

TOPIC 9: ORGANIC CHEMISTRY II

Topic competency: *The learner analyses reaction mechanisms, evaluates reaction pathways and conditions, and designs multi-step syntheses to achieve target compounds (considering alcohols, phenols, carbonyl compounds)*

SUB-TOPIC 9.1: Alcohols and Phenols

Learning outcomes:

The learner should be able to;

- (a) Analyse the structure, nomenclature, physical and chemical properties of alcohols and phenol (*u,s*)

Suggested learning activities as pre the syllabus

(i) Individually, learners search for information about the structure, nomenclature, preparation and physical properties of alcohols and phenols , discuss their findings in groups and make reports (preparation of phenols not required)
(ii) Individually, learners search for information about the chemical properties of alcohols and phenols and their mechanisms , discuss their findings in groups and make reports.
(iii) In pairs, learners use problem-based learning to carryout exercise on chemical reactions of alcohols and phenols and their mechanisms.
(iv) In groups, learners perform test tube experiments on the identification and reactions of alcohols (include distinction between classes) and phenols and write reports.

- (b) Evaluate the applications of alcohols and phenols in real life (*u, v/a*)

Suggested learning activities as per the syllabus

(i) In groups, learners analyse case studies to evaluate the applications of alcohols and phenols in real life and make presentations.
(ii) In groups, learners carryout projects to make useful products from alcohols and phenols.

ALCOHOLS (ALKANOLS) AND PHENOLS

ALCOHOLS (ALKANOLS)

These are organic compounds containing a hydroxyl group ($-OH$) attached to the saturated carbon atom in the chain or ring.

Alcohols containing only one hydroxyl group are called monohydric alcohols and hence have a general molecular formula $C_nH_{2n+1}OH$ and those with more than one hydroxyl group per molecule are known as polyhydric alcohols.

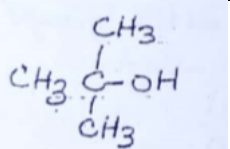
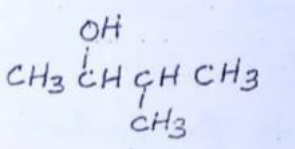
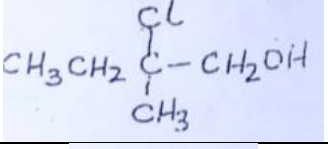
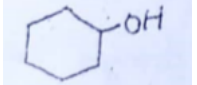
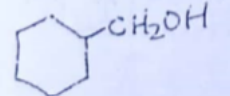
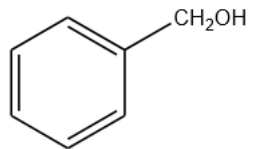
Nomenclature

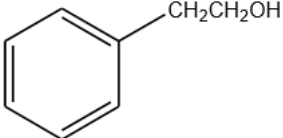
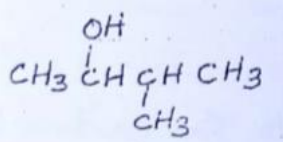
Monohydric alcohols are named by replacing the final letter 'e' of the corresponding alkane with 'ol'

The longest chain containing the hydroxyl group is chosen.

The carbon atoms are numbered to give the carbon atom with the hydroxyl group the lowest number. For some alcohols, the position of the functional group has to be indicated by numbering.

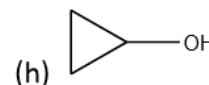
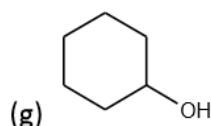
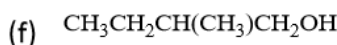
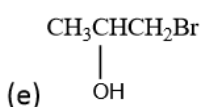
When naming the polyhydric alcohols, the final letter 'e' of the corresponding alkane is not replaced. The name of the alkane is then followed by numbers to indicate the positions of the hydroxyl groups then the name ends either 'diol' if there are two hydroxyl groups or 'triol' if there are three hydroxyl groups in the molecule. For example

Structure	IUPAC name
CH_3OH	Methanol
CH_3CH_2OH	Ethanol
$CH_3CH_2CH_2OH$	Propan-1-ol
$CH_3CH(CH_3)CH_2OH$	
	
	
	
	
	Cyclohexylmethanol
	

	2-phenylethanol
	

Name the following compounds using the IUPAC System

- (a) CH_3OH (b) $\text{CH}_3\text{CH}_2\text{OH}$ (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (d) $(\text{CH}_3)_3\text{CCH}_2\text{OH}$



Solution

- (a) Methanol (b) Ethanol (c) Propan-1-ol (d) 2,2-dimethylpropan-1-ol
 (e) 1-bromopropan-2-ol (f) 2-methylbutan-1-ol (g) Cyclohexanol (h) Cyclopropanol

Classification of alcohols

The classification is done according to;

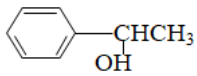
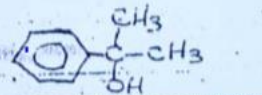
- (a) The number of hydroxyl groups in the molecule.
 (b) The number of alkyl groups attached to the carbon atom bearing the hydroxyl group.

Classification according to the number of hydroxyl group in the molecule

(i) Monohydric alcohols	These have only one hydroxyl group in the molecule e.g. CH_3OH , $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
(ii) Dihydric alcohols (Diols)	These contain two hydroxyl groups per molecule. E.g. Ethane-1,2-diol
(iii) Trihydric alcohols (Triols)	These contain three hydroxyl groups per molecule e.g. propane-1,2,3-triol (glycerol)

Note: dihydric and Trihydric alcohols are generally termed as polyhydric or polyols.

Classification according to the number of alkyl groups attached to the carbon atom bearing the hydroxyl group.

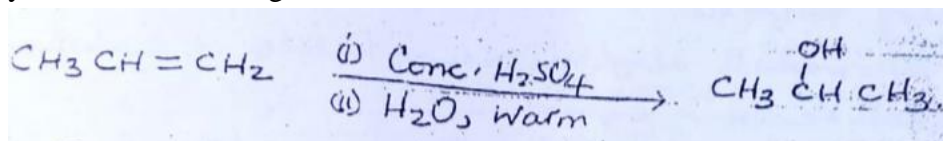
(i) Primary alcohols	<p>These have only one alkyl group attached to the carbon atom bearing the hydroxyl group i.e. $R - CH_2OH$ e.g. $CH_3CH_2CH_2OH, CH_3CH_2OH$</p>
(ii) Secondary alcohols	<p>These have two alkyl groups attached to the carbon atom bearing the hydroxyl group i.e.</p> $R - \underset{\substack{ \\ OH}}{CH} - R'$ <p>e.g.</p> $CH_3 - \underset{\substack{ \\ OH}}{CH} - CH_3$ 
(iii) Tertiary alcohols	<p>These have three alkyl groups attached to the carbon atom bearing the hydroxyl group i.e.</p> $R - \underset{\substack{ \\ OH}}{C} - R'$ <p>e.g.</p> $CH_3 - \underset{\substack{ \\ CH_3}}{C} - OH$ 

Preparation of alcohols

There are many methods of synthesizing monohydric alcohols;

(a) By warming alkenes with acidified water:

- (i) Using concentrated sulphuric acid; When an alkene is reacted with concentrated sulphuric acid, an alkyl hydrogen sulphate is formed which when warmed in water yields an alcohol. E.g.



Mechanism:

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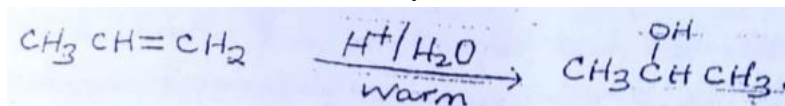
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The above reaction is commonly written as;

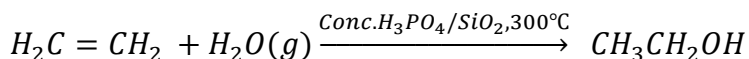


Mechanism:

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(ii) By direct hydration using concentrated phosphoric(V) acid

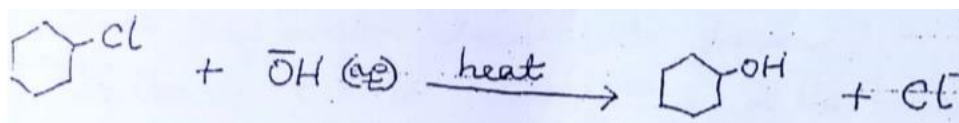
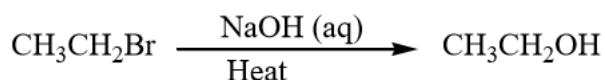
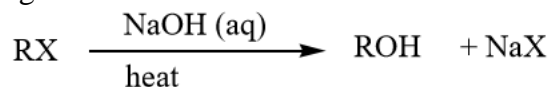
Ethanol can be got by directly hydrating ethene with steam in the presence of concentrated phosphoric(V) acid at a temperature of 300°C.



(b) By hydrolysis of alkyl halides with aqueous alkalis.

When an alkyl halide is heated with an aqueous solution of alkali, an alcohol is formed.

e.g.



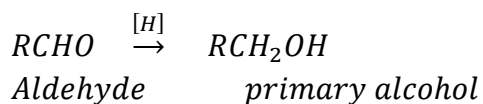
(c) By reduction of carbonyl compounds

When an aldehyde is reduced, a primary alcohol is formed.

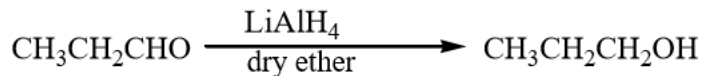
The reducing agents which can be used include;

- Lithium aluminium hydride (LiAlH_4) or Lithium tetrahydrido aluminate(III) dissolved in dry ether (solvent). Ether must be dry because the hydride reacts with water.
- Sodium boron tetrahydride (NaBH_4) or sodium tetrahydrido borate(III) dissolved in water or alcohol (solvent)
- Hydrogen in the presence of a metal catalyst.
- Sodium in an alcohol.

i.e.



E.g.



Other examples are;

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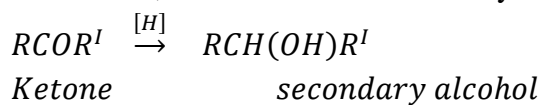
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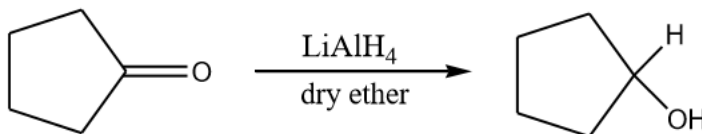
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Meanwhile, the reduction of a ketone yields a secondary alcohol.



E.g.



Other examples are;

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Task

Using equations only, show how the following conversions can be effected.

(i) CH_3CHO to $BrCH_2CH_2Br$

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Task

Using equations only, show how the following conversions can be effected.

(i) CH_3CH_2COOH to 2-bromopropane.

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(ii) Propanoic acid to propan-2-ol

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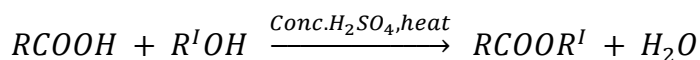
(e) From esters

(i) By reduction of an ester

An ester can be formed by reacting a carboxylic acid with an alcohol, in what is known as an *esterification reaction*.

In this reaction, some concentrated sulphuric acid has to be added to the mixture which has to be warmed/ heated as well.

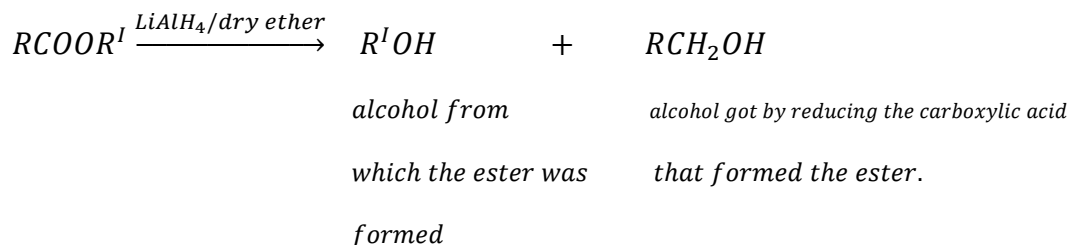
i.e.



Note: This reaction is reversible.

When an ester is treated with lithium aluminium hydride in dry ether, two alcohols are obtained, an alcohol from which the ester was formed during esterification and an alcohol obtained by reducing the carboxylic acid from which the ester was formed.

i.e

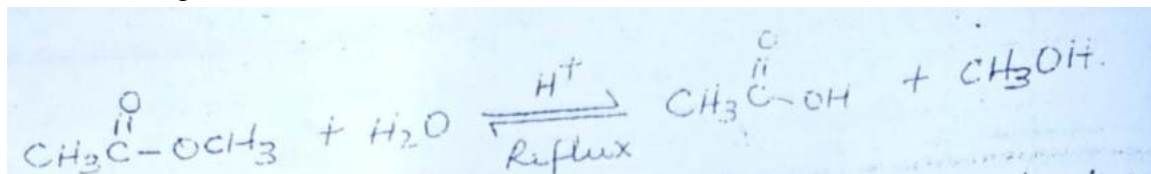


e.g.

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(ii) By hydrolysis of an ester

Esters are hydrolysed, catalyzed by use of either dilute sulphuric acid or a base such as sodium hydroxide to form a mixture of a carboxylic acid and an alcohol. The reaction is reversible. E.g.



The two products can be separated by fractional distillation.

Mechanism:

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Task:

(a) Benzyl ethanoate can be reduced to two alkanols

(i) Write the structural formula of benzyl ethanoate.

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(ii) Give one reagent that can be used for the reduction.

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(iii) Write the structural formula of the alkanols

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(b)Hydrolysis of esters using mineral acids gives alkanols and alkanolic acids. Briefly describe a method which can be used to determine whether the oxygen atom in alkanol comes from the ester or water

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Hint: in the mechanism for esterification, this would be determined;

This was determined using radioactive Oxygen (18). The primary alcohol containing oxygen-18 is reacted with monocarboxylic acid. The mass spectrometer is used to analyse the ester and water formed. The oxygen-18 is found in the ester only and not water indicating that carbon-oxygen single bond in the acid and oxygen-hydrogen bond in the alcohol are bonded.

(f) **By the cannizzaro reaction:**

This reaction involves two aldehydes namely, methanal ($HCHO$) and benzaldehyde. They both lack an alpha hydrogen atom. Alpha hydrogen is a hydrogen atom directly bonded on the carbon atom adjacent to the carbon atom of the functional group i.e. the carbonyl carbon atom. E.g. the aldehydes below have α -hydrogen atoms;



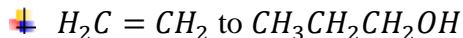
When methanal and benzaldehyde (the aldehydes lacking α -hydrogen atoms) are each treated with concentrated sodium hydroxide (or potassium hydroxide) solution, two organic products are formed. A product due to reduction of an aldehyde (i.e. a primary alcohol) and a product due to oxidation of an aldehyde (i.e. in this case the sodium salt of a carboxylic acid)

i.e.

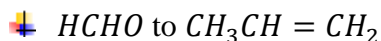
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Note: In this method the primary alcohol formed has one carbon atom more than the starting carbonyl compound (aldehyde).

Task:

Using equations only, show how the following conversions below can be effected.



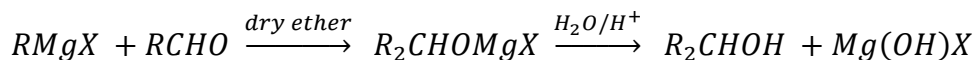
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(ii) Using other aldehydes (RCHO) as the carbonyl compound.

When a Grignard reagent is reacted with an aldehyde which is not methanal and the subsequent intermediate treated with acidified water, a secondary alcohol is formed. i.e.



e.g.

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Task:

Using equations only, show how the conversions below can be effected.

(a) CH_3CHO to $CH_3CH = CHCH_3$

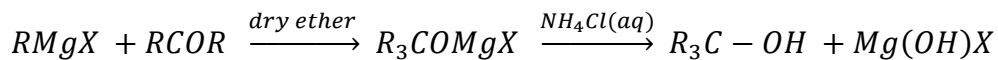
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(b) CH_3MgCl to propane

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(iii) *Using a ketone as a carbonyl compound.*

When a Grignard reagent is reacted with a ketone and the subsequent intermediate is reacted with aqueous ammonium chloride, a tertiary alcohol is formed. i.e.

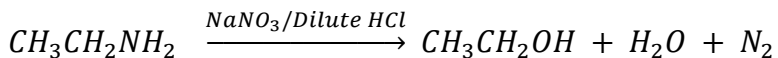


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Note:

(i) Primary alcohols can be prepared from primary amines by reacting the amine with sodium nitrite and concentrated / dilute hydrochloric acid.

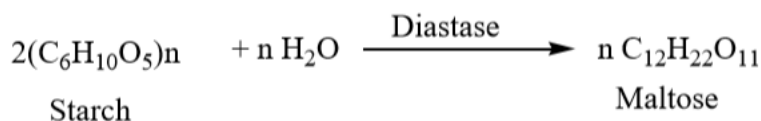


(ii) In the preparation of tertiary alcohols, aqueous ammonium chloride is used for hydrolysis as the dilute acid brings about dehydration of a tertiary alcohol to yield an alkene.

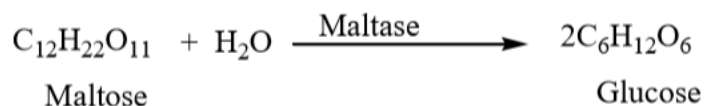
(h) By fermentation:

Fermentation is a process in which sugars are decomposed by enzymes to form alcohol.

Raw materials like molasses, potatoes and cereals that contain starch, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, are warmed with malt at 60°C for a specific period of time to convert starch into maltose by the enzyme diastase contained in the malt.



On addition of yeast which contains enzyme maltase, the maltose is broken down into glucose.



The glucose formed is maintained at 15°C and then is then converted into alcohol by an enzyme zymase also contained in the yeast.



PHYSICAL PROPERTIES OF ALCOHOLS

Physical state:

Most simple aliphatic alcohols and lower aromatic alcohols are colourless liquids at room temperature with a spirit smell.

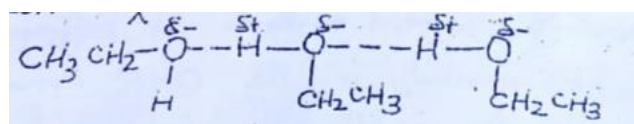
Aliphatic alcohols containing more than 12 carbon atoms and higher aromatic alcohols are waxy solids.

Boiling and melting points:

Just like alkanes, the boiling points of alcohols increases with increasing molecular mass and decreases with increased branching. However, alcohols have higher boiling points than the corresponding alkanes of comparable molecular mass.

Reason:

Alcohols contain oxygen-hydrogen ($O - H$) bond, in which the highly electronegative oxygen atom is directly bonded to hydrogen and thus the bond is highly polar. This makes the alcohol molecules to associate through intermolecular hydrogen bonds which are strong and require a lot of heat to be broken. i.e.



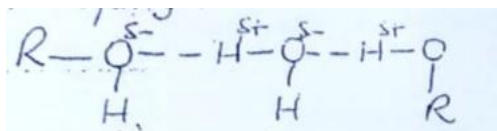
However, in alkanes, the molecules associate through van der waals forces of attraction which are weak and thus require little heat energy to be broken.

Solubility:

Alcohols with low relative molecular mass for example, methanol, ethanol and propan-1-ol are completely soluble/ miscible with water in all proportions to form neutral solutions.

Reason:

Alcohol molecules can form hydrogen bonds with water molecules i.e.



The hydrogen bonds formed between alcohol and water molecules increase the interaction between them (i.e. the alcohol and the water molecules) thus enhancing solubility (miscibility).

However, higher alcohols are less soluble in water and generally solubility (miscibility) of the alcohols in water decreases with increasing molecular mass. This is attributed to the increasing proportion of the water insoluble alkyl group in the molecule.

Note:

Alcohols are generally soluble in organic solvents and the simple alcohols themselves such as methanol and ethanol can be used as organic solvents.

CHEMICAL PROPERTIES OF ALCOHOLS

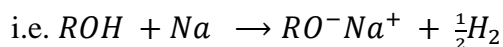
The reactions of alcohols can be divided into three categories;

- (a) Reactions involving cleavage of the oxygen-hydrogen bond.
- (b) Reactions involving cleavage of the carbon-oxygen bond.
- (c) Reactions involving the carbon skeleton.

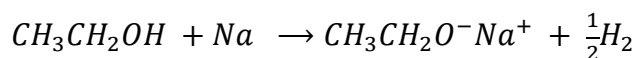
(a) **Reactions involving cleavage of the oxygen-hydrogen bond.**

(i) **Reaction with sodium.**

Alcohols react with sodium metal releasing hydrogen gas.



E.g.



(Sodium ethoxide)

In this reaction, the alcohol is behaving as an acid by reacting with a highly electropositive metal (sodium) to liberate hydrogen gas and form a salt.

This reaction can be used in testing the presence of a hydroxyl group in an organic compound i.e. all organic compounds containing a hydroxyl group (e.g. alcohols, phenols and carboxylic acids) react with sodium metal releasing hydrogen gas.

Therefore, when sodium metal is added to such compounds, the metal dissolves with effervescence of a colourless gas.

Task:

1. Name a reagent that you can use to distinguish between ethanol and methoxymethane. State what is observed and write equation for the reaction if any when each member is separately treated with the reagent.

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2. 2.3 g of a piece of sodium metal was dropped in ethanol.

(a) Write an equation for the reaction

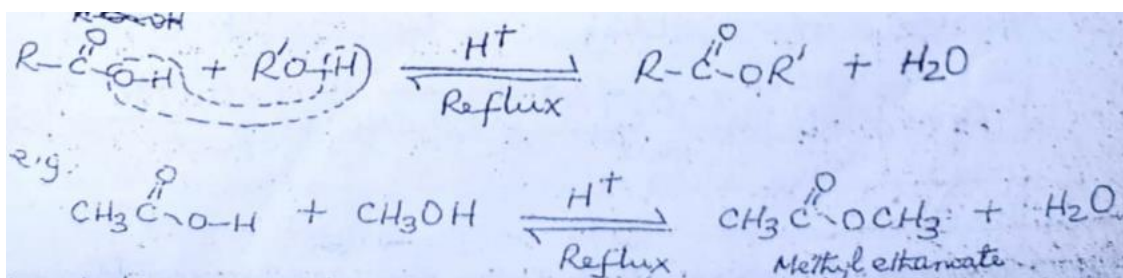
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(b) Calculate the volume of gas evolved measured at s.t.p.

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(c) Bromomethane was added to the resultant solution in (b).
(i) Name the type of reaction that takes place.

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(ii) Write an equation for the reaction and outline the mechanism.

(ii) Esterification

When an alcohol is heated/ refluxed with a carboxylic acid in the presence of concentrated sulphuric acid, an ester is formed. This reaction is reversible. i.e.



Mechanism:

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Esterification reaction can be used in qualitative analysis for detecting the presence of either an alcohol or a carboxylic acid. If on heating a mixture of some unknown organic **compound A** with a carboxylic acid (ethanoic acid) and concentrated sulphuric acid, a sweet fruity smell is detected, then the conclusion is that **compound A** is an alcohol.

Similarly, if a sweet fruity smell is detected, on heating a mixture of some unknown **compound B** with an alcohol and concentrated sulphuric acid, then the conclusion is carboxylic acid.

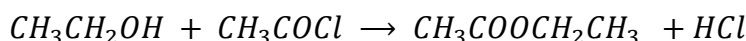
Note:

- ❖ *The sweet fruity smell of an ester is rather faint but usually becomes more intense if the mixture resulting from esterification reaction is poured in cold water in a beaker.*
- ❖ *During esterification reaction, the bond broken in the alcohol is the oxygen-hydrogen bond while the bond broken in the carboxylic acid is the carbon-oxygen bond.*

(iii) Reaction with Acid halides (Acyl halides)

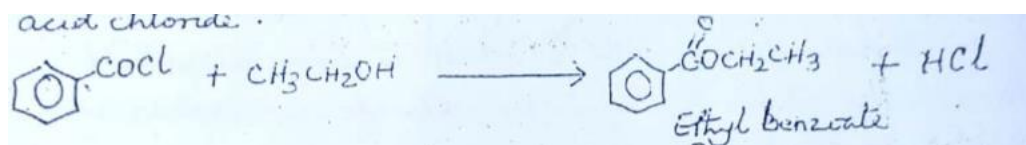
Alcohols react with acid halides forming esters. This reaction can also be termed as esterification.

e.g.



Mechanism:

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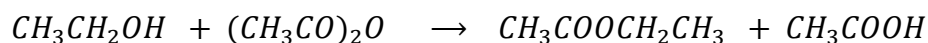
Mechanism:

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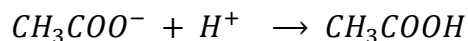
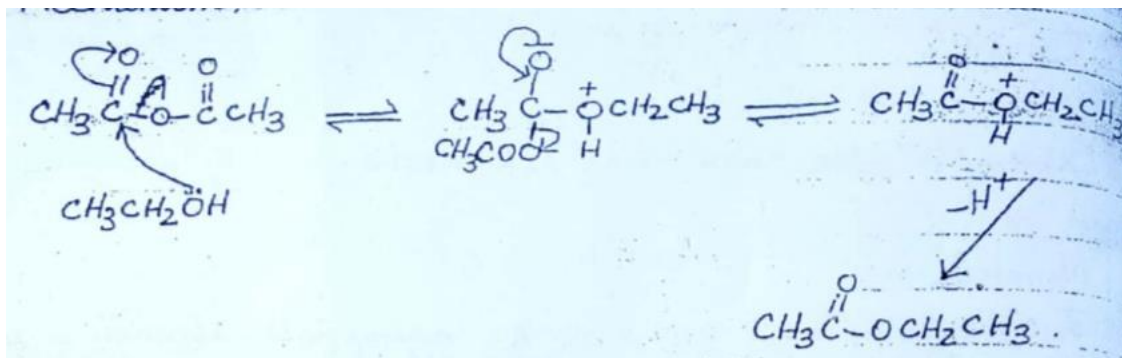
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(iv) Reaction with Acid anhydrides

When an alcohol is reacted with an acid anhydride, an ester and a carboxylic acid are formed. i.e



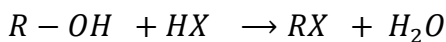
Mechanism:



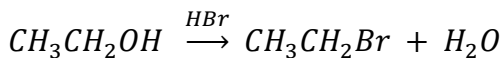
(b) Reactions involving cleavage of the carbon-oxygen bond.

(i) Reaction with hydrogen halides.

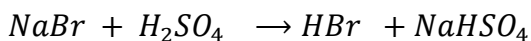
Alcohols react with hydrogen halides to form alkyl halides. i.e.



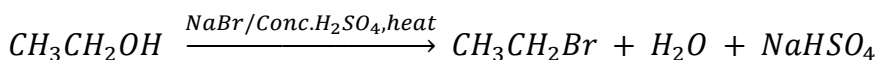
E.g.



The hydrogen bromide used in the above reaction is generated 'in situ' from a heated mixture of sodium bromide or potassium bromide with concentrated sulphuric acid.



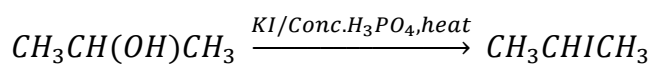
Hence, the best way of representing the above reaction is



Mechanism:

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Likewise, hydrogen iodide can be generated 'in situ' from a heated mixture of sodium iodide or potassium iodide with concentrated phosphoric(V) acid



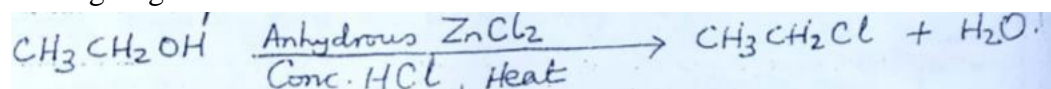
Mechanism:

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In this case, concentrated sulphuric acid is not used to generate HI in situ but rather concentrated phosphoric(V) acid because concentrated sulphuric acid would readily oxidise the HI formed to iodine.

The reaction involving hydrogen chloride as the hydrogen halide is catalyzed by anhydrous zinc chloride and the hydrogen chloride gas is readily provided by concentrated hydrochloric acid due to its high volatility.

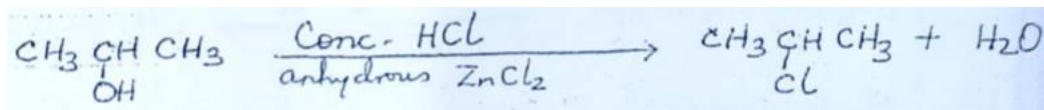
For primary alcohol, the reaction does not take place at room temperature but rather on heating. E.g.



Mechanism:

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For secondary alcohols, the reaction takes place within about 5-10 minutes at room temperature. E.g.



Mechanism:

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For tertiary alcohols, the reaction occurs immediately at room temperature. E.g.

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In these reactions, the chloroalkane formed makes the solution to turn cloudy (due to a suspension of the insoluble chloroalkane particles in solution).

We can therefore base on this fact to distinguish between the three classes of alcohols using the above reagent (i.e. anhydrous zinc chloride and concentrated hydrochloric acid)

When a primary alcohol is treated with the above reagents at room temperature, there is no observable change (since the reaction does not occur at room temperature.)

When a secondary alcohol is treated with the above reagents at room temperature, a cloudy solution is formed within about 5-10 minutes since the reaction occurs within that time frame.

When a tertiary alcohol is treated with the above reagents at room temperature, a cloudy solution is formed immediately since the reaction occurs immediately.

Summary

Reagent: Anhydrous zinc chloride and concentrated hydrochloric acid

Observations:

Primary alcohols give no observable change at room temperature.

Secondary alcohols give a cloudy solution within about 5-10 minutes

Tertiary alcohols give a cloudy solution immediately.

Note:

- The mixture of anhydrous zinc chloride and concentrated hydrochloric acid is commonly known as **Lucas reagent**.
- This reaction employs the fact that tertiary alcohols are the most reactive while primary alcohols are the least reactive.

Reason:

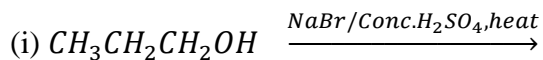
The reaction of alcohols with hydrogen halides generally proceeds via formation of carbonium ion as intermediate.

With tertiary alcohols, the intermediate carbonium ion is a tertiary one. Since a tertiary carbonium ion is stable. This reaction is favoured hence making tertiary alcohols to react readily.

With primary alcohols, the intermediate carbonium ion is a primary one, which is unstable. Therefore, the reaction is not favoured hence making the primary alcohol not to react at room temperature.

Task:

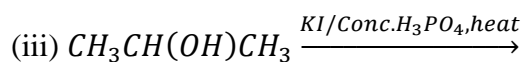
(a) Complete the following equations of reaction and suggest a mechanism for each reaction.



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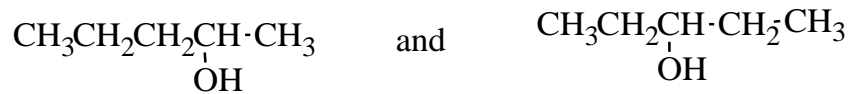


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(b) Name a reagent that can be used to distinguish between $CH_3CH_2CH_2CH_2OH$ and $(CH_3)_3C - OH$, stating what would be observed and giving reason for your answer.

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(c) Name one reagent that can be used to distinguish between each of the following pairs of compounds. In each case, state what is observed if the reagent is separately treated with each member of the pair.



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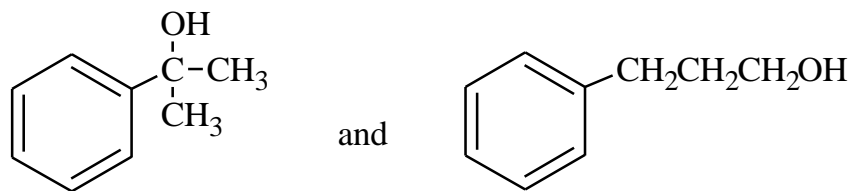
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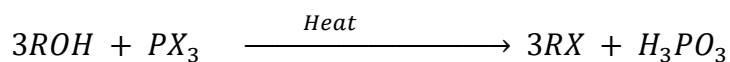
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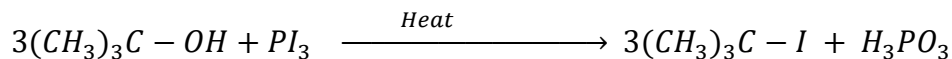
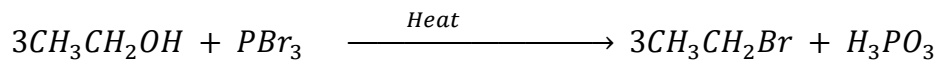
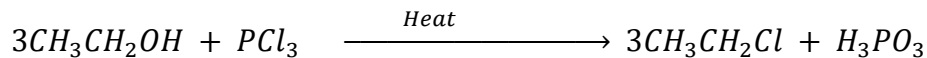
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(ii) **Reaction with phosphorus(III) halides (PX₃)**

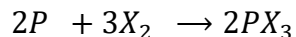
When an alcohol reacts with a phosphorus(III) halide, an alkylhalide and phosphorus acid are formed. This reaction occurs on heating. i.e.



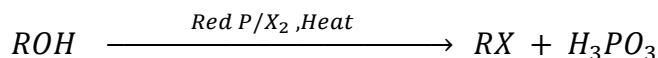
E.g.



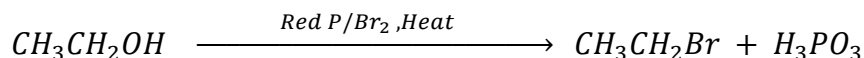
The phosphorus(III) halide in this case can be generated in situ by heating the phosphorus with the corresponding halogens i.e.



Hence the general equation of the reaction above can also be written as

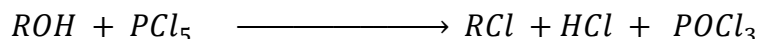


e.g.

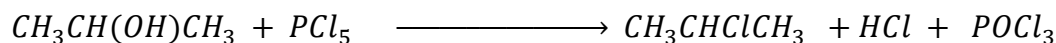
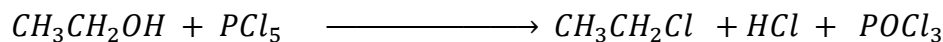


(iii) Reaction with phosphorus(V) chloride.

When an alcohol reacts with phosphorus(V) chloride, a chloroalkane is formed together with misty fumes of hydrogen chloride gas and phosphorus trichloride oxide ($POCl_3$). This reaction occurs at room temperature. i.e.



e.g.



NOTE:

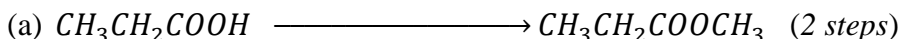
This reaction is common to all organic compounds containing the hydroxyl group (i.e. alcohols, phenols and carboxylic acids)

It can therefore be used as a basis for distinguishing between an alcohol or carboxylic acid and any other organic compound lacking the hydroxyl group.

On treatment with phosphorus(V) chloride, an alcohol or carboxylic acid evolves misty fumes.

Task:

Using equations only, describe how each of the following conversions can be effected.



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Note:

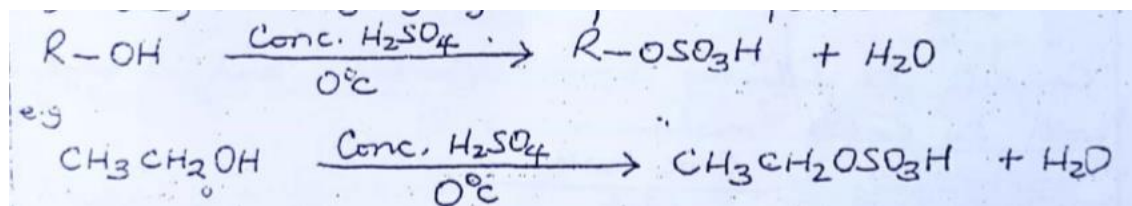
In this reaction, the hydrochloric acid formed can promote other parallel and undesired reactions. In practice, a small quantity of pyridine (a weak base) is usually included in the reaction mixture to absorb the hydrogen chloride as it is formed.

(c) Reactions involving the carbon skeleton

(i) Reaction with concentrated sulphuric acid

When an alcohol reacts with concentrated sulphuric acid, the major organic product formed depends on the conditions of the reaction particularly the temperature of the reaction mixture.

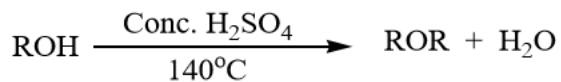
At 0°C, an alcohol reacts with concentrated sulphuric acid forming an alkyl hydrogen sulphate. i.e.



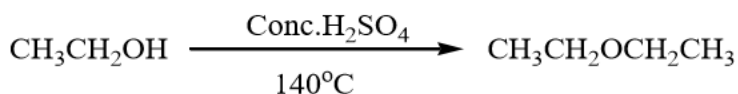
Mechanism:

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At 140°C, an excess of the primary alcohol reacts with concentrated sulphuric acid forming an ether. i.e.



E.g.



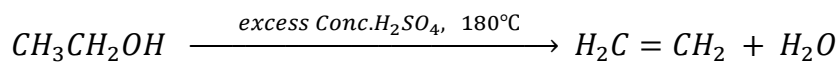
Mechanism:

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Note: *This reaction is mainly undergone by primary alcohols.*

At a temperature in the range of 170-180°C, a primary alcohol reacts with excess concentrated sulphuric acid to form an alkene in a dehydration reaction.

e.g.



Mechanism:

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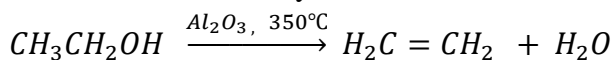
Note:

Secondary and tertiary alcohols also undergo dehydration even at lower temperatures to form alkenes.

i.e.

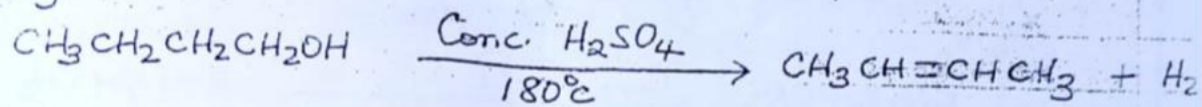
Note:

- The reaction of alcohols with concentrated sulphuric acid between 170-180°C and concentrated phosphoric acid at 360°C to form alkenes is an example of elimination reactions undergone by alcohols.
- Dehydration is easiest with tertiary alcohols and difficult with primary alcohols. This explains why in practice for the case of a primary alcohol, not only should acid be in excess but also a very high temperature range, i.e. of 170-180°C, is necessary. On the contrary, dehydration of tertiary alcohols can occur at lower temperature including 140°C.
- Dehydration of ethanol can also be achieved by passing ethanol vapour over heated aluminium oxide catalyst at 350°C.

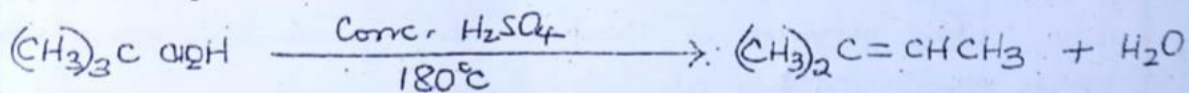
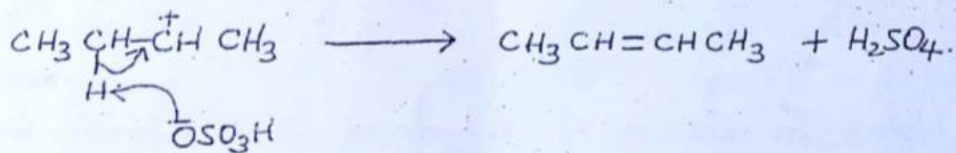
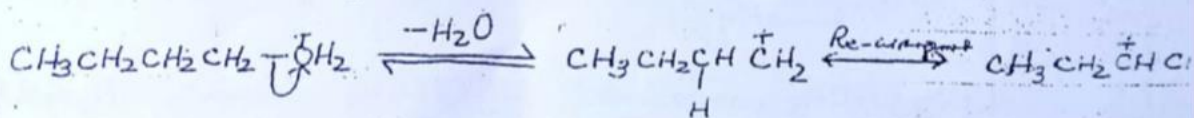
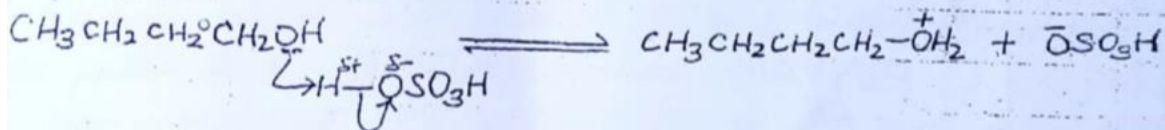


- In some dehydration reactions of alcohols, re-arrangement of the carbonium ion occurs to give a more stable carbonium ion.

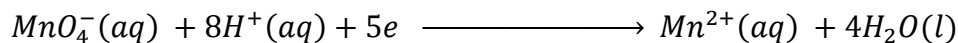
e.g.



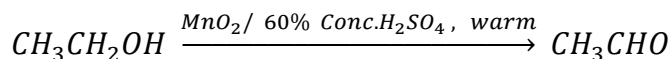
Mechanism:



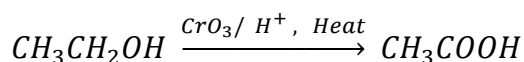
In the reaction, the purple manganate(VII) ions are reduced to colourless manganese(II) ions according to the half equation below;



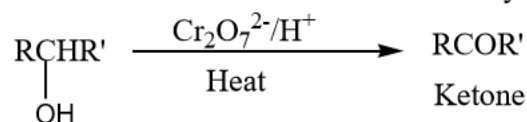
When a mild oxidizing agent such as manganese(IV) oxide in 60% concentrated sulphuric acid is warmed with a primary alcohol, the final product is an aldehyde.



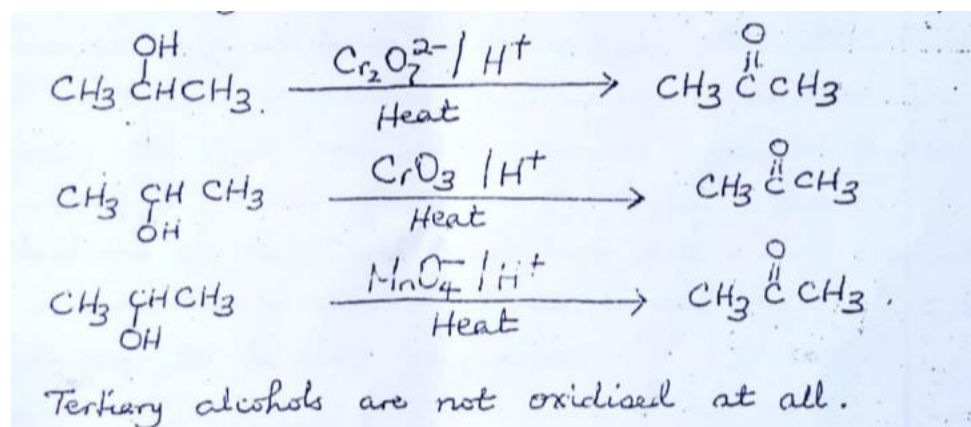
Acidified chromium(VI) oxide oxidizes primary alcohols to aldehydes on heating.



Secondary alcohols are oxidized to corresponding ketones. i.e.

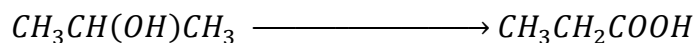


e.g.



Task:

Using equations, show how the conversion below can be effected

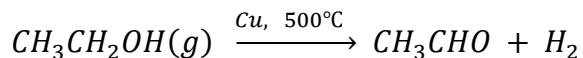


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Note:

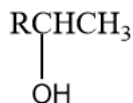
It therefore implies that primary and secondary alcohols are reducing agents. Tertiary alcohols are not oxidized at all and hence are not reducing agents. Hence, when a tertiary alcohol is heated with either acidified potassium dichromate(VI) solution or acidified potassium manganate(VII) solution, there is no observable change.

It is also possible to oxidize ethanol vapour in absence of oxygen by passing it over copper catalyst at



(d) Iodoform reaction (reaction with aqueous iodine and sodium hydroxide solution)

This reaction is undergone by alcohols with a methyl group directly bonded to the carbon atom bearing the hydroxyl group. E.g. **Ethanol** ($\text{CH}_3\text{CH}_2\text{OH}$) and secondary alcohols with structure;

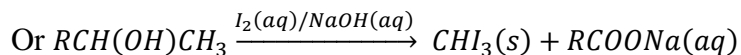
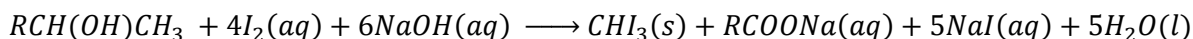


Observation: A yellow precipitate of **triiodomethane** is formed.

Ethanol is the only primary alcohol that gives a yellow precipitate with this mixture of iodine solution in the presence of sodium hydroxide solution.

In the reaction, iodine acts as a mild oxidizing agent initially oxidizing the alcohol to a ketone. The ketone formed then reacts with excess iodine to form triiodomethane and a salt of a carboxylic acid.

The overall equation for the reaction can be illustrated as;



Task:

1. Name a reagent that can be used to distinguish the following, state what is observed and write equation for the reaction.

(a) $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

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(b) $CH_3CH_2CH_2CH(OH)CH_3$ and $CH_3CH_2CH_2CH_2CH_2OH$

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2. (a) A saturated organic compound **G** contains 72% carbon, 12% hydrogen and the rest being oxygen.
- Determine the empirical formula of **G**.
 - Given that the vapour density of **G** is 50, determine the molecular formula of **G**.
- (b) **G** is neutral to litmus and reacts with sodium metal to form bubbles of hydrogen gas and compound **T**. Identify **G** and **T**
- (c) Write equation and suggest a mechanism for the reaction between;
- G** and hot orthophosphoric acid.
 - G** and ethanoyl chloride.
- (d) **G** was heated with acidified chromium(VI) oxide
- State what was observed and write equation for the reaction.
 - The organic product formed in (d)(i) was treated with semi carbazide in dilute sulphuric acid. Write equation for the reaction and suggest a mechanism for the reaction.
3. A compound **Q** with vapour density=30, consists 60.0% carbon, 13.3% hydrogen and the rest being oxygen.
- Calculate the empirical formula of **Q**.
 - Determine the molecular formula of **Q**.
- (b) Write the names and structural formulae of all possible isomers of **Q**.
- (c) When **Q** was reacted with iodine solution and sodium hydroxide solution and the mixture warmed, a yellow precipitate was formed.
- Identify **Q**.
 - Write equation for the reaction that took place.
 - State what would be observed when **Q** is heated with acidified potassium manganate(VII) solution, name the major organic product and write equation for the reaction that took place.
- (d) When **Q** was heated with excess concentrated sulphuric acid, a gas **W** which turned acidified potassium manganate(VII) from purple to colourless was evolved. Write equation for the reaction between;
- Q** and sulphuric acid and suggest a mechanism for the reaction.
 - W** and acidified potassium manganate(VII) and name the product.
4. (a) When 6.1g of an organic compound **P** was burnt completely in oxygen, 15.4g of carbon dioxide and 2.7g of water were formed. 0.252g of **P** when vapourised at 273°C and 2.15atmospheres, 43.04cm³ of vapour was formed.
- Calculate the empirical formula of **P**.

- (ii) Determine the molecular formula of **P**.
- (b) **P** burns with a sooty flame. Identify **P**.
- (c) When **P** was treated with lithium tetrahydrido aluminate(III) in dry ethoxyethane, compound **Q** was formed. When **Q** was warmed with acidified solution of chromium trioxide, compound **R** was formed.
- (i) Identify **Q** and **R**.
- (ii) Write equations leading to the formation of **Q** and **R**.
- (d) Write equation and suggest a mechanism for the reaction between;
- (i) **Q** and propanoyl bromide.
- (ii) **R** and 2, 4-dinitrophenylhydrazine in acidic medium.
- (e) Without using equations, describe how **P** can be synthesized from benzene.
5. Explain each of the following observations and illustrate your answer with equations where necessary.
- (a) The reactivity of alcohols with hydrogen halides is in the order;
Tertiary > secondary > primary alcohol
- (b) Alcohols are neutral organic compounds whereas phenol is weakly acidic, and yet both have hydroxyl group.
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