-}Cr_2O_3$

Solution

Reduction of CO using H_2 and $ZnO\text{-}Cr_2O_3$ is commercially used method for the preparation of methanol.

$$CO + 2H_2 \xrightarrow[\substack{300\text{-}400\ ^{\circ}C \\ 200\text{-}300\ atm}]{ZnO\text{-}Cr_2O_3} CH_3OH$$

Therefore, option (d) is the correct answer.

Phenol is heated with $CHCl_3$ and aqueous KOH when salicylaldehyde is produced. This reaction is known as:

BOARDS

(a) Rosenmund’s reduction reaction

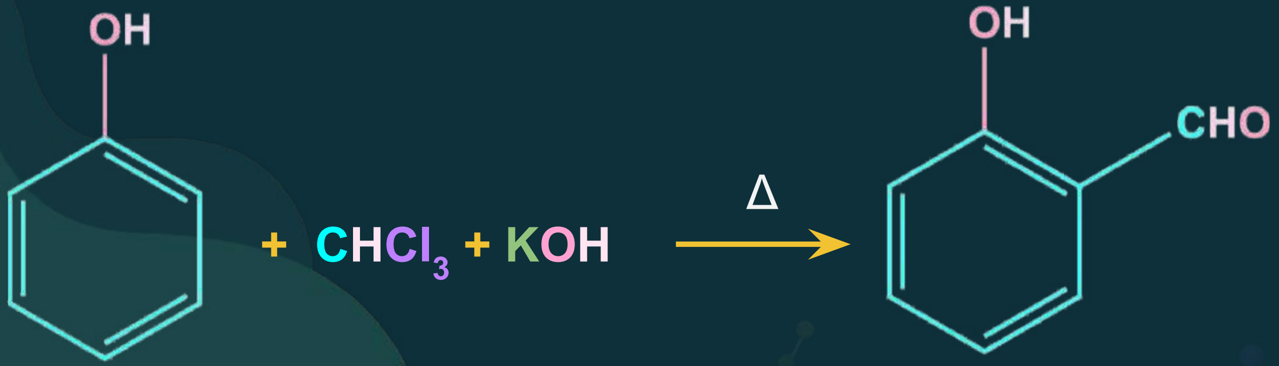
(b) Reimer-Tiemann reaction

(c) Friedel-Crafts reaction

(d) Sommelet reaction

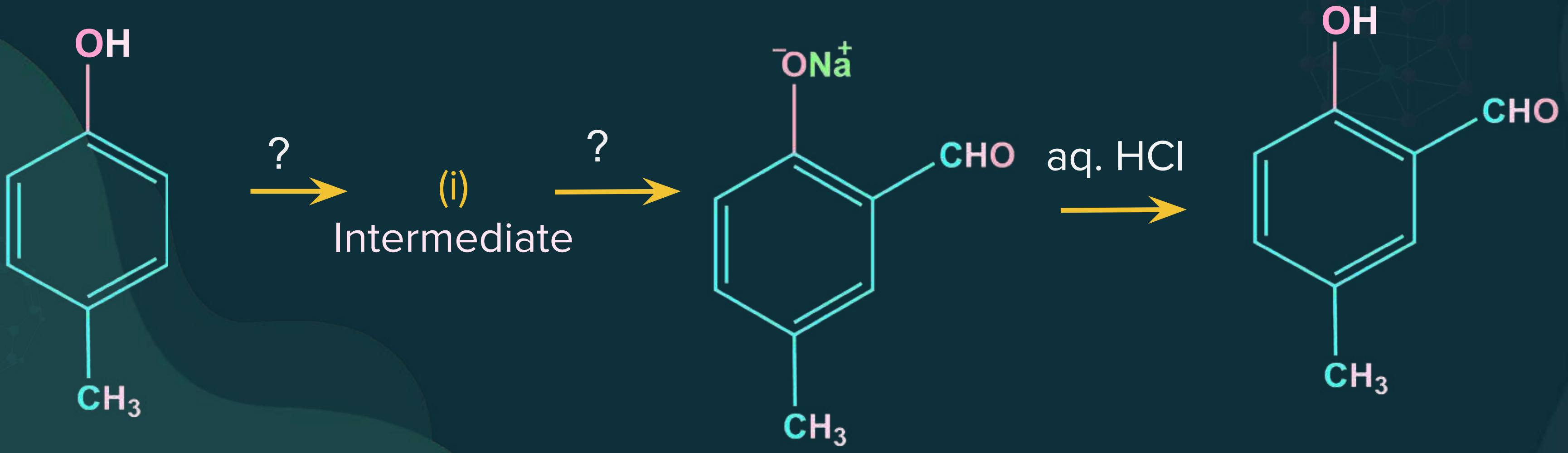
Solution

Phenol is heated with $CHCl_3$ and aqueous KOH when salicylaldehyde is produced. This reaction is known as Reimer-Tiemann reaction.



Therefore, option (b) is the correct answer.

Which one of the following reagents is used in the given reaction?



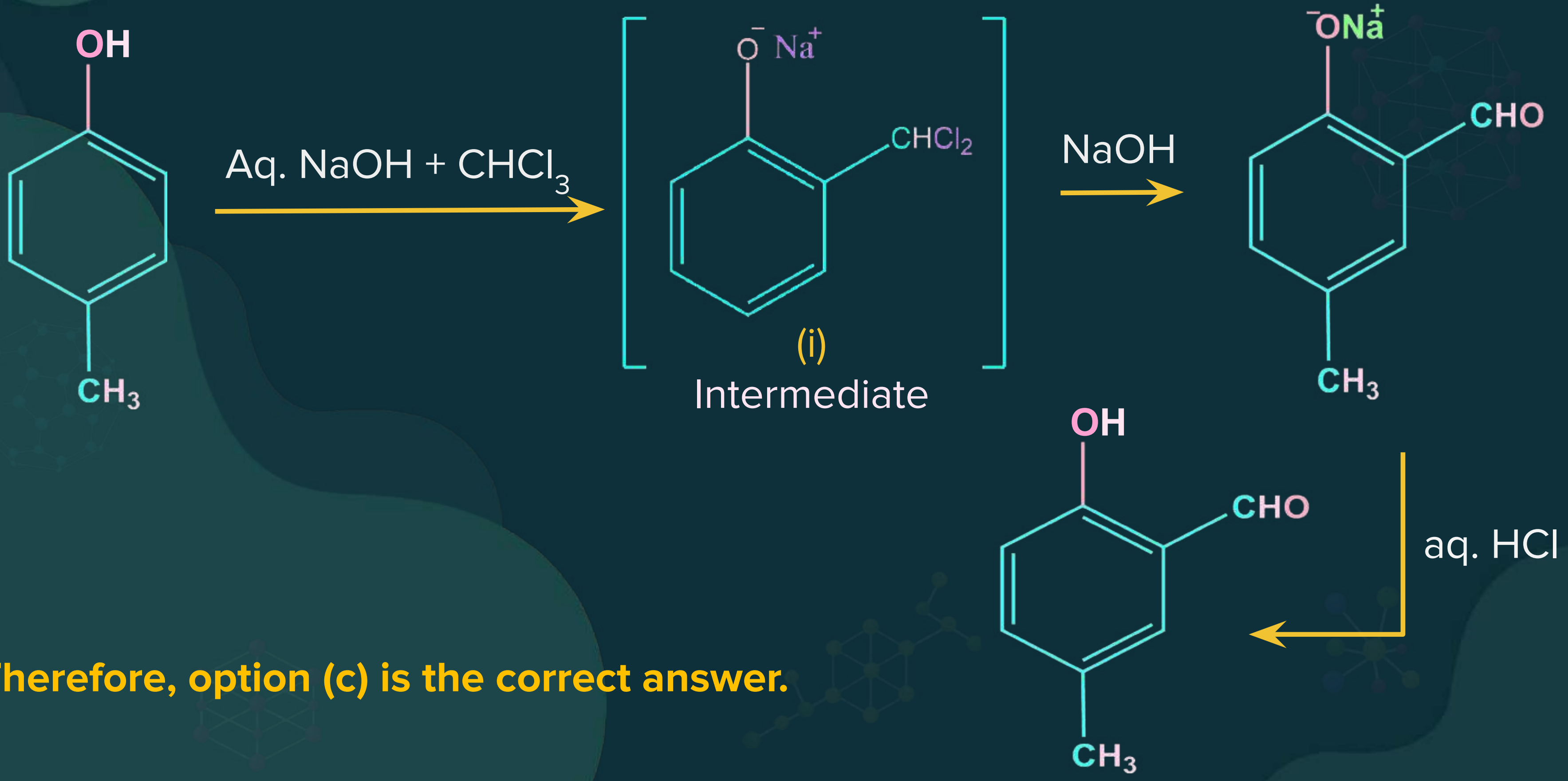
(a) Aq. NaOH + CH_3Cl

(b) Aq. NaOH + CH_2Cl_2

(c) Aq. NaOH + $CHCl_3$

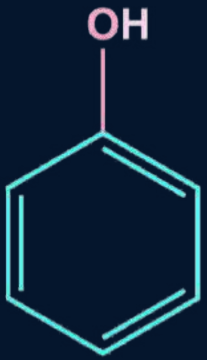
(d) Aq. NaOH + CCl_4

Solution



Therefore, option (c) is the correct answer.

Select the correct options:



$$\xrightarrow[\text{(ii) } H^+]{\text{(i) } CHCl_3 + NaOH,\ \Delta} \text{P > Q (\% yield)}$$

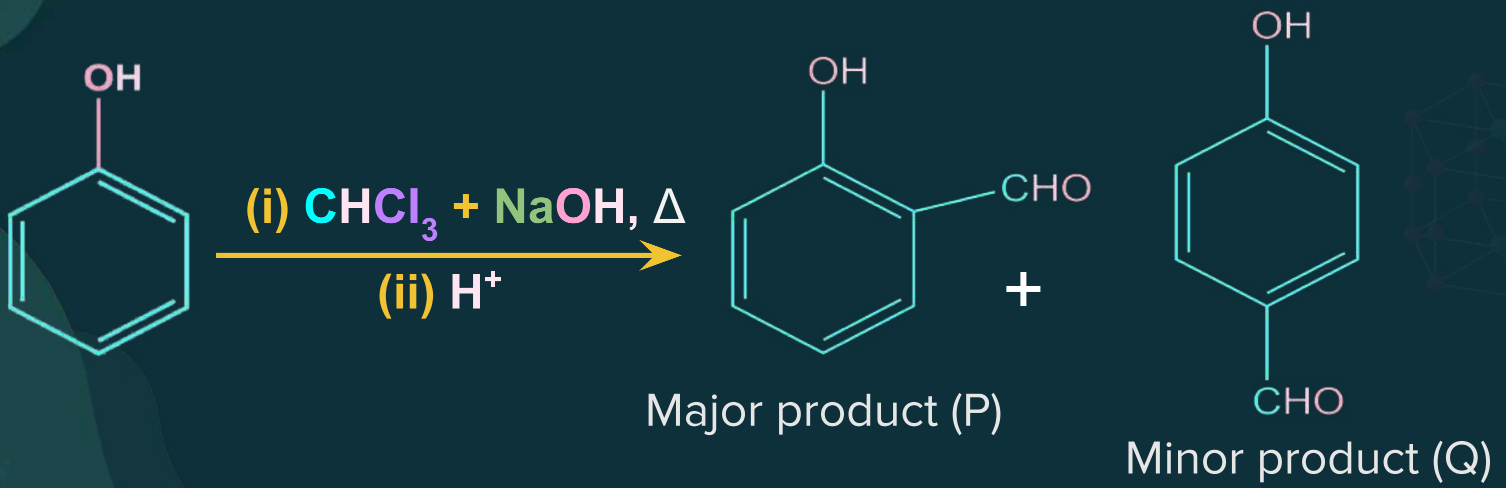
(a) Boiling point, (P > Q)

(b) Melting point, (P > Q)

(c) Water solubility, (P < Q)

(d) Acid strength, (Q < P)

Solution

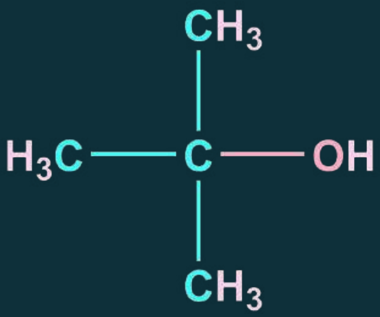


Since this reaction is known as the Reimer-Tiemann reaction the product formed is o-salicylaldehyde and p-salicylaldehyde as P and Q respectively. Since, there will be intramolecular hydrogen bonding in case of o-salicylaldehyde hence boiling point of P is less than that of Q. Due to intramolecular hydrogen bonding in case of o-salicylaldehyde its melting point, solubility in water as well as acid strength also decreases.

Hence, option (c) is correct answer.

PhMgBr + (x) $\longrightarrow$  ; (x) is:

(a) CH_4

(b) 

$(CH_3)_3C{-}OH$

(c) 

(d) Ether

Solution

Here (x) must have the acidic hydrogen; in given option only option (b) has acidic hydrogen.

Hence, option (b) is correct answer.

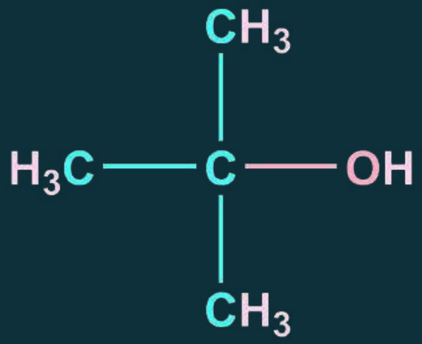
Which among the following compounds is the most acidic in nature?

(a) HOH

(b) CH_3OH

(c) CH_3CH_2OH

(d)



$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH$

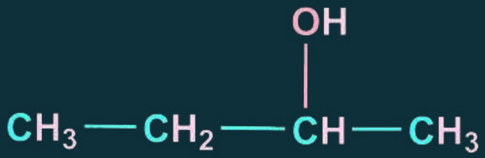
Solution

Water is more acidic than all alcohols except methanol CH_3OH.

Therefore, option (b) is the correct answer.

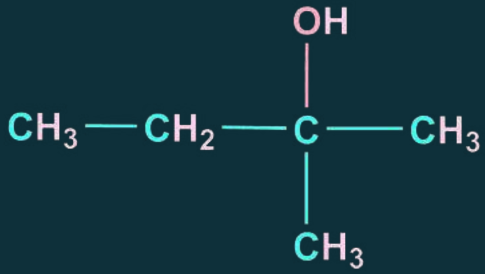
When vapour of an alcohol is passed over Cu at 300 °C, the product is isobutene. Alcohol in this reaction will be:

(a)



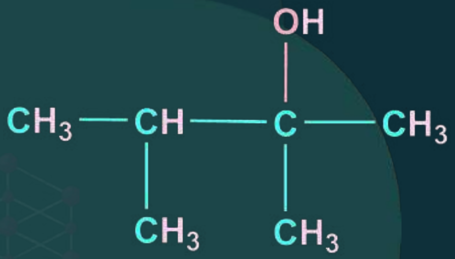
$$CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-CH_3$$

(b)



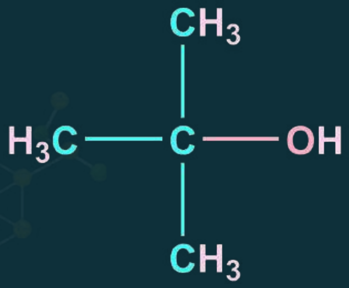
$$CH_3-CH_2-\overset{OH}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_3$$

(c)



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

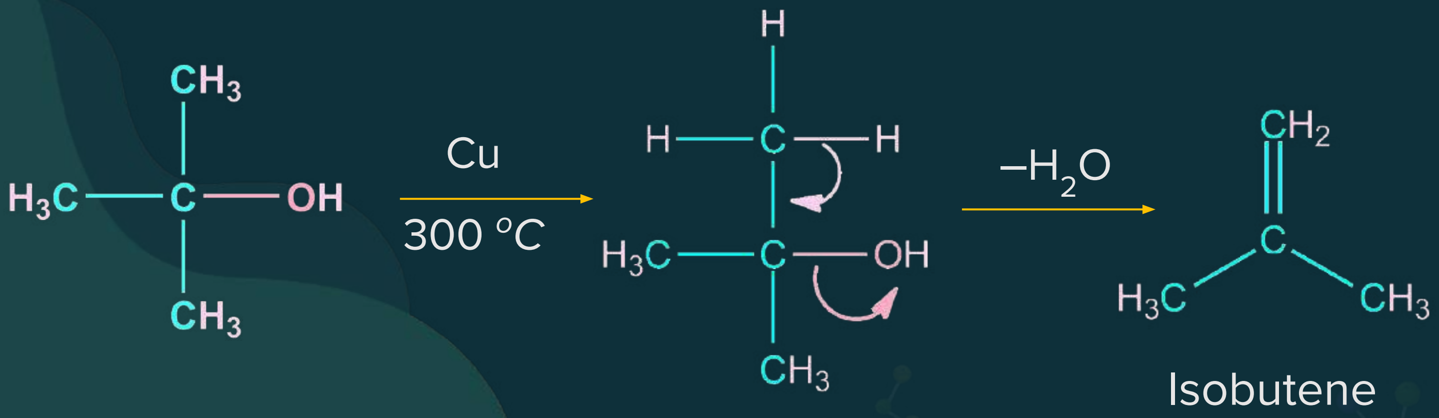
(d)



$$H_3C-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-OH$$

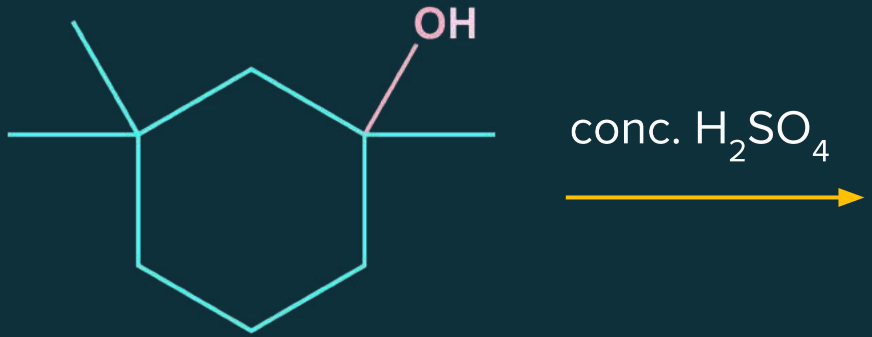
Solution

Tertiary alcohols, when heated with copper get dehydrated to give alkenes.

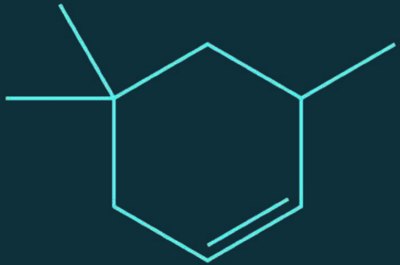


Therefore, option (d) is the correct answer.

Which is not a likely product formed when the following alcohol is treated with concentrated sulfuric acid?

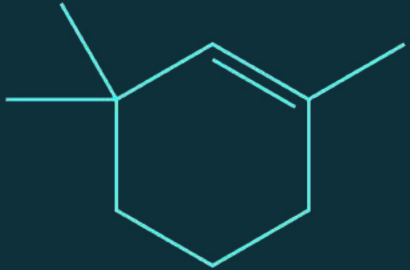


(a)



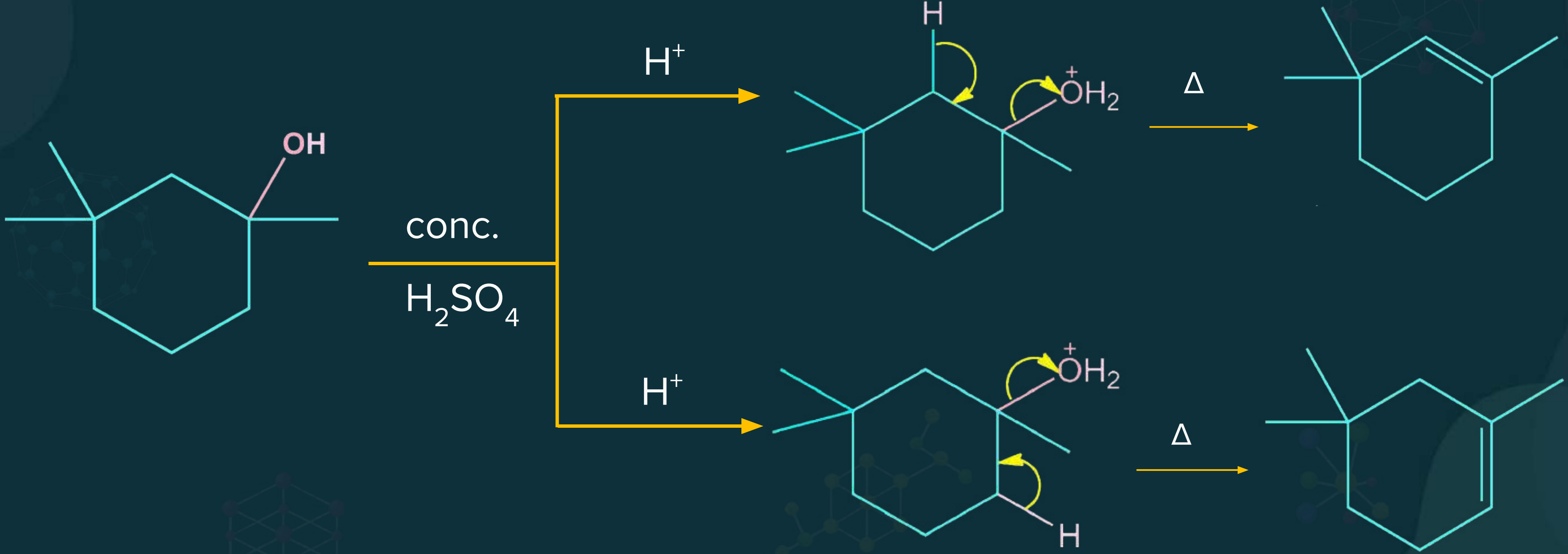
(b)

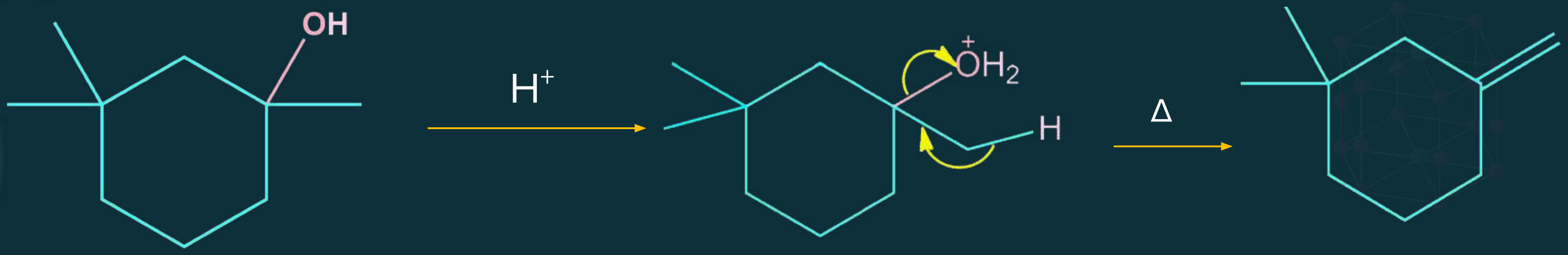
(c)



(d)

Solution



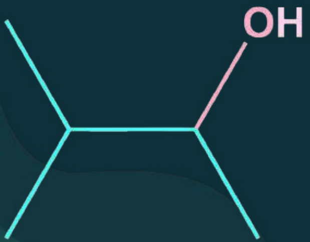


Since, option (a) is not a possible product.

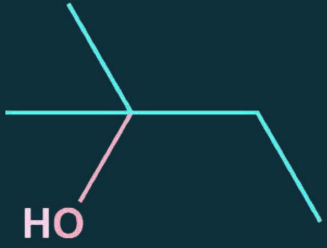
Therefore, option (a) is the correct answer.

; Structure of (A) is:

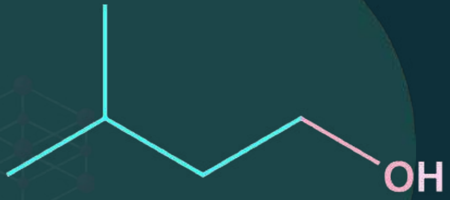
(a)



(b)



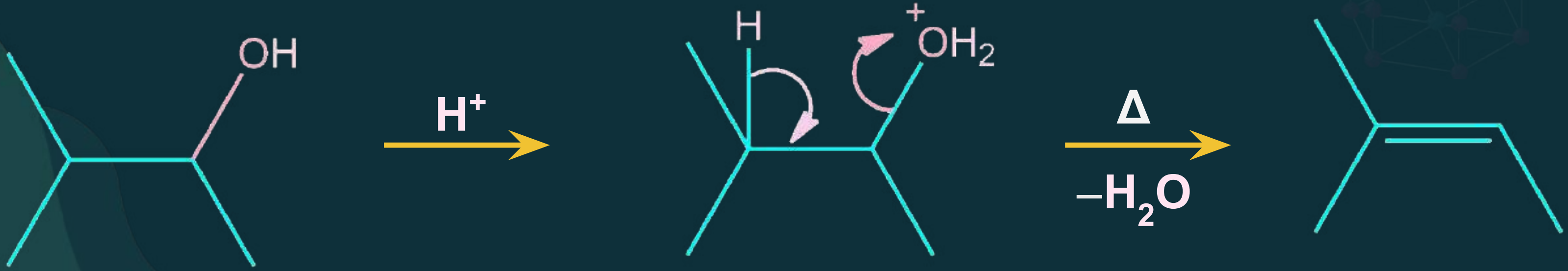
(c)



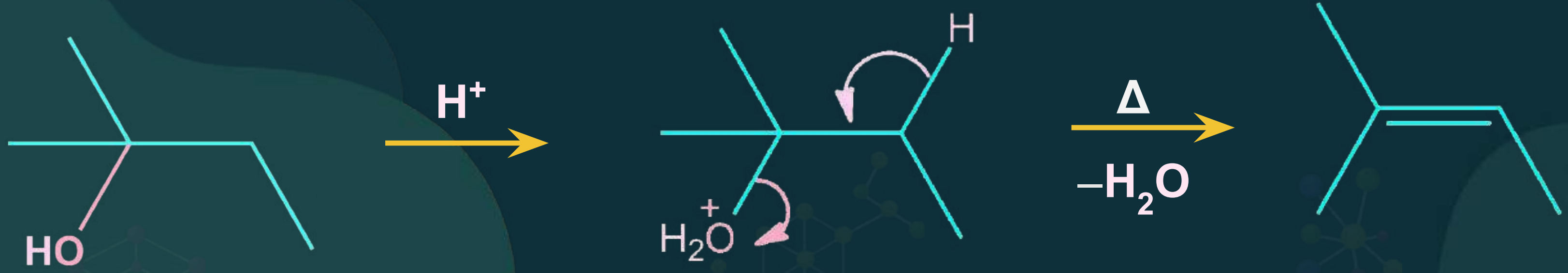
(d) All of these

Solution

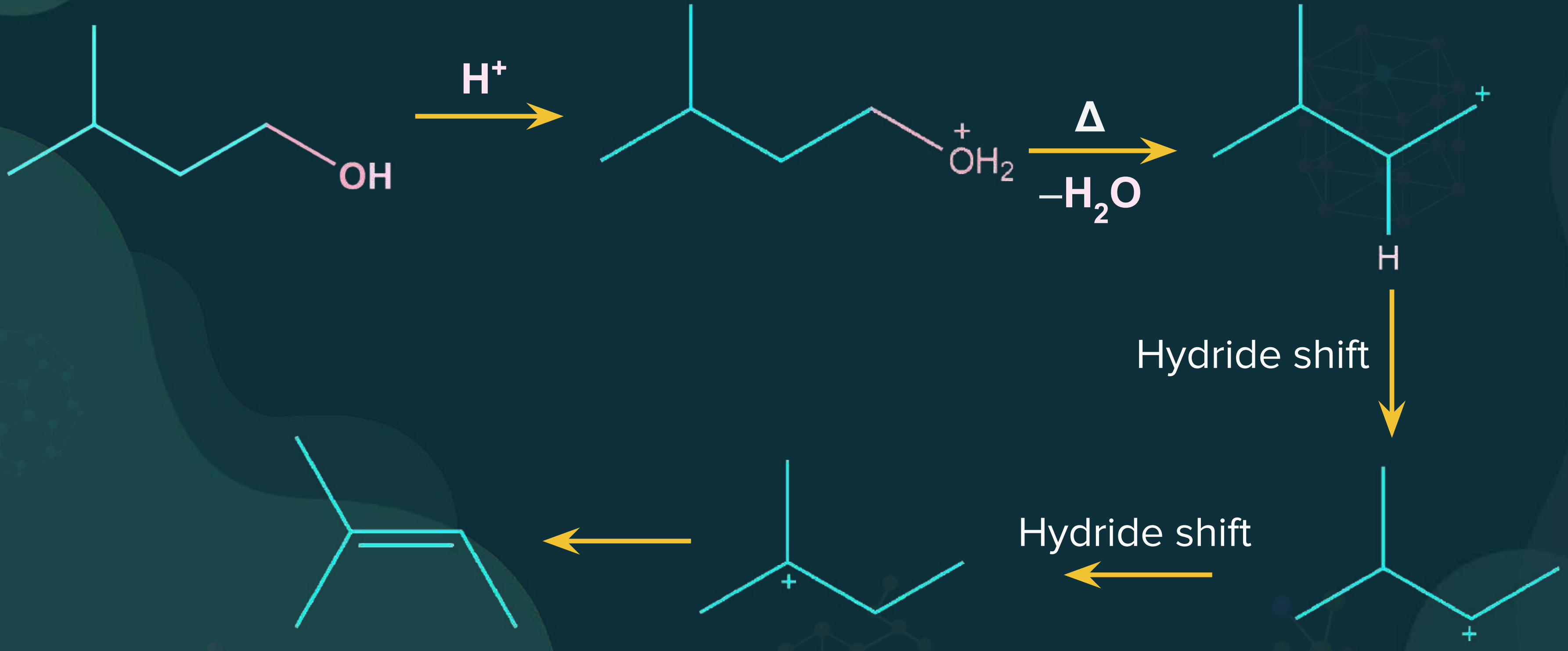
(a)



(b)



(c)

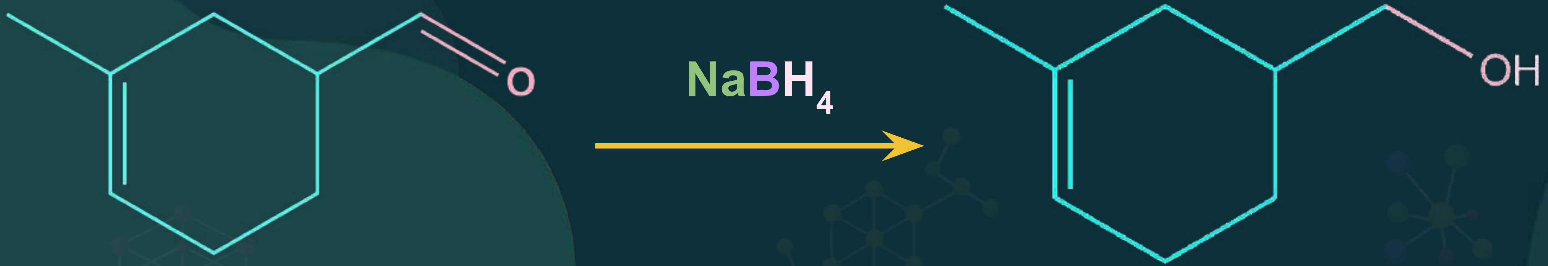


Therefore, option (d) is the correct answer.

What is the major product of the following reaction?

Solution

$NaBH_4$ is a mild reducing agent. It reduces aldehyde to primary alcohols.



Chemical Properties of Ethers

Chemical reactions of ethers

1. Cleavage of C–O bond in ethers
2. Electrophilic substitution reaction

Cleavage of C–O bond in ethers

Ethers are **unreactive towards most bases**, but they can react under acidic conditions.

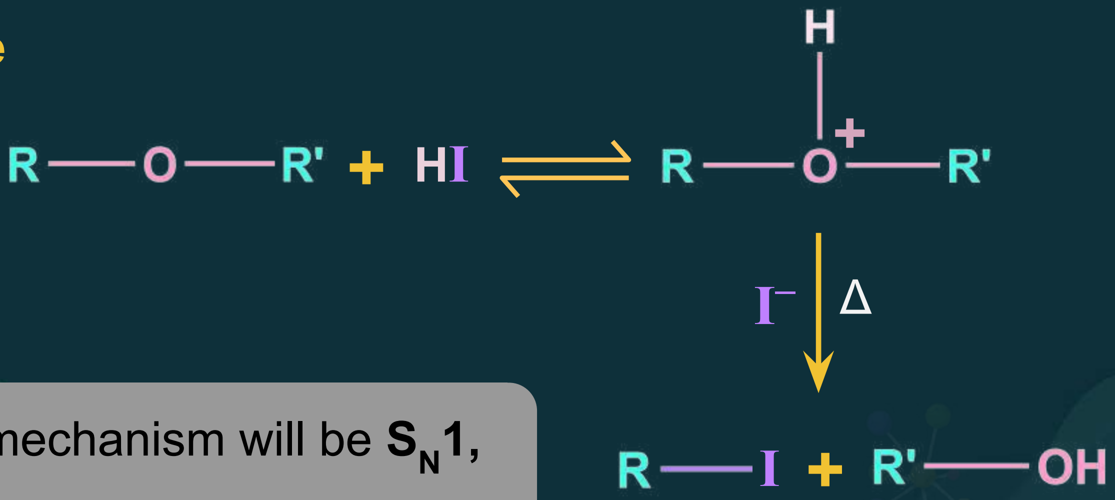
A protonated ether can undergo **substitution** with the expulsion of an alcohol.

Chemical Properties of Ethers

Reactions of Ethers with HX

Ethers react with **conc. HBr & HI** because these reagents are **sufficiently acidic** to protonate the ether. **Bromide** & **iodide** are good nucleophiles for the **substitution reaction**

General reaction

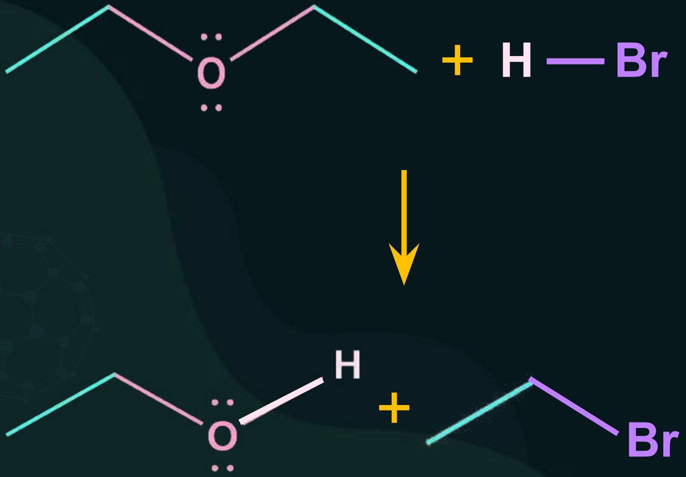


$$R-O-R' + HI \rightleftharpoons R-\overset{\overset{\displaystyle H}{|}}{O^{+}}-R' \xrightarrow[\Delta]{I^-} R-I + R'-OH$$

If R or R’ is 3º, then mechanism will be **S_N1,** otherwise **S_N2**.

Chemical Properties of Ethers

S_N2 Reaction of Ethers



Mechanism of S_N2 Reaction

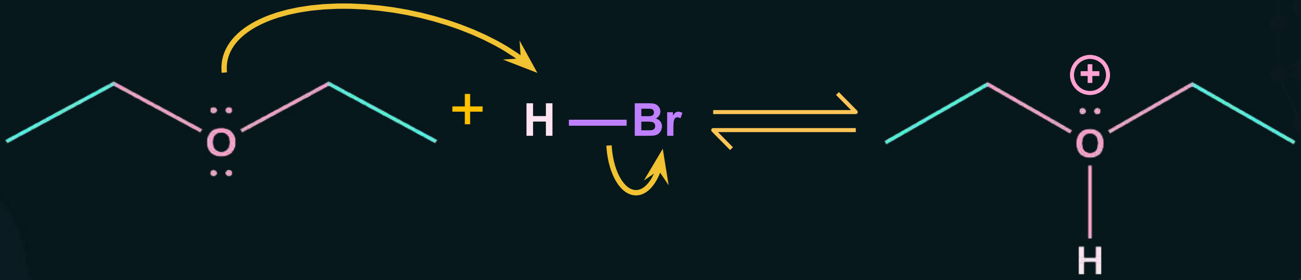
Step 1 Protonation of ether

Step 2 Attack of nucleophile

If HBr is present in **excess**, ethanol (just formed) reacts with HBr (present in excess) to form a **second equivalent** of ethyl bromide.

Chemical Properties of Ethers

Protonation of ether

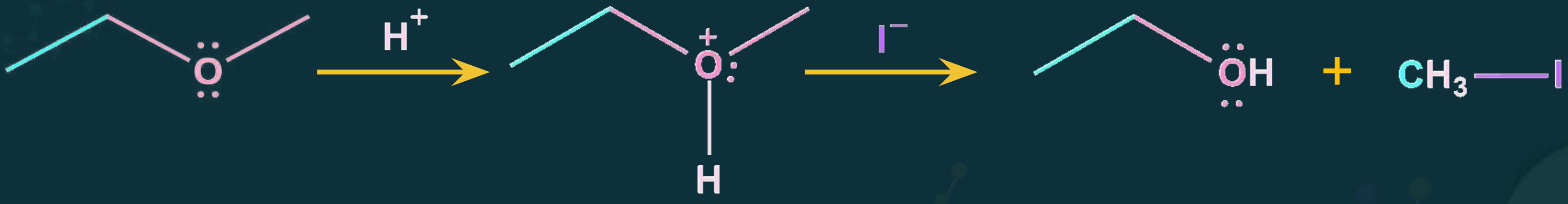


Attack of nucleophile

The **major product** of this reaction is:

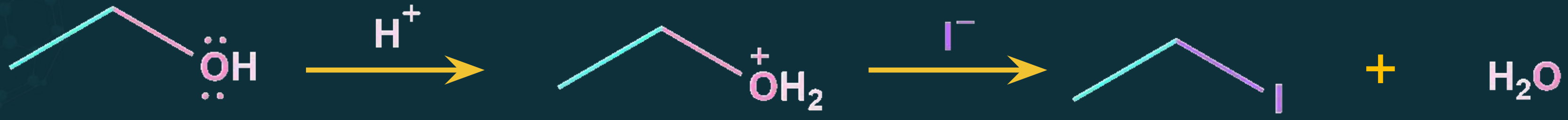
Solution

When HI is added to the compound, following reaction occurs:



S_N2 attack will happen on that substrate which is less sterically hindered therefore the attack happen on carbon of methyl group side not ethyl side.

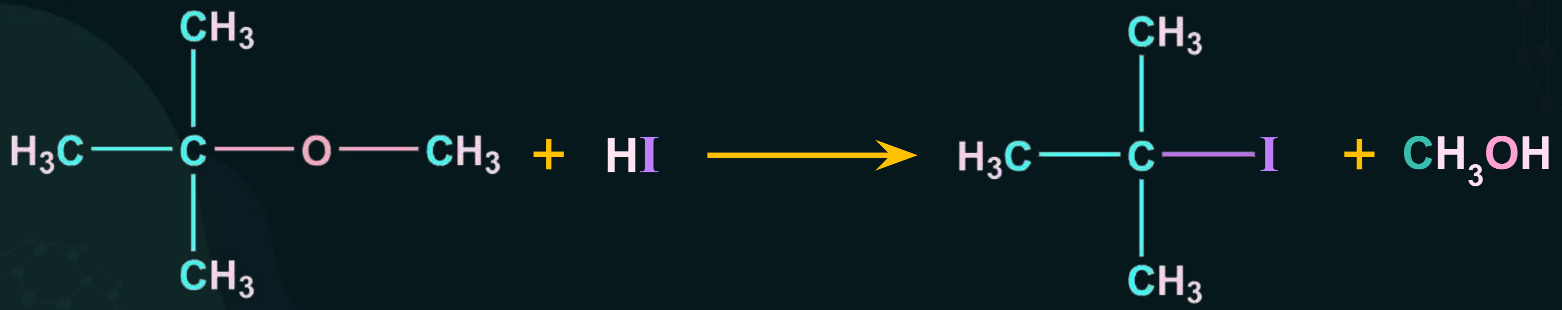
When excess HI is added to the compound then the alcohol which is formed as product abstract H^+ from HI and the attack of nucleophile (I^-) take place on the electrophilic carbon which is attached with oxygen. The reaction is given as follow:



Ethyl iodide is formed in case of excess HI.

Chemical Properties of Ethers

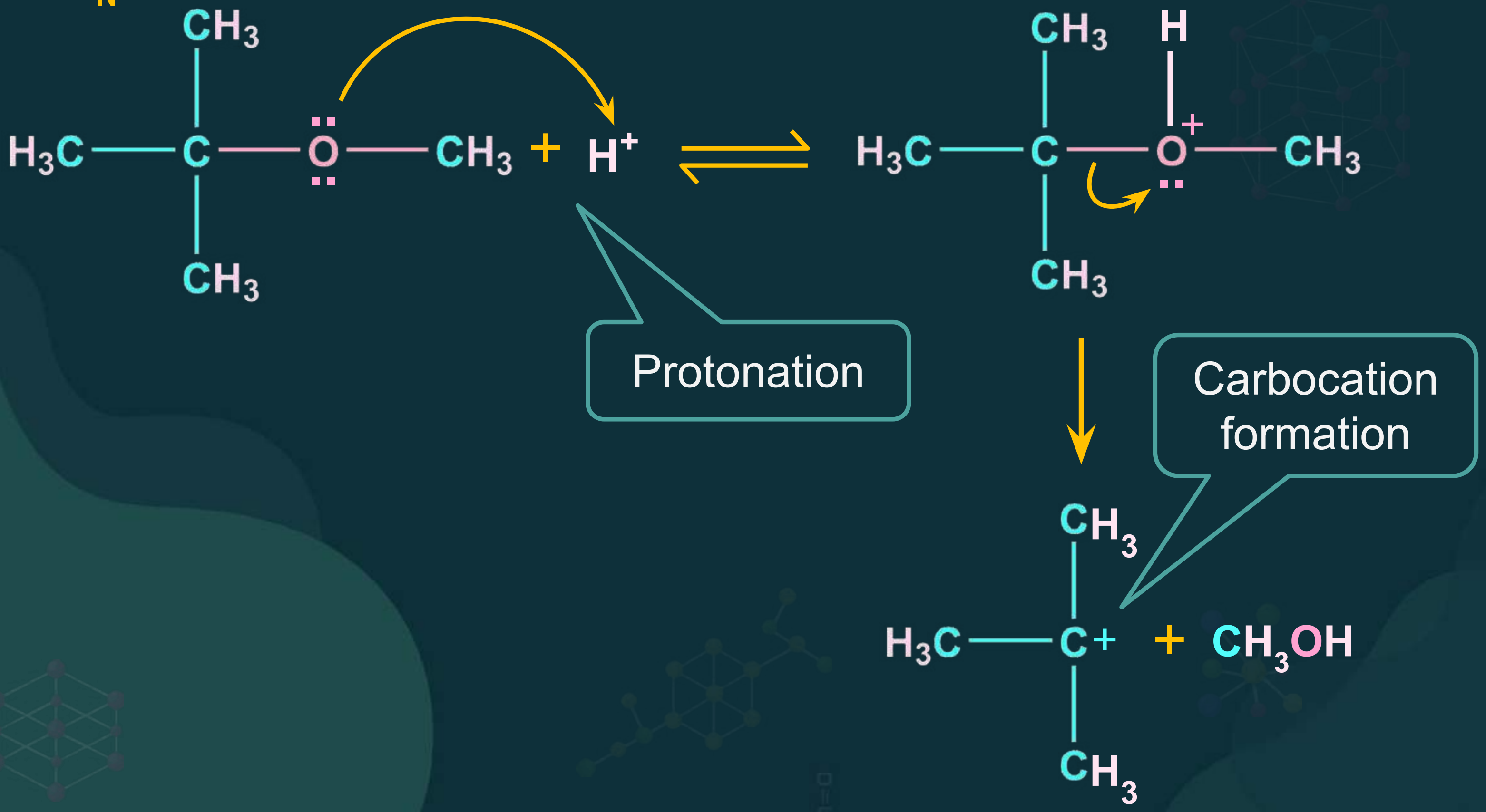
S_N1 Reaction of Ethers



$$\mathrm{H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-O-CH_3 + HI \longrightarrow H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-I + CH_3OH}$$

Chemical Properties of Ethers

Mechanism of S_N1 Reaction

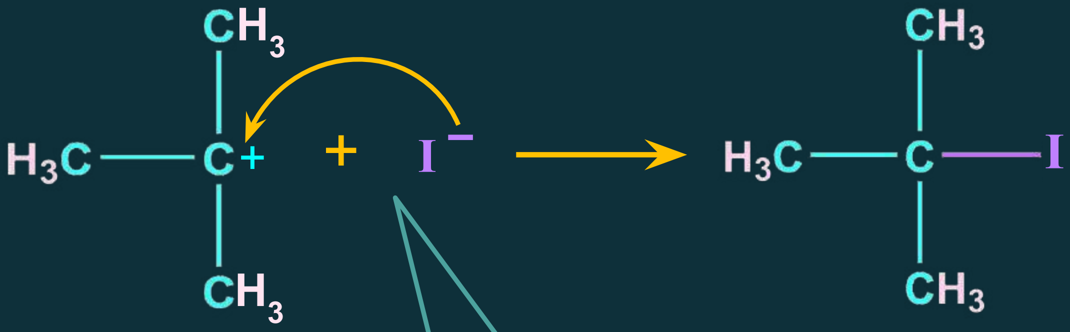


$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\ddot{\underset{\cdot\cdot}{O}}-CH_3 + H^+ \rightleftharpoons H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{\cdot\cdot}{O^+}}-CH_3 \longrightarrow H_3C-\overset{CH_3}{\underset{CH_3}{C^+}} + CH_3OH$$

Protonation

Carbocation formation

Chemical Properties of Ethers

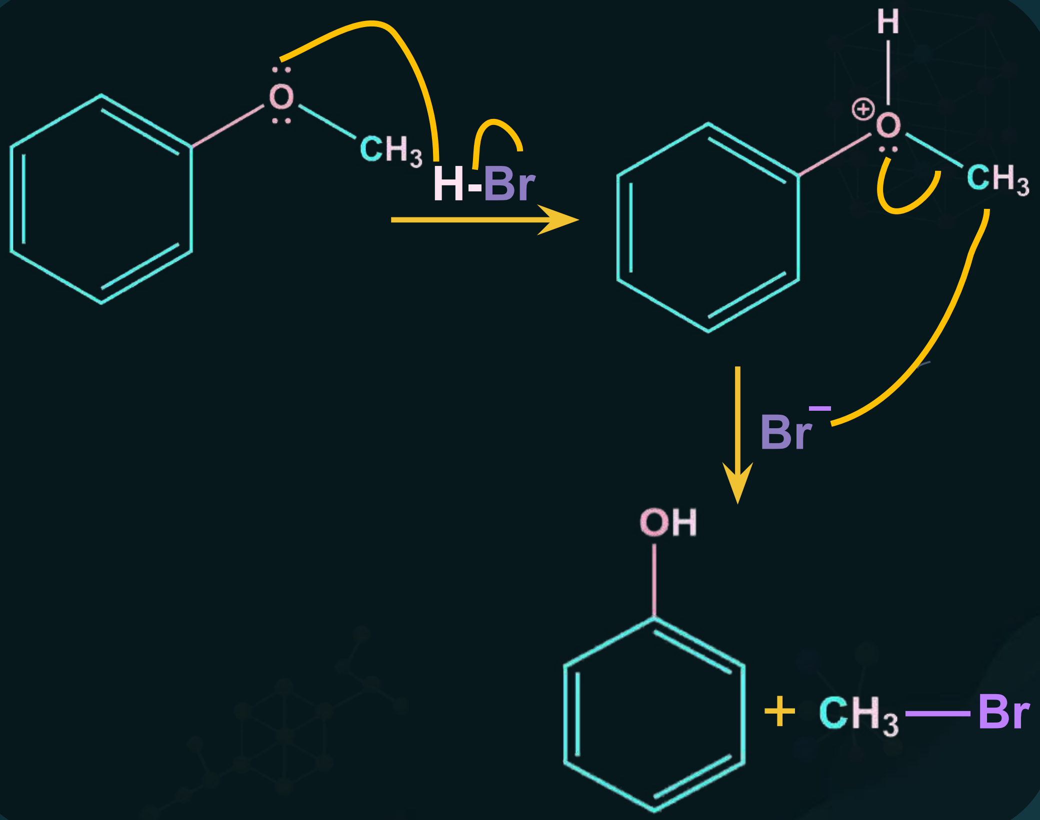


Attack of the nucleophile

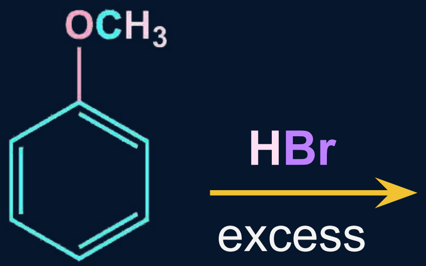
Chemical Properties of Ethers

Alkyl Aryl Ether

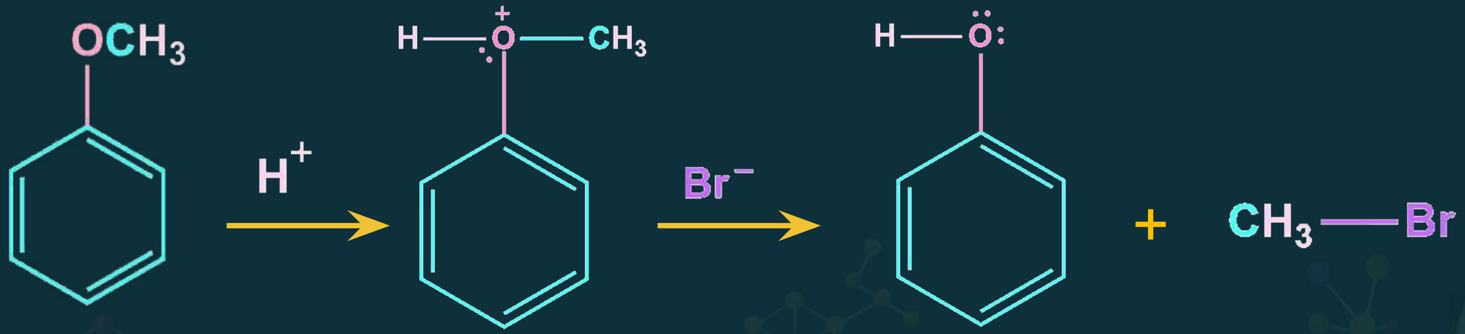
Alkyl aryl ethers are cleaved at the **alkyl-oxygen bond** due to the more stable aryl-oxygen bond.



The major product of this reaction is:

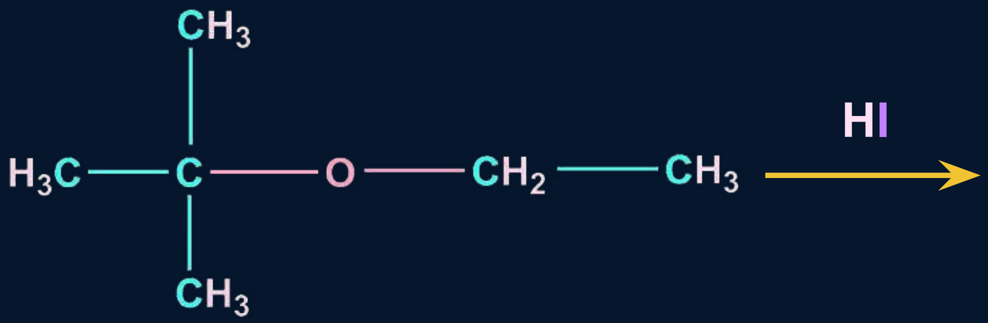


Solution



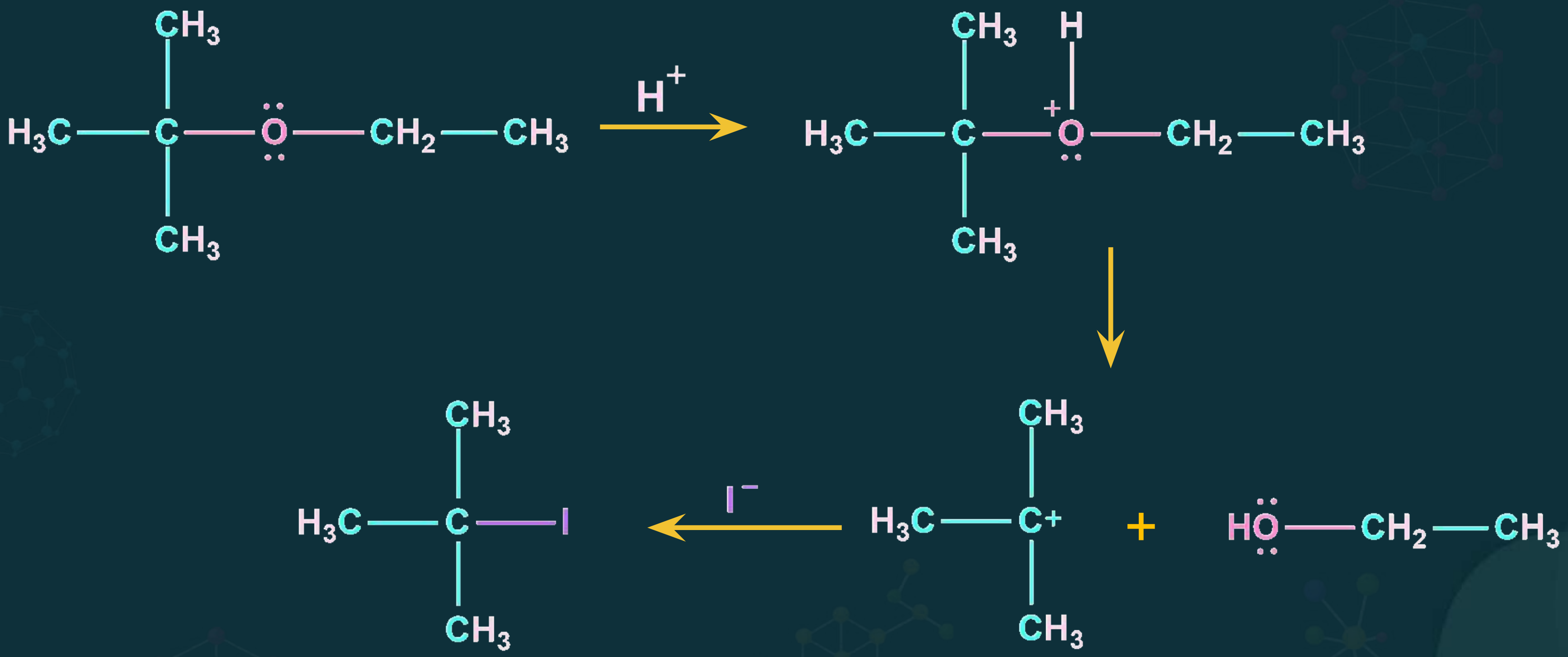
This reaction proceed via **S_N2 mechanism.**

The products of the following reaction are:



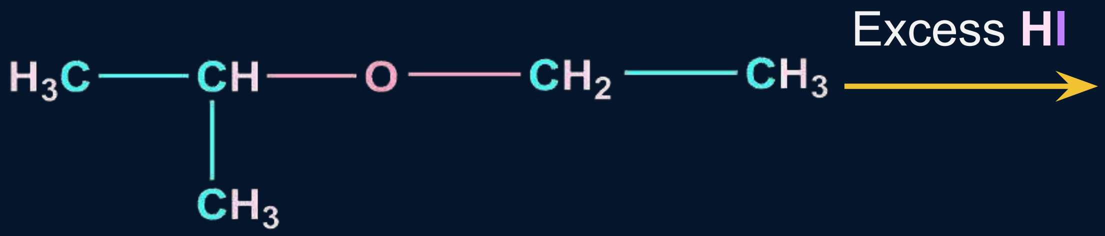
$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-O-CH_2-CH_3 \xrightarrow{HI}$$

Solution



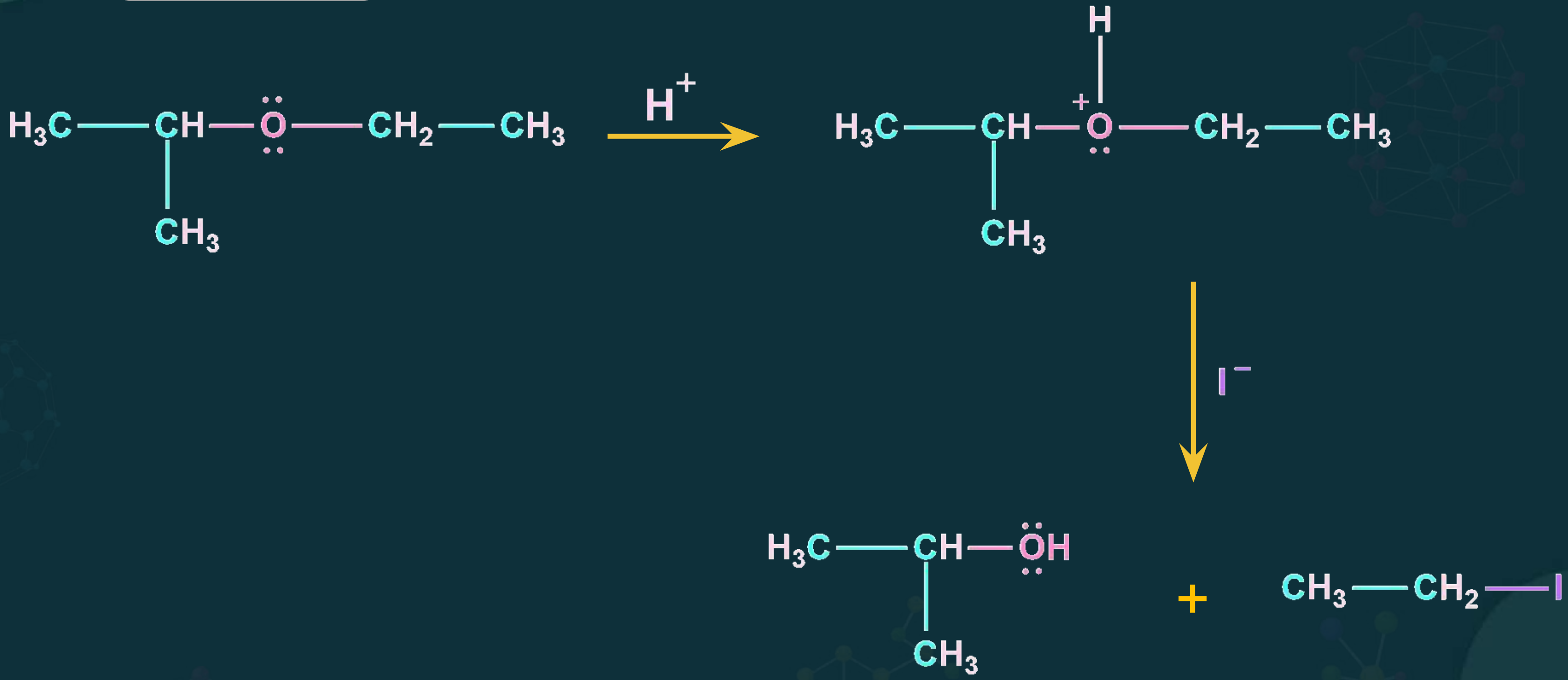
Since t-butyl cation is there, reaction will proceed via **S_N1 mechanism**.

The products of the following reaction are:



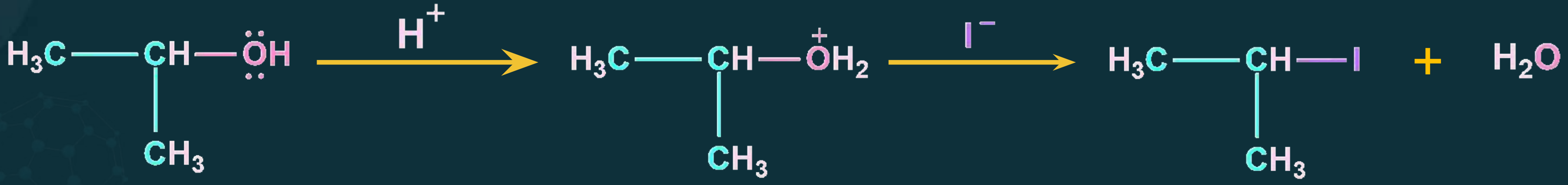
$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-CH_2-CH_3 \xrightarrow{\text{Excess HI}}$$

Solution



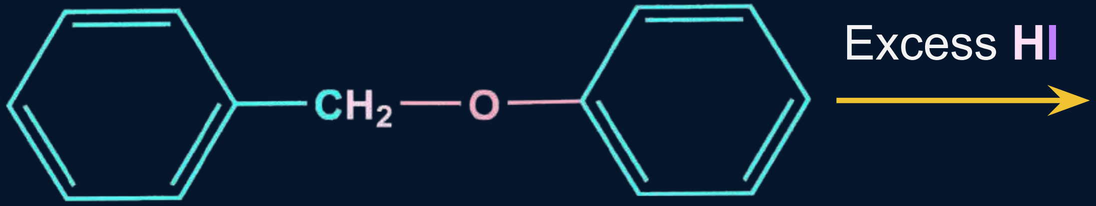
Attack of I⁻ happens from less hindered side as the reaction proceeds via S_N2 mechanism

When excess HI is added to the compound, then it abstract H^+ from HI and the attack of nucleophile (I^-) take place on the electrophilic carbon which is attached with oxygen. Thus, following reaction occurs:



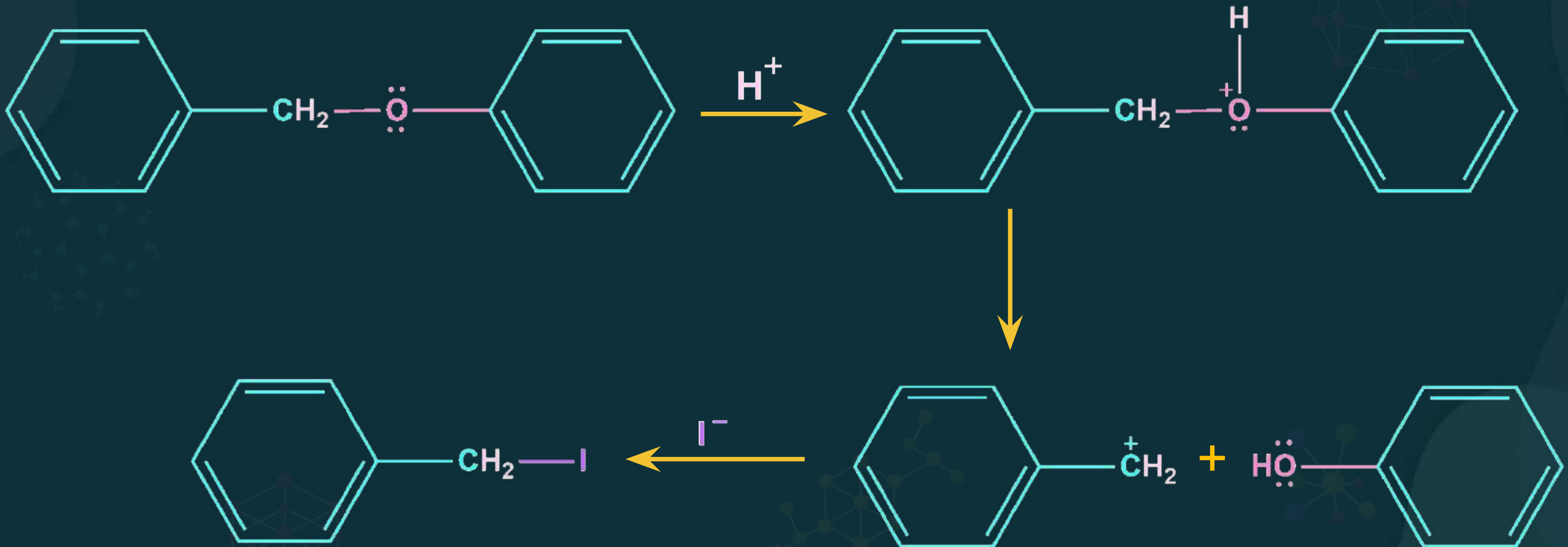
$$H_3C-\underset{\underset{CH_3}{|}}{CH}-\underset{..}{\ddot{O}}H \xrightarrow{H^+} H_3C-\underset{\underset{CH_3}{|}}{CH}-\overset{+}{O}H_2 \xrightarrow{I^-} H_3C-\underset{\underset{CH_3}{|}}{CH}-I + H_2O$$

The products of the following reaction are:



Solution

Here, cleavage of C-O bond of benzyl side takes place.



Assertion: Ethyl phenyl ether on reaction with HBr form phenol and ethyl bromide.

Reason: Cleavage of C–O bond takes place on ethyl-oxygen bond due to the more stable phenyl-oxygen bond.

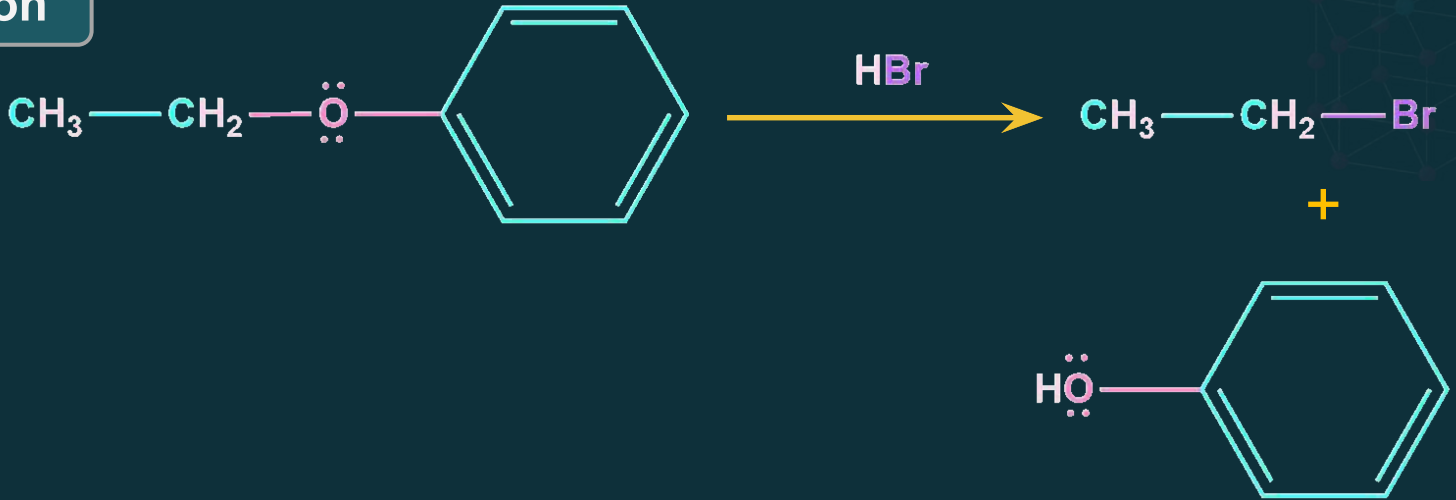
a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

c) If the Assertion is correct but Reason is incorrect.

d) If both the Assertion and Reason are incorrect.

Solution



Ethyl phenyl ether on reaction with HBr form phenol and ethyl bromide. The **reason is** that Phenyl-Oxygen bond is stable because oxygen delocalise its lone pair of electrons over the phenyl ring thereby the phenyl-oxygen bond has a partial double bond character. **Hence, option (a) is the correct answer.**

The heating of Phenyl methyl ether with HI produces:

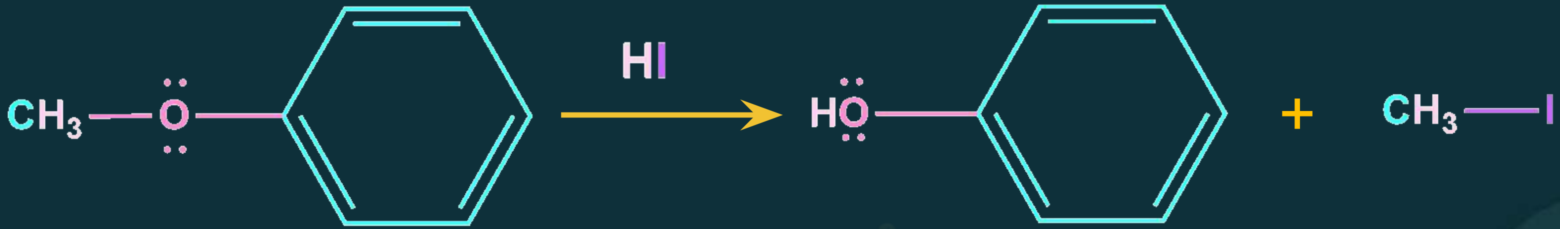
a) Iodobenzene

b) Phenol

c) Benzene

d) Ethyl chloride

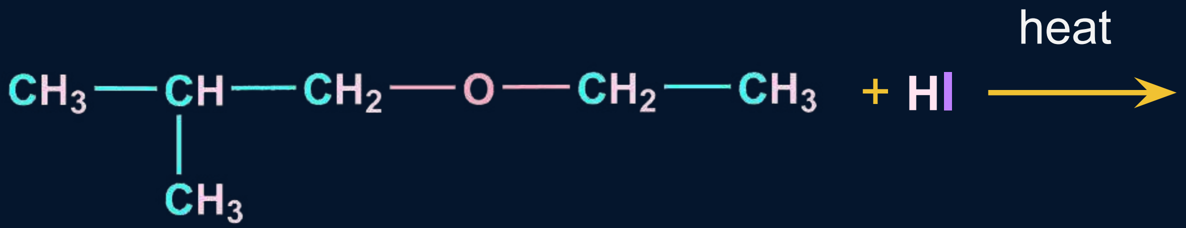
Solution



The heating of Phenyl methyl ether with HI produces phenol and methyl iodide.

Hence, option (b) is the correct answer.

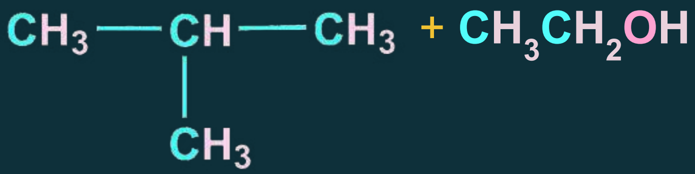
In the reaction,



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-O-CH_2-CH_3 + HI \xrightarrow{heat}$$

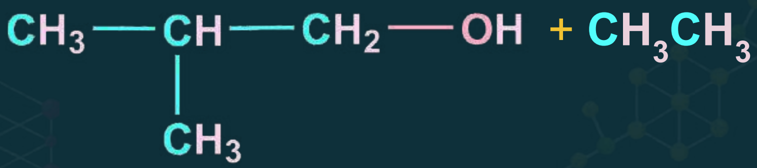
Which of the following compounds will be formed?

a)



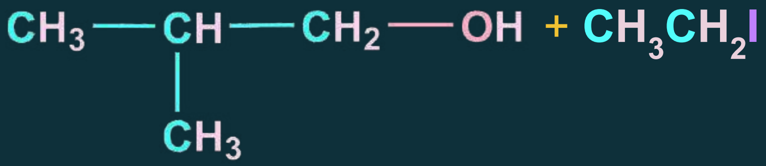
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3 + CH_3CH_2OH$$

b)



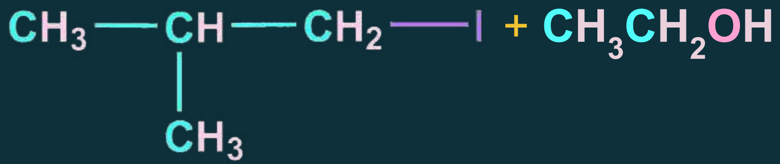
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH + CH_3CH_3$$

c)



$$CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2-OH + CH_3CH_2I$$

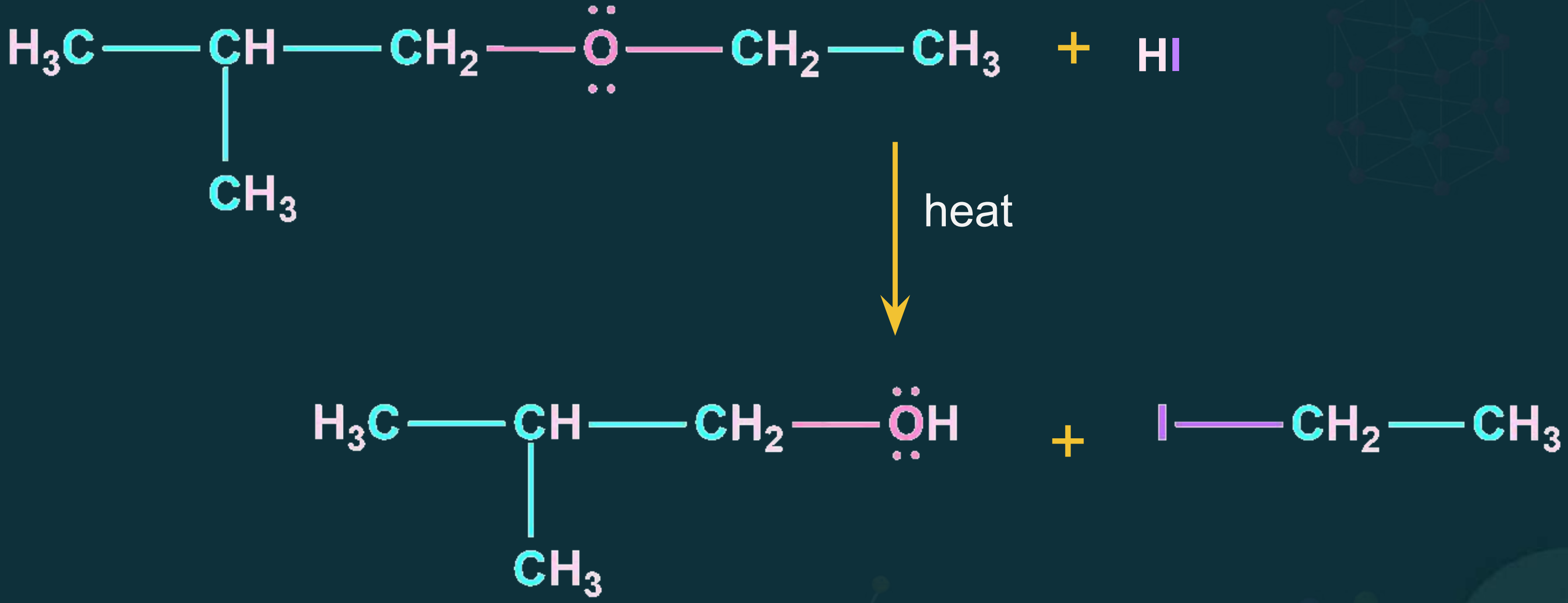
d)



$$CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2-I + CH_3CH_2OH$$

Solution

$(CH_3)_2CH—CH_2$ and $CH_3—CH_2$, both are primary alkyl groups , so the reaction will proceed via **S_N2 mechanism.**



$$H_3C-\underset{\underset{CH_3}{|}}{CH}-CH_2-\ddot{\underset{..}{O}}-CH_2-CH_3 + HI \xrightarrow{\text{heat}} H_3C-\underset{\underset{CH_3}{|}}{CH}-CH_2-\ddot{\underset{..}{O}}H + I-CH_2-CH_3$$

Hence, option (c) is the correct answer.

The major organic product in the reaction is:

$$CH_3OCH(CH_3)_2 + HI \longrightarrow \text{Products}$$

a) $CH_3I + (CH_3)_2CHOH$

b) $CH_3OH + (CH_3)_2CHI$

c) $ICH_2OCH(CH_3)_2$

d) $CH_3OC(I)H(CH_3)_2$

Solution

CH_3 and $(CH_3)_2CH$ are primary and secondary alkyl groups respectively, so reaction will proceed via **S_N2 mechanism.**

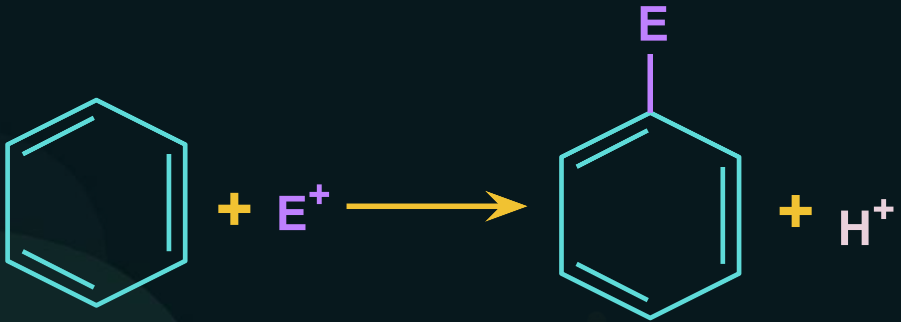
$$CH_3OCH(CH_3)_2 + HI \longrightarrow CH_3I + (CH_3)_2CHOH$$

Hence, option (a) is the correct answer.

Chemical Properties of Ethers

Electrophilic substitution reaction

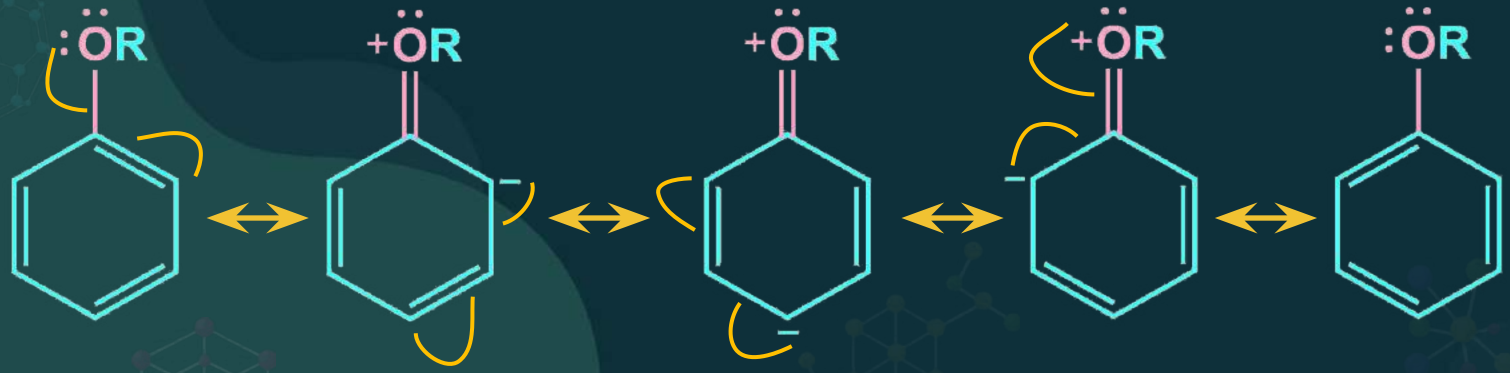
General reaction



Chemical Properties of Ethers

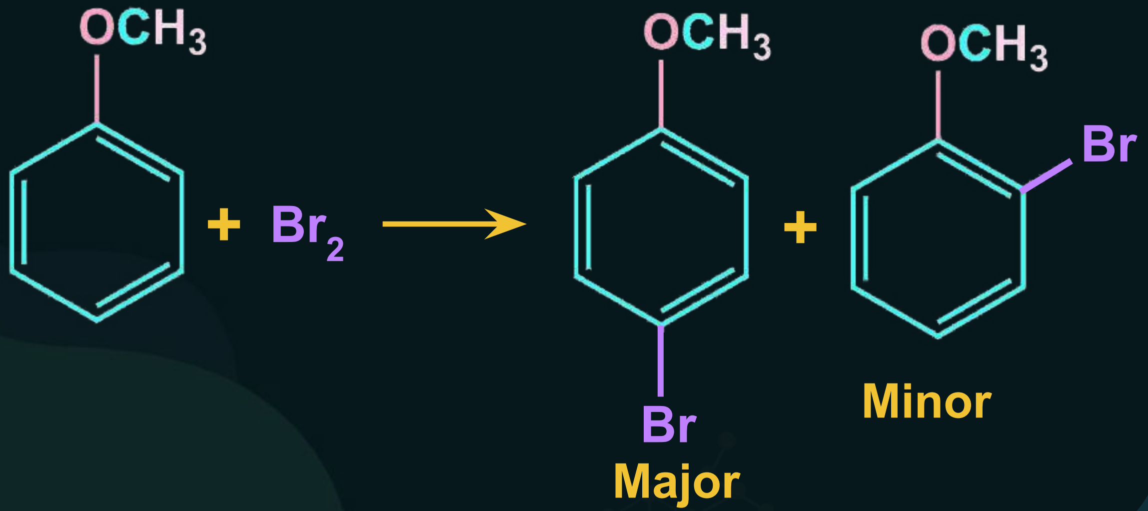
The **alkoxy group (-OR) is ortho-para directing** and activates the aromatic ring towards electrophilic substitution.

Resonance structures



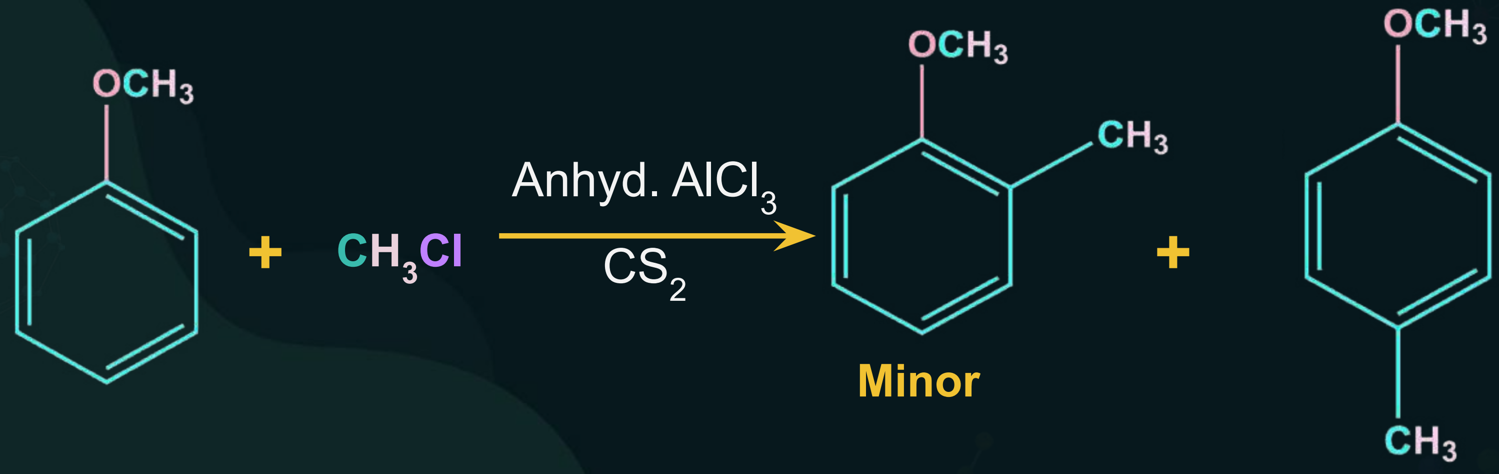
Chemical Properties of Ethers

Halogenation



Chemical Properties of Ethers

Friedel-Crafts Reaction - Alkylation

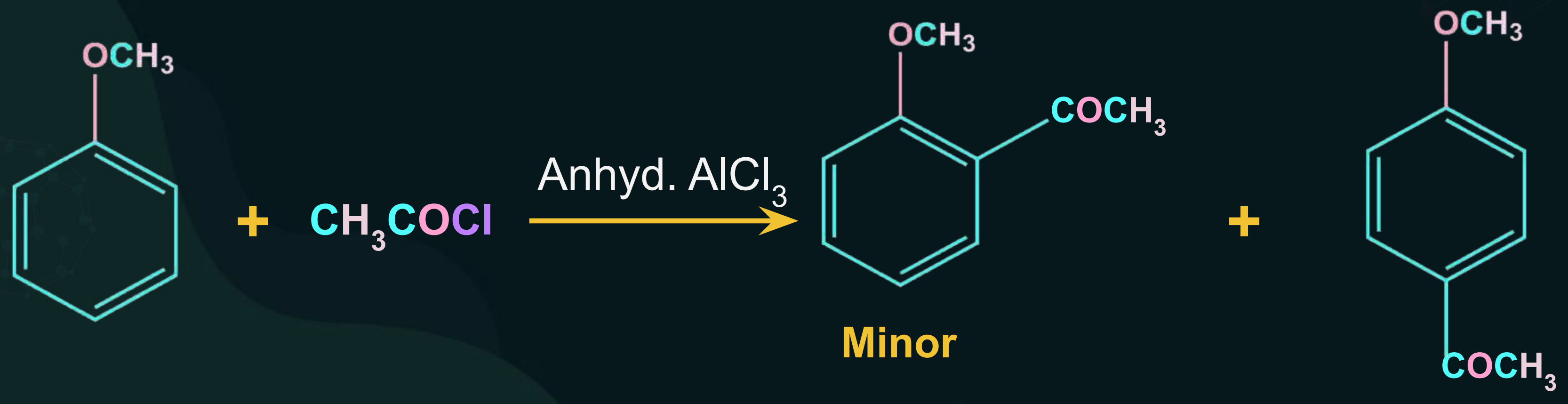


Minor

Major

Chemical Properties of Ethers

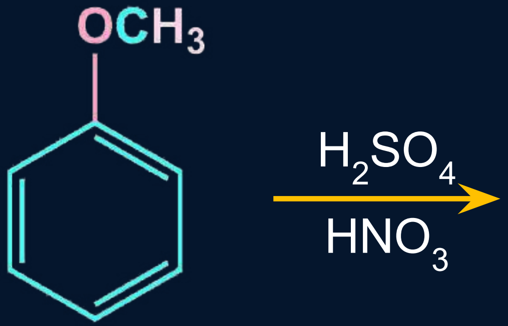
Friedel-Crafts Reaction - Acylation



Minor

Major

The major and minor product for the given reaction are:



Solution

Mixture of concentrated sulphuric acid and concentrating nitric acid is known as nitrating mixture which generates NO_2^+ as follows:

$H_2SO_4 + HO\text{-}NO_2 \rightleftharpoons HSO_4^- + H_2O^+\text{-}NO_2$

Here **$H_2O^+\text{-}NO_2$** will dissociate as :

$H_2O^+\text{-}NO_2 \rightleftharpoons H_2O + NO_2^+$

NO_2^+ will attack on ortho and para position to give 1-Methoxy-4-nitrobenzene as major and 1-Methoxy-2-nitrobenzene as minor product.

The ether that undergoes electrophilic substitution reactions:

a) $CH_3OC_2H_5$

b) $C_6H_5OCH_3$

c) CH_3OCH_3

d) $C_2H_5OC_2H_5$

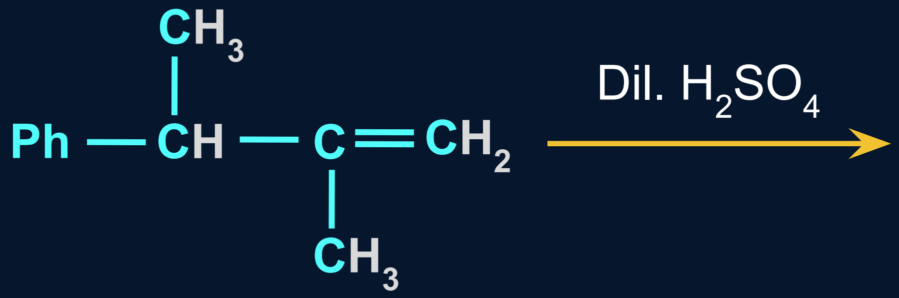
Solution

For electrophilic substitution reaction, ether should be aromatic. Here all the options except option (b) do not contain aromatic ring.

Hence, option (b) is the correct answer.

Practice Questions

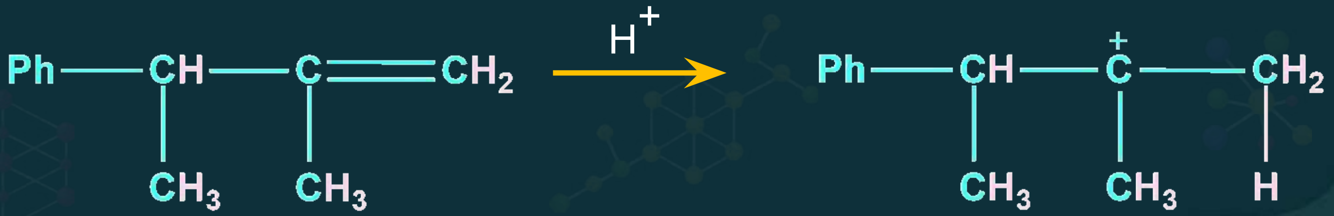
Give the major product of the following reaction.



$$\mathrm{Ph-\overset{CH_3}{\overset{|}{CH}}-\underset{\underset{CH_3}{|}}{C}=CH_2} \xrightarrow{\text{Dil. } H_2SO_4}$$

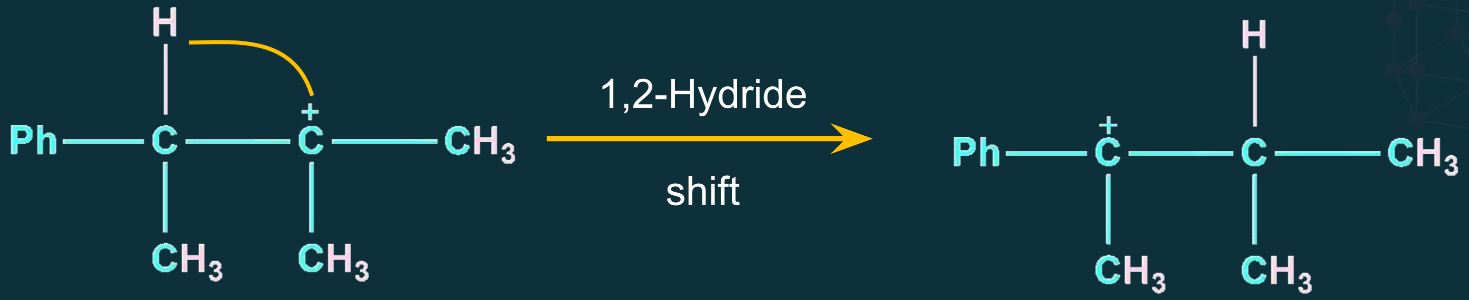
Solution

Here H^+ ion from the sulphuric acid will attack on the pi bond of the reactant to form tertiary carbocation as follows:

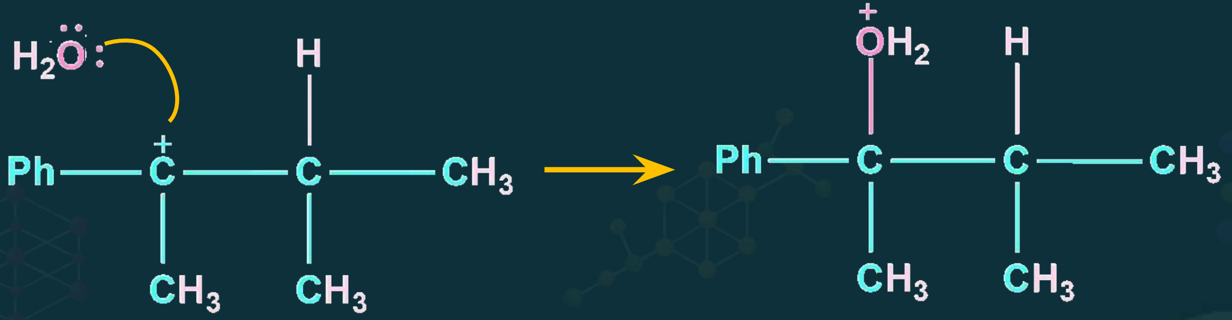


$$\mathrm{Ph-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{C}=CH_2} \xrightarrow{H^+} \mathrm{Ph-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{\overset{+}{C}}-\underset{\underset{H}{|}}{CH_2}}$$

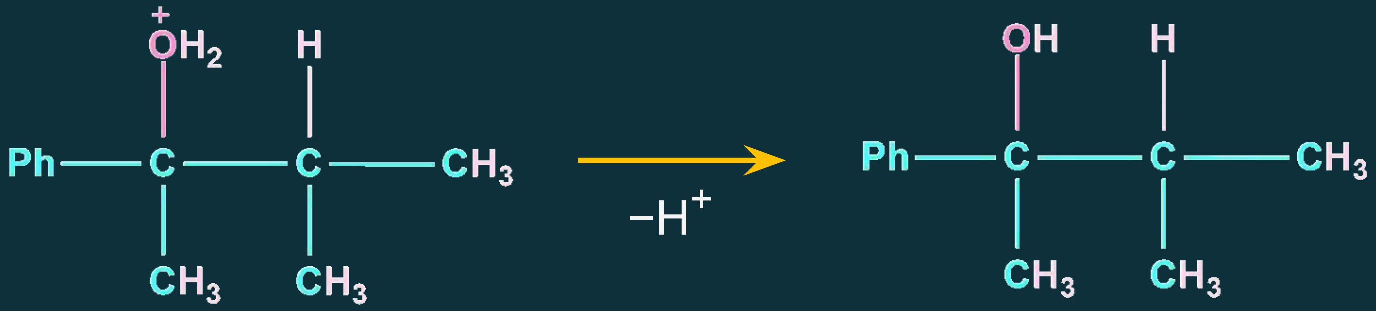
Since tertiary carbocation with benzyl group is most stable because of resonance therefore 1, 2 hydride shift take place.



Now, H_2O will attack on the carbocation.

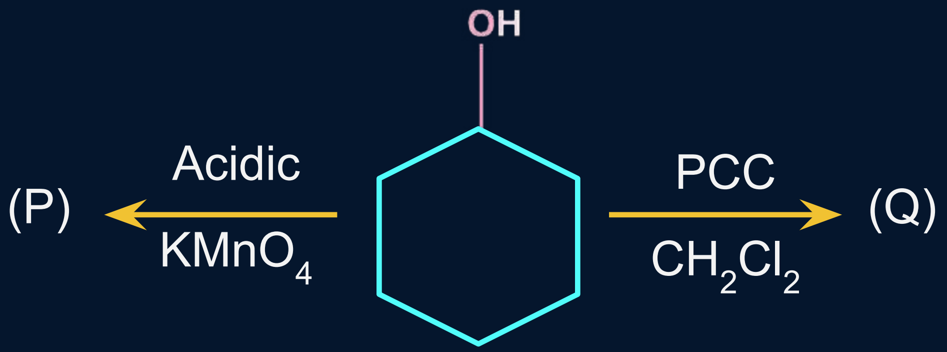


Finally removal of H^+ will take place to give **3-Methyl-2-phenylbutan-2-ol** as final product.



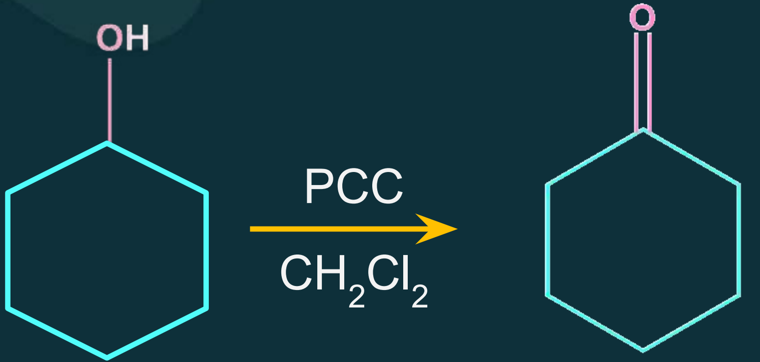
3-Methyl-2-phenylbutan-2-ol

Identify (P) and (Q) respectively in the given reaction.



Solution

PCC in CH_2Cl_2 solvent is used to oxidise primary alcohol to aldehyde and secondary alcohol to ketone.

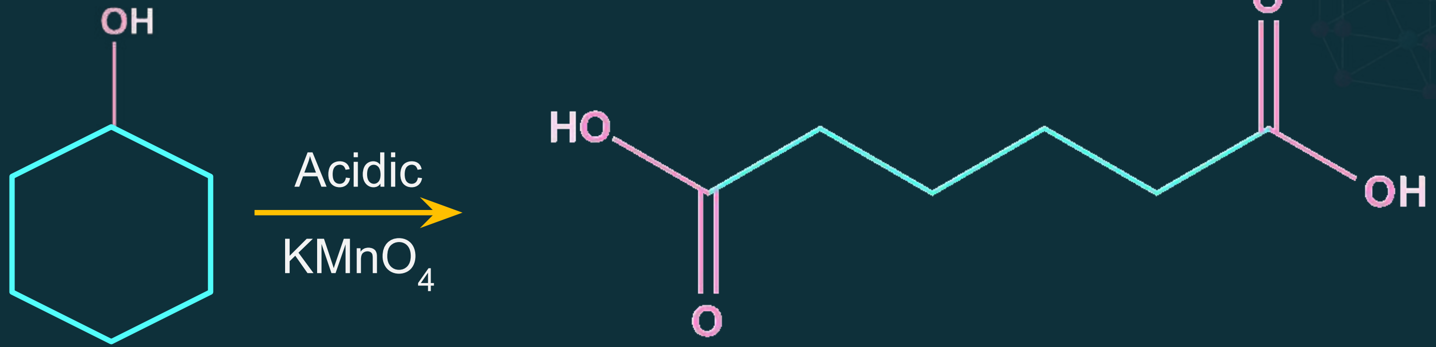


Cyclohexanone

At room temperature: Acidic $KMnO_4$ is used to oxidise primary alcohol to aldehyde and secondary alcohol to ketone.

Cyclohexanone

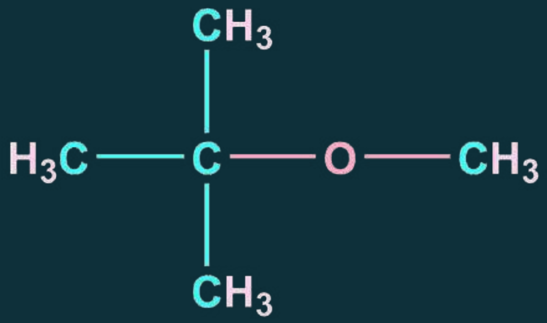
On heating: Acidic $KMnO_4$ converts alcohol to acid.



Adipic acid

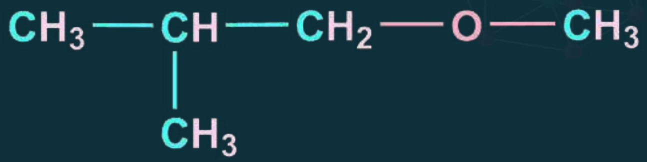
Among the following ethers, which one will produce Methyl alcohol on treatment with HI?

a)



$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_3$

b)



$CH_3-\underset{CH_3}{CH}-CH_2-O-CH_3$

c) $CH_3-CH_2-CH_2-O-CH_3$

d) None of these

Solution

Option (a) follows S_N1 mechanism. Thus, tertiary halide and methanol is formed.

$$(CH_3)_3C\text{-}O\text{-}CH_3 + HI \longrightarrow (CH_3)_3C\text{-}I + CH_3OH$$

Option (b) and (c) follows S_N2 mechanism. Thus, methyl iodide is formed.

Hence, option (a) is the correct answer.

$CH_3OC_2H_5$ and $(CH_3)_3C\text{-}OCH_3$ are treated with hydroiodic acid. The fragments obtained after reactions are:

a) $CH_3I + C_2H_5OH$; $(CH_3)_3CI + CH_3OH$

b) $CH_3OH + C_2H_5I$; $(CH_3)_3CI + CH_3OH$

c) $CH_3OH + C_2H_5I$; $(CH_3)_3COH + CH_3I$

d) $CH_3I + C_2H_5OH$; $CH_3I + (CH_3)_3COH$

Solution

In case of **$CH_3OC_2H_5$**, the reaction will proceeds with S_N2 mechanism to give methyl iodide and ethanol whereas in case of **$(CH_3)_3C\text{-}OCH_3$**, the reaction will proceed via S_N1 mechanism to give tertiary butyl iodide and methanol.

Hence, option (a) is the correct answer.

Assertion: The major products formed by heating $C_6H_5CH_2OCH_3$ with HI are $C_6H_5CH_2I$ and CH_3OH.
Reason: Benzyl cation is more stable than methyl cation.

a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

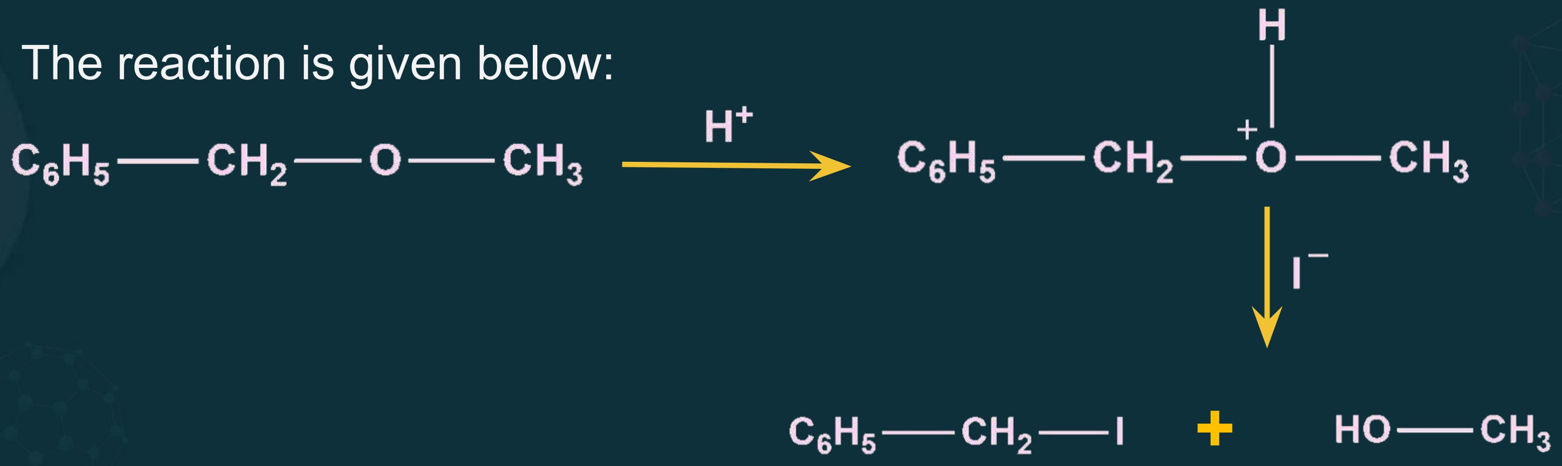
b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

c) If the Assertion is correct but Reason is incorrect.

d) If both the Assertion and Reason are incorrect.

Solution

The reaction is given below:



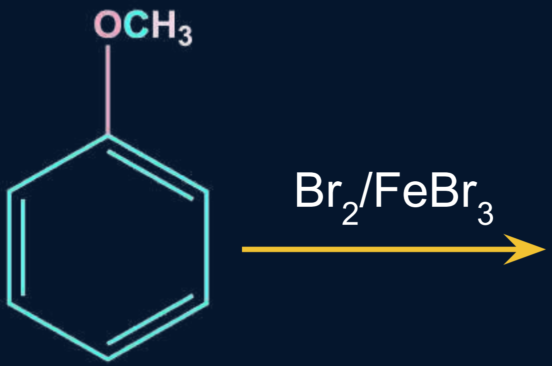
$$C_6H_5-CH_2-O-CH_3 \xrightarrow{H^+} C_6H_5-CH_2-\overset{\overset{H}{|}}{\overset{+}{O}}-CH_3$$

$$\xrightarrow{I^-} C_6H_5-CH_2-I + HO-CH_3$$

Since benzyl carbocation is most stable, reaction proceeds via S_N1 mechanism and the products obtained are **$C_6H_5CH_2I$ and CH_3OH.** Here both assertion and reason are correct but reason is not the correct explanation of the assertion as the actual reason is -CH_2-O bond energy is lower than CH_3-O bond energy.

Hence, option (b) is the correct answer.

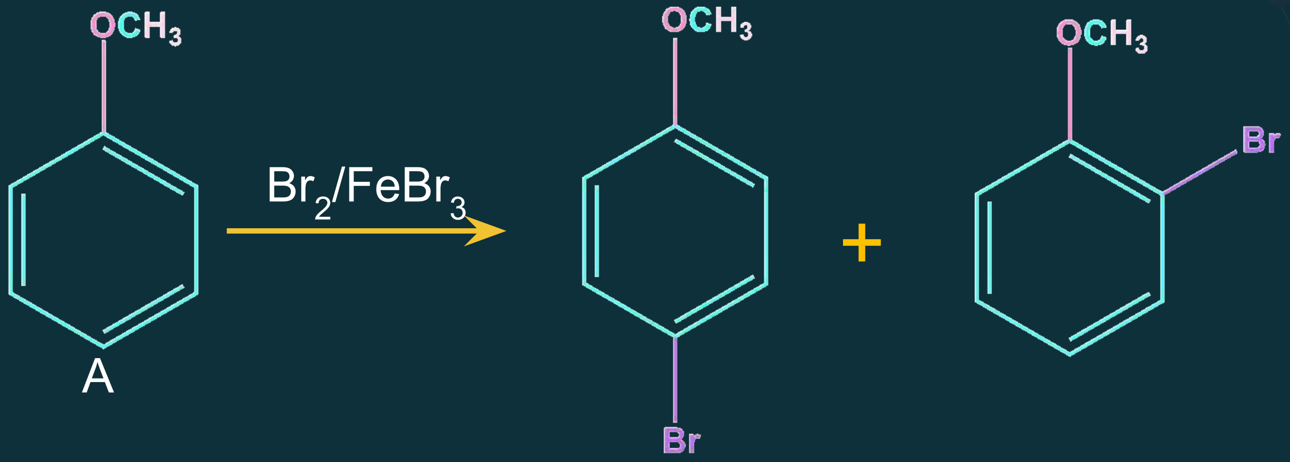
The major product obtained on the monobromination (with Br_2 /$FeBr_3$) of the following compound A is:



A

Solution

During the addition of bromine, Br_2 dissociate into Br^+ which act as an electrophile. The bromonium ion will attack on the ortho or para position of anisole ring.



***p*-Bromoanisole** ***o*-Bromoanisole**

Here *p*-Bromoanisole will be the major product whereas *o*-bromoanisole will be the minor product due to steric hindrance.

In Reimer-Tiemann reaction, molecular weight of phenol increases by:

a) 28

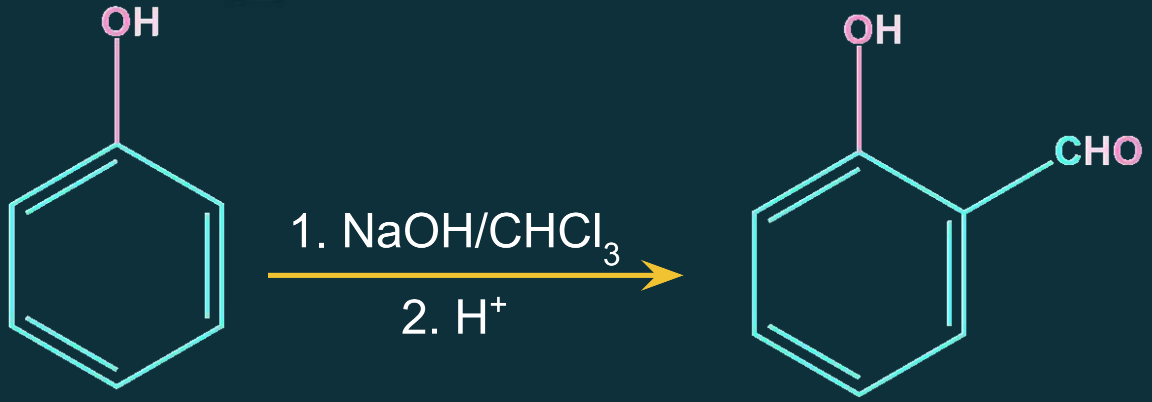
b) 29

c) 30

d) 31

Solution

Reimer-Tiemann reaction is known as the reaction which is used for the ortho formylation of the phenol and the rection is given as follows:



In the product, there is addition of —CHO group by replacing the hydrogen of phenol

Molecular weight of —CHO functional group = 29

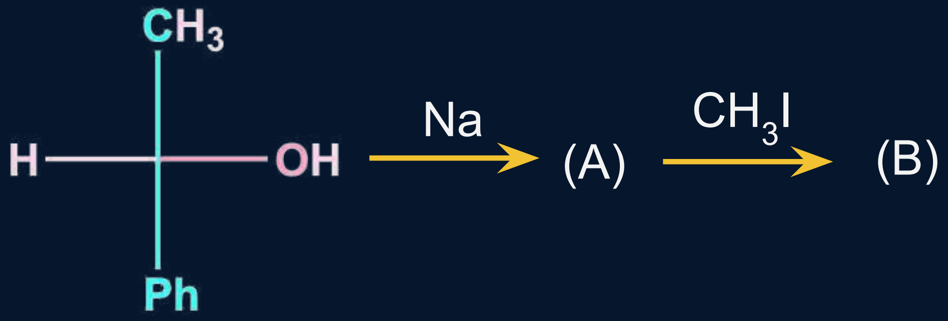
Molecular weight of —H = 1

molecular weight increase = 29 - 1 = 28

Hence, the molecular weight of phenol increases by 28.

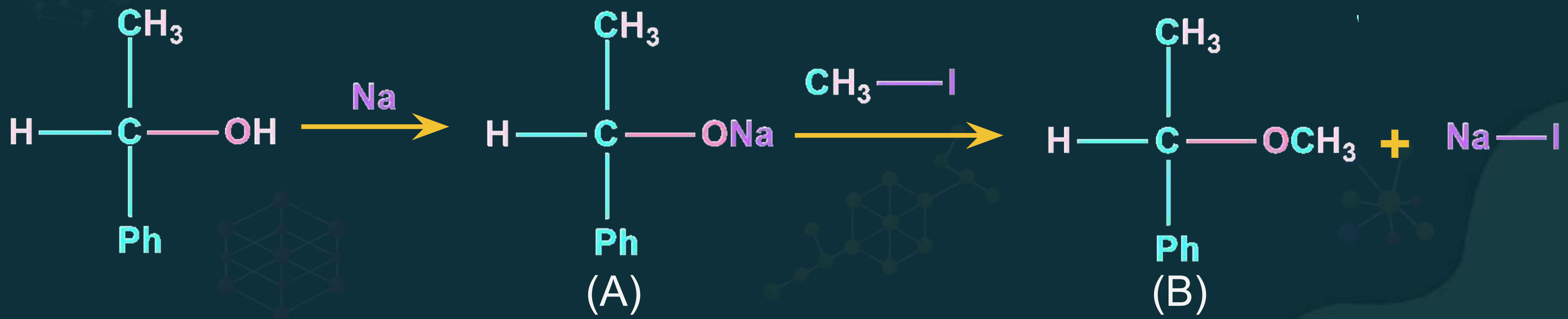
Hence, option (a) is the correct answer.

The major product (B) formed is:



$$\mathrm{H-\underset{Ph}{\overset{CH_3}{|}}-OH} \xrightarrow{\mathrm{Na}} (A) \xrightarrow{\mathrm{CH_3I}} (B)$$

Solution



$$\mathrm{H-\underset{Ph}{\overset{CH_3}{C}}-OH} \xrightarrow{\mathrm{Na}} \underset{(A)}{\mathrm{H-\underset{Ph}{\overset{CH_3}{C}}-ONa}} \xrightarrow{\mathrm{CH_3-I}} \underset{(B)}{\mathrm{H-\underset{Ph}{\overset{CH_3}{C}}-OCH_3}} + \mathrm{Na-I}$$

How many compounds (including stereoisomers) with molecular formula $C_5H_{10}O$ may be reduced with $NaBH_4$ to a primary alcohol?

a) 2

b) 3

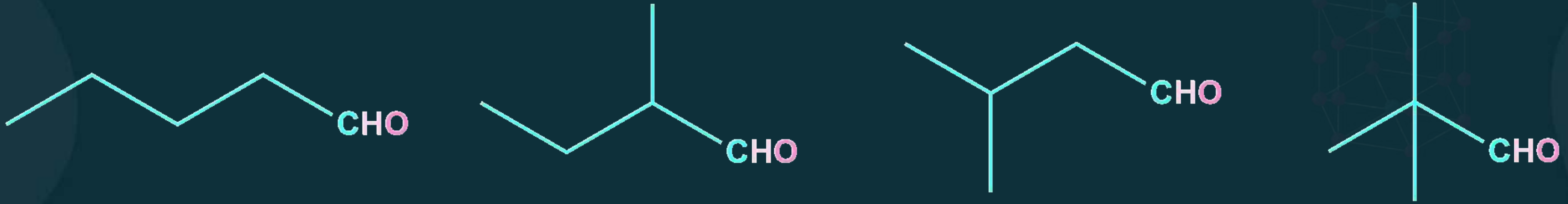
c) 4

d) None of these

Solution

The compound will be aldehyde as it is reduced to primary alcohol with $NaBH_4$.

The following are the compounds:

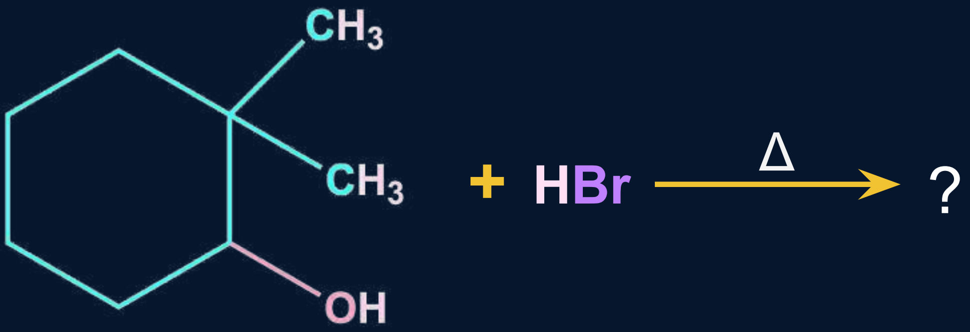


As the carbon is chiral, it
have 2 stereoisomers.

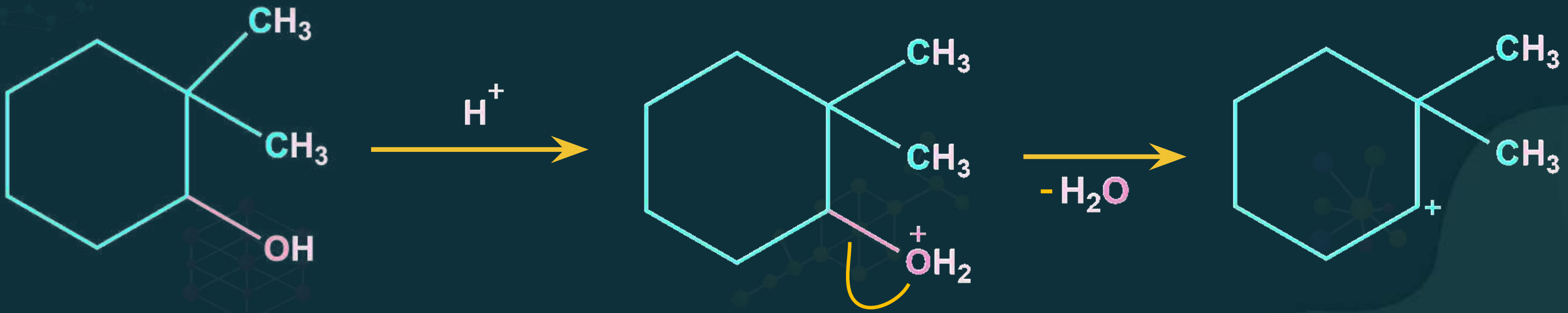
Here, a total of five isomers can be reduced to primary alcohol.

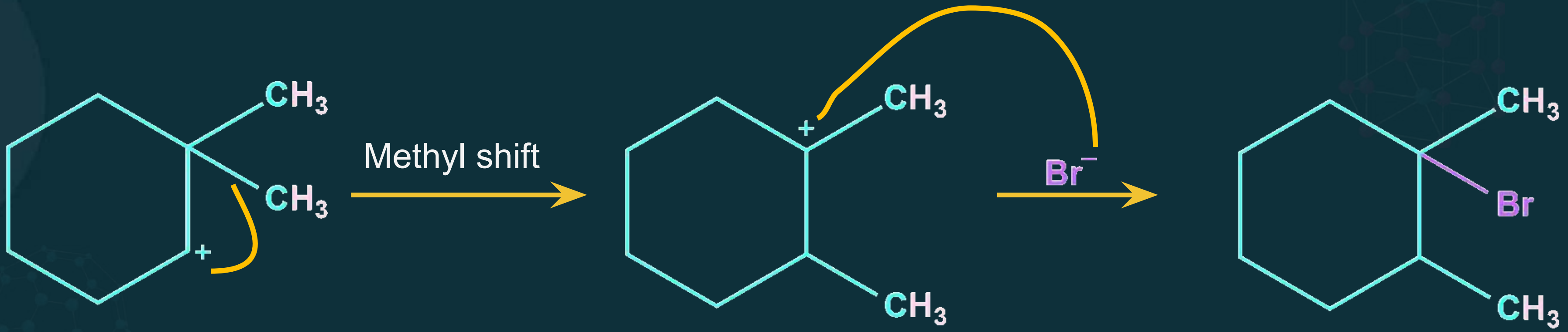
Hence, option (d) is the correct answer.

What is the major product of the following reaction?



Solution




CH3
CH3
+
Methyl shift
+
CH3
CH3
Br⁻
CH3
Br
CH3

Substrate of Dow’s process for the manufacture of phenol is:

a) Chlorobenzene

b) Benzenediazonium chloride

c) Benzenesulphonic acid

d) Cumene

Solution

In dow’s process, chlorobenzene is treated with NaOH at 300 ℃ to give sodium phenoxide ion. Hence the substrate is Chlorobenzene.

Hence, option (a) is the correct answer.

K_a value of phenol is more than that of ethanol because:

a) Phenoxide ion is a stronger base than ethoxide ion.

b) Phenoxide is more stable than ethoxide ion due to resonance.

c) Phenoxide is less stable than ethoxide ion.

d) Phenoxide is bulkier than ethoxide ion

Solution

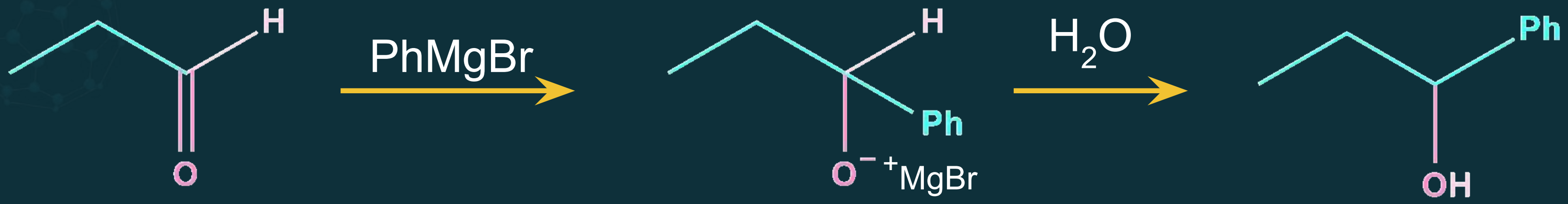
K_a value of phenol is more than that of ethanol because phenoxide is more stable than ethoxide ion due to resonance.

Hence, option (b) is the correct answer.

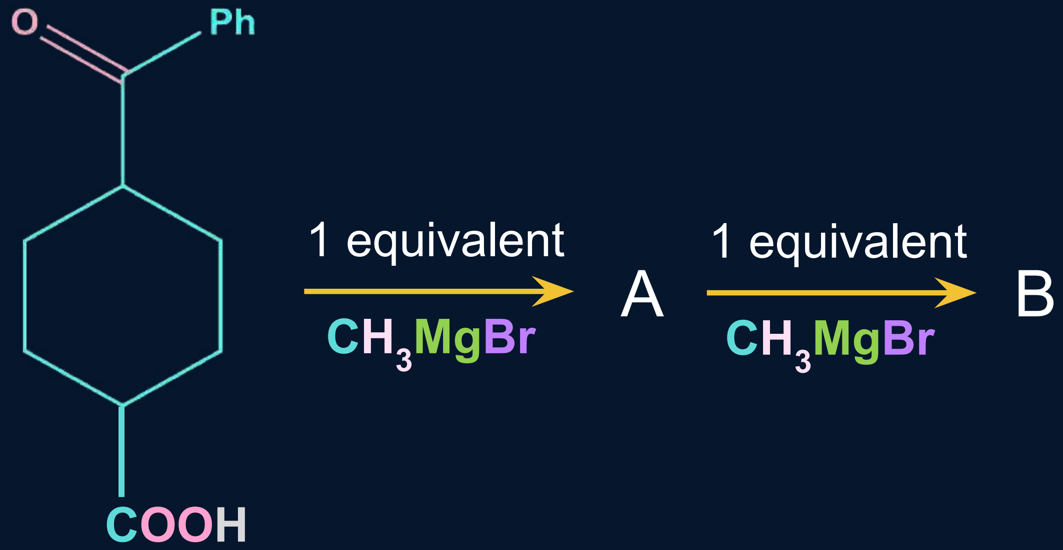
What is the major product of the following reaction?

$$CH_3-CH_2-CHO \xrightarrow[2.\ H_2O]{1.\ PhMgBr}$$

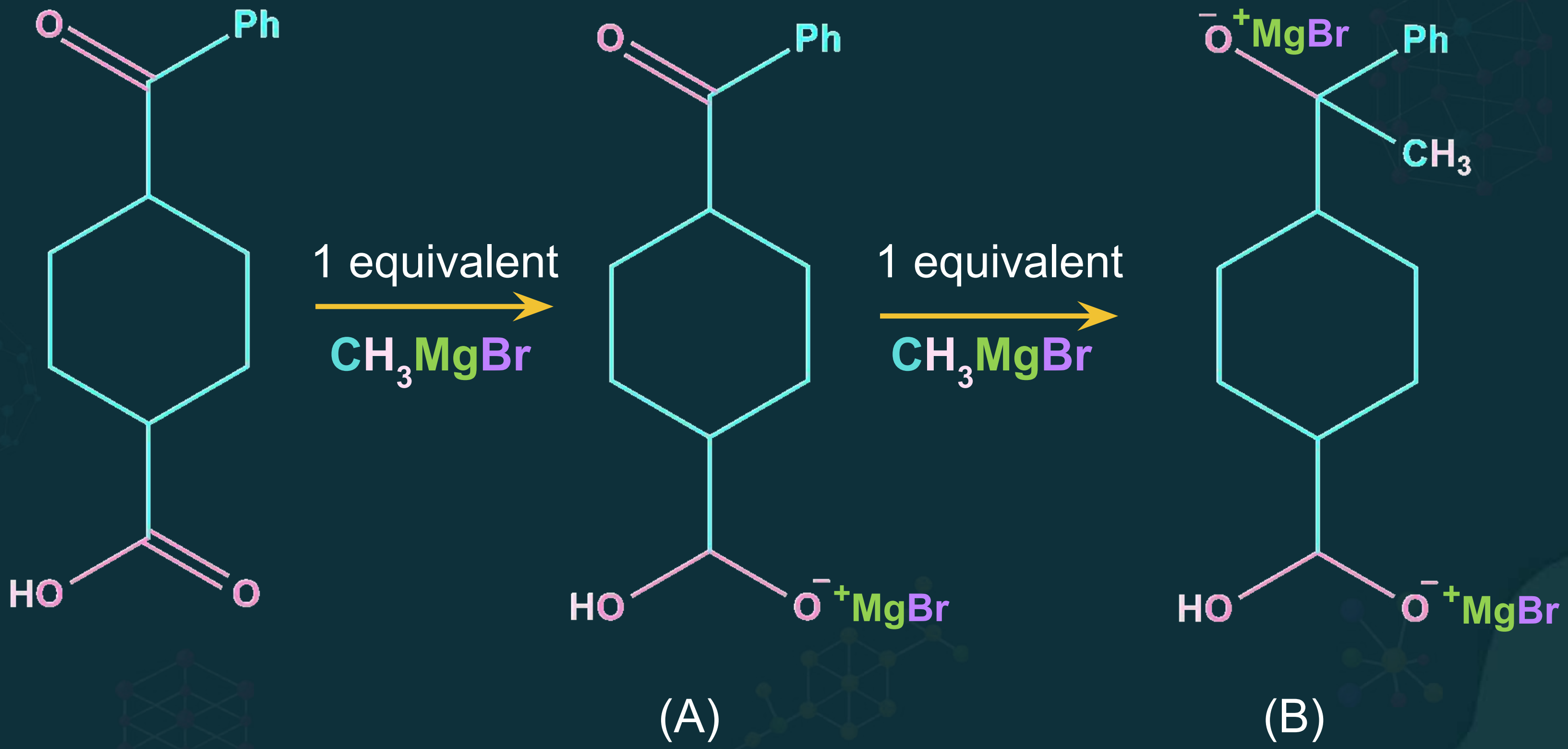
Solution



What is the product A & B of the following reaction?



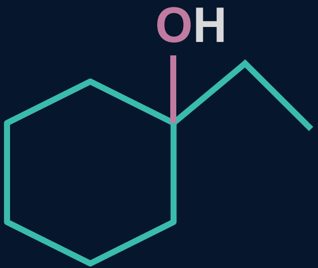
Solution



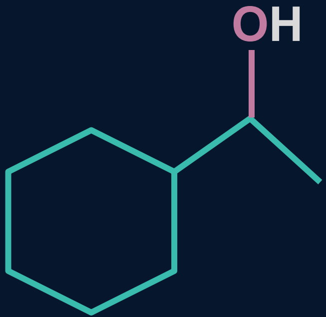
O
Ph
HO
O
1 equivalent
CH3MgBr
O
Ph
HO
O⁻ ⁺MgBr
1 equivalent
CH3MgBr
O⁻ ⁺MgBr
Ph
CH3
HO
O⁻ ⁺MgBr
(A)
(B)

Which of the following alcohols gives a rearranged carbocation when dehydrated?

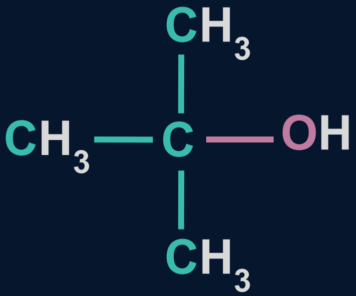
a)



b)

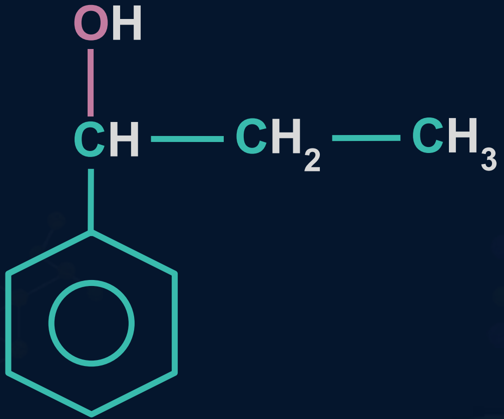


c)



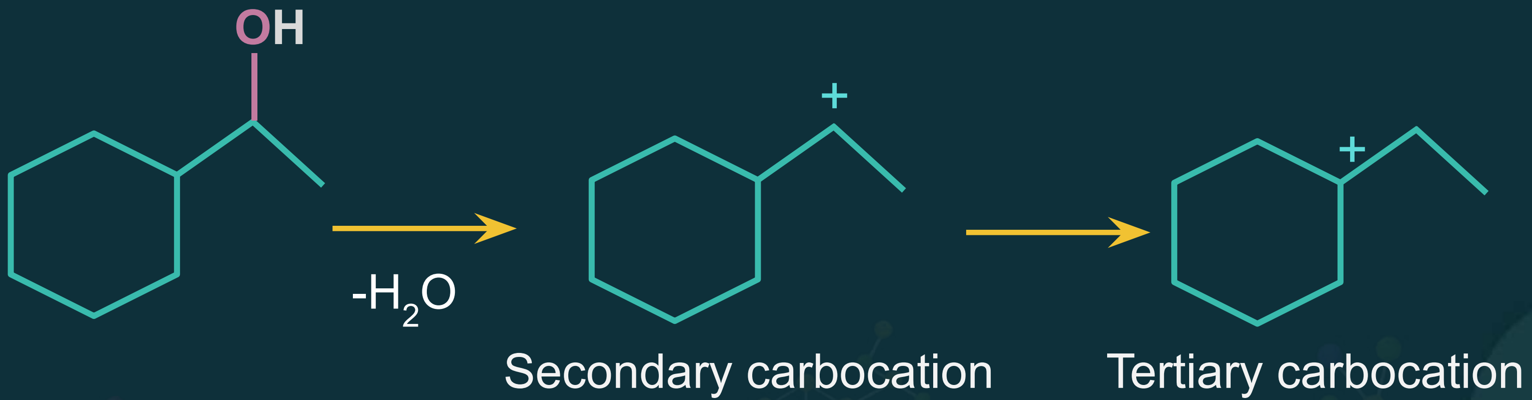
$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH$

d)



Solution

In option (a) and (c), tertiary carbocation is formed and it is highly stable. In case of option (d), secondary benzylic carbocation is formed which is also stable, hence it does not undergo rearrangement whereas in option (b), secondary carbocation is formed, hence it rearranges to give tertiary carbocation.



Hence, option (b) is the correct answer.