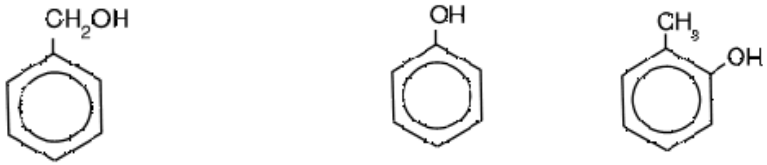
Hydroxy compounds

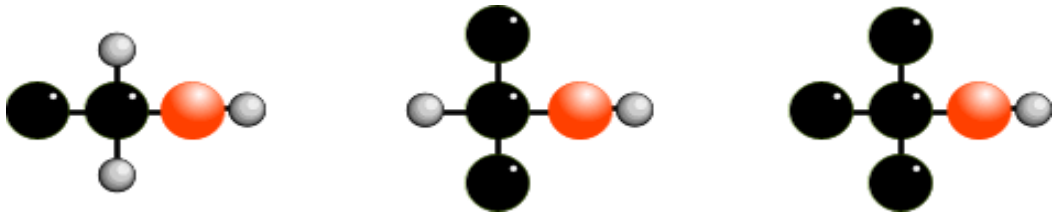
Introduction: Classification

Alcohols

Phenols



- Boiling point of alcohols are much higher than those of ethers or hydrocarbons with similar molecular mass, M_r
- This is due to the presence of intermolecular hydrogen bonding in alcohols
- Greater branching = lower inter-molecular forces



PRIMARY 1° SECONDARY 2° TERTIARY 3°

Substitution to give halogenoalkanes

- Reagent: hydrogen halide
- Alcohol is **refluxed** with **NaX** & **H_2SO_4** (for iodoalkanes, **H_3PO_4** is used instead)

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$$

$$C_2H_5OH + HCl \rightarrow C_2H_5Cl + H_2O$$

- Reagent: Phosphorus halide

-Alcohols react with PI_3 to give iodoalkanes

- $3C_2H_5OH + PI_3 \rightarrow 3C_2H_5I + H_3PO_3$

Substitution to give halogenoalkanes

-Alcohols react with PCl_5 to give chloroalkane

$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$

Reaction is used as test for alcohol – white fumes of HCl.

- Reagent: thionyl chloride ($SOCl_2$)
- Reagent : **$SOCl_2(l)$**
- Condition : **Reflux**
- $C_2H_5OH + SOCl_2 \rightarrow C_2H_5Cl + SO_2 + HCl$

Combustion

- $ROH + O_2 \rightarrow CO_2 + H_2O$
- E.g : $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

- In **excess** of O_2 ethanol burns with a **pale blue** (non-luminous) flame.
- In **limited** supply of O_2 ➔ ethanol burns with a **yellow** (luminous) flame and some soot is formed.

Reaction with sodium

- Conditions : room temperature

- $C_2H_5OH + Na \rightarrow C_2H_5O^-Na^+ + \frac{1}{2} H_2$

  ethanol(acid) sodium ethoxide

- Alcohols are organic chemistry's equivalent of water
- Water reacts with sodium to produce hydrogen and so do alcohols
- The reaction is slower with alcohols than with water since ethanol is a much weaker acid than water
- Alkoxides are white, ionic crystalline solids e.g. $CH_3CH_2O^-Na^+$

Dehydration to produce alkenes

- Reagent/catalyst: conc. sulphuric acid (H_2SO_4) or conc. phosphoric acid (H_3PO_4)
- Conditions: heat/reflux at 170°C

e.g.

$$\underset{\text{ethanol}}{CH_3CH_2OH} \xrightarrow[\text{heat at } 170\,^{\circ}C]{\text{excess c.}H_2SO_4} \underset{\text{ethene}}{CH_2{=}CH_2} + H_2O$$

- If ***excess ethanol*** is used at *140°C*, ether is produced instead of ethene.

$$CH_3CH_2OH + H_2SO_4 \rightarrow CH_3CH_2HSO_4 + H_2O$$

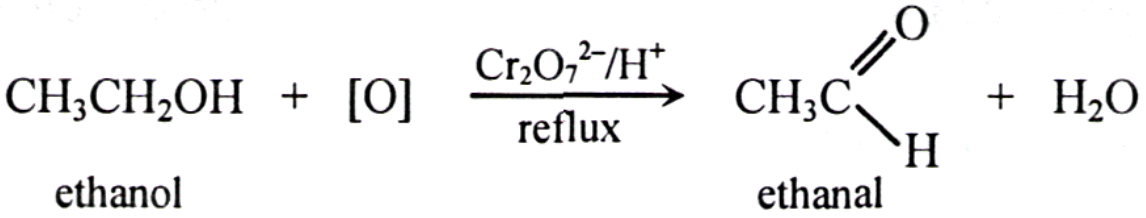
Excess c.H_2SO_4 at 170°C → $CH_2{=}CH_2$

Excess ethanol at 140°C → $CH_3CH_2OCH_2CH_3$ ethoxyethane

Oxidation

- Reagent: $K_2Cr_2O_7$ or $KMnO_4$ and dilute H_2SO_4
- Condition: heat/reflux
- Observation: $K_2Cr_2O_7$: orange turns green (Cr^{3+})
  $KMnO_4$: purple decolourised (Mn^{2+})

- Primary alcohols are easily oxidised to aldehydes
  e.g.



- It is essential to distil off the aldehyde before it gets oxidised to the acid.
- In reflux condition, carboxylic acid is formed.

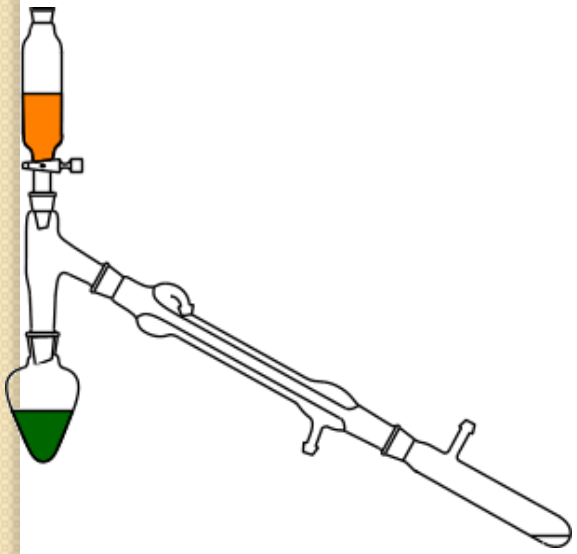
OXIDATION OF PRIMARY ALCOHOLS

Controlling the products

e.g. $CH_3CH_2OH(l) + [O] \longrightarrow CH_3CHO(l) + H_2O(l)$

then $CH_3CHO(l) + [O] \longrightarrow CH_3COOH(l)$

OXIDATION TO ALDEHYDES: DISTILLATION



Aldehyde has a lower boiling point so distils off before being oxidised further

OXIDATION TO CARBOXYLIC ACIDS: REFLUX

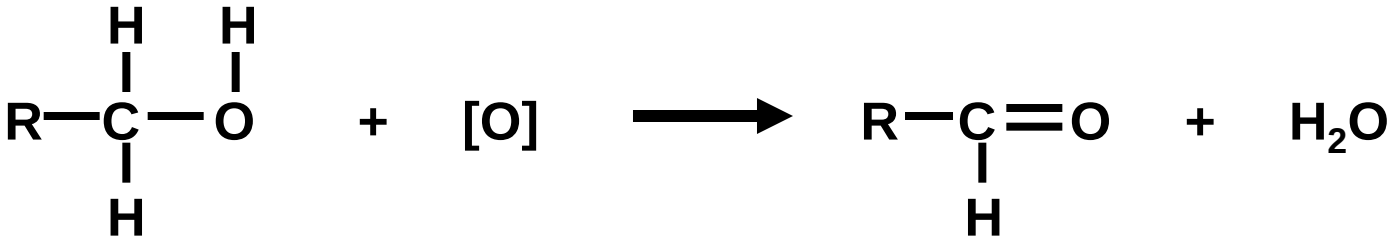
Aldehyde condenses back into the mixture and gets oxidised to the acid

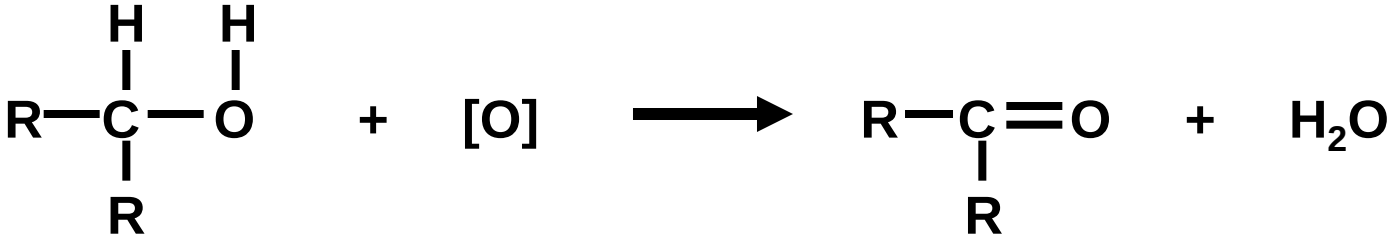
Oxidation

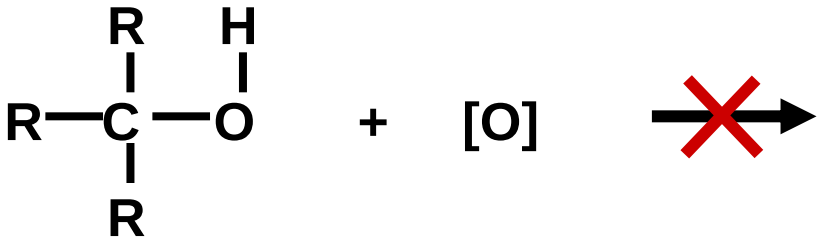
- Secondary alcohols are easily oxidised to ketones

e.g. $CH_3CHOHCH_3(l) + [O] \rightarrow CH_3COCH_3(l) + H_2O(l)$

propan-2-ol propanone

1° 

2° 

3° 

For oxidation to take place easily you must have two hydrogen atoms on adjacent C and O atoms.

ESTERIFICATION OF ALCOHOLS

Reagent(s): carboxylic acid+strong acid catalyst (e.g conc. H_2SO_4)

Conditions: reflux

e.g.

$$CH_3CH_2OH + CH_3COOH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$

Concentrated H_2SO_4 is a dehydrating agent - it removes water causing the equilibrium to move to the right and increases the yield

Esters are fairly unreactive but is used as flavourings

Distinguish between classes of alcohols

- Primary, secondary & tertiary can be distinguished by oxidation.
- Primary alcohols are oxidised to ……

……

- The presence of carboxylic acid is indicated by the *effeversence of CO_2 on adding Na_2CO_3*
- Secondary alcohols are oxidised to ……
- The presence of ketones is indicated by *orange ppt formed when 2,4-dinitrophenylhydrazine is added.*

Commercial paint and varnish removers contain a mixture of dichloromethane, CH_2Cl_2, and methanol, CH_3OH.

(a) What would be observed when the following reactions are carried out?
In each case, give the name or formula of the reaction product which is responsible for the observation you have made.

(iii) CH_3OH is reacted with sodium.

observation .....

product responsible .....