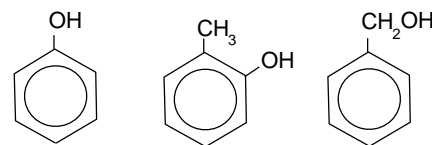


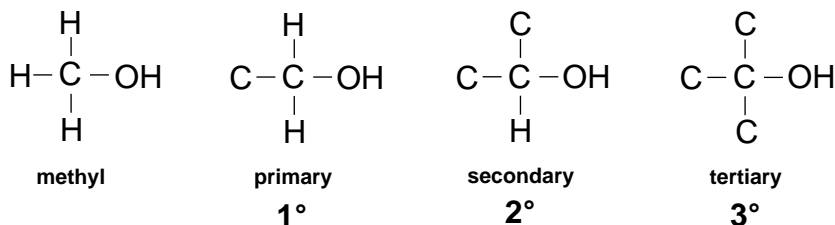
## ALCOHOLS

- Aliphatic**
- **general formula  $C_nH_{2n+1}OH$**  - provided there are no rings
  - named as substituted alkanes by removing the final -e and adding -ol
  - for isomers the position of the OH is given a number - *propan-1-ol* / *propan-2-ol*
- Aromatic**
- the OH must be **attached directly to a benzene ring**; known as **phenols**
  - an OH on a side chain of a benzene ring behaves as a typical aliphatic alcohol.

**Q.1** Which of the structures is/are classified as phenols?



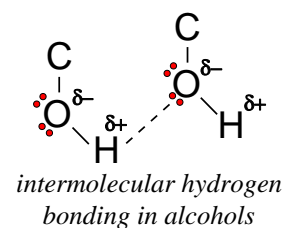
- Structures**
- alcohols are classified according to the environment of the OH functional group
  - chemical behaviour, especially with oxidation, often depends on the structure



## Physical properties

**Boiling point** Increases with molecular size due to **higher induced dipole-dipole interactions**. Alcohols have **higher boiling points** than similar molecular mass alkanes due to the added presence of **inter-molecular hydrogen bonding**. More energy is required to separate the molecules.

		$M_r$	bp / $^\circ\text{C}$
ethanol	$C_2H_5OH$	46	+78
propane	$C_3H_8$	44	-42

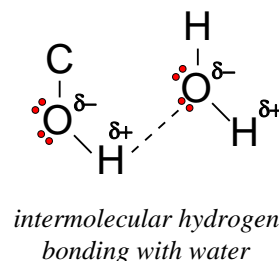


Boiling point also increases for “straight” chain isomers.  
Greater branching = lower inter-molecular forces.

		bp / $^\circ\text{C}$
butan-1-ol	$CH_3CH_2CH_2CH_2OH$	118
butan-2-ol	$CH_3CH_2CH(OH)CH_3$	100
2-methylpropan-2-ol	$(CH_3)_3COH$	83

- Solubility**
- Low molecular mass alcohols are **miscible with water** due to **hydrogen bonding** between the two molecules.

Alcohols are themselves very good solvents, being able to dissolve a large number of organic molecules.



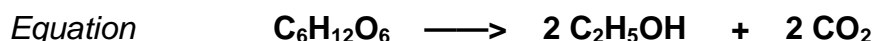
## PREPARATION OF ALCOHOLS

- Laboratory*
- **from haloalkanes** - reflux with aqueous sodium or potassium hydroxide.
  - **from aldehydes** - reduction with sodium tetrahydridoborate(III) - NaBH<sub>4</sub>.
  - **from alkenes** - acid catalysed hydration using conc. sulphuric acid.

*Industrial*      **Fermentation**

*Reagent(s)*      GLUCOSE - from hydrolysis of starch

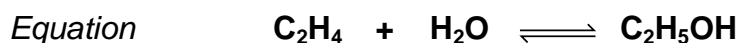
*Conditions*      yeast  
warm but no higher than 37°C



**Direct hydration**

*Reagent(s)*      ETHENE - from cracking of fractions from distilled crude oil

*Conditions*      • catalyst - phosphoric acid  
• high temperature and pressure



**Q.2** List some advantages and disadvantages of the two major industrial methods.

**Fermentation**      *advantage(s)*

*disadvantage(s)*

**Hydration**      *advantage(s)*

*disadvantage(s)*

**Uses**      *ethanol*      •

- 
- 

*methanol*      • fuel, **added to petrol** to improve combustion properties  
• **solvent**  
• a **feedstock** for important industrial processes

## CHEMICAL PROPERTIES

**General** Lone pairs on the oxygen atom makes alcohols **Lewis Bases** (lone pair donors).

- They can use a lone pair to
- pick up protons
  - behave as nucleophiles.

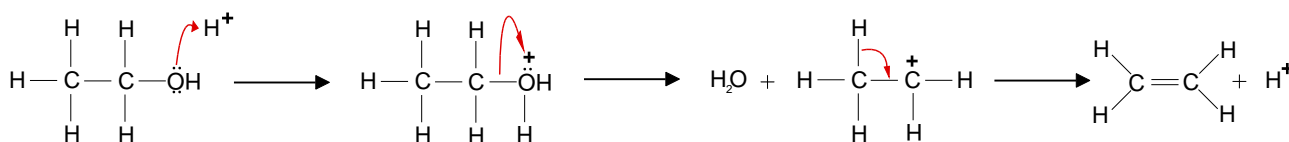
**Elimination** *Reagent* conc. sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) or conc. phosphoric acid (H<sub>3</sub>PO<sub>4</sub>)

*Conditions* reflux 180°C

*Product* alkene

*Equation* e.g.  $\text{C}_2\text{H}_5\text{OH}(\text{l}) \longrightarrow \text{CH}_2 = \text{CH}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

*Mechanism*

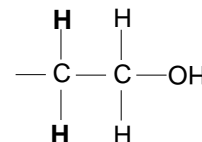


**Step 1** protonation of the alcohol using a lone pair on oxygen

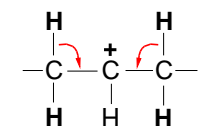
**Step 2** loss of a water molecule to generate a carbocation

**Step 3** loss of a proton (H<sup>+</sup>) to give the alkene

*Note 1* There must be a hydrogen atom on a carbon atom adjacent the carbon with the OH on it



*Note 2* Alcohols with the OH in the middle of a chain have two ways of losing water. In **Step 3** of the mechanism, a proton can be lost from either side of the carbocation. This can give a **mixture of alkenes from unsymmetrical alcohols**



## Elimination

**Method 2** *Conditions* Pass vapour over a heated catalyst of pumice or aluminium oxide

**Q.3** *Butan-2-ol reacts with concentrated sulphuric acid to give **THREE** isomeric alkenes. What are they and how are they formed?*

## Oxidation of Alcohols

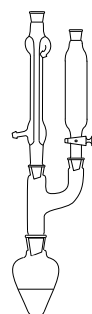
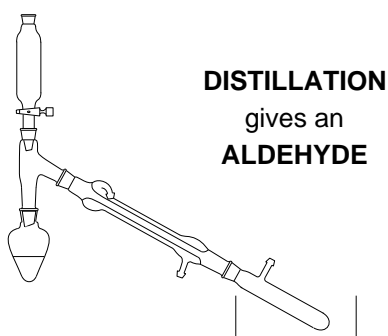
Provides a way of differentiating between primary, secondary and tertiary alcohols. Reagents include acidified potassium dichromate(VI) or potassium manganate(VII)

Primary

**Easily oxidised to aldehydes and then to carboxylic acids.**



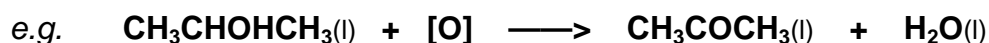
- it is essential to **distil off the aldehyde** before it gets oxidised to the acid
- the alcohol is dripped into a warm solution of acidified  $\text{K}_2\text{Cr}_2\text{O}_7$
- the **aldehyde has a low boiling point** - no hydrogen bonding - it distils off
- if it didn't distil off it would be oxidised to the equivalent carboxylic acid
- to oxidise an alcohol straight to the acid you would reflux the mixture



compound	formula	intermolecular bonding	boiling point
ETHANOL	$\text{C}_2\text{H}_5\text{OH}$	HYDROGEN BONDING	$78^\circ\text{C}$
ETHANAL	$\text{CH}_3\text{CHO}$	PERMANENT DIPOLE-DIPOLE	$23^\circ\text{C}$
ETHANOIC ACID	$\text{CH}_3\text{COOH}$	HYDROGEN BONDING	$118^\circ\text{C}$

Secondary

**Easily oxidised to ketones**



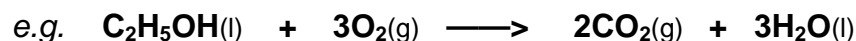
N.B.

On prolonged treatment with a powerful oxidising agent they can be further oxidised to a mixture of acids with fewer carbon atoms than the original alcohol.

Tertiary

**Not oxidised under these conditions.** They do break down with vigorous oxidation

**Combustion** Alcohols make useful fuels



- have high enthalpies of combustion
- do not contain sulphur so there is less pollution
- can be obtained from renewable resources

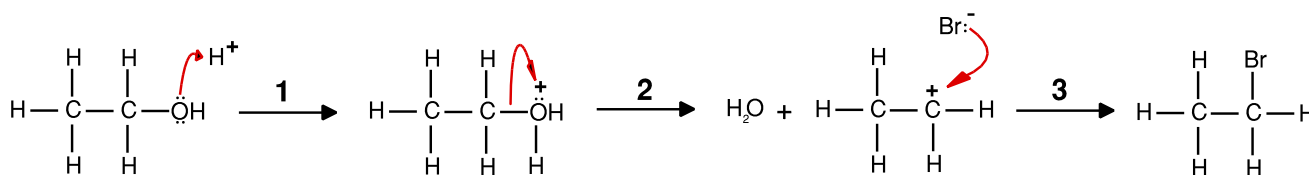
**Bromination** *Reagent(s)* either conc. hydrobromic acid  $\text{HBr}(\text{aq})$   
or sodium (or potassium) bromide and conc. sulphuric acid

*Conditions* reflux

*Product* haloalkane



*Mechanism* The mechanism starts off in a similar way to the dehydration (protonation of the alcohol and loss of water) but the carbocation (*carbonium ion*) is attacked by a nucleophilic bromide ion in step 3.



**Step 1** protonation of the alcohol using a lone pair on oxygen

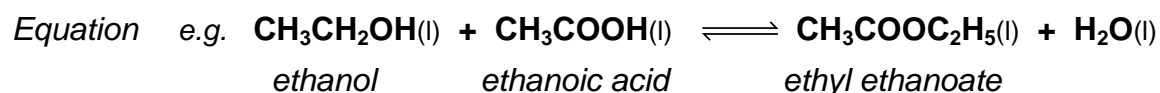
**Step 2** loss of a water molecule to generate a carbocation (*carbonium ion*)

**Step 3** a bromide ion behaves as a nucleophile and attacks the carbocation

**Esterification** *Reagent(s)* carboxylic acid + strong acid catalyst (e.g. conc.  $\text{H}_2\text{SO}_4$ )

*Conditions* reflux

*Product* ester



An **advantage of concentrated  $\text{H}_2\text{SO}_4$**  is that it is also a **dehydrating agent** and removes water as it is formed causing the equilibrium to move to the right and thus **increasing the yield** of ester.

**Q.4** Name these esters;  $\text{HCOOC}_2\text{H}_5$   
 $\text{CH}_3\text{CH}_2\text{COOCH}_3$

Complete the equations;



## IDENTIFYING ALCOHOLS USING INFRA RED SPECTROSCOPY

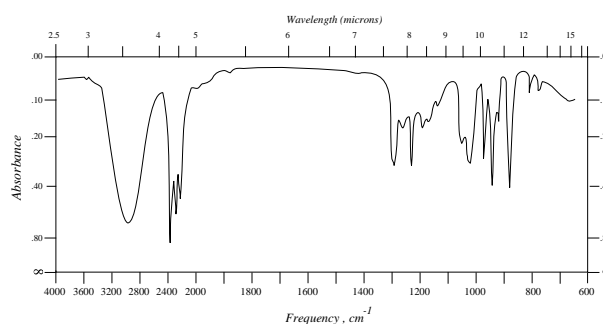
BOND	COMPOUND	ABSORBANCE	RANGE
O-H	alcohols	broad	3200 $\text{cm}^{-1}$ to 3600 $\text{cm}^{-1}$
O-H	carboxylic acids	medium to broad	2500 $\text{cm}^{-1}$ to 3500 $\text{cm}^{-1}$
C=O	ketones, aldehydes esters and acids	strong and sharp	1600 $\text{cm}^{-1}$ to 1750 $\text{cm}^{-1}$

### Differentiation

Compound	O-H	C=O
ALCOHOL	<b>YES</b>	NO
ALDEHYDE / KETONE	NO	<b>YES</b>
CARBOXYLIC ACID	<b>YES</b>	<b>YES</b>
ESTER	NO	<b>YES</b>

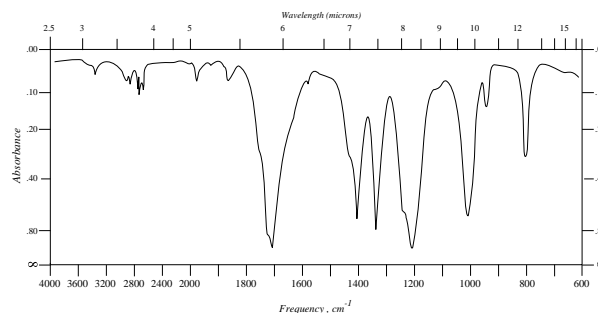
### ALCOHOL

O-H absorption



### ALDEHYDE

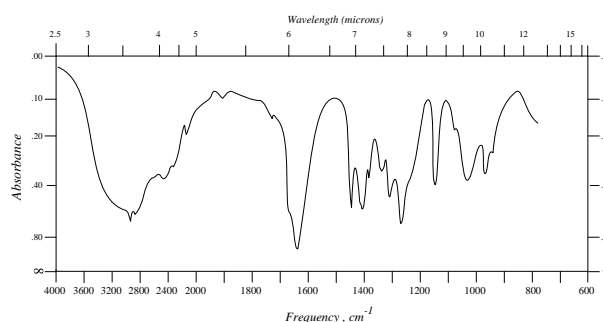
C=O absorption



### CARBOXYLIC ACID

O-H absorption

C=O absorption



## INDUSTRIAL PREPARATION OF ETHANOL - SUMMARY

### FERMENTATION

*Reagent(s)*      GLUCOSE - from hydrolysis of starch

*Conditions*      yeast  
warm but no higher than 37°C

*Equation*       $\text{C}_6\text{H}_{12}\text{O}_6 \longrightarrow 2 \text{C}_2\text{H}_5\text{OH} + 2 \text{CO}_2$



- **LOW ENERGY PROCESS**
- **USES RENEWABLE RESOURCES - PLANTS**
- **SIMPLE EQUIPMENT**



- **SLOW**
- **PRODUCES IMPURE ETHANOL**
- **BATCH PROCESS**

### HYDRATION OF ETHENE

*Reagent(s)*      ETHENE - from cracking of fractions from distilled crude oil

*Conditions*      catalyst - phosphoric acid  
high temperature and pressure

*Equation*       $\text{C}_2\text{H}_4 + \text{H}_2\text{O} \longrightarrow \text{C}_2\text{H}_5\text{OH}$



- **FAST**
- **PURE ETHANOL PRODUCED**
- **CONTINUOUS PROCESS**



- **HIGH ENERGY PROCESS**
- **EXPENSIVE PLANT REQUIRED**
- **USES NON-RENEWABLE FOSSIL FUELS TO MAKE ETHENE**

### USES

- **ALCOHOLIC DRINKS**
- **SOLVENT** - industrial alcohol / methylated spirits (methanol is added)
- **FUEL** - used as a petrol substitute in countries with limited oil reserves

## BIOFUELS

*What are they?*

Liquid fuels made from plant material and recycled elements of the food chain

- **biodiesel**            diesel alternative
- **bioethanol**        petrol additive / substitute

### Biodiesel

*What is it?*

Biodiesel is an alternative fuel which can be made from waste vegetable oil or from oil produced from seeds. It can be used in any diesel engine, either neat or mixed with petroleum diesel.

It is a green fuel, does not contribute to the carbon dioxide (CO<sub>2</sub>) burden and produces drastically reduced engine emissions. It is non-toxic and biodegradable.

*Advantages*

- renewable - derived from sugar beet, rape seed
- dramatically reduces emissions
- carbon neutral
- biodegradable
- non-toxic
- fuel & exhaust emissions are less unpleasant
- can be used directly in unmodified diesel engine
- high flashpoint - safer to store & transport
- simple to make
- used neat or blended in any ratio with petroleum diesel

*Disadvantages*

- poor availability - very few outlets & manufacturers
- more expensive to produce
- poorly made biodiesel can cause engine problems

*Future problems*

- there isn't enough food waste to produce large amounts of biodiesel
- crops grown for biodiesel use land for food crops
- a suitable climate is needed to grow most crops
- some countries have limited water resources

**Q.5**

*Is it sensible, in a world that is short of food, that land should be turned over to the production of biofuels? What are your ideas?*