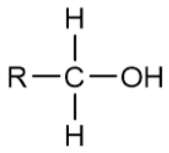
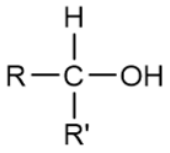
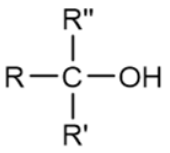
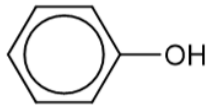
7 HYDROXY COMPOUNDS

Hydroxy Compounds
contain –OH group

Alcohols
–OH group attached to saturated C atom
(Part A)

Phenols
–OH group directly attached to C atom of benzene ring
(Part B)

Primary (1^o) alcohols	**Secondary** (2^o) alcohols	**Tertiary** (3^o) alcohols	
			

(where R, R', R" are alkyl or aryl groups)

If R = alkyl group, it is an aliphatic alcohol.
If R = C_6H_5– group, it is an aromatic or aryl alcohol.

7A: Alcohols

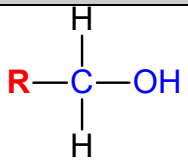
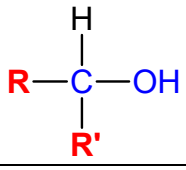
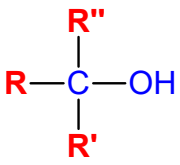
7A.1 INTRODUCTION

- Alcohols are organic compounds containing hydroxyl functional group (−OH).
- General chemical formula of an aliphatic alcohol is $C_nH_{2n+1}OH$.
- Aliphatic alcohols are also often represented as "R-OH" where R = alkyl groups.

7A.2 CLASSIFICATION AND NOMENCLATURE OF ALIPHATIC ALCOHOLS

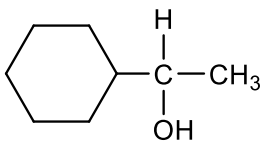
7A.2.1 Classification

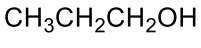
There are 3 classes of aliphatic alcohols - differ in the no. of alkyl groups on the C atom to which –OH is attached.

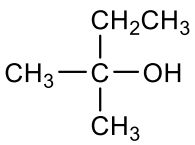
Type of Alcohol	No. of alkyl groups on C atom to which –OH is attached to	
Primary (1°)	**1**	
Secondary (2°)	**2**	
Tertiary (3°)	**3**	

Checkpoint 1

Classify each of the following aliphatic alcohols as a primary, secondary or tertiary alcohol.







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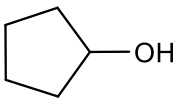

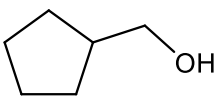

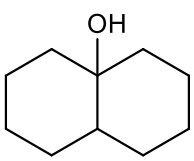

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7A.2.2 Nomenclature

- Alcohols are named by replacing the terminal '-e' of the corresponding alkane by '-ol'.
- The parent chain must be the longest chain containing the –OH group.
- The carbon with the –OH attached is given the lowest number possible.
- Substituents are numbered according to their position on the parent chain, and listed in alphabetical order.
- If more than one –OH group is present, the terms, di and tri are used, together with their respective numbers.

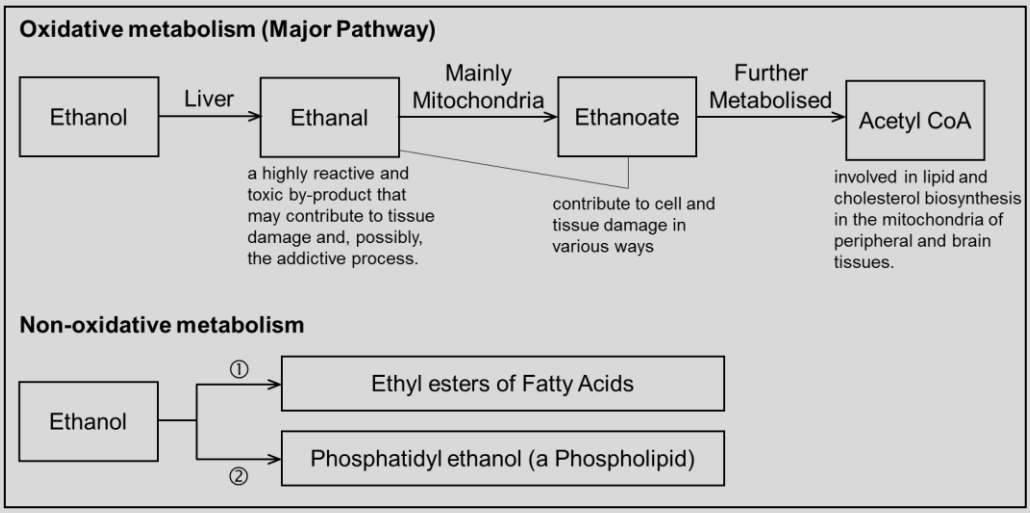
Checkpoint 2

Fill in the correct structural formula of the alcohol.

(a)	(b)	(c)
Propane-1,3-diol	2-methylpropan-2-ol	2-ethylcyclohexanol

Negative effects of excessive alcohol consumption (FYI)

In Singapore, binge drinking (defined as having four or more alcoholic drinks in one session for women, and five or more for men) is most common among 18- to 29-year-olds: 18.7% of men and 12.2% of women. In 2010, the Singapore Mental Health Study found that about 3.5% of our citizens suffered from alcohol abuse at some point in their lives and 0.5% from alcohol addiction (or alcoholism).[1]



Alcohol is eliminated from the body by various metabolic mechanisms. In general, alcohol metabolism is achieved by both oxidative and non-oxidative pathways.

A person's brain develops until the age of about 24. During this time, alcohol abuse can result in learning difficulties and social problems. Alcohol is also a known cause of cancers of the mouth, throat (pharynx), voice box (larynx), oesophagus, liver, colon and rectum, and breast.[3] Alcohol may increase the risk of cancer of the pancreas too. For each of these cancers, the risk increases with the amount of alcohol consumed.

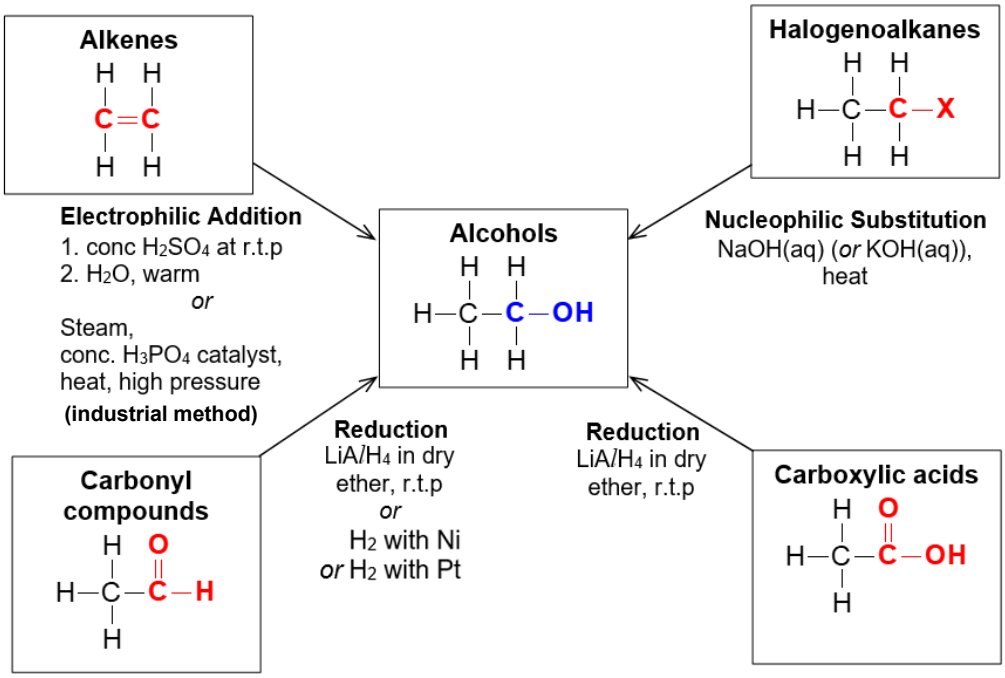
The exact way alcohol affects cancer risk isn't completely understood. In fact, there might be several different ways it can raise risk, and this might depend on the type of cancer.

1 *Health Promotion Board and National Addictions Management Service (2012). When does drinking become a problem? Retrieved from http://www.nams.sg/resources/Documents/Problem%20Drinking%20Resource%20Booklet.pdf*
2 *Zakhari, S. (n.d.). Overview: How is alcohol metabolized by the body? Retrieved from http://pubs.niaaa.nih.gov/publications/arh294/245-255.htm*
3 *American Cancer Society. Retrieved from http://www.cancer.org/index*

7A.3 PREPARATION OF ALCOHOLS

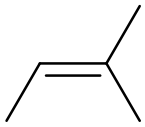
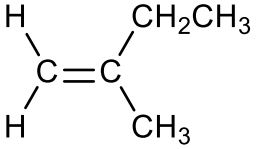
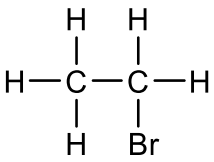
Success Criteria:

- I can state the reagents and conditions to convert various functional groups to alcohol.
- I know that LiA*l*H$_4$ cannot reduce C=C.
- I know that LiA*l*H$_4$ is the only reducing agent that can reduce RCOOH.



Checkpoint 3

Fill in the blanks.

Reactant	Reagents and conditions	Major Product	Type of Reaction
	Steam, conc H_3PO_4, Heat, high pressure		Electrophilic addition
	conc H_2SO_4, room temp, followed by warm with H_2O		
	NaOH(aq), heat		Nucleophilic substitution

7A.3.1 Reduction of Carbonyl Compounds (Aldehydes and Ketones) and Carboxylic Acids

There are several reducing agents which will be covered in the A level syllabus. However, not all reducing agents will work on all functional groups. Heterogeneous catalysis such as Pt and Ni may be used to reduce alkenes and carbonyl compounds, but is not suitable for carboxylic acid.

The table below summarizes the reducing agents/conditions and the organic compounds that can be reduced to alcohols.

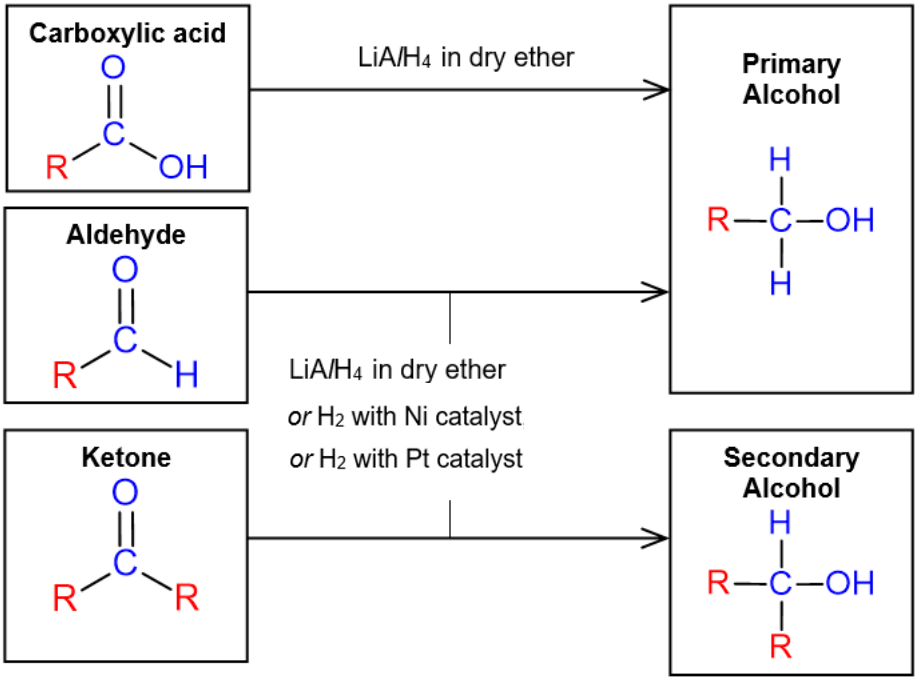
Note:
$LiAlH_4$ is the only reducing agent that can reduce carboxylic acid.

Reducing agent/ conditions \ Organic compounds	**Carboxylic acid**	**Ketone**	**Aldehyde**
$LiAlH_4$ in dry ether, room temperature	✓	✓	✓
H_2 with Ni catalyst or H_2 with Pt catalyst	✗	✓	✓

Carboxylic acids and aldehydes are reduced to primary alcohols but ketones are reduced to secondary alcohols.

Note:
−COOH group in carboxylic acid is resonance stabilized. Hence we need a stronger reducing agent to reduce the −COOH group.

Note:
Aldehydes are reduced to their corresponding primary alcohols, while ketones are reduced to their corresponding secondary alcohols.

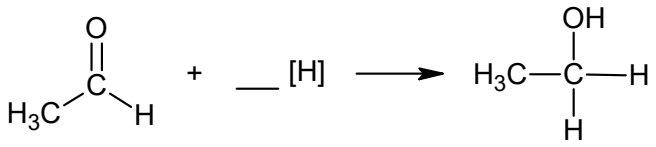


Note:
In A level questions, you are to use [H] to represent the reducing agent, LiA/H_4 to balance the equations. Other atoms in the equation are balanced using H_2O.

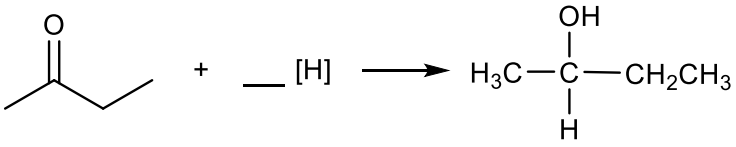
Note:
H^- from LiA/H_4 is an nucleophile and does not react with electron rich C=C because the C=C bond lacks an electrophilic carbon for nucleophilic attack.

Checkpoint 4

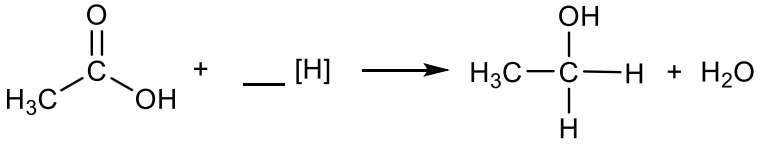
Fill in the blanks provided. Place a '✓' next to the reducing agent which allows the reduction to be carried out.



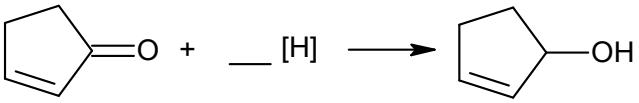
☐ LiA/H_4 in dry ether
☐ H_2/Ni



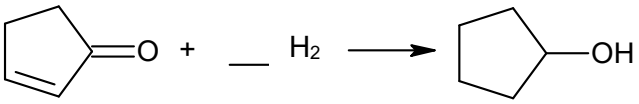
☐ LiA/H_4 in dry ether
☐ H_2/Ni



☐ LiA/H_4 in dry ether
☐ H_2/Ni



☐ LiA/H_4 in dry ether
☐ H_2/Ni



☐ LiA/H_4 in dry ether
☐ H_2/Ni

Alternative form of fuel: Bioethanol

A biofuel is an organic compound made *by* or *from* a living organism, which humans can use to power something. In practical consideration, any organic fuel that is produced from organic matter (living or once-living material) in a short period of time (days, weeks or even months) is a biofuel. This contrasts with fossil fuels, which take millions of years to form, and with other types of fuel, which are not based on organic compounds (nuclear fission, for instance). Bioethanol is an alcohol made by fermentation, mostly from carbohydrates in the form of sugar and starch produced by crops such as corn and sugarcane.

However, there are concerns about the production of bioethanol, such as the fact that it requires more energy for production than it can supply and that it directly competes for land for growing crops.

7A.4 CHEMICAL REACTIONS OF ALCOHOLS

Success Criteria:

1. I am able to give the reagents and conditions for different types of reactions involving alcohol and the structure of products formed.

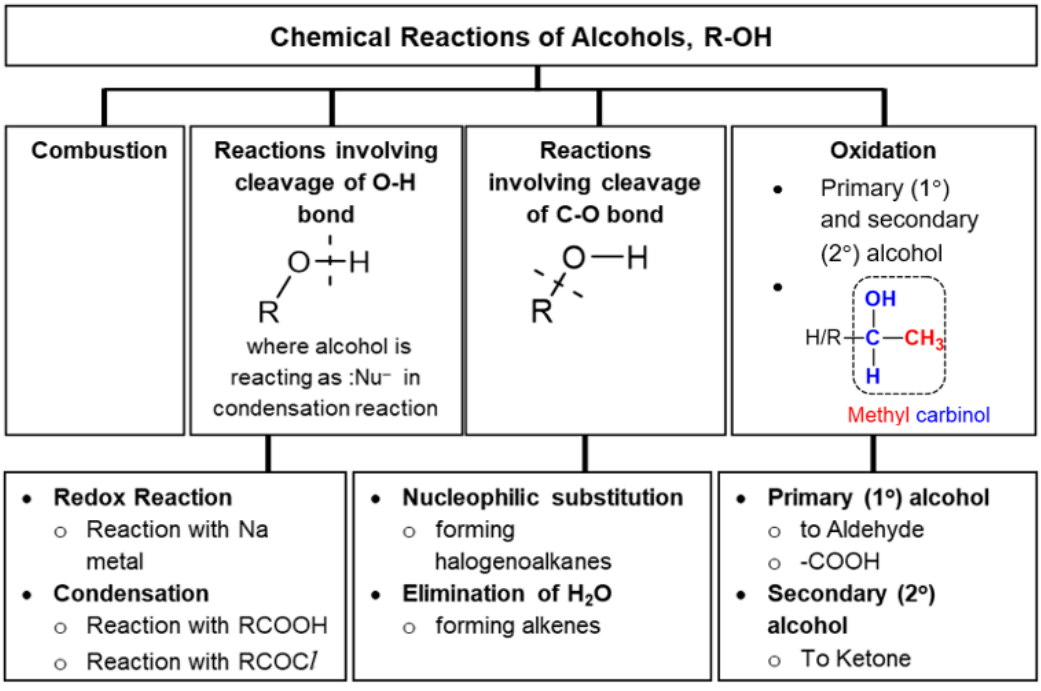
2. I know that C–O bond is cleaved when alcohol undergoes elimination and substitution reaction while O–H bond is cleaved when alcohol are involved in
   (i) redox reaction
   (ii) reaction when O in alcohol is the nucleophile e.g. esterification.

3. I know that alcohol is not acidic in aqueous medium due to the RO^- more unstable (stronger base) than OH^-.

4. I am able to state the 2 different sets of reagents and conditions for formation of ester, and able to explain their difference in reactivity and yield.

5. I know that C—OH (BE: 360 kJmol^{-1}) bond in alcohol cannot be substituted by C*l*$^-$, Br$^-$ ion to form C—X bond (BE (C—C*l*): 340 kJmol^{-1} BE(C—Br): 280 kJmol^{-1}) (ie. X must be introduced in the form of HX, SOC*l*$_2$, PC*l*$_5$ etc)

6. I am able to state and explain the conditions and reagents required to obtain
   (i) aldehyde from oxidation of a primary alcohol
   (ii) carboxylic acid or ketone from primary and secondary alcohols respectively.



Distinguishing Tests for Alcohols

- **Sodium metal** : effervescence of H_2 observed
- **Anhydrous PC*l*$_5$ / SOC*l*$_2$** : white fumes of HC*l* observed
- **$K_2Cr_2O_7$, H_2SO_4, heat** (1° and 2° alcohols) : orange $K_2Cr_2O_7$ turns green
- **$KMnO_4$, H_2SO_4, heat** (1° and 2° alcohols) : purple $KMnO_4$ decolourises
- **Warm with I_2, NaOH(aq)** *(only for methyl cabinol) :* yellow ppt of CHI_3 observed

7A.4.1 Combustion

Lower members of alcohols burn with a clean, smokeless flame, producing carbon dioxide and water.

Eg. $C_2H_5OH\ (l) + 3\ O_2\ (g) \longrightarrow 2\ CO_2\ (g) + 3\ H_2O\ (l)$

7A.4.2 Reactions Involving Cleavage of O−H bond

(i) Acidity of Alcohol

Note:
K_a value is a measure of extent of dissociation of weak acid to give H^+.

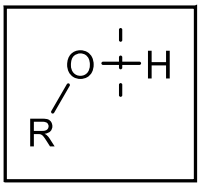
$$HA \rightleftharpoons H^+ + A^-$$
$$K_a = \frac{[H^+][A^-]}{[HA]}$$

The larger the value of K_a, the more a reaction favours the products of the written equation.

Eg

large K_a value, large degree of acid dissociation

O–H group in different covalent compounds may dissociate to different extent to give H^+ and conjugate base (see equations below).



At 25 °C,

(a) $RO{-}H + H_2O \rightleftharpoons \underset{\text{conjugate base}}{RO^-} + H_3O^+$ $\quad K_a = 1.3 \times 10^{-16}$ mol dm^{-3}

(b) $HO{-}H + H_2O \rightleftharpoons \underset{\text{conjugate base}}{HO^-} + H_3O^+$ $\quad K_a = 2.0 \times 10^{-16}$ mol dm^{-3}

K_a value increases with greater stability of the products
∴ extent of acid dissociation depends on stability of the conjugate base.

From equations **(a)** and **(b)**, structures of the conjugate base are different. The electron-donating alkyl group (R) destabilises the RO^- ion by **intensifying its negative charge**. ∴RO^- is less stable than HO^-.
Hence, ROH dissociates less readily into its ions as compared to H_2O.
Thus K_a of RO−H < K_a of HO−H

Note:
Since alcohols are neutral, they do not react with bases such as NaOH(aq), Na_2CO_3(aq) or $NaHCO_3$ (aq).

Alcohols are *weaker* acids than water; so an aqueous solution of alcohol is **neutral**.

(ii) Redox Reaction: Reaction with reactive Sodium metal

The protonic H in alcohol is easily reduced by reactive metals such as sodium to form H_2 gas. This redox reaction takes place at **room temperature**, is highly exothermic and vigorous. **Effervescence of H_2 gas** is observed.

Eg. $CH_3CH_2\mathbf{OH}\ (l) + Na\ (s) \longrightarrow \underset{\text{sodium ethoxide}}{CH_3CH_2\mathbf{O^-}Na^+} + \frac{\mathbf{1}}{\mathbf{2}}\ \mathbf{H_2\ (g)}$

Type of reaction	Redox
Reagent and condition	Sodium metal, Na (s)
Observation	Effervescence of colourless H_2 gas (extinguishes a burning splint with a 'pop')

(iii) Condensation Reaction *(See Chapter 9: Carboxylic acid and Derivatives)*

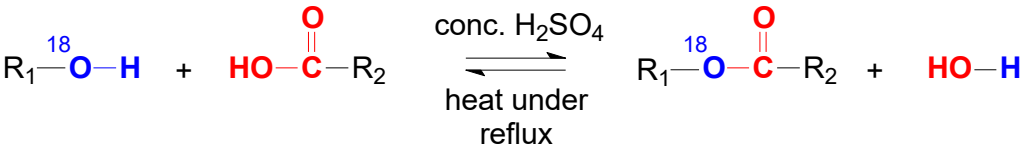
Lone pairs on the oxygen atom of OH group of alcohol enable alcohol to act as nucleophiles in reactions with carboxylic acid and acyl chloride.

Note:
During condensation to form ester, alcohol loses H atom while carboxylic acid loses OH group.

The ^{18}O isotope of the alcohol –OH group remains in the C–O bond of ester.

(i) Esterification with carboxylic acid, RCO_2H

- Alcohol reacts with carboxylic acid to form ester, a group of sweet-smelling organic compounds through ***condensation.***

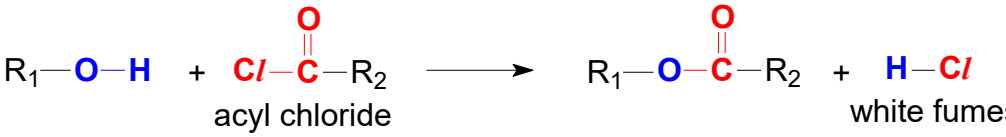


Type of reaction	Condensation
Reagent and condition	Carboxylic acid, concentrated H_2SO_4, heat

- It is a slow and reversible reaction.
- To speed up the reaction, heat is supplied and an acid catalyst, concentrated H_2SO_4, is added.
- According to Le Chatelier's principle, the yield of a reaction can be improved by removing the product, therefore the yield of this condensation reaction can be increased by:
  - addition of conc. H_2SO_4 to absorb the water produced
  - distillation to collect the ester produced

(ii) Esterification with acyl chloride, RCOC*l*

Esters can also be formed by reacting alcohols with acyl chlorides (acid chlorides).



Note:
During condensation to form ester, alcohol loses H atom while acyl chloride loses C*l* group.

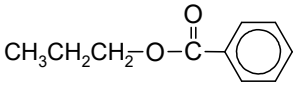
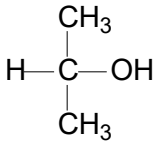
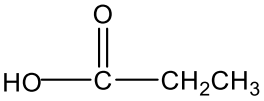
Type of reaction	Condensation
Reagent and condition	Acyl chloride, room temperature

Advantages of using acyl chloride over carboxylic acid:

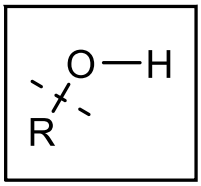
- More efficient way of forming esters since acyl chlorides are more reactive
  - reaction can take place at room temperature (no heating required)
  - no catalyst required
- **Reaction goes to completion ➔ Higher yield of ester.**

Checkpoint 5

Fill in the blanks provided.

Structure of alcohol used	Structure of acid used	Ester prepared
		
		

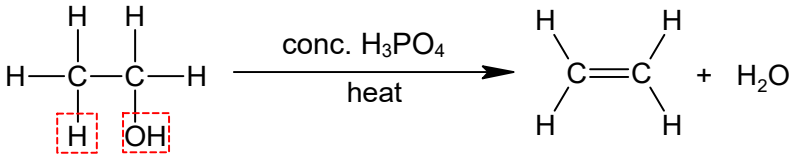
7A.4.3 Reactions Involving Cleavage of C−O bond



Alcohols can undergo the following reactions upon cleavage of the C−O bonds:

- **Elimination** to form alkenes *(Refer to 'Chapter 4: Alkenes' notes)*
- **Nucleophilic Substitution** to form halogenoalkanes *(Refer to 'Chapter 6: Halogen Derivatives' notes)*

(i) Elimination of H_2O from alcohols to form alkene



Type of reaction	Elimination
Reagent and condition	Concentrated H_3PO_4, heat OR Al_2O_3(s), heat (or excess concentrated H_2SO_4, heat)

Zaitsev's Rule

The more highly substituted alkenes are more stable and hence more readily formed in an elimination reaction.

Checkpoint 6

Butan-2-ol undergoes elimination to gives 2 different alkenes.
Draw the structures of the 2 alkenes and indicate the major product.

(ii) Nucleophilic substitution of –OH group in alcohols

(a) Reaction with HX(g)

$CH_3CH_2\mathbf{OH} + H\mathbf{X}(g) \longrightarrow CH_3CH_2\mathbf{X} + H_2O$ $\mathbf{X}$ = C*l*, Br, I

Reagent and condition	Gaseous HX [X = Br or C*l* or I]

(b) Reaction with PX_3

$3CH_3CH_2\mathbf{OH} + P\mathbf{X}_3 \longrightarrow 3CH_3CH_2\mathbf{X} + H_3PO_3$ $\mathbf{X}$ = C*l*, Br, I

Reagent and condition	Anhydrous PX_3 , room temperature

(c) Reaction with PCl_5

$CH_3CH_2\mathbf{OH} + P\mathbf{Cl}_5 \longrightarrow CH_3CH_2\mathbf{Cl} + POCl_3 + HCl(g)$

Reagent and condition	Anhydrous PCl_5 , room temperature
Observation	White fumes HC*l* (g) observed

(d) Reaction with $SOCl_2$

$CH_3CH_2\mathbf{OH} + SO\mathbf{Cl}_2 \longrightarrow CH_3CH_2\mathbf{Cl} + SO_2(g) + HCl(g)$

Reagent and condition	Anhydrous $SOCl_2$, room temperature
Observation	White fumes HC*l* (g) observed

(For Your Info)

Cl^- ion is more stable than HO^- ion. Therefore, **hydroxide (OH^-) is a much poorer leaving group** compared to the halides, and hence alcohols generally do not undergo nucleophilic substitution, unlike the halogenoalkanes.

R–C*l* + OH^- ⟶ R–OH + Cl^- (Nucleophilic substitution by OH^-)

R–OH + Cl^- ⟶✗ R–C*l* + OH^- (Direct reaction with Cl^- is **NOT** possible)

The following can be done to convert the hydroxyl group into a better leaving group:

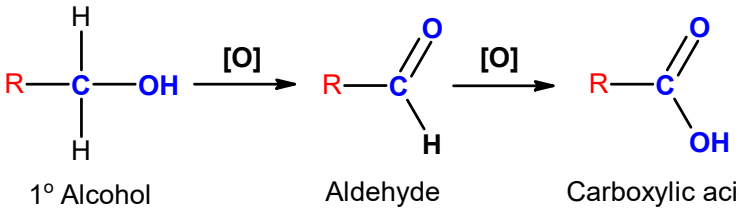
- Protonation of the −OH group using a strong acid to give R–OH_2^+, where electrically neutral H_2O is a much better leaving group

- Oxygen of the –OH group forms strong bonds with the sulfur or phosphorus atoms when reacted with $SOCl_2$, PCl_3, PCl_5, favouring the substitution of C–O bond in alcohol.

7A.4.4 Oxidation of Alcohols

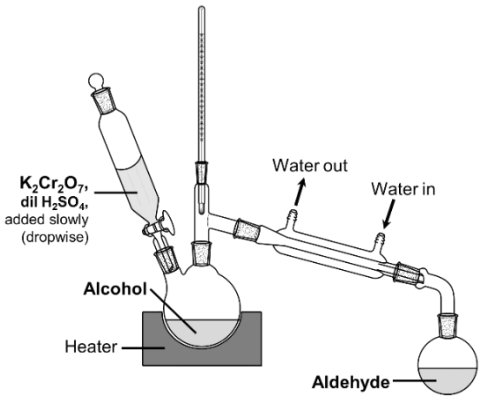
(i) Oxidation of PRIMARY (1°) ALCOHOLS

Primary alcohols can be first oxidised to **aldehydes,** which are easily further oxidised to **carboxylic acids**:



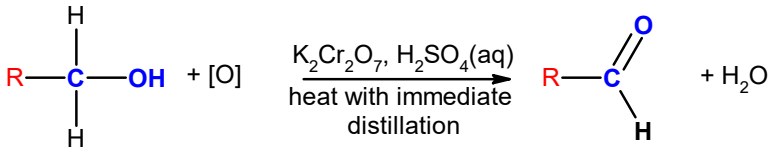
1° Alcohol Aldehyde Carboxylic acid

Acidified $K_2Cr_2O_7$, being a milder oxidising agent, oxidises 1° alcohol in a stepwise manner i.e. aldehyde first then carboxylic acid.



The volatile aldehyde is **distilled** out of the reaction mixture before it can be further oxidised.
Take note that acidified $K_2Cr_2O_7$ are added to the alcohol slowly. This is another precaution to prevent further oxidation.

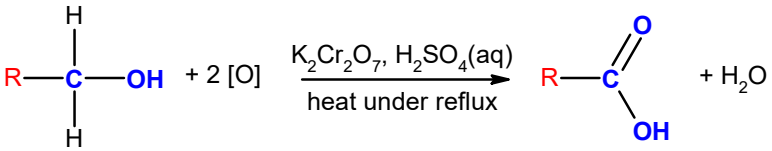
Aldehyde can be **isolated** via **distillation.** Removal of aldehyde from the oxidsing agent prevents further oxidation of aldehyde to carboxylic acid.



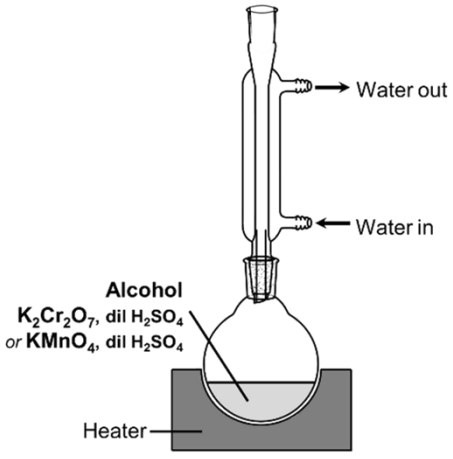
1° Alcohol Aldehyde

Note:
Aldehyde has a lower boiling point than alcohol, hence it can be distilled out from the reaction mixture.

Heating under reflux allows aldehyde to undergo further oxidation with acidified $K_2Cr_2O_7$, converting 1° alcohol to carboxylic acid only.

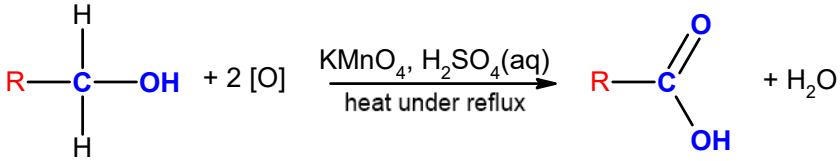


1° Alcohol Carboxylic acid



The mixture is heated under reflux so that the volatile aldehyde formed initially is returned from the condenser to the mixture to be further oxidised.

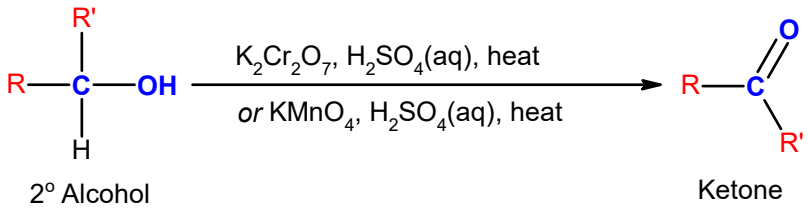
Acidified $KMnO_4$ is a stronger oxidising agent as compared to acidified $K_2Cr_2O_7$. Use of acidified $KMnO_4$ oxidises 1° alcohol to carboxylic acid. The aldehyde formed in the process is oxidised almost immediately into carboxylic acid by $KMnO_4$, hence aldehyde cannot be isolated.



1° Alcohol Carboxylic acid

(ii) Oxidation of SECONDARY (2°) ALCOHOLS

Secondary alcohols are oxidised to **ketones**, by either $K_2Cr_2O_7$ or $KMnO_4$.



2° Alcohol Ketone

Note: Ketones cannot be further oxidised.

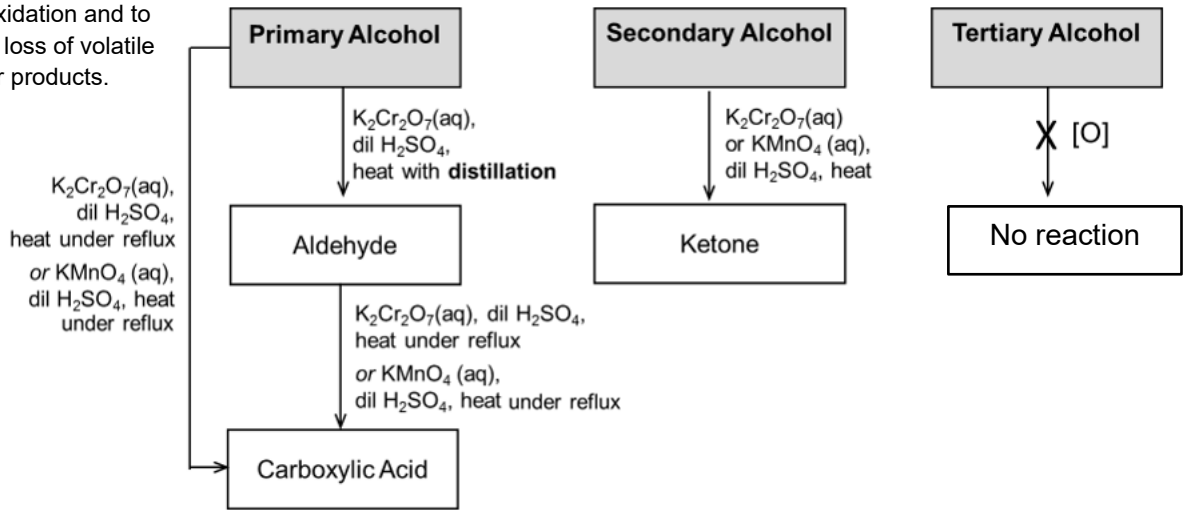
(iii) TERTIARY ALCOHOLS are resistant to oxidation

Oxidation reactions can be used in distinguishing 1° and 2° alcohols from 3° alcohols. Oxidising agent remain unchanged in colour when it is added to tertiary alcohol.

Summary for oxidation of alcohols

Primary and secondary alcohols form different products from the oxidation process. Tertiary alcohol cannot be oxidised.

Note:
Heating under reflux is used only for the synthesis of carboxylic acids from primary alcohols to ensure complete oxidation and to prevent the loss of volatile reactants or products.



Observation for oxidation of alcohols (Distinguishing test)

Note:
For the distinguishing test of alcohols using oxidation, **gentle heating** is used because the test is carried out in a test tube.

Reagent and condition	$KMnO_4$, H_2SO_4(aq), **heat**
Observation	Purple $KMnO_4$ decolourises. (resultant Mn^{2+}(aq) is colourless/pale pink)

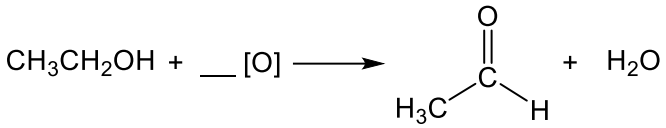
Reagent and condition	$K_2Cr_2O_7$, H_2SO_4(aq), **heat**
Observation	Orange $K_2Cr_2O_7$ turns green. (resultant Cr^{3+}(aq) is green)

Note:
[O] are used to represent oxidising agent and to combine with the H removed to form H_2O.

Checkpoint 7

1 Fill in the blanks provided. Indicate the reagents and conditions required for each reaction and the corresponding observation.

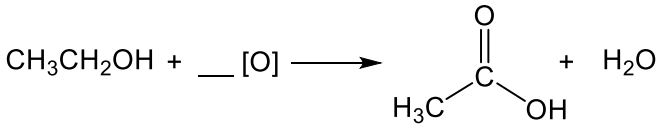
(a)



Reagent and Condition:

Observation

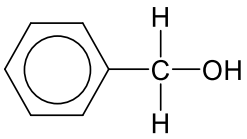
(b)



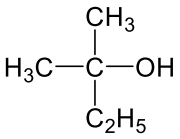
Reagent and Condition:

2 Which alcohol does **not** result in a colour change when warmed with acidified potassium dichromate(VI)?

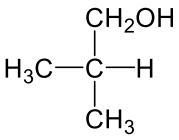
A



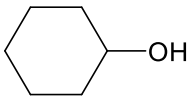
B



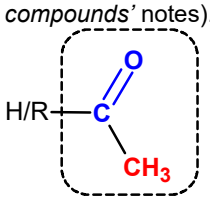
C



D

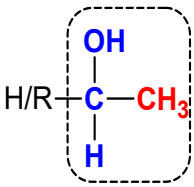


Note:
Methyl carbonyl compounds will also give positive tri-iodomethane test (Refer to *'Carbonyl compounds'* notes).



Methyl carbonyl

(iv) Oxidation of Methyl Carbinol [Triiodomethane (CHI_3) / iodoform test]

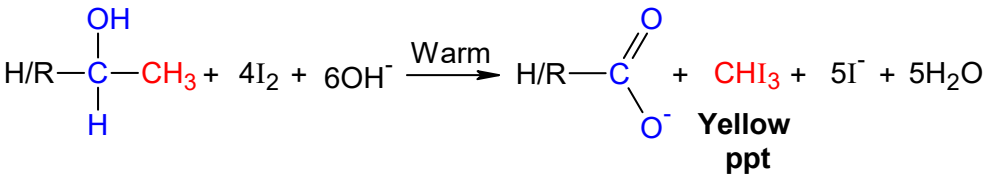


Methyl carbinol

This test is positive only for alcohols containing a methyl group and a hydrogen atom attached to the carbon at which the –OH group is attached to:

When such an alcohol is warmed with alkaline I_2 (aq), a **carboxylate salt** along with a pale **yellow precipitate** of tri-iodomethane, **CHI_3** (iodoform) is formed.

Ethanol is the simplest alcohol which can give a positive iodoform test.

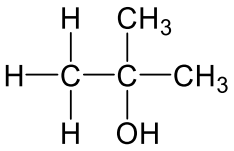


Type of reaction	Redox
Reagent and condition	I_2, NaOH(aq), warm
Observation	Yellow precipitate of CHI_3 observed

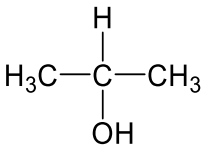
Checkpoint 8

1 Identify the alcohol that would give a yellow precipitate on warming with aqueous alkaline iodine?

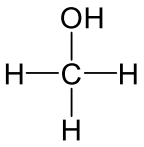
A



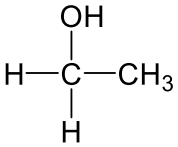
B



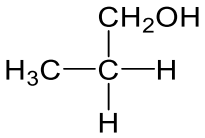
C



D

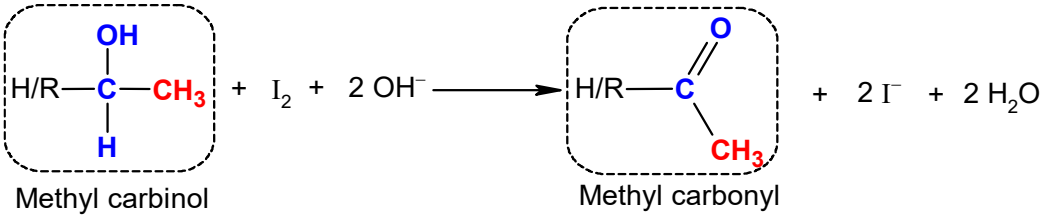


E



The tri-iodomethane reaction takes place through the following steps:

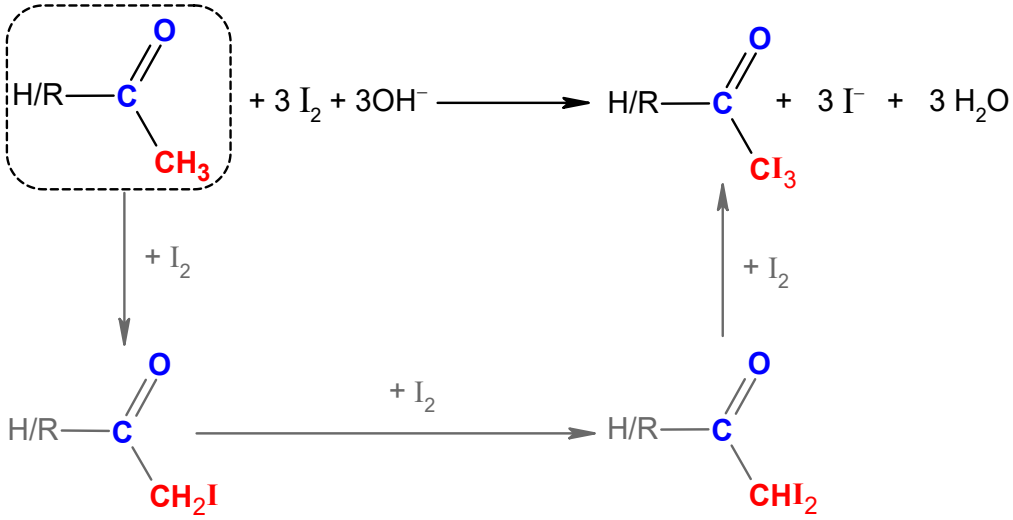
Step 1: Oxidation of alcohol to aldehyde or ketone



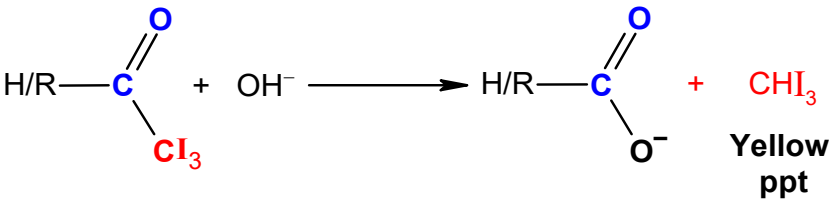
Methyl carbinol Methyl carbonyl

where R = H, alkyl, or aryl group

Step 2: Step-wise substitution of H atoms in methyl group by I atoms



Step 3: Hydrolysis under alkaline conditions to form tri-iodomethane



7A.5 TESTS AND IDENTIFICATION

Success Criteria:

- I am able to describe the chemical tests that identify –OH group from other functional groups.
- I am able to distinguish a 3° alcohol from 1° and 2° alcohols via oxidation.
- I am able to describe the chemical test to verify the presence of methyl carbinol structure in the alcohol.
- I am able to write the balanced equations for all reactions, including the tri-iodomethane test.

7A.5.1 Using Sodium metal (Redox Reaction)

$$R\text{–}OH + Na \xrightarrow{\text{room temperature}} RO^{-}Na^{+} + \tfrac{1}{2}\,\mathbf{H_2(g)}$$

Type of reaction	Redox
Reagent and condition	Sodium metal, Na(s)
Observation	Effervescence of colourless H_2 gas (extinguishes a burning splint with a 'pop')

7A.5.2 Using PCl_5 / $SOCl_2$

$$R\text{–}OH + PCl_5 \xrightarrow{\text{room temperature}} R\text{–}Cl + POCl_3 + \mathbf{HCl}$$

(*White fumes*)

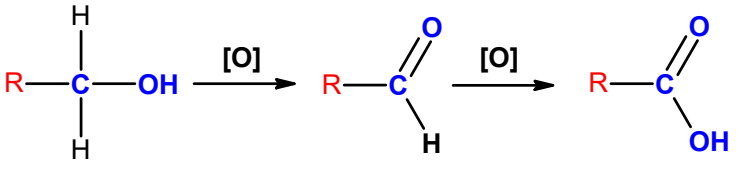
$$R\text{–}OH + SOCl_2 \xrightarrow{\text{room temperature}} R\text{–}Cl + SO_2 + \mathbf{HCl}$$

(*White fumes*)

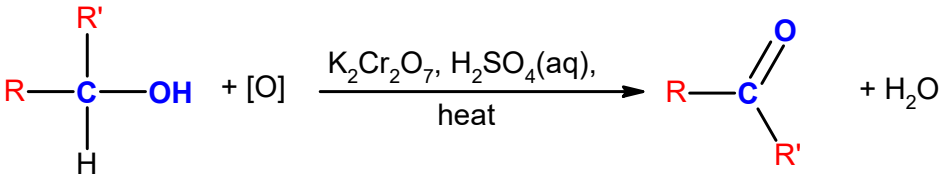
Note:
$SOCl_2$ will be a better reagent than PCl_5 as the side products formed are gases.

Type of reaction	Substitution
Reagent and condition	Anhydrous PCl_5 / $SOCl_2$, room temperature
Observation	White fumes HCl (g) observed

7A.5.3 Using $K_2Cr_2O_7$, H_2SO_4(aq), heat



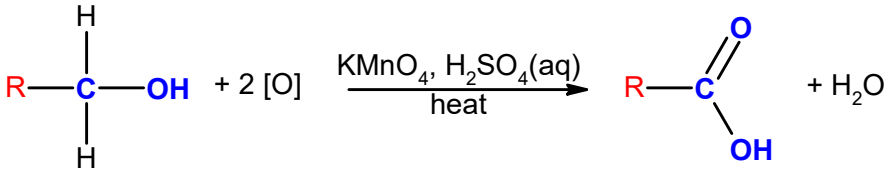
1° Alcohol — Aldehyde — Carboxylic acid



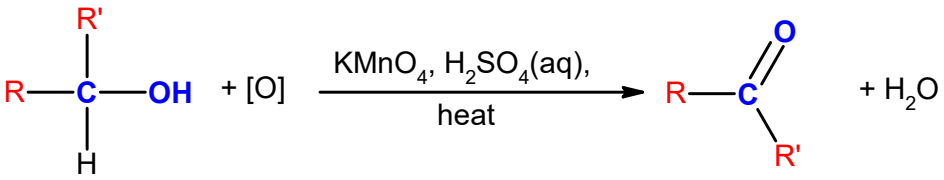
2° Alcohol — Ketone

Type of reaction	Oxidation
Reagent and condition	$K_2Cr_2O_7$, H_2SO_4(aq), heat
Observation	Orange $K_2Cr_2O_7$ turns green. (resultant Cr^{3+}(aq) is green)

7A.5.4 Using $KMnO_4$, H_2SO_4(aq), heat



1° Alcohol — Carboxylic acid

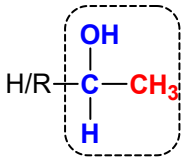


2° Alcohol — Ketone

Type of reaction	Oxidation
Reagent and condition	$KMnO_4$, H_2SO_4(aq), heat
Observation	Purple $KMnO_4$ decolourises. (resultant Mn^{2+}(aq) is colourless/pale pink)

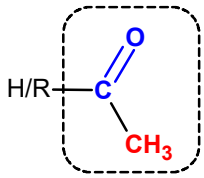
7A.5.5 Tri-iodomethane Test (Iodoform Test)

Note:



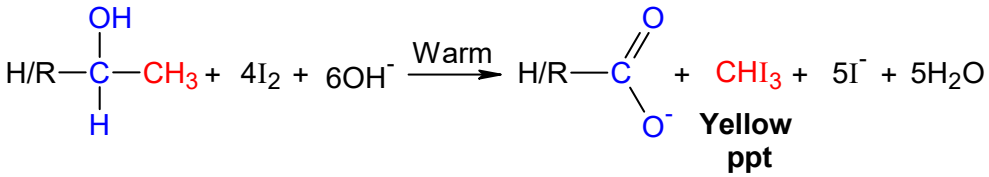
Methyl carbinol

Methyl carbonyl compounds will also give positive tri-iodomethane test (Refer to *'Carbonyl compounds'* notes).

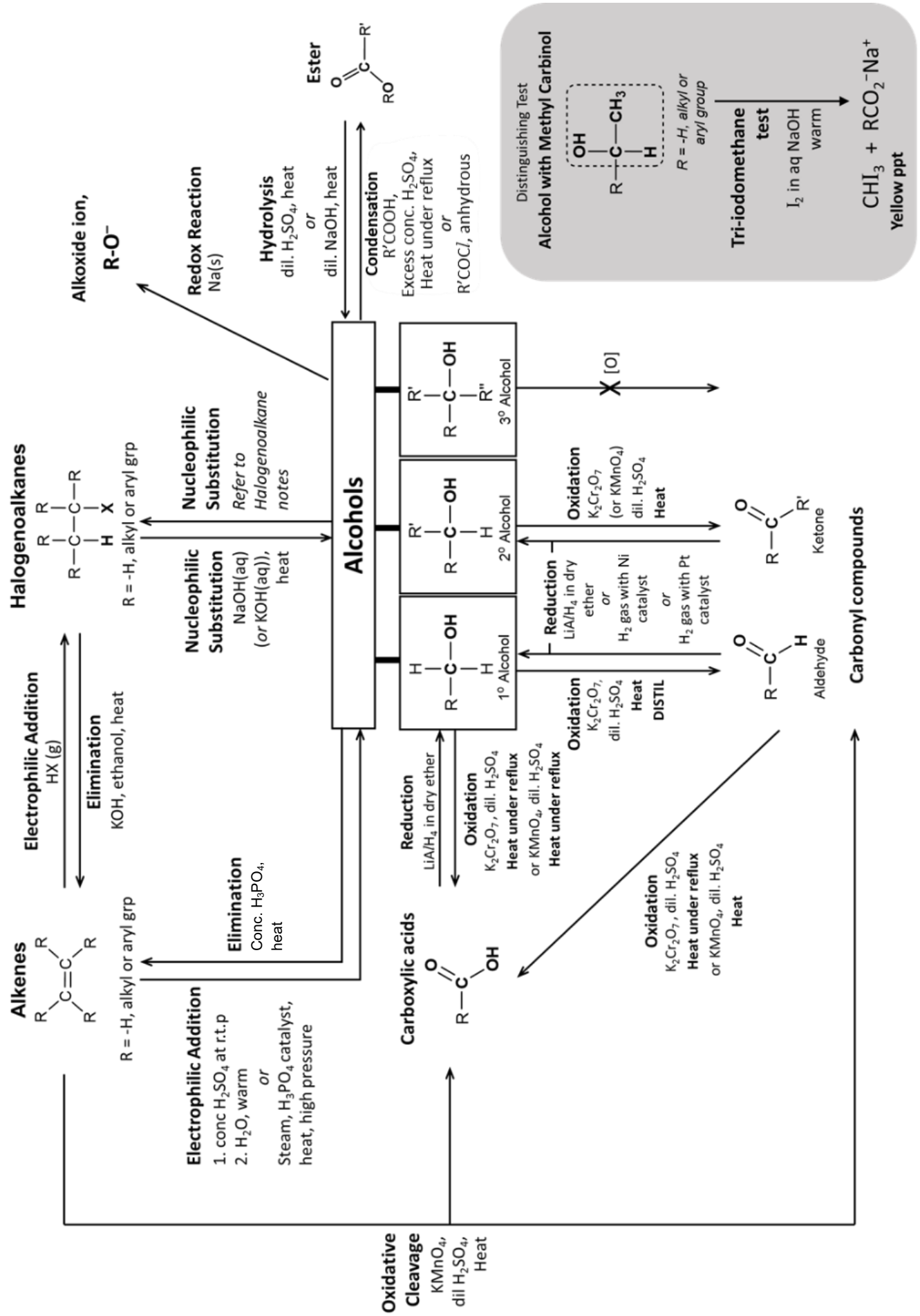


Methyl carbonyl

This test is positive only for methyl carbinol (alcohols containing a methyl group and a hydrogen atom attached to the carbon at which the –OH group is attached to



Type of reaction	Redox
Reagent and condition	I_2, NaOH(aq), warm
Observation	Yellow precipitate of CHI_3 observed


Alkenes
R = -H, alkyl or aryl grp
Electrophilic Addition
1. conc H_2SO_4 at r.t.p
2. H_2O, warm
or
Steam, H_3PO_4 catalyst, heat, high pressure
Electrophilic Addition
HX (g)
Elimination
KOH, ethanol, heat
Halogenoalkanes
R = -H, alkyl or aryl grp
Nucleophilic Substitution
Refer to Halogenoalkane notes
Nucleophilic Substitution
NaOH(aq) (or KOH(aq)), heat
Elimination
Conc. H_3PO_4, heat
Alcohols
1° Alcohol
2° Alcohol
3° Alcohol
Alkoxide ion, R-O⁻
Redox Reaction
Na(s)
Hydrolysis
dil. H_2SO_4, heat
or
dil. NaOH, heat
Condensation
R'COOH,
Excess conc. H_2SO_4,
Heat under reflux
or
R'COCl, anhydrous
Ester
Reduction
$LiAlH_4$ in dry ether
Oxidation
$K_2Cr_2O_7$, dil. H_2SO_4
Heat under reflux
or $KMnO_4$, dil. H_2SO_4
Heat under reflux
Oxidation
$K_2Cr_2O_7$,
dil. H_2SO_4
Heat
DISTIL
Reduction
$LiAlH_4$ in dry ether
or
H_2 gas with Ni catalyst
or
H_2 gas with Pt catalyst
Oxidation
$K_2Cr_2O_7$
(or $KMnO_4$)
dil. H_2SO_4
Heat
[O]
Aldehyde
Ketone
Carbonyl compounds
Carboxylic acids
Oxidation
$K_2Cr_2O_7$, dil. H_2SO_4
Heat under reflux
or $KMnO_4$, dil. H_2SO_4
Heat
Oxidative Cleavage
$KMnO_4$,
dil H_2SO_4,
Heat
Distinguishing Test
Alcohol with Methyl Carbinol
R = -H, alkyl or aryl group
Tri-iodomethane test
I_2 in aq NaOH
warm
CHI_3 + $RCO_2^-Na^+$
Yellow ppt

Success Criteria	Relevant Tutorial questions	What do you still struggle with? Write your queries here.
1. I am able to name alcohols correctly using IUPAC nomenclature and classify them as primary, secondary or tertiary alcohols.	DQ8a	
2. I can state the reagents and conditions to convert various functional groups to alcohol. 3. I know that $LiAlH_4$ cannot reduce C=C. 4. I know that $LiAlH_4$ is the only reducing agent that can reduce RCOOH.	DQ4 DQ8b(ii)	
4. I am able to give the reagents and conditions for different types of reactions involving alcohol and the structure of products formed. 5. I know that C–O bond is cleaved when alcohol undergoes elimination and substitution reaction while O–H bond is cleaved when alcohol are involved in (iii) redox reaction (iv) reaction when O in alcohol is the nucleophile e.g. esterification. 6. I know that alcohol is not acidic in aqueous medium due to the RO^- more unstable (stronger base) than OH^-. 7. I am able to state the 2 different sets of reagents and conditions for formation of ester, and able to explain their difference in reactivity and yield. 8. I know that C–OH (BE: 360 $kJmol^{-1}$) bond in alcohol cannot be substituted by Cl^-, Br^- ion to form C-X bond (BE (C-Cl): 340 $kJmol^{-1}$ BE(C-Br): 280 $kJmol^{-1}$) (ie. X must be introduced in the form of HX, $SOCl_2$, PCl_5 etc) 9. I am able to state and explain the conditions and reagents required to obtain **(i)** aldehyde from oxidation of a primary alcohol **(ii)** carboxylic acid or ketone from primary and secondary alcohol respectively.	SQ3, DQ2, DQ5, DQ6, DQ7 SQ2 DQ8b(i)/(iii)	
10. I am able to describe the chemical tests that identify –OH group from other functional groups. 11. I am able to distinguish a 3° alcohol from 1° and 2° alcohols via oxidation. 12. I am able to describe the chemical test to verify the presence of methyl carbinol structure in the alcohol. 13. I am able to write the balanced equations for all reactions, including the tri-iodomethane test.	DQ9 DQ8c	

7A Alcohols Tutorial

Self-attempt questions

Physical Properties

1 The table below shows the boiling points of some organic compounds.

Compound	Formula	M_r	Boiling point/ °C
Propane	C_3H_8	44	–42
Ethanol	C_2H_5OH	46	78
Ethane-1,2-diol	$CH_2(OH)CH_2OH$	62	197
Butan-1-ol	$CH_3CH_2CH_2CH_2OH$	74	118
Methylpropan-1-ol	$(CH_3)_2CHCH_2OH$	74	108

Explain the difference in boiling points of the following pairs of compounds:

(a) Propane and ethanol

(b) Ethanol and ethane-1,2-diol

(c) Butan-1-ol and methylpropan-1-ol

2 Which compound reacts with its own oxidation product (an oxidation which involves no loss of carbon) to give a sweet-smelling liquid containing the ester functional group? [J95/IV/26]

A propanal

B propanoic acid

C propanone

D propan-1-ol

3 In which processes is at least one product a gas at room temperature and pressure? [N04/I/24]

A dehydration of ethanol

B esterification of ethanoic acid by ethanol

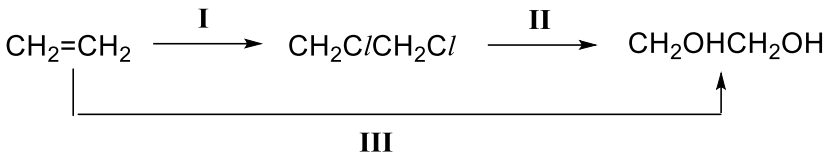
C oxidation of ethanal by $Cr_2O_7^{2-}$ / H^+

D substitution of ethanol by HBr

Discussion Questions

Preparation and reactions of Alcohol

4 There are two ways to attain ethane-1,2-diol from ethane as shown in the reaction scheme below.



Which are the correct reagents and conditions for the reactions **I** to **III** above?

	I	II	III
A	PCl_5	aqueous NaOH, heat	cold $KMnO_4$, KOH
B	PCl_5	alcoholic NaOH, heat	aqueous KOH
C	Cl_2 in CCl_4	aqueous NaOH, heat	cold $KMnO_4$, KOH
D	Cl_2 in CCl_4	alcoholic NaOH, heat	$KMnO_4$, KOH, heat

5 In its reaction with sodium, 1 mol of a compound **X** gives 1 mol of $H_2(g)$.

Which compound might **X** be?

1 $(CH_3)_3COH$

2 $CH_3CH(OH)CH_2CHO$

3 $CH_3CH(OH)CH_2OH$

A 1 and 2 only

B 2 and 3 only

C 1 only

D 3 only

6 Which compound is a product of the reaction between phenylmethanol, $C_6H_5CH_2OH$, and ethanoyl chloride, CH_3COCl?

A $C_6H_5CH_2COOCH_3$

B $C_6H_5COCH_3$

C $C_6H_5CH_2COCl$

D $C_6H_5CH_2OCOCH_3$

7 Suggest how the following compounds can be prepared from the given starting material, giving the reagents and conditions for each step of the reaction synthesis.

	Starting material	**Final product**
(a)	butan-1-ol	butan-2-ol
(b)	1,2-dibromoethane	Ethanedioic acid
(c)	cyclohexanol	hexanedioic acid
(d)	pentanoic acid	pentane-1,2-diol

8 **(a)** Draw the structural formulae for all the alcohols with the molecular formula $C_4H_{10}O$ and classify them as primary, secondary or tertiary alcohols.

(b) **(i)** Using one of the alcohols identified in **(a)**, give the reagents and conditions required to oxidise primary alcohol to different extent.

Write equations to form the two different oxidised product, use [O] to represent the oxidising agent.

(ii) Give the reagent and conditions required to convert both of the oxidised products obtained in **b(i)** back to the primary alcohol. Write equations to represent both the processes, using [H] to represent reducing agent if applicable.

(iii) $HOCH(CH_3)CH_2CH=CH_2$ is a secondary alcohol. Give the structures of the products formed when it is heated with acidified $KMnO_4$.

(c) One of the alcohols identified in **(a)** is found to have the following properties:

- On warming with iodine and aqueous sodium hydroxide, a pale-yellow precipitate is obtained.
- On heating with concentrated phosphoric acid, a mixture of but-1-ene and but-2-ene is obtained.

Identify the alcohol and explain your reasoning with appropriate equations.

(d) When an excess of the alcohol identified in **(c)** is heated with concentrated sulfuric acid, a compound of molecular formula $C_8H_{18}O$ is formed. Suggest a structure of the product.

Distinguishing Test

9 Describe a simple chemical test that can be used to distinguish between each pair of compounds:

(a) Propan-1-ol and propene

(b) Propan-1-ol and propanoic acid

(c) 2-methylpropan-2-ol and propan-2-ol

(d) 1-bromopropane and propan-1-ol

Structure Elucidation Questions

10 Alcohol **B** has the molecular formula $C_5H_{12}O$. Reaction of **B** with hot acidified potassium dichromate(VI) produces compound **C**, $C_5H_{10}O_2$. Heating **B** over Al_2O_3 produces **D**, C_5H_{10}. Vigorous oxidation of **D** forms 2−methylpropanoic acid as one of the products.

Suggest structures for **B**, **C** and **D** and explain the reactions involved.

Suggested approach for structure elucidation questions.

Information	**Deductions (identify <u>type of reaction</u> & <u>functional group/ part structure</u>)**
B, $C_5H_{12}O$ reacts with hot acidified potassium dichromate(VI) to produce compound **C**, $C_5H_{10}O_2$.	Type of reaction : Functional group: **C** is **B** is
B is heated over Al_2O_3 to produce **D**, C_5H_{10}.	Type of reaction : Functional group: **D** is
Vigorous oxidation of **D** forms 2−methylpropanoic acid as one of the products.	Type of reaction : Functional group: **D** is and **D** has a specific structure of

Note: since we have two sets of information on the functional group and specific structure of **D**, we should deduce structure of **D** first, to understand the arrangement of the C atoms in the carbon chain.

After identifying the arrangement of C atoms in carbon chain, we can use the structure of **D** to confirm the identity of compound **B**, and subsequently, compound **C**.

<u>Extra Practice questions</u>

11 A liquid **L** contains 12.8% of carbon, 2.1% of hydrogen and 85.1% of bromine by mass. When 0.376 g of **L** is evaporated in a syringe, the volume of vapour produced is 45.4 cm^3, at s.t.p.

L is hydrolysed by aqueous sodium hydroxide to give compound **M**. **M** can be oxidised in several stages by nitric acid and the final product of this oxidation is an acid, **N**, of relative molecular mass 90.

Identify **L**, **M** and **N**, giving their structural formulae and explain your reasoning.

Note: Use the same approach as Q10 to explain your answer

12 Suggest structures for the compounds **V** to **Y**. Explain the reactions involved in each case, giving equations where appropriate.

An optically active compound **V**, $C_9H_{12}O$, reacts with acidified $K_2Cr_2O_7$ to give **W**, $C_9H_{10}O$. **V** reacts with iodine in aqueous sodium hydroxide to give yellow precipitate and the sodium salt of acid **X**, $C_8H_8O_2$. **X** reacts with acidified $KMnO_4$ to form **Y,** $C_8H_6O_4$.

Note: Use the same approach as Q10 to explain your answer