

S.SHANMUGAM PG Assistant

UNIT - 11

St.John's M.H.S.S porur Chennai -116
THERS Mob: 9841945665

HYDROXY COMPOUNDS AND ETHERS

1. Identify the product (s) is / are formed when 1 – methoxy propane is heated with excess HI. Name the mechanism involved in the reaction

The carbon-oxygen bond is ethers can be cleaved by heating with HI to form an alcohol and an alkyl halide at 373K. In case of unsymmetrical ethers which contains two different alyl groups, the site of cleavege is such that the halide is formed from the alkyl group which is smaller in size.

Thus the products formed in this case are iodomethane and Propan-2-ol

$$CH_3-CH_2-CH_2-OCH_3+HI \xrightarrow{excess of HI} CH_3I+CH_3-CH-CH_3$$

i) Name the mechanism involved in the reaction - S_N 1 reaction.

In the presence of conc.HI I think $(CH_3)_2CH$ -OH changes to $(CH_3)_2CH$ - I. Also since a secondary carbon is present SN_1 mechanism may occur then the products are different $(CH_3OH)_2CH$ -I).

- 2. Draw the major product formed when 1-ethoxyprop-1-ene is heated with one equivalent of HI
 - 1-Ethoxyprop-1-ene reacts with HI to form iodoethane and prop-1-en-1-ol.

$$C_2H_5$$
-OCH = CH - CH $_3$ + HI one equivalent of HI $_2$ C $_2$ H $_5$ - I + HO - CH = CH- CH $_3$

Not easy to break this bond as it is enaged in resonance so

$$HO - CH = CH - CH_3 \leftarrow Tautomerism \rightarrow O = CH - CH_2 - CH_3 (aldehyde)$$

3. Suggest a suitable reagent to prepare secondary alcohol with identical group using Grignard reagent.

4. What is the major product obtained when two moles of ethyl magnesium bromide is treated with methyl benzoate followed by acid hydrolysis.

$$\begin{array}{c} O \\ C_6H_5\text{-} C\text{-} OCH_3 + C_2H_5\text{-}MgBr & O \\ C_6H_5\text{-} C\text{-} OCH_3 & -MgBr/CH_3O^- \\ C_2H_5 & C_5H_5 \end{array}$$

3-phenyl-pentan-3-ol

- 5. Predict the major product, when 2-methyl but -2-ene is converted into an alcohol in each of the following methods.
 - (i.) Acid catalysed hydration (ii.) Hydroboration (iii.) Hydroxylation using bayers reagent
 - i) 2-methyl but -2-ene is converted into an alcohol in Acid catalysed hydration

$$H_3C$$
 $C = C$ H_3 $H^+/50\%H_2O$ CH_3 CH_3 CH_2 CH_3 CH_3 CH_3 CH_3 CH_3

follows Markovnikov's rule

2-Methyl-butan - 2-ol

ji2-methyl but -2-ene is converted into an alcohol in Hydroboration

$$\begin{array}{c} \text{H}_{3}\text{C} \\ \text{H}_{3}\text{C} \\ \text{C} = \text{C} \\ \text{C} \\ \text{H}_{3}\text{C} \\ \text{C} \\ \text{C} \\ \text{H}_{3}\text{C} \\ \text{C} \\ \text{C} \\ \text{H}_{3} \\ \text{C} \\ \text{O} \\ \text{D}^{-} \\ \text{| ii) } 3 \text{ H}_{2}\text{O}_{2} \\ \text{follows anti Markovnikov's rule} \\ \\ \begin{array}{c} \text{CH}_{3} \text{ CH}_{3} \\ \text{C} \\ \text{H}_{3} \\ \text{C} \\ \text{C} \\ \text{H}_{3} \\ \text{C} \\$$

$$\begin{array}{c} \text{H}_{3}\text{C} \\ \text{H}_{3}\text{C} \end{array} \xrightarrow{\text{CH}_{3}} \begin{array}{c} \text{H} & \text{OH} & \text{OH} \\ \text{Alkaline KMnO}_{4} \\ \text{CH}_{3} \end{array} \xrightarrow{\text{CH}_{3}} \begin{array}{c} \text{OH} & \text{OH} \\ \text{CH}_{3} - \text{C} - \text{CH} - \text{CH}_{3} \\ \text{CH}_{3} \\ \text{2-Methyl-butan - 2,3-diol} \end{array}$$

iii) 2-methyl but -2-ene is converted into an alcohol in Hydroxylation using bayers reagent

6. Arrange the following in the increasing order of their boiling point and give a reason for your ordering

- (i) Butan 2- ol, Butan -1-ol, 2 -methylpropan -2-ol
- (ii) Propan -1-ol, propan -1,2,3-triol, propan -1,3 diol, propan -2-ol
- a) Among isomeric alcohols primary alcohols have higher boiling point and the tertiarly alcohols have lower boiling points
- b) The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surfacearea).
- i) increasing order of their boiling point
- 2 -methyl propan -2-ol < Butan 2- ol < Butan -1-ol
- ii) increasing order of their boiling point

propan -2-ol < Propan -1-ol < propan -1,3 - diol < propan -1,2,3-triol

7. Can we use nucelophiles such as NH₃,CH₃O⁻ for the Nucleophilic substitution of alcohols

Because the OH group of the alcohol must be protonated before it can be displaced by a nucleo-phile, only weakly basic nucleophiles (I^- , Br^- , CI^-) can be used in the substitution reaction.Moderately and strongly basic nucleophiles (NH_3 , RNH_2 , and CH_3O^-) cannot be used because theytoo would be protonated in the acidic solution and, once protonated, would no longer be nucleo-philes (H_4^+ , H_4^+ , H_3^+) or would be poor nucleophiles (H_3^+).

- i) Tertiary alcohol does not allow for their oxidation because of absence **Q- hydrogen** atom.
- ii) This is why tertiary alcohols are said to be resistant to oxidation But at elevated temperatures it possible to oxidise, under strong oxidising agent like acidified K₂Cr₂O₇ / H⁺ cleavage of C –C bond takes place to give a mixture of carboxylic acid like formic acid and acetic acid
- 9. What happens when 1-phenyl ethanol is treated with acidified KMnO₄.

10. Write the mechanism of acid catalysed dehydration of ethanol to give ethene.

The mechanism of acid dehydration of ethanol to yield ethene involves the following three steps:

Primary alcohols undergo dehydration by E₂ mechanism

Step 1: Protonation of ethanol to form ethyl oxonium ion:

$$\mathsf{CH_3^-\,CH_2^-\, \overset{\bullet}{\Omega}^-\,H} \ + \ \mathsf{H^+} \ \rightleftharpoons \ \ \mathsf{CH_3^-\,CH_2^-\, \overset{\bullet}{\Omega}^-\,H}$$

Step 2:Formation of carbocation (rate determining step):

$$CH_3-CH_2-O \xrightarrow{H} Slow CH_3-CH_2 + H_2O$$

Step 3:Elimination of a proton to form ethene:

$$H - CH_2 - CH_2 \implies CH_2 = CH_2 + H^+$$

- 11. How is phenol prepared form
 - i) chloro benzene ii) isopropyl benzene
 - i) chloro benzene to phenol

Chlorobenzene ii) isopropyl benzene phenol

Phenol

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12. Explain Kolbe's reaction

13. Write the chemical equation for Williamson synthesis of 2-ethoxy – 2- methyl pentane starting from ethanol and 2 – methyl pentan -2-ol

Step 1: alcohol into alkylhalide

$$\text{CH}_3 - \text{CH}_2 - \text{OH} + \text{HBr} \xrightarrow{\Delta} \text{CH}_3 - \text{CH}_2 - \text{Br} + \text{H}_2\text{O}$$

Step 2: 2 - methyl pentan -2-ol into sodium alkoxide

Step 3: sodium alkoxide into 2-ethoxy - 2- methyl pentane

$$\begin{array}{c} \operatorname{CH_3} \\ \operatorname{CH_3-CH_2-CH_2-CH_2-CH_3^++CH_3-CH_2Br} \\ \operatorname{CH_3} \end{array} \longrightarrow \begin{array}{c} \operatorname{CH_3} \\ \operatorname{CH_3-CH_2-CH_2-CH_2-CH_3^++NaBr} \\ \operatorname{CH_3} \end{array}$$

14. Write the structure of the aldehyde, carboxylic acid and ester that yield 4- methylpent-2-en-1-ol.

$$CH_3$$
- CH - CH = CH - CHO CH_3

ii) carboxylic acid yield 4- methylpent-2-en-1-ol

$$CH_3$$
- CH - CH = CH - $COOH$ CH_3

iii) ester yield 4- methylpent-2-en-1-ol

$$CH_3$$
- CH - CH = CH - $COOCH_3$
 CH_3

aldehyde, carboxylic acid and ester undergoes reduction that yield 4- methylpent-2-en-1-ol

15. What is metamerism? Give the structure and IUPAC name of metamers of 2-methyoxy propane

Metamerism:

It is a special isomerism in which molecules with same formula, same functional group, differing only in the nature of the alkyl group attached to oxygen.

For example an ether having molecular formula C₄H₁₀O exhibits following **metamers**

СН ³	Comman Name	IUPAC name
CH ₃ -O-ĊH - CH ₃	Methyl isopropyl ether	2- methoxy propane
$\mathrm{CH_3CH_2\text{-}O\text{-}CH_2CH_3}$	dietyl ether	ethoxy ethane
CH ₃ -O-CH ₂ CH ₂ CH ₃	methyl propyl ether	1 - methoxy propane

Ethoxy ethane and 1 - methoxy propane are metamers 2- methoxy propane

16. How are the following conversions effected

i) benzylchloride to benzylalcohol ii) benzyl alcohol to benzoic acid

i) benzylchloride to benzylalcohol:

$$\begin{array}{c} \text{CH}_2\text{CI} & \text{CH}_2\text{OH} \\ \\ & \\ \text{Benzyl chloride} & \text{Benzyl alcohol} \end{array} + \text{NaCl}$$

ii) benzyl alcohol to benzoic acid

OH

KMnO₄

HCl

Benzyl alcohol

Benzoic acid

17. Complete the following reactions

i)
$$CH_3 - CH_2 - OH \xrightarrow{PBr_3} A \xrightarrow{(aq)NaOH} B \xrightarrow{Na} C$$

$$\mathbf{CH_3} - \mathbf{CH_2} - \mathbf{OH} \xrightarrow{\mathsf{PBr_3}} \mathbf{CH_3} - \mathbf{CH_2} - \mathbf{Br} \xrightarrow{\mathsf{(aq)NaOH}} \mathbf{CH_3} - \mathbf{CH_2} - \mathbf{OH} \xrightarrow{\mathsf{Na}} \mathbf{CH_3} - \mathbf{CH_2} - \mathbf{ONa} + \frac{1}{2}\mathbf{H_2}$$

A - ethyl bromide B- ethanol C - Sodium ethoxide

i)
$$C_6H_5$$
 - OH \xrightarrow{Zn} A $\xrightarrow{CH_3CI/anhydrous\ AICI_3}$ B $\xrightarrow{KMnO_4/H^+}$ C

$$\mathbf{C_6H_5}\text{-}\mathbf{OH} \xrightarrow{Zn} \mathbf{C_6H_6} \xrightarrow{CH_3Cl} \mathbf{C_6H_5}\text{-}\mathbf{CH_3} \xrightarrow{KMnO_4/H^+} \mathbf{C_6H_5}\text{-}\mathbf{COOH}$$

A - benzene

B-Toluene

C - Benzoic acid

iii) Anisole t-butylchloride/AlCl₃ A
$$Cl_2/FeCl_3$$
 B HBr C OCH_3 OCH_3

A - 4-tert-butyl-1-anisole

B-2-chloro-4-tert-butyl-1-anisole

C - 2-chloro-4-tert-butyl-1-phenol

iv)
$$A \xrightarrow{\text{CHOHCH}_3} A \xrightarrow{i) O_3} B$$

1-(1-methyl-cyclohexyl)-ethanol to nonane-2,8 -dione

OH
$$CH_3$$
 H_3 C $CH - CH_3$ H_3 C $CH - CH_3$ H_3 C $CH - CH_3$ H_4 CH_3 H_4 CH_3 H_4 CH_3 H_4 CH_3 H_5 CH_5 CH_5

18. 0.44g of a monohydric alcohol when added to methyl magnesium iodide in ether liberates at STP 112 cm³ of methane with PCC the same alcohol form a carbonyl compound that answers silver mirror test. Identify the compound.

Monohydric alcohol means a alcohol which contains one hydroxyl group. PCC is an oxidising agent which convert alcohols to aldehyde or ketones. Aldehydes show silver mirror test not ketones. So, aldehyde is formed and primary alcohols give aldehyde on oxidation. Secondary alcohols give ketones. Consider the formula of monohydric alcohol is $\mathbf{C_nH_{2n+1}OH}$. Alcohols react with grignard reagent form alkyl magnesium halide with the evolution of alkane.

$$\mathsf{CnH}_{2\mathsf{n}+1}\mathsf{OH} + \mathsf{CH}_{3}\mathsf{MgI} \longrightarrow \mathsf{CH}_{4} + \mathsf{C}_{\mathsf{n}}\mathsf{H}_{2\mathsf{n}+1}\mathsf{OMgI}$$

112 cm³ of methane is produced from 0.44 g of alcohol

22400 cm3 of methane is produced from =
$$\frac{22400 \times 0.44}{112}$$
 = 88 g

This is the molar mass of alcohol as 1 mole of alcohol which is equivalent to molar mass produces 22400 cm³ of gas at STP.

Molar mass of alcohol = 81 g

Subtract the mass of hydroxyl group from it = 88 - (16 + 1) = 71 g

$$C_n H_{2n+1} = 71 g$$

Number of carbon can be possible with this molar mass is 5 which comprises mass 60 g and the rest mass is the mass of hydrogen.

So, the formula of alcohol is $C_5H_{11}OH$.

19. Complete the following reactions

i) OH
$$C_6H_5COCI \rightarrow A$$

$$OH^- \rightarrow B$$
(major product)

ii)
$$C_6H_5$$
-CHCH(OH)CH(CH₃)₂ $\xrightarrow{\text{ConH}_2SO_4}$

i) Phenol on treatment with acid chlorides gives esters. The acetylation and benzoylation of phenol are called **Schotten-Baumann reaction.**

20. Phenol is distilled with Zn dust followed by friedel – crafts alkylation with propyl chloride to give a compound B, B on oxidation gives (c) Identify A,B and C.

i) Phenol to benzene

A-benzene

B-Cumene

C- Cumene hydro peroxide

ii) benzene to phenol

CH₃MgBr+
$$\longrightarrow$$
 A \xrightarrow{HBr} B $\xrightarrow{Mg / \text{ ether}}$ C $\xrightarrow{HCHO / H_3O^+}$ D

Identify A,B,C,D and write the complete equation

22. What will be the product (X and A)for the following reaction

$$\begin{array}{c} \text{acetylchloride} & \xrightarrow{i) \ CH_3MgBr} & X \xrightarrow{acid \ K_2Cr_2O_7} & A \\ \\ \text{CH}_3\text{-COCl} & \xrightarrow{i) \ CH_3MgBr} & \text{CH}_3\text{-COCH}_3 & \xrightarrow{acid \ K_2Cr_2O_7} & \text{CH}_3\text{-COOH} + \text{H-COOH} \\ \\ & X \text{-Acetone} & \text{A-Acetic acid} \\ \end{array}$$

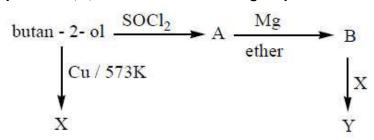
23. How will you convert acetylene into n-butyl alcohol.

$$\begin{array}{lll} \text{step -1:} & \text{H-C} \equiv \text{C-H} & \underline{\qquad} 42\% \, \text{H}_2 \text{SO}_4 \, / \, 1\% \text{Hg}^{2+} & \text{CH}_3\text{-COCH}_3 \\ & \textbf{Aldol condesation} \\ & \text{step -2:} & \text{CH}_3\text{-} & \text{C} - \text{CH}_3 + \text{H-CH}_2\text{-CO-CH}_3 & \underline{\qquad} & \text{NaOH} \\ & & & & \text{OH} \end{array} \\ & \text{step -3:} & \text{CH}_3\text{-} & \text{CH - CH - CHO} & \underline{\qquad} & \text{CH}_3\text{-} & \text{CH = CH - CHO} + \text{H}_2\text{O} \\ & & & \text{OH} & \text{H} \end{array}$$

step-4 Reduction of crotonaldehyde to n-butyl alcohol.

$$CH_3$$
- CH = CH - $CHO \xrightarrow{H_2/Ni} CH_3$ - $CH_2 CH_2$ - $COOH$

24. Predict the product A,B,X and Y in the following sequence of reaction



$$\begin{array}{c} \text{CH}_3\text{-}\text{CH}_2\text{-}\text{CH}\text{-}\text{CH}_3 & \underline{\text{SOCl}_2} \\ \text{OH} & \underline{\text{CH}_3\text{-}\text{CH}_2\text{-}\text{CH}\text{-}\text{CH}_3} & \underline{\text{Mg}/\text{Ether}} \\ \text{OH} & \underline{\text{CH}_3\text{-}\text{CH}_2\text{-}\text{C}\text{-}\text{CH}\text{-}\text{CH}_3} \\ \\ \text{CH}_3\text{-}\text{CH}_2\text{-}\text{C}\text{-}\text{CH}_3 \\ \\ \text{CH}_3\text{-}\text{CH}_2\text{-}\text{C}\text{-}\text{CH}_3 \\ \\ \text{OH} & \underline{\text{CH}_3\text{-}\text{CH}_2\text{-}\text{C}\text{-}\text{CH}_3} \\ \\ \text{CH}_3\text{-}\text{CH}_2\text{-}\text{C}\text{-}\text{CH}_3 \\ \\ \text{CH}_3\text{-}\text{CH}_2\text{-}\text{C}\text{-}\text{C}\text{-}\text{CH}_3 \\ \\ \text{CH}_3\text{-}\text{CH}_2\text{-}\text{C}\text{-}\text{C}\text{-}\text{CH}_3 \\ \\ \text{CH}_3\text{-}\text{CH}_2\text{-}\text{C}\text{-}\text{C}\text{-}\text{CH}_3 \\ \\ \text{CH}_3\text{-}\text{CH}_2\text{-}\text{C}\text{-}\text{C}\text{-}\text{CH}_3 \\ \\ \text{OMgCl} \\ \\ \end{array}$$

Compound- A: 2- chloro - butane
Compound- B: 2- butanone

Compound- X: 2- butanone

Compound- Y: 3, 4-dimethyl-hexan-3-ol

$$\begin{array}{c} & \text{H} \\ \text{CH}_3\text{-CH}_2\text{-}\text{C} \text{-}\text{CH}_3 \\ \text{CH}_3\text{-}\text{CH}_2\text{-}\text{C} \text{-}\text{CH}_3 \\ \text{OH} \end{array}$$

25. 3,3 – dimethylbutan-2-ol on treatment with conc. H₂SO₄ to give tetramethyl ethylene as a major product. Suggest a suitable mechanism

The mechanism is as follows:

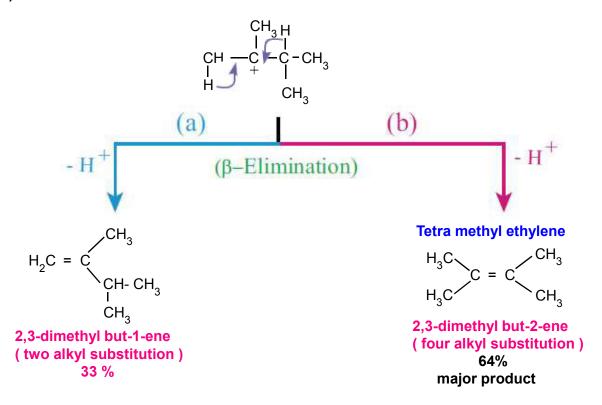
Step-1: protonation of 3,3-dimethylbutan-2-ol

2) Removal of a water molecule from the carbonium ion formed above

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3) Conversion of 2 degree carbonium to 3 degree carbonium by methyl shift:

4) Removal of H⁺ ion to form a double bond:



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