

With 2018 NCEA  
Exam included



# Chemistry AS 91391

## C3.5 Organic Chemistry

# Achievement Criteria



This achievement standard involves describing the structure, physical properties, and reactions of organic compounds.

- Organic compounds will be limited to those containing one or more of the following functional groups: alkene, haloalkane, amine, alcohol, aldehyde, ketone, carboxylic acid, ester (including triglycerides), acyl chloride, amide.

Reactivity of organic compounds will be limited to

- substitution reactions using the following reagents: concentrated HCl, HBr,  $\text{ZnCl}_2/\text{HCl}$ ,  $\text{SOCl}_2$ ,  $\text{PCl}_3$ , NaOH, KOH (in alcohol or aqueous solution), concentrated  $\text{NH}_3$ , primary amines, primary alcohols/ $\text{H}^+$ , primary alcohols,  $\text{H}_2\text{O}/\text{H}^+$ ,  $\text{H}_2\text{O}/\text{OH}^-$  (Substitution reactions include esterification, condensation, hydrolysis, and polymerisation.)
- oxidation reactions using the following reagents:  $\text{MnO}_4^-/\text{H}^+$ ,  $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ , Tollens', Fehling's and Benedict's. Reduction of aldehydes and ketones with  $\text{NaBH}_4$
- elimination reactions using the following reagents: KOH in alcohol and concentrated  $\text{H}_2\text{SO}_4$  (includes major and minor products from asymmetric alcohols and haloalkanes)
- polymerisation reactions of formation of polyesters and polyamides including proteins
- addition reactions of alkenes (used for the identification of the products of elimination reactions).

Appropriate information relating to other oxidants or reductants will be provided.

Physical properties of organic compounds will be limited to

- solubility
- melting point and boiling point
- rotation of plane-polarised light.

## Special notes

Constitutional isomers are those that have the same molecular formula, but a different structural formula.

Systematic naming of amines is restricted to primary amines. Candidates will not be expected to recall the common names of amino acids.

Knowledge of principles of organic chemistry covered in [Chemistry Level 2 AS 91165](#) will be assumed.

# Contents

- 1. Functional groups – Naming and properties:** Alkanes, alkenes, haloalkanes (primary, secondary, tertiary), alcohol, amines, carboxylic acids, Aldehydes, ketones, acids chlorides, amides and esters
- 2. Isomers:** cis/trans and optical isomers (enantiomers)
- 3. Addition reactions** of alkenes: to alcohol ( $\text{H}_2\text{O}/\text{H}^+$ ) or haloalkane ( $\text{PCl}_5$ ) using Markovnikov's rule / major ( $2^\circ$ ) minor ( $1^\circ$ )  
Comparing Addition (Oxidation) of alkenes: alkene +  $\text{MnO}_4^- \rightarrow$  -diol OR alkene +  $\text{H}_2\text{O}/\text{H}^+ \rightarrow$  -ol
- 4. Elimination reactions** of alcohol (conc  $\text{H}_2\text{SO}_4$ ) /haloalkanes (alc KOH) : to alkenes Saytzeff's rule (poor get poorer) major (-2-) /minor (-1-)
- 5. Substitution reactions:**  
alcohols ( $\text{SOCl}_2$ )  $\rightleftharpoons$  haloalkanes (aq KOH)  
carboxylic acids  $\rightarrow$  acids chlorides ( $\text{PCl}_5$  or  $\text{SOCl}_2$ ) reflux  
acid chlorides + ammonia  $\rightarrow$   $1^\circ$  amide + HCl ( $\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl}$ )
- 6. Oxidation reactions of alcohols:**  $1^\circ$  alcohol (+  $\text{MnO}_4^-$ )  $\rightarrow$  aldehyde (distillation)  
aldehyde  $\rightarrow$  carboxylic acids (reflux)  
 $2^\circ$  alcohol (+  $\text{MnO}_4^-$ )  $\rightarrow$  ketone
- 7. Reduction reactions of aldehydes/ketones:** ( $\text{NaBH}_4$ ) aldehyde  $\rightarrow$   $1^\circ$  alcohol / ketone  $\rightarrow$   $2^\circ$  alcohol
- 8. Distinguishing tests/redox equations:** aldehyde positive for Tollens/Benedicts/permanganate

# Contents

9. Acid/base reactions with Amines: amine + water  $\rightarrow$  conjugate + OH<sup>-</sup>  
amine + base  $\rightarrow$  salt + water

10. Acids base reactions with Carboxylic acids: carboxylic acid + base  $\rightarrow$  salt + water (+ CO<sub>2</sub> if carbonate)

11. Esterification reactions: alcohol + carboxylic acid  $\rightarrow$  ester (conc H<sub>2</sub>SO<sub>4</sub>) reflux with Na<sub>2</sub>CO<sub>3</sub> and anhydrous MgSO<sub>4</sub>

12. Esterification reactions of acid chlorides: acid chloride + alcohol  $\rightarrow$  Ester + HCl

13. Hydrolysis reactions of esters: acid: ester  $\rightarrow$  alcohol + carboxylic acid  
base: (NaOH) ester  $\rightarrow$  alcohol + salt

14. Hydrolysis reactions of amides: acid: amide + H<sub>3</sub>O<sup>+</sup>  $\rightarrow$  carboxylic acid + NH<sub>4</sub><sup>+</sup>  
base: amide + OH<sup>-</sup>  $\rightarrow$  carboxylate ion<sup>-</sup> + NH<sub>3</sub>

15. Condensation polymerisation: dicarboxylic + diol  $\rightarrow$  polyester + water  
dicarboxylic + diamides  $\rightarrow$  polyamide + water

16. Amino acids: forming dipeptides

## Background Knowledge

We define organic chemistry *as the chemistry of compounds that contain both carbon and hydrogen.*

Carbon has four valence electrons and forms covalent bonds, either as single, double or triple bonds, with a large number of other elements, including the hydrogen, nitrogen, oxygen, phosphorus, and sulfur.

### Mass number

Number of protons and neutrons in atom



### Atomic symbol

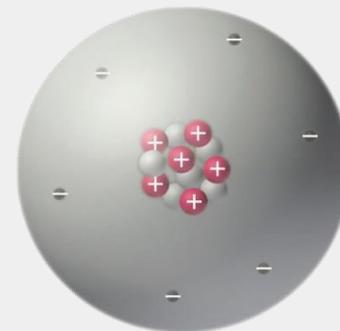
Abbreviation used to represent atom in chemical formulas

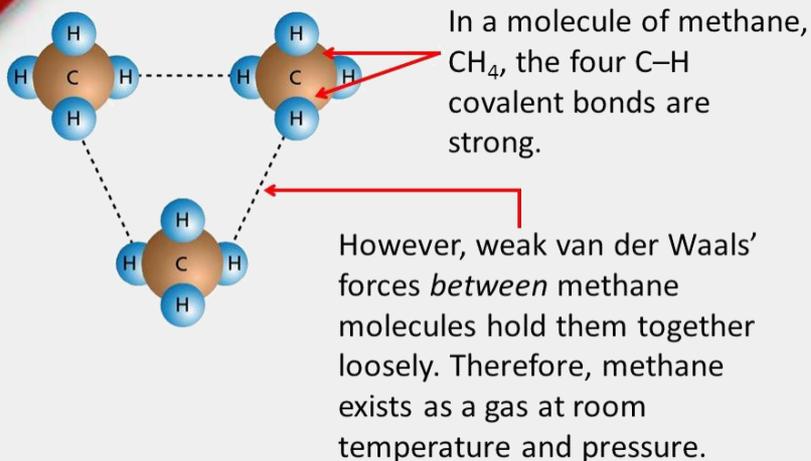
### Atomic number

Number of protons in atom

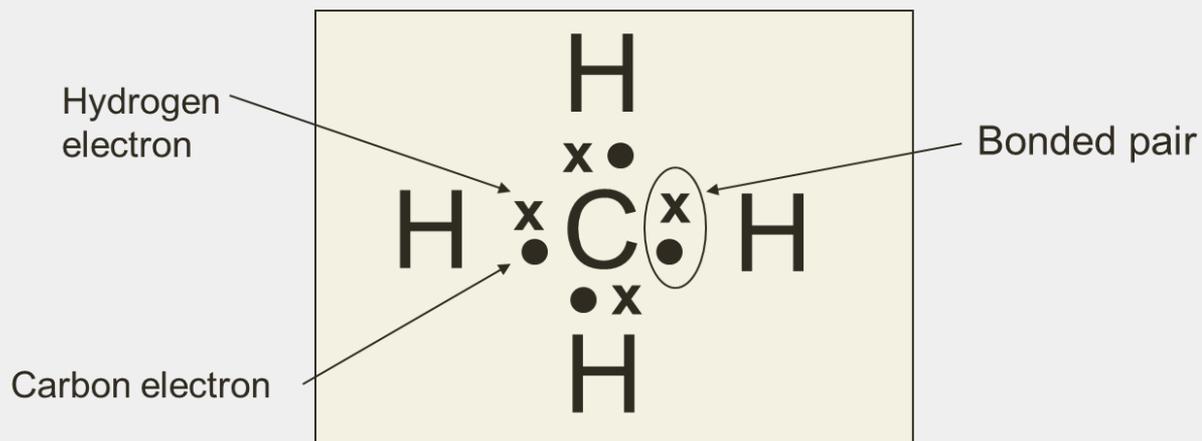


6 protons   
6 neutrons   
6 electrons 

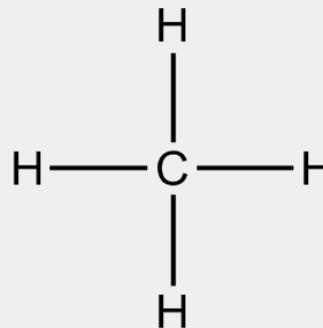




**Covalent bonding** occurs where valence electrons around atoms are shared between neighbouring atoms. This type of bonding is found between the C and H atoms in hydrocarbons and the C, H and O atoms in alcohol and is called **intramolecular** bonding. This bonding is very strong. The bonding between molecules is called **intermolecular** bonding and this is much weaker. When hydrocarbons are heated and they change state into liquids and gases it is this bonding between molecules that is broken **not** the covalent bonding.

Lewis diagram of CH<sub>4</sub> (methane)

Lewis diagrams can be used to show how atoms are arranged in a molecule and which valence electrons are used in bonding. A bonding pair of electrons can also be shown as a line:

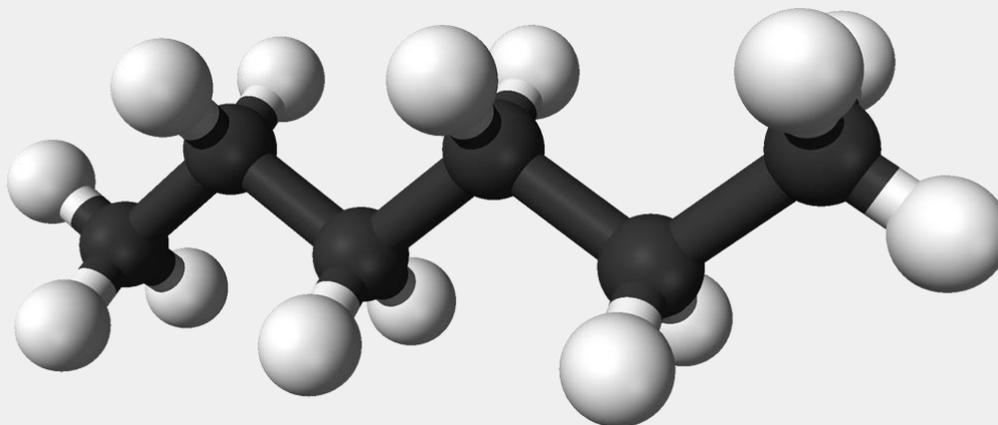


**Molecular Formula** – type and number of each atom.

i.e. Propane  $C_3H_8$

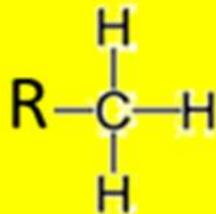
**Structural Formula** – placement of each atom.

**Condensed Structural Formula**

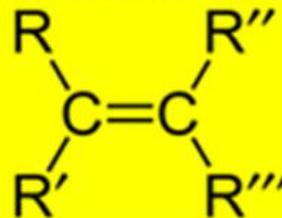


Structural **isomers** are molecules with the same molecular formula but **different** structural formula.

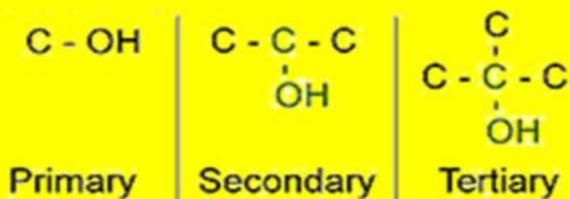
## Alkanes



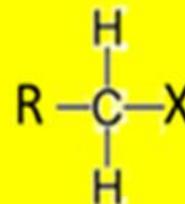
## Alkenes



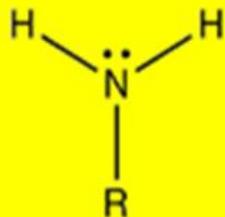
## Alcohols



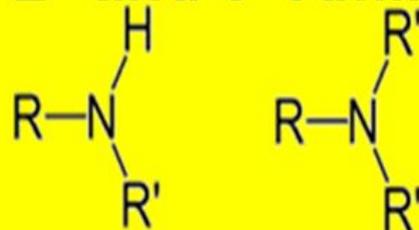
## Haloalkanes

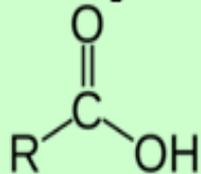
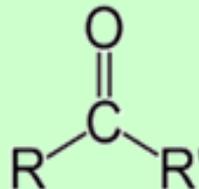
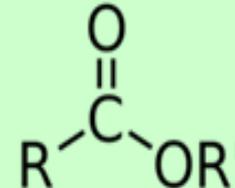
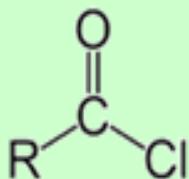
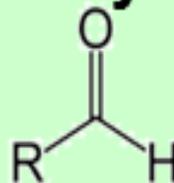
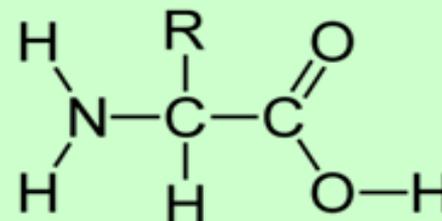
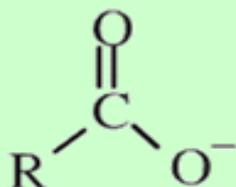
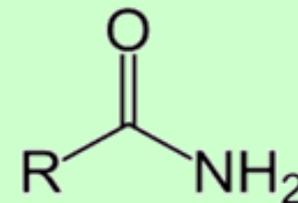


## 1° Amines



## 2° and 3° Amines



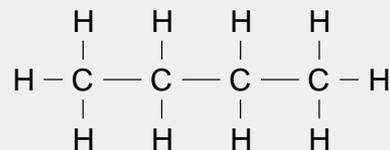
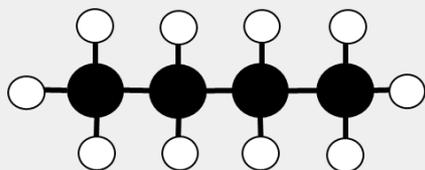
**Carboxylic Acids****Ketones****Esters****Acid Chlorides****Aldehydes****Amino Acid****Carboxylic salt****Amide**

## Alkanes

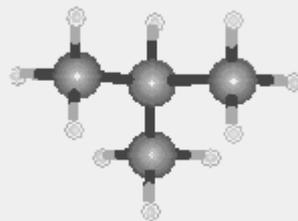
generic formula  
 $C_nH_{2n+2}$ 

Compounds that contain only carbon and hydrogen are known as **hydrocarbons**. Those that contain as many hydrogen atoms as possible are said to be *saturated*. The saturated hydrocarbons are also known as **alkanes**.

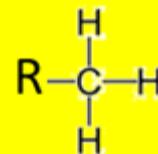
**Straight-chain hydrocarbons**, in which the carbon atoms form a chain that runs from one end of the molecule to the other .i.e. butane



Alkanes also form **branched** structures. The smallest hydrocarbon in which a branch can occur has four carbon atoms. This compound has the same formula as butane ( $C_4H_{10}$ ), but a different structure, known as a structural isomer.



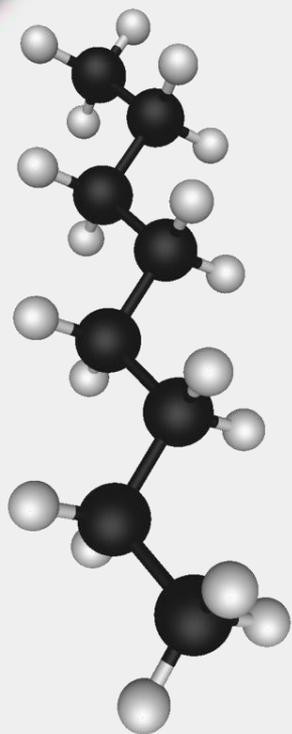
## Alkanes



## Chemical properties of Alkanes



Background  
Knowledge



1. **Non reactivity of alkanes** (in relation to acids, alkalis, metals, water, because they are non-polar molecules).
2. **Low melting and boiling points** – intermolecular forces are weak van der Waal forces.
3. **Odour** – hydrocarbons are volatile because they have weak intermolecular forces and they have characteristic smells.
4. Do not conduct heat or electricity.
5. As the C chain gets longer the hydrocarbons change from gas to liquid to solid.
6. Combustion of alkanes. Alkanes are very good fuels.



Write name as –

1. Identify the longest C chain
2. Identify any branches
3. Number the C atoms in longest chain
4. so branches are on the lowest numbers

5. Write the name

1. Location of branch
2. Name of branch
3. Prefix of long chain
4. -ane



## IUPAC Rules for Alkane Nomenclature

1. Find and name the longest continuous carbon chain.
2. Identify and name groups attached to this chain.
3. Number the chain consecutively, starting at the end nearest a substituent group.
4. Designate the location of each substituent group by an appropriate number and name.
5. Assemble the name, listing groups in alphabetical order.

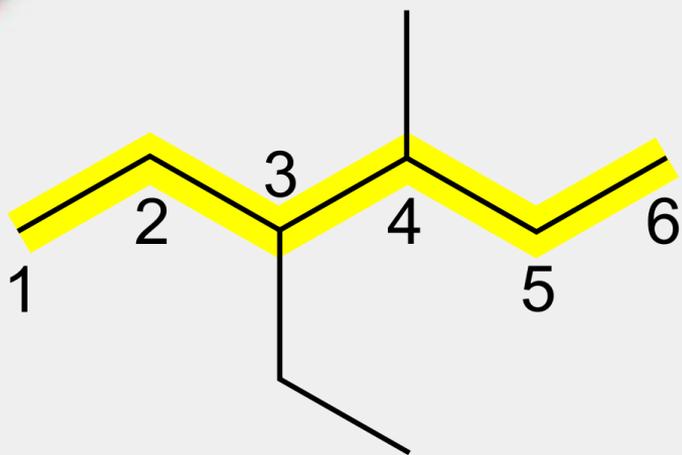
The prefixes di, tri, tetra etc., used to designate several groups of the same kind, are not considered when alphabetising.

<b>methyl</b>	<b>ethyl</b>	<b>propyl</b>
<b>1</b>	<b>2</b>	<b>3</b>
<b>-CH<sub>3</sub></b>	<b>-CH<sub>2</sub>CH<sub>3</sub></b>	<b>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub></b>

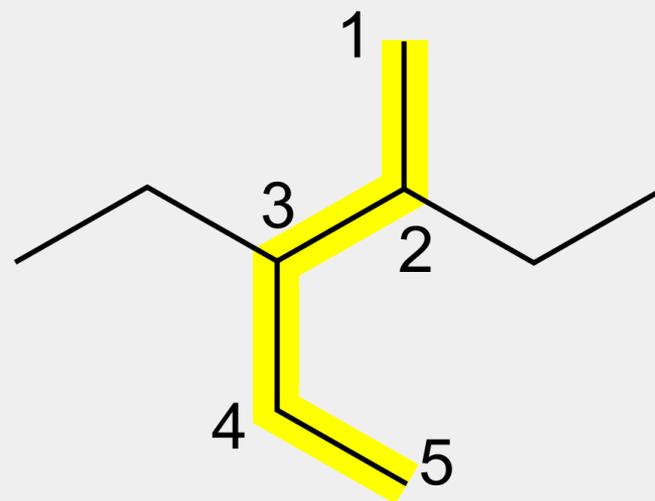


## Naming Branched chain Alkanes

Always make sure the longest possible chain of carbons – and therefore the shortest possible branches – is used.



3-ethyl-4-methylhexane



2,3-diethylpentane  
(incorrect)

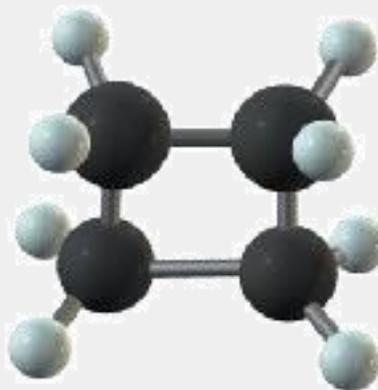


## Naming cyclic Alkanes

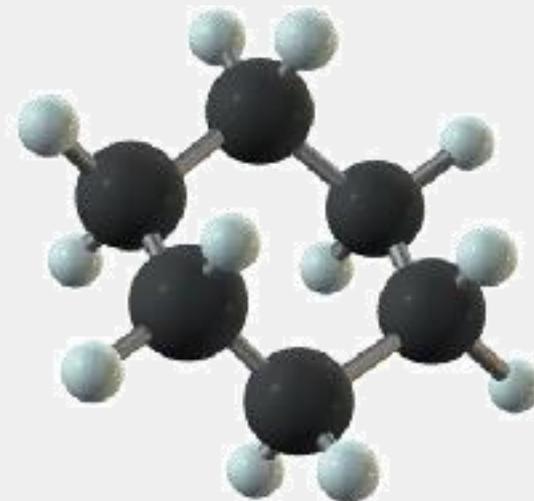
Alkanes can also form cyclic molecules. These are named by placing cyclo- in front of the longest chain.



cyclopropane



cyclobutane



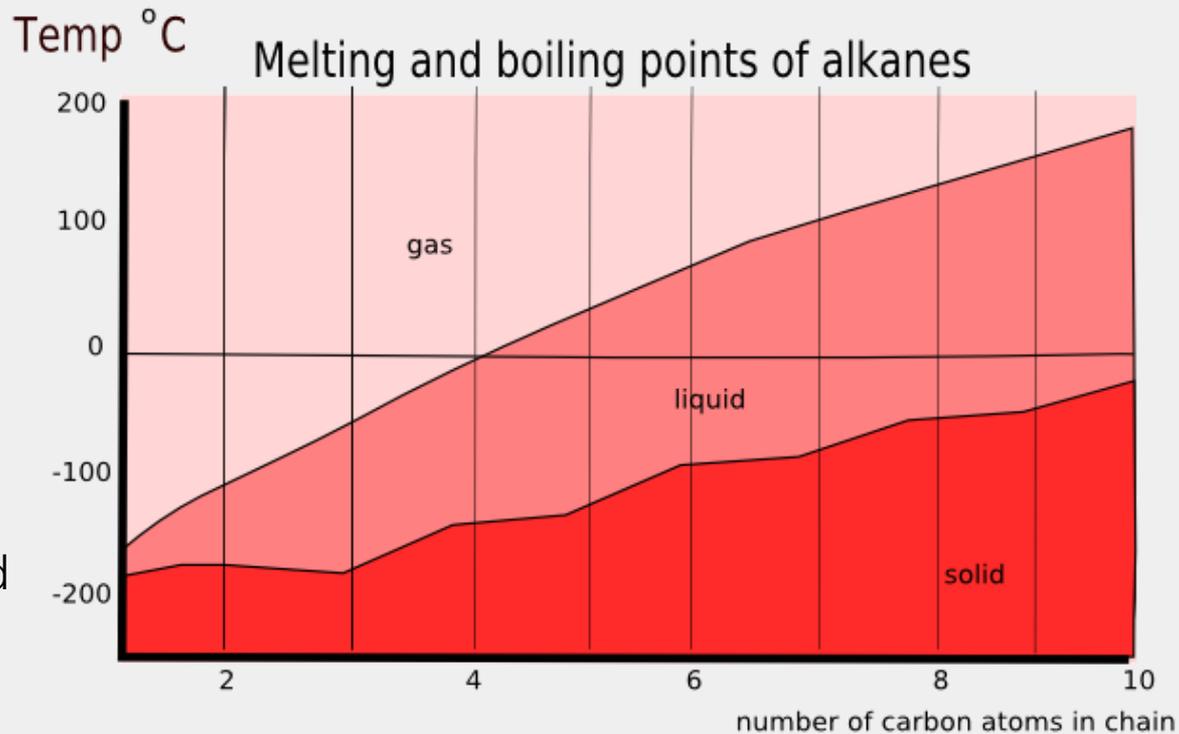
cyclohexane

## Background Knowledge

Alkanes are non-polar molecules and are bonded together by weak intermolecular forces. As the number of carbons increase so does the Molar Mass of the molecule. The larger the molar mass the more total valence electrons are available.

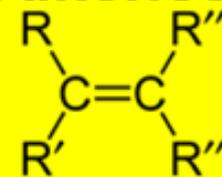


## Melting and boiling points of alkanes

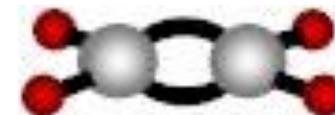


These valence electrons can randomly cluster on one side or the other creating an instantaneous polar end – thereby creating a bond to another molecule's instantaneous polar end. The greater the number of carbons, the stronger the bond between molecules therefore the higher the melting and boiling point.

## Alkenes



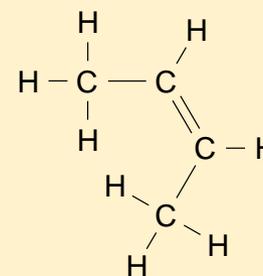
**Functional Group** – One double carbon-carbon bond C=C  
 A **functional group** is the part of the molecule responsible for reactions typical of the homologous series.

Alkene Nomenclature

Alkenes are named in a similar way to alkanes, *but the longest continuous carbon chain is numbered to give the carbon atoms in the double bond the lowest possible numbers.*

The position of the double bond is given by the smaller number of the two carbon atoms involved.

After numbering the longest chain C1-C2=C3-C4, the compound is named 2-butene or but-2-ene, but not 3-butene nor but-3-ene.



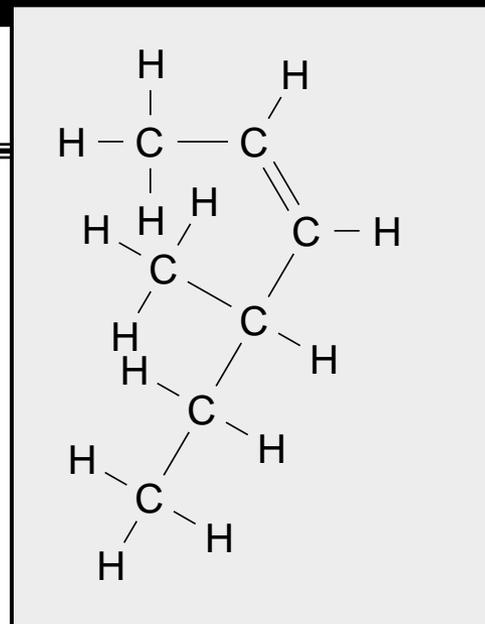
generic formula



Write name as

1. Location of branch
2. Name of branch
3. Prefix of long chain
4. Location of C=C
5. -ene
6. If in an alkene there are more than one double bond is present, it named as a -diene or -triene.

For example; 2,5-Dimethyl-2,4-hexadiene, here double bond located at 2 and 4 position with two substituent (methyl group) at 2 and 5 positions.



Number carbons so double bond has the lowest number.

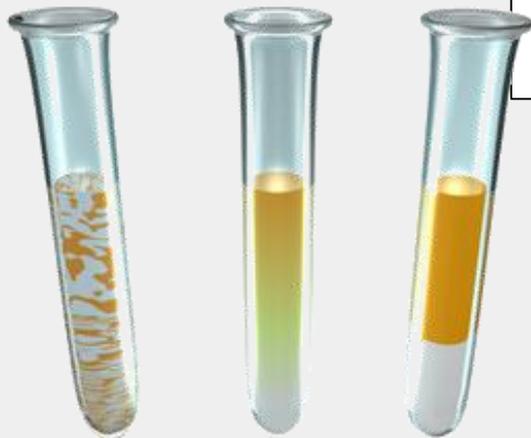
The Alkene shown above is found to be 4-methylhex-2-ene by numbering the chain C1-C2=C3-C4-C5-C6.

## Background Knowledge

# Summary of solubility in Water –Alkanes and Alkenes



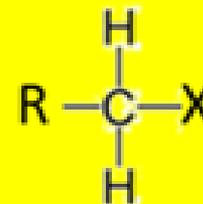
Alkanes and Alkenes: **Not soluble in water.** These molecules are non-polar (there is no negative or positive ends to the molecule) compared with water which is polar (having a negative area near the oxygen atom and positive area near the hydrogen atoms) so they are not attracted to each other. Alkanes and alkenes are **immiscible** (two or more liquids that will not mix together to form a single homogeneous substance) and form a distinct layer from the water. Smaller C chained alkanes and alkenes are less dense than water and float on top.



If either an Alkane or Alkene is mixed into water eventually the two liquids will form separate **immiscible** layers

Named as a chloroalkane or bromoalkane etc, with the position of the halogen given by the appropriate number of the carbon that it is attached to in the chain.

## Haloalkanes

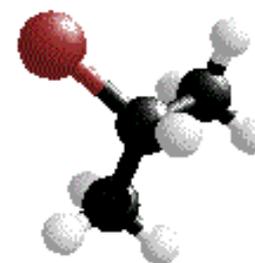


The haloalkanes can be classified as

**Primary**  $\text{RCH}_2\text{X}$  - the C atom to which X is attached is only attached to one other C atom

**Secondary**  $\text{R}_2\text{CHX}$  - the C atom to which X is attached, is attached to two other C atoms

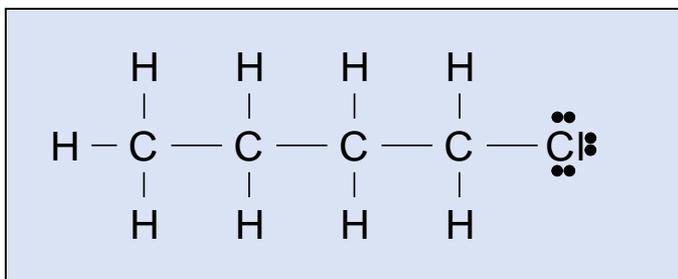
**Tertiary**  $\text{R}_3\text{CX}$  - the C atom to which X is attached, is attached to three other C atoms.



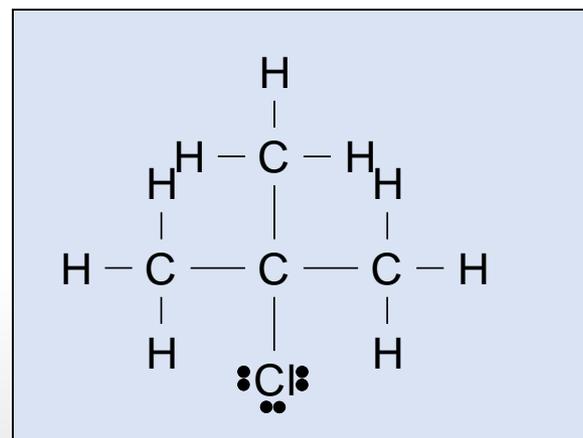
Haloalkanes are classified according to the position of the halogen atom bonded in the molecule.

This leads to the existence of

- > primary ( $1^\circ$ ) – bonded to a C that is bonded to only 1 other C
- > secondary ( $2^\circ$ ) – bonded to a C that is bonded to 2 other C
- > tertiary ( $3^\circ$ ) – bonded to a C that is bonded to 3 other C

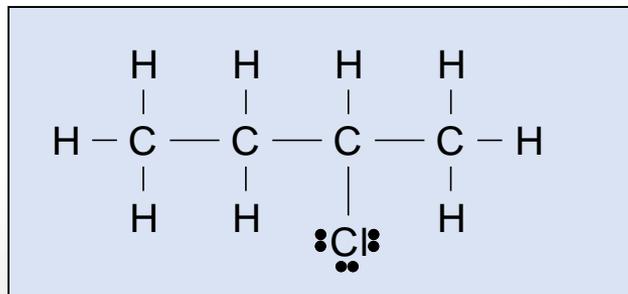


1-chlorobutane  
( $1^\circ$ haloalkane)

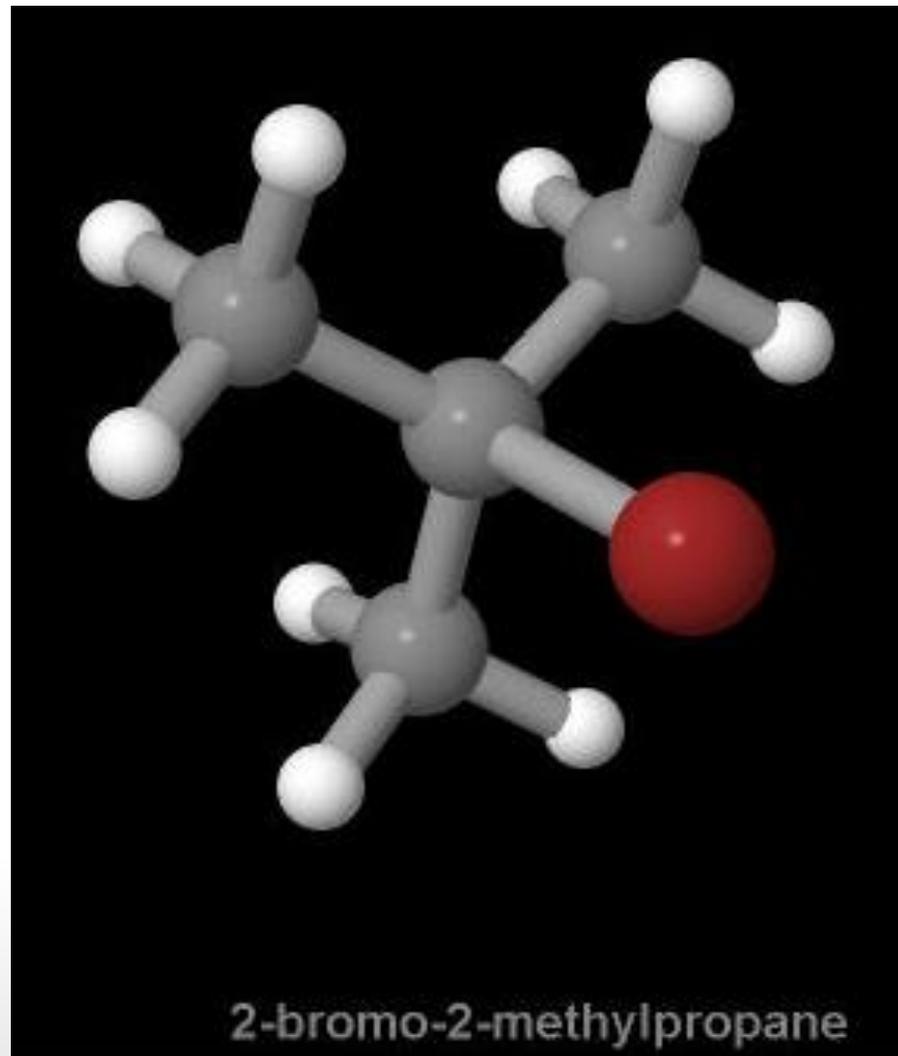


2-chloro-2-methylpropane  
( $3^\circ$ haloalkane)

2-chlorobutane  
( $2^\circ$ haloalkane)

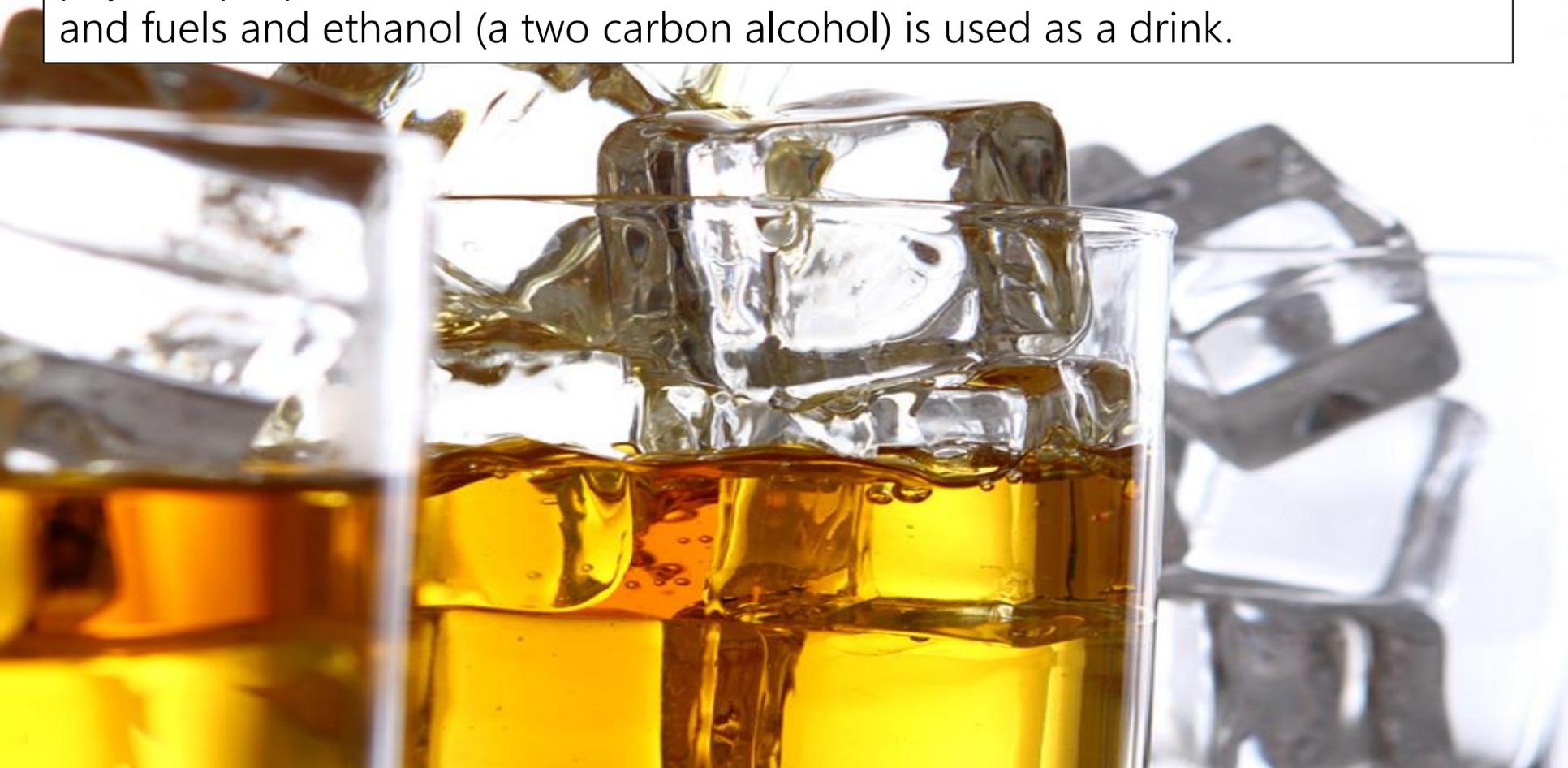


Atom	Name used in haloalkane
Bromine	Bromo
Chlorine	Chloro
Fluorine	Fluoro
iodine	iodo

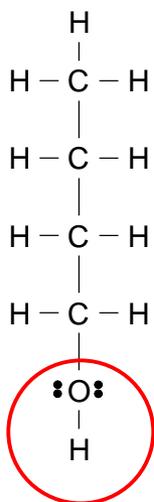




Alcohols are not considered hydrocarbons as they have one or more oxygen atoms attached in addition to the hydrogen and carbon atoms. Alcohols are organic substances however and share many of the same chemical and physical properties of the alkanes and alkenes. Alcohols are used as solvents and fuels and ethanol (a two carbon alcohol) is used as a drink.



Functional group is the hydroxyl group –OH (not a hydroxide)



Butan-1-ol

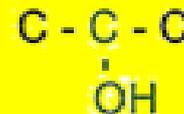
### Naming alcohols

1. Location of branch
2. Name of branch
3. Prefix of long chain
4. an-
5. Location of OH  
(if multiple di, tri, tetra)
6. -ol

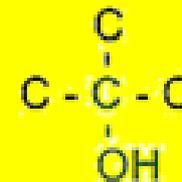
## Alcohols



Primary



Secondary



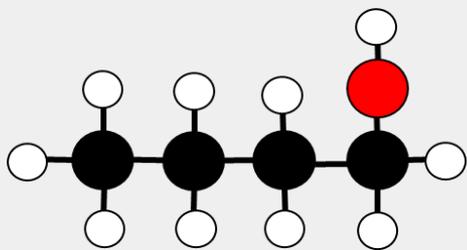
Tertiary

Alcohols are classified according to the position of the hydroxyl group bonded in the molecule.

This leads to the existence of

- > primary ( $1^\circ$ ) – bonded to a C that is bonded to only 1 other C
- > secondary ( $2^\circ$ ) – bonded to a C that is bonded to 2 other C
- > tertiary ( $3^\circ$ ) – bonded to a C that is bonded to 3 other C

Small alcohol molecules are polar and the presence of the OH group means they are able to undergo intermolecular **hydrogen bonding**. The large difference in electronegativity between the O and H atoms means the O-H bond is very polar and the slightly positive charge on this H atom is attracted to the non-bonding electron pairs of the oxygen on another molecule. This means small alcohol molecules are highly soluble in water. However as the length of the non-polar hydrocarbon chain increases this solubility in water decreases.

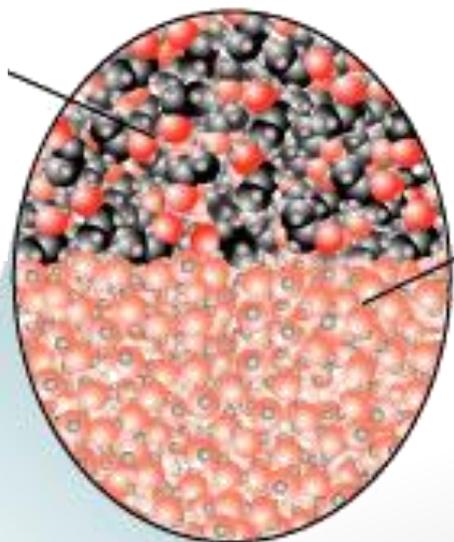


Aqueous solutions are neutral. The presence of the OH group in this molecule is NOT the same as the OH<sup>-</sup> in sodium hydroxide, NaOH (an ionic compound).

Alcohols: **Soluble in water.** These molecules are polar (due to the  $-OH$  end) and water, also being polar, will bond with the alcohol. The alcohol molecules will therefore disperse and mix within the water molecules.

At the instant ethanol and water are mixed the ethanol floats on top of the water

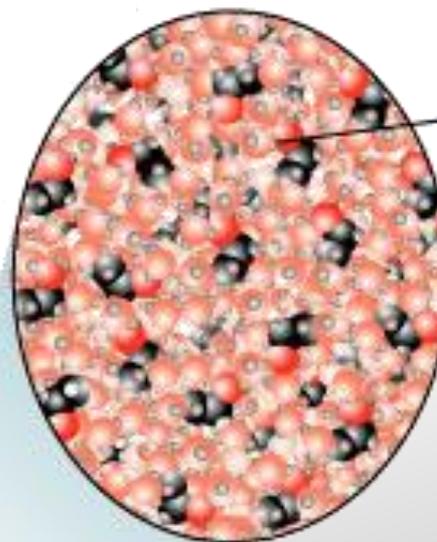
Hydrogen bonds between ethanol molecules.



Hydrogen bonds between water molecules.

Because the attractions between their molecules are similar, the molecules mix freely, allowing each substance to disperse into the other

Hydrogen bonds between ethanol and water molecules.



Ethanol and water mix.



**Alkanes:** The smaller the alkane molecule the lower the boiling point and the more volatile (easier to combust) the alkane. As the molar mass (Mass number of all the atoms combined) increases, the boiling points also increase as the strength of the intermolecular (between molecules) attractions increases.

The alkanes methane to butane (C1 – C4) are all gases at room temperature

Alkanes with between 5C and 15C atoms are all liquids

Alkanes with over 15 C atoms are soft solids

**Alkenes:** The boiling point trend is similar to alkanes where the larger the number of C atoms in the chain the higher the boiling point. The equivalent length C chain alkene has a slightly higher point than that of the alkanes.

**Alcohols:** The boiling point trend is similar to both alkanes and alkenes where the larger the number of C atoms in the chain the higher the boiling point.

The boiling point is higher than both alkanes and alkenes as the intermolecular bonding is stronger due to being a polar molecule– which creates a positive and negative end and hold the individual alcohol molecules together stronger and thus needs more energy to break them (heat energy)

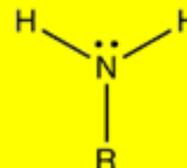
Even small chain alcohols are liquid at room temperature

Functional group is the amino group  $\text{-NH}_2$

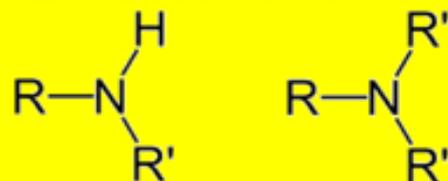
Amines are named as substituents e.g. aminomethane,  $\text{CH}_3\text{NH}_2$ . These may be classed as primary, secondary or tertiary, but their classification depends on the number of C atoms attached to the N atom. Primary  $\text{RNH}_2$ , secondary  $\text{R}_2\text{NH}$ , tertiary  $\text{R}_3\text{N}$ .

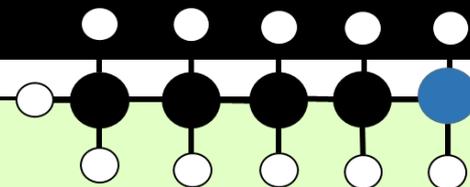
Amines have an unpleasant "ammonia" smell. The smaller amines, up to C5, are soluble in water but larger amino alkanes are insoluble, as the size of the non-polar hydrocarbon chain cancels out the effect of the polar amino (mainly due to lone pair of electrons on the N) functional group.

### 1° Amines



### 2° and 3° Amines





Write name as –

1. Identify the longest C chain - Identify any branches
2. Number the C atoms in longest chain so number Carbon 1 attached to amino group ( $\text{NH}_2$ )
3. Write the name
  1. Location of branch
  2. Name of branch
  3. Amino-
  4. Prefix of long chain
  5. -anee.g. 1-aminobutane (4C)

Either will be accepted in NCEA assessments

### Alternative naming method

1. Identify the longest C chain - Identify any branches
2. Number the C atoms in longest chain so number Carbon 1 attached to amino group ( $\text{NH}_2$ )
3. Write the name
  1. Location of branch
  2. Name of branch
  3. Prefix of long chain
  4. -anaminee.g. butanamine (4C)

# Names and Classification of primary, secondary and tertiary amines



Amines can be classified as 1°, 2° or 3° according to the number of R groups on the nitrogen. The N is a placeholder for a number as it is not off a carbon.

1°	1 R group on amino nitrogen (and 2H)		
2°	2 R groups on amino nitrogen (and 1H)		
3°	3 R groups on amino nitrogen (and no H)		

If the amino group –NH<sub>2</sub> is not on the end carbon then name the compound as you would a branch  
For example  
2-amino ...

If the groups off the N are different then name each separately  
For example  
N-ethyl – N-methyl

1

Systematic naming of amines is limited to primary amines.

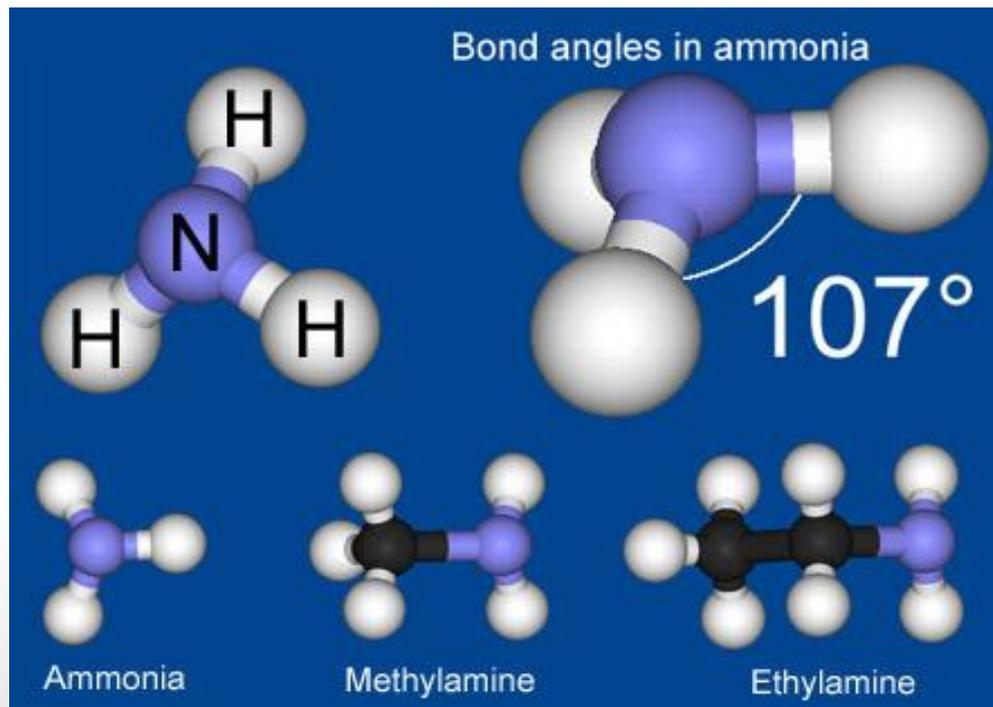
**Intermolecular bonding** results from hydrogen bonding between the N-H groups as well as ID-ID attractions from the molecule.

### States

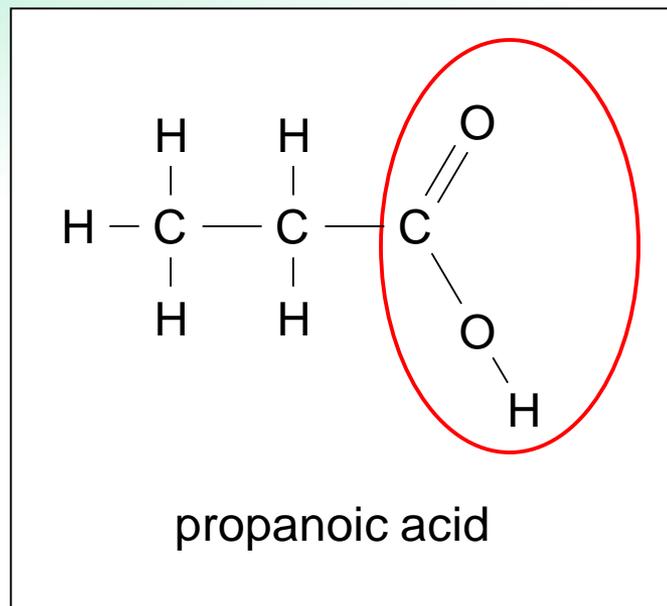
- aminomethane and aminoethane are **gases**.
- Aminopropane and aminobutane are volatile **liquids** with fishy smells.
- Heavier aminoalkanes are **solids**.

### Solubility in water

Lower molecular mass aminoalkanes are soluble in water due to hydrogen bonding. Solubility in water decreases as hydrocarbon portion increases.



Functional group is the carboxyl group  $\text{-COOH}$



### Naming carboxylic acids

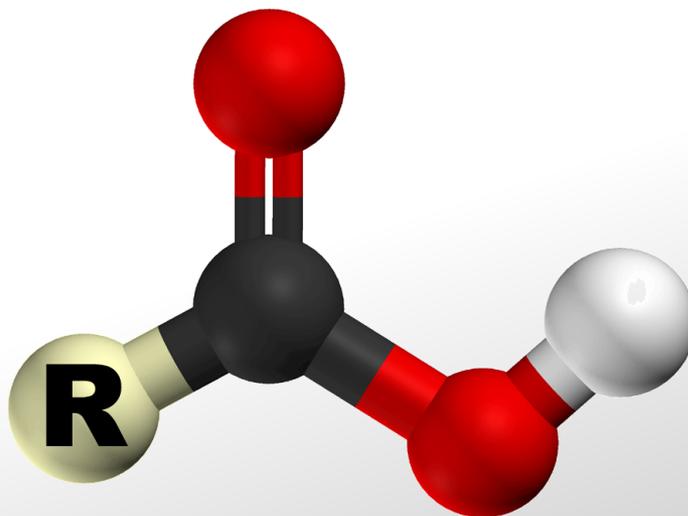
1. Longest  $\text{-C}$  chain with  $\text{-COOH}$
2. Identify branches
3. No. 1 C is the C in  $\text{-COOH}$
4. Location of branches
5. Name branch
6. Prefix
7.  $\text{-anoic acid}$

- polar molecules as short chains ~ non-polar molecules as long chains
- boiling points and melting points decrease with chain length
- turn blue litmus red (weakly acidic)
- conduct electricity
- react with metal to form salt and  $\text{H}_2$
- react with metal oxides to form salt and  $\text{H}_2\text{O}$
- react with metal carbonates to form salt and  $\text{H}_2\text{O}$  and  $\text{CO}_2$

All the simple, straight-chain carboxylic acids up to ten carbons are liquids at room temperature. The liquids have sharp pungent odours and all have high boiling points.

Smaller molecules, less than 10 carbons, are completely miscible in water due to the formation of hydrogen bonds with the water.

The highly polar carboxylic acids dimerise in the liquid phase and in non-aqueous solvents ( $\text{CCl}_4$ ) and form two hydrogen bonds between each pair. This extra degree of hydrogen bonding causes carboxylic acids to have higher boiling points compared to their corresponding alcohols.

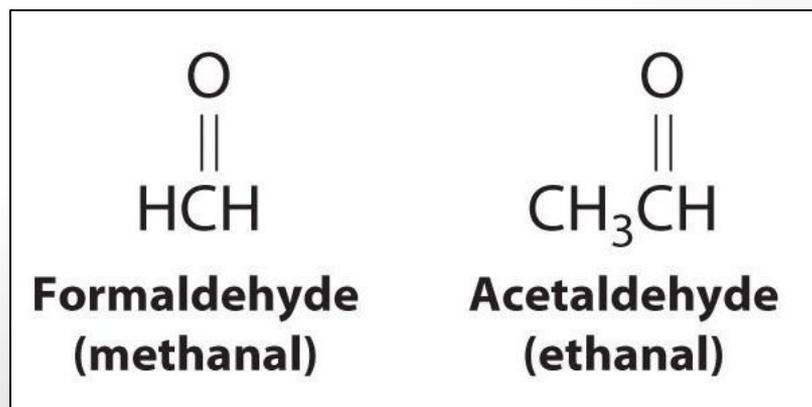
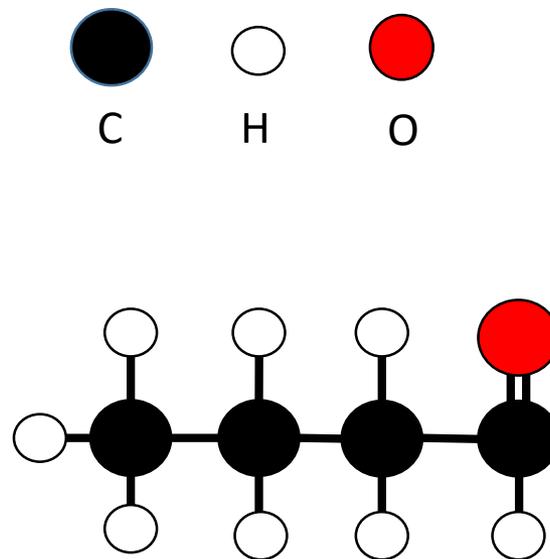


Aldehydes are a class of organic compounds that are important in the manufacture of plastics, dyes, food additives, and other chemical compounds. Aldehydes have the general formula -RCHO

Where R is either a hydrogen atom, as in the case of formaldehyde, or an aromatic hydrocarbon group.

Formaldehyde is used extensively in the chemical industry in the synthesis of organic compounds. Its most important use is in the manufacture of synthetic resins.

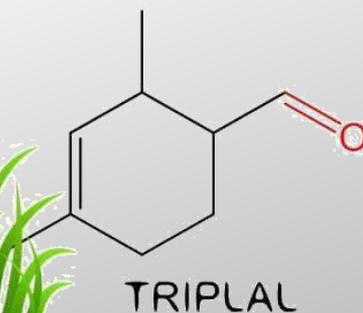
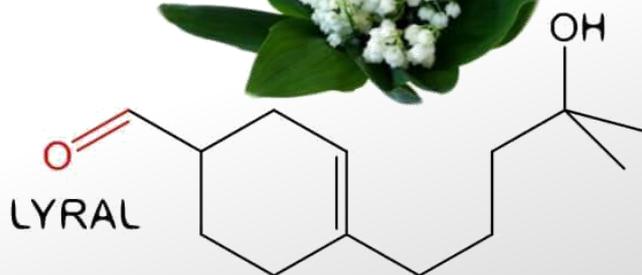
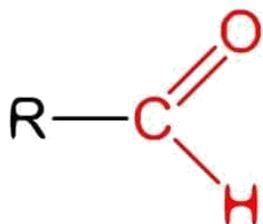
Recent tests have indicated that it is a carcinogen.



Functional group is the group – RCHO

Aldehydes are named by changing “-e” at the end of the alkane to “-al”.

The aldehyde group does not need to be numbered when naming an aldehyde as it **must always be on the end carbon** (carbon number 1). If there are other substituents in the molecule, then numbering is always from the aldehyde end of the chain.

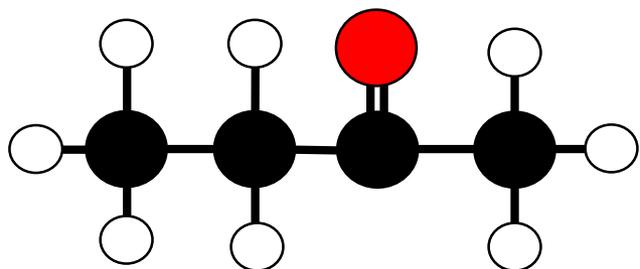


Functional group is the group – (alkanones - RCOR')

Ketones are named by changing “-e” on alkanes to “-one”.

Ketones (apart from propanone and butanone where there is no choice) need a number to indicate the position of the carbonyl (C=O) group.

pentan-2-one



C



H



O

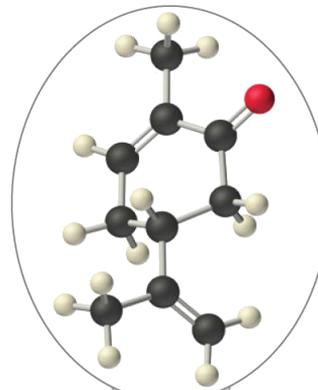




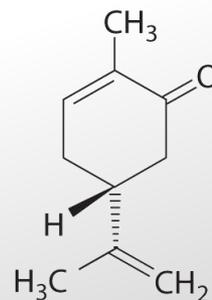
Ketones are a class of organic compounds of the general structure  $\text{RCOR}'$ , in which R and R' represent organic radicals. The simplest ketone is acetone ( $\text{CH}_3\text{COCH}_3$ ). Acetone is a product of the metabolism of fats, but under ordinary conditions, it oxidizes quickly to water and carbon dioxide. In diabetes mellitus, however, acetone accumulates in the body. Other ketones are camphor, many steroids, some fragrances, and some sugars. Ketones are relatively reactive organic compounds and thus are invaluable in synthesizing other compounds; they are also important intermediates in cell metabolism.

Carvone is a ketone that forms two optical isomers or enantiomers: (–) carvone smells like spearmint. Its mirror image, (+) carvone, smells like caraway. Humans have olfactory receptors in their noses, which can distinguish between the chiral ketones, allowing them to notice significant differences in smell between spearmint and caraway.

(+)-Carvone

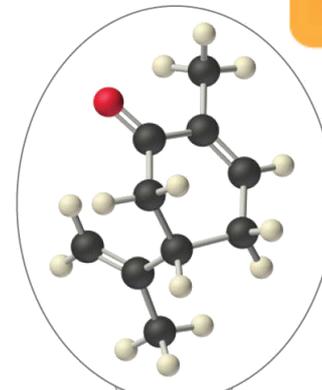


Caraway seeds

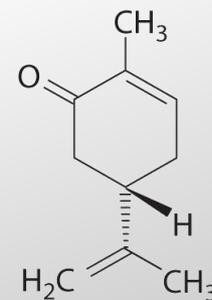


(+)-Carvone

(–)-Carvone

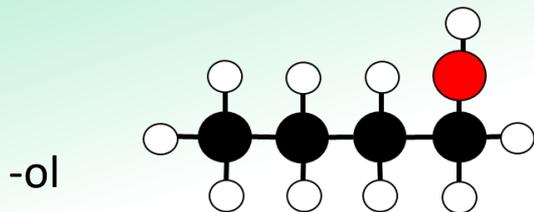


Spearmint oil

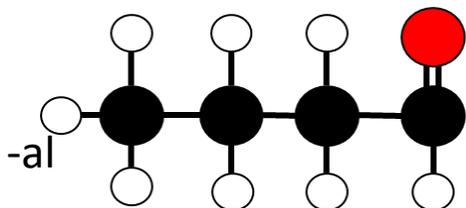


(–)-Carvone

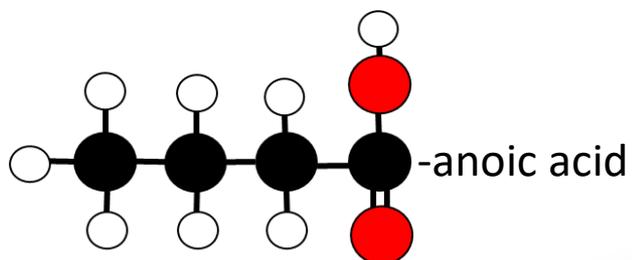
Primary alcohol



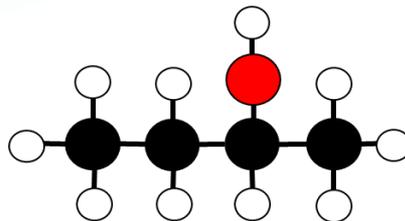
aldehyde



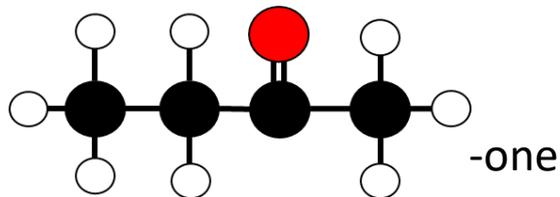
Carboxylic acid



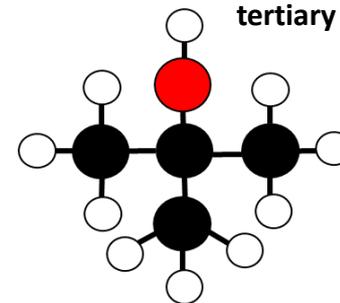
Secondary alcohol



ketone



tertiary alcohol



No Reaction



C



H



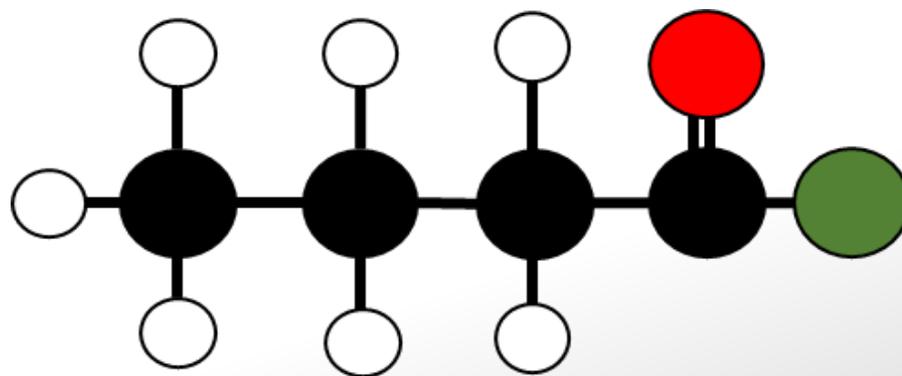
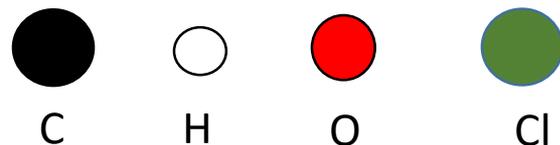
O

Formed from carboxylic acids, with a -Cl replacing the -OH

Functional Group: -COCl

## Naming

- ❑ suffix is "-oyl chloride"
- ❑ prefix is alkyl group including the carbon on the -COCl group  
e.g. "butan-"



Butanoyl chloride

## Acid Chloride Properties

- ❑ low MPs and BPs as there is no H bonding on the functional group.
- ❑ liquids which fume in moist air and have an irritating smell (due to rapid hydrolysis reaction)
- ❑ They are very reactive with water

**Functional Group**  $\text{-CONH}_2$  Formed from carboxylic acids with a  $\text{-NH}_2$  substituting the  $\text{-OH}$ .

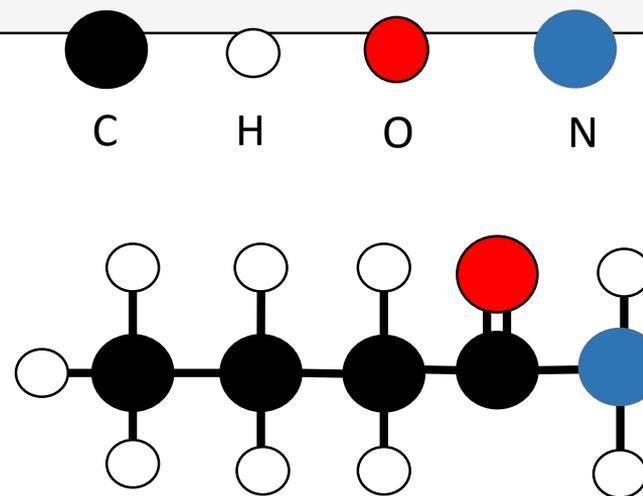
### Naming

- suffix is "-anamide"
- prefix is alkyl group including the carbon on the  $\text{-CONH}_2$  group e.g. "but-"

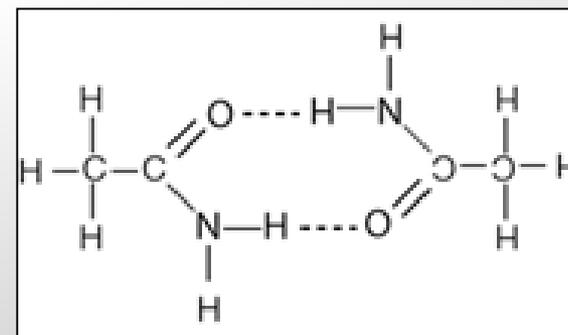
### Physical Properties

- methanamide is liquid, the rest are odourless solids.  
(impure ethanamide smells like mice)
- The higher melting points are due to dimerisation caused by hydrogen bonding.

A **dimer** is a chemical entity consisting of two structurally similar subunits called monomers joined by bonds that can be either strong or weak

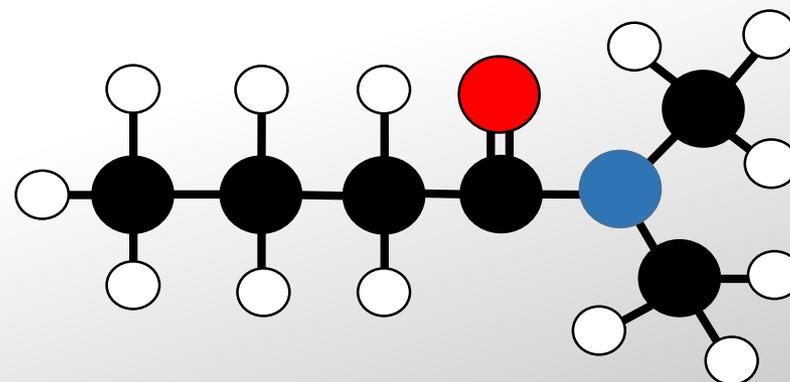
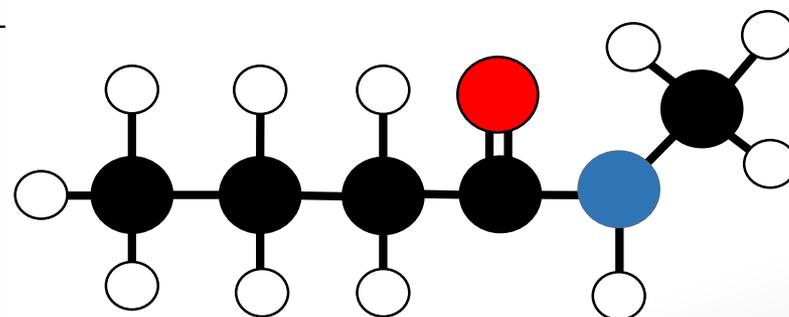
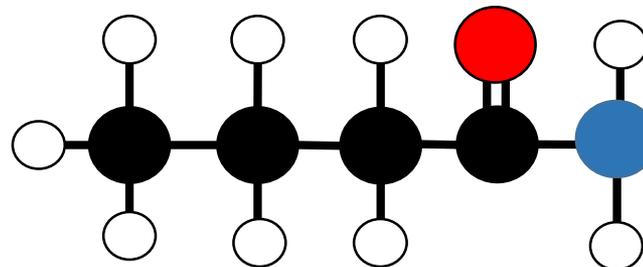


Butanamide

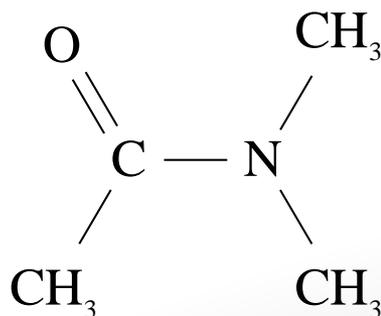


**Classification as 1°, 2°, 3°**

1°	no alkyls and 2 hydrogens on N	$\text{R}-\text{C} \begin{array}{l} \text{=O} \\ \backslash \\ \text{NH}_2 \end{array}$ 
2°	1 alkyl and 1 hydrogen on N	$\text{R}-\text{C} \begin{array}{l} \text{=O} \\ \backslash \\ \text{NH}-\text{R}' \end{array}$ 
3°	2 alkyls and no hydrogen on N	$\begin{array}{l} \text{O} \\ \text{=C} \\ \text{R} \end{array} - \text{N} \begin{array}{l} \text{R}' \\ \text{R}' \end{array}$ 

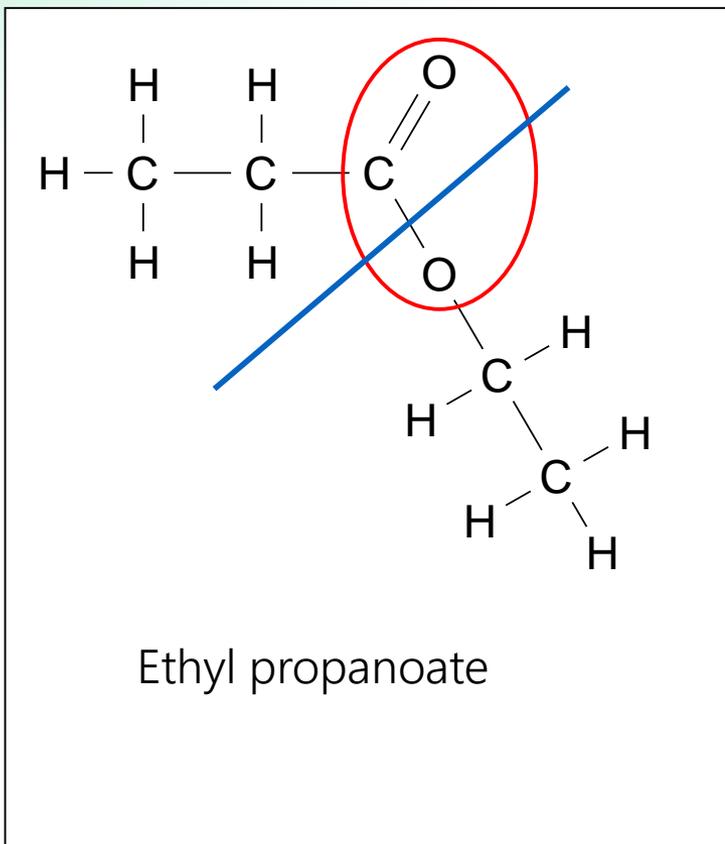


1. Indicate whether 1° - The N is only attached to one C group (no N in front of name)
2. Indicate whether 2° - The N is attached to 2 C groups ( place an 'N' in front of the name)
3. Indicate whether 3° - The N is attached to 3 C groups (place an 'N,N' in front of the name)
4. Name the groups off the N (not the long 'parent C chain') as branches
5. Name the longest C chain
6. Suffix - anamide



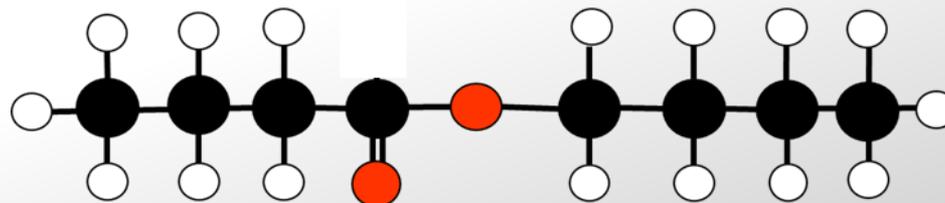
**N,N-dimethylethanamide**

Functional group is  $\text{-COO-}$



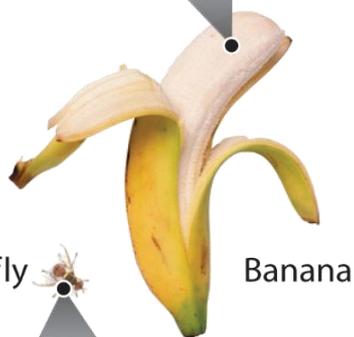
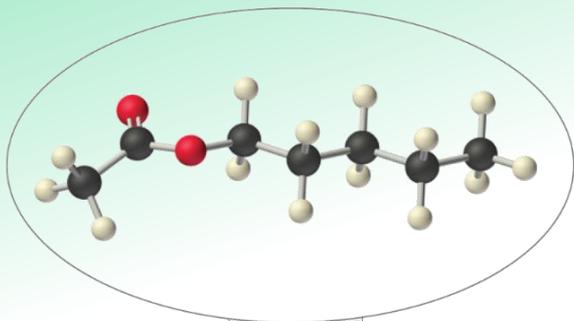
### Naming esters

1. Split between C-O bond
2. Identify name for side with  $\text{-O-}$
3. Prefix of C chain
4. -yl
5. Identify name for side with  $\text{C=O}$
6. Prefix of C chain
7. -anoate



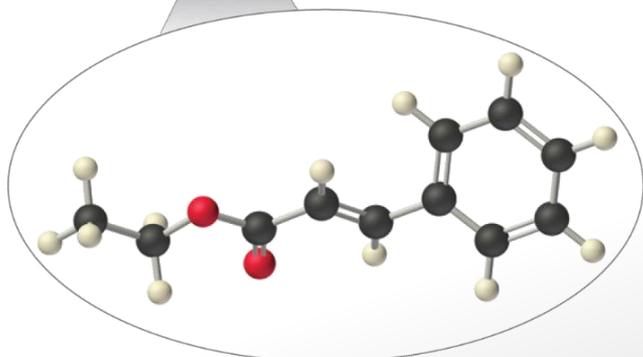
Esters often have fruity or distinctive smells  
Prepared by the process of esterification

Amyl acetate (pentyl acetate)  
(banana scent)



Fruit fly

Banana



Ethyl cinnamate (a pheromone)

Esters are chemical compounds responsible for the fruity smells present in processed food. Many natural flavours and smells are due to the presence of esters in flowers and fruits.

The higher the molecular weight, the weaker the odours they carry are.

alcohol	organic acid	ester made	smell of ester
pentanol	ethanoic acid	pentyl ethanoate	pears
octanol	ethanoic acid	octyl ethanoate	bananas
pentanol	butanoic acid	pentyl butanoate	strawberries
methanol	butanoic acid	methyl butanoate	pineapples

# NCEA 2013 Functional Groups

Merit  
Question

**Question 1a:** Complete the table below by giving the IUPAC systematic name or the structural formula for each compound.

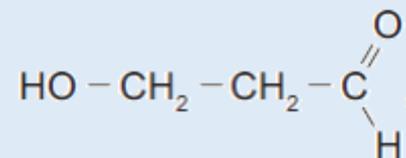
Structural formula	IUPAC systematic name
$\text{HO}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-hydroxy propanal / 3-hydroxyl propanal
$\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$	propanamide
$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	4-methyl pentan-2-one

# NCEA 2013 Functional Groups

Merit  
Question

**Question 1c:** Draw the structural formulae of three different isomers of which show the following properties:

- Isomer 1 turns moist blue litmus paper red.
- Isomer 2 is an ester.
- Isomer 3 is a ketone.



Property	Structural formula
turns moist blue litmus paper red	$\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$
is an ester	$\text{CH}_3\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_3 \quad \text{HC}\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_3$
is a ketone	$\text{HO}-\text{CH}_2\overset{\text{O}}{\parallel}{\text{C}}\text{CH}_3$

## NCEA 2013 Functional groups

Merit  
Question

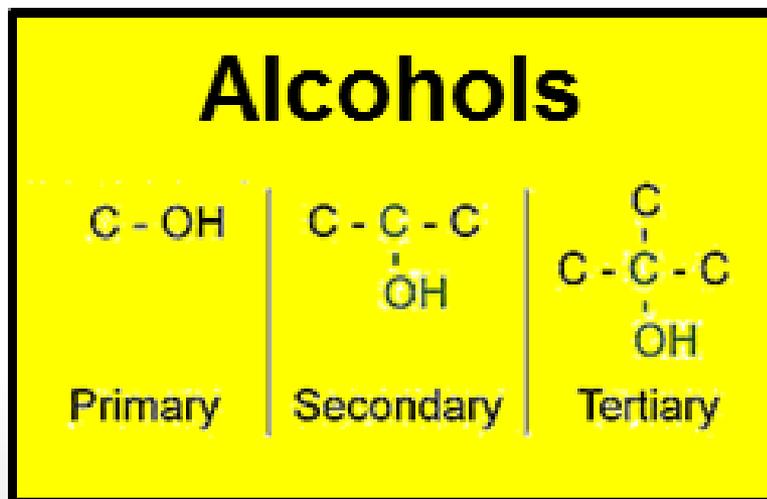
**Question 3a:** (i) Three alcohol compounds are listed below.  
methylpropan-2-ol butan-1-ol butan-2-ol  
Compare and contrast the structures of the compounds above.

The three alcohols are (structural) isomers / they have the same molecular formula but different structural formula.

Methyl propan-2-ol is a tertiary alcohol

Butan-2-ol is a secondary alcohol

Butan-1-ol is a primary alcohol



## NCEA 2014 Functional Groups

Achieved  
Question

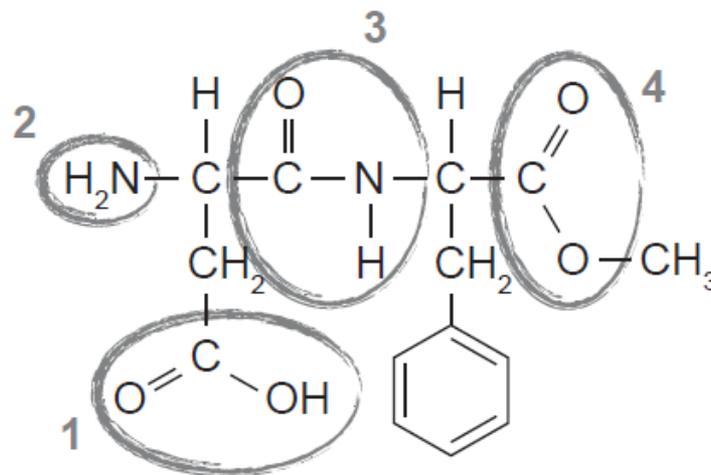
**Question 1(a):** Complete the table below giving the IUPAC systematic name or the structural formula for each compound.

Structural formula	IUPAC systematic name
$\begin{array}{c} \text{Cl} \quad \text{O} \\   \quad    \\ \text{CH}_3 - \text{CH} - \text{C} - \text{CH}_3 \end{array}$	3-chlorobutanone
$\text{CH}_3 - \text{CH}_2 - \text{CO} - \text{NH}_2$	propanamide
$\begin{array}{c} \text{CH}_3 - \text{O} - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\    \\ \text{O} \end{array}$	methylbutanoate

## NCEA 2015 Functional Groups

Achieved  
Question

**Question 1(a):** The structure of aspartame is given below. Aspartame is often used as an artificial sweetener in drinks. Identify the FOUR different functional groups within the aspartame molecule that are circled and numbered below:



**Answer:**

1. Carboxylic acid or carboxyl
3. Amide

2. Amine or aminoalkane
4. Ester

# NCEA 2015 Functional Groups

Achieved  
Question

**Question 1(b):** Complete the table below by drawing the structural formula for the named compounds.

IUPAC systematic name	Structural formula
propanoyl chloride	$\text{H}_3\text{CCH}_2\overset{\text{O}}{\parallel}{\text{C}}\text{Cl}$
3-bromopentan-2-one	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{C}-\text{CH}(\text{Br})-\text{CH}_2-\text{CH}_3 \end{array}$
2-methylbutanal	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{CH}_2-\underset{\text{CH}_3}{\text{C}}-\text{C}-\text{H} \end{array}$

## NCEA 2015 Isomers (Haloalkanes)

Merit  
Question

Question 1(c) (i): In the boxes below, draw the three structural isomers of  $C_4H_9Cl$  that represent a primary, secondary and tertiary haloalkane.

Primary haloalkane	Secondary haloalkane
$H_3C-CH_2-CH_2-CH_2-Cl$ or $H_3C-CH_2-CH(CH_3)-Cl$	$H_3C-CH(Cl)-CH_2-CH_3$

Tertiary haloalkane
$H_3C-CCl(CH_3)CH_3$

# NCEA 2016 Functional Groups

Achieved  
Question

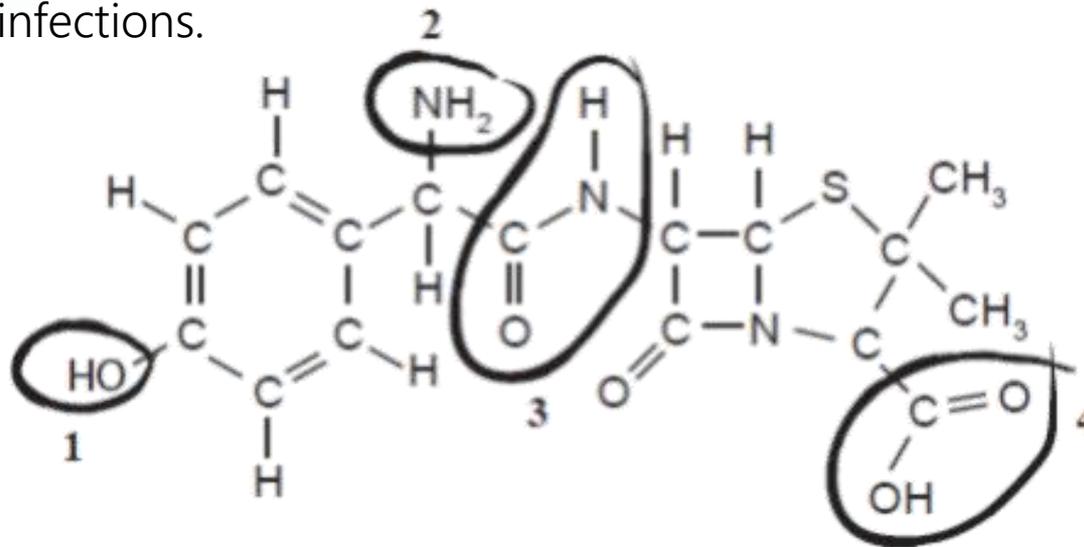
**Question 1a:** Complete the table below by drawing the structural formula for the named compounds.

IUPAC systematic name	Structural Formula
butylethanoate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} \\ \backslash \\ \text{O} - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$ <p>butylethanoate</p>
2-hydroxybutanal	$\begin{array}{c} \text{OH} \\   \\ \text{CH}_3\text{CH}_2 - \text{CH} - \text{C} \\ \parallel \\ \text{H} \end{array}$ <p>2-hydroxybutanal</p>
ethanamide	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} \\ \backslash \\ \text{NH}_2 \end{array}$ <p>ethanamide</p>

# NCEA 2016 Functional Groups

Achieved  
Question

**Question 1b:** The structure of amoxicillin is given below. It is an antibiotic used in the treatment of bacterial infections.



Name the four different functional groups circled within the amoxicillin molecule above.

<b>1</b>	Hydroxyl (alcohol).
<b>3</b>	Amide / peptide.

<b>2</b>	Amine / amino.
<b>4</b>	Carboxylic acid.

# NCEA 2016 Functional Groups

Achieved  
Question

## Question 2b:

The structures of four different organic substances are shown in the table below. (i) Name the organic substances **A** to **D**.

Letter	Structure	Name
<b>A</b>	$\text{CH}_3\text{CH}_2\text{CH}_2-\text{NH}_2$	Propan-1-amine. (1-propanamine)
<b>B</b>	$\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	Propanal.
<b>C</b>	$\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	Propanoyl chloride.
<b>D</b>	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	Propan-2-one. (propanone)

# NCEA 2017 Functional Groups

Merit  
Question

**Question 1a:** Complete the table below to indicate the IUPAC name, functional group, and / or the structural formula for organic compounds that contain **only four carbon atoms**. The first row has been completed for you.

Functional group	Structural formula	IUPAC (systematic) name
Alkene	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	but-1-ene
Amine	$\begin{array}{c} \text{CH}_3\text{CHCH}_2-\text{N}-\text{H} \\   \quad   \\ \text{CH}_3 \quad \text{H} \end{array}$	2-methylpropan-1-amine
Acyl chloride	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{C}-\text{Cl} \\    \\ \text{O} \end{array}$	butanoyl chloride 2-methylpropanoyl chloride
Ester	$\begin{array}{c} \text{H}-\text{C}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3 \\    \\ \text{O} \end{array}$	propyl methanoate
Ketone	$\begin{array}{c} \text{CH}_3\text{CH}_2-\text{C}-\text{CH}_3 \\    \\ \text{O} \end{array}$	Butanone Butan-2-one
Aldehyde	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2-\text{C}-\text{H} \\    \\ \text{O} \end{array}$	Butanal 2-methylpropanal
Amide	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2-\text{C}-\text{NH}_2 \\    \\ \text{O} \end{array}$	butanamide

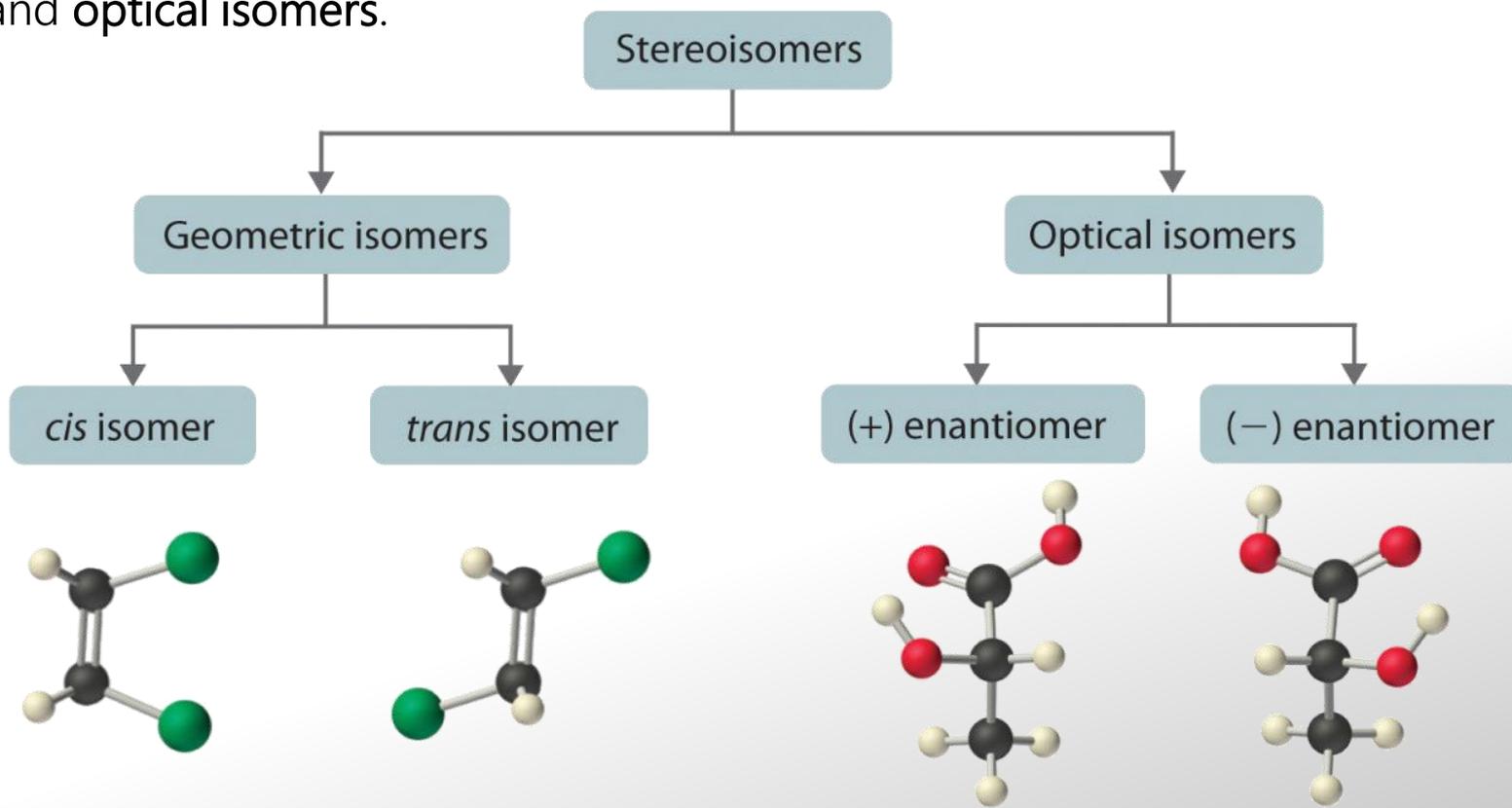
# NCEA 2018 Functional Groups

Achieved  
Question

**Question 1a:** Complete the table below to show either the structural formula or the IUPAC (systematic) name for each organic molecule.

Structural Formula	IUPAC (systematic) name
$\begin{array}{c} \text{Cl} \\   \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{C} \begin{array}{l} \text{=O} \\ \text{-Cl} \end{array} \end{array}$	3-chlorobutanoyl chloride
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3$	pentan-2-one
$\text{CH}_3 - \text{CH}_2 - \text{CH}(\text{CH}_3) - \text{CH}_2 - \text{CH}_2 - \text{CHO}$	4-methylhexanal
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{C} \\   \\ \text{NH}_2 \end{array}$	propanamide

Two molecules are described as stereoisomers of each other if they consist of the same atoms, that are connected in the same sequence, but the atoms are positioned differently in space. The difference between two stereoisomers can only be seen from the three dimensional arrangement of the molecules. Stereoisomers are a type of isomer (variety). Stereoisomers can be subdivided into **geometric isomers** and **optical isomers**.



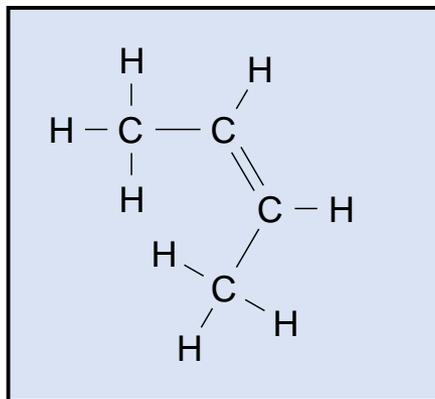
Examples: *cis*-Dichloroethene    *trans*-Dichloroethene

L-(+)-Lactic acid

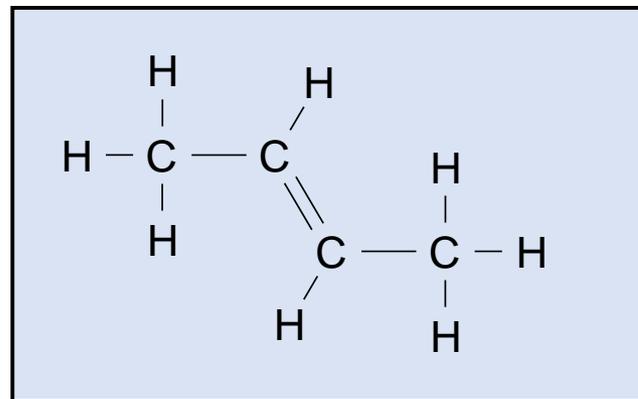
D-(-)-Lactic acid

Alkenes can exist as **geometrical** or *cis-trans* isomers, a form of stereoisomerism. A simple example is but-2-ene.

To exist as geometrical isomers the C atoms at **both** ends of the double bond must each have **two different groups (or atoms) attached**. It is impossible for a 1-alkene to have geometric isomers since the first C atom in the chain has two identical H atoms.



Cis but-2-ene



Trans but-2-ene

**NOTE:**

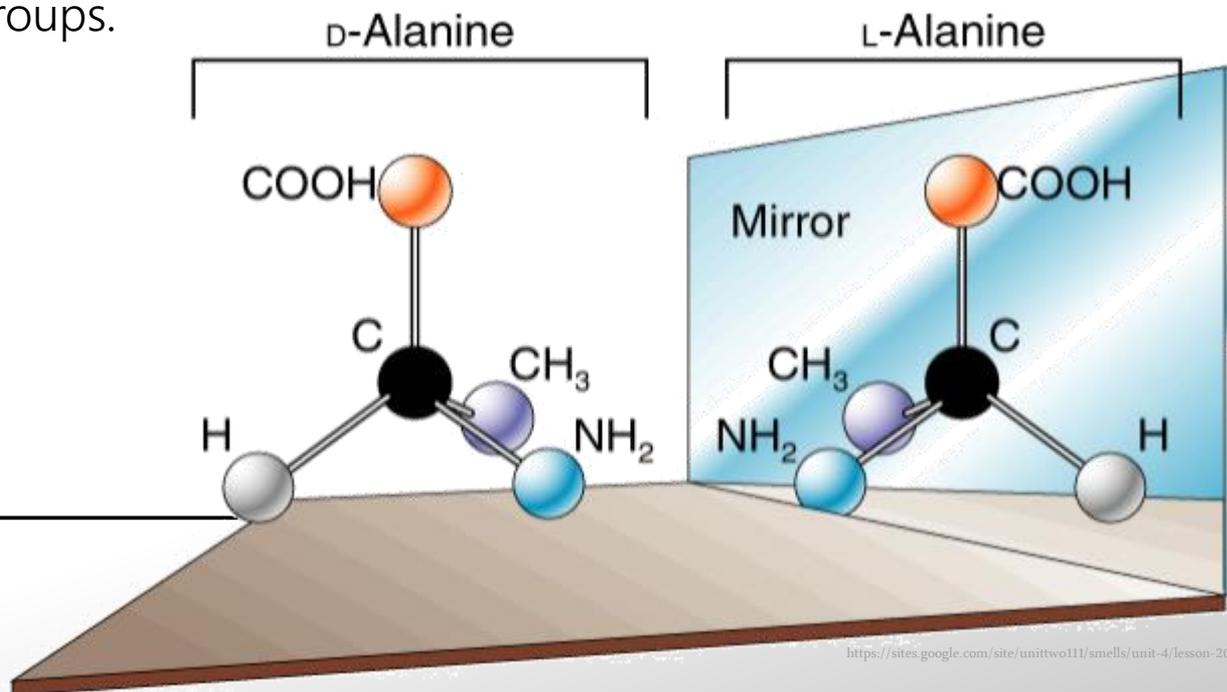
- (i) The *cis* or *trans* prefix must be included when naming these alkenes.
- (ii) Bond angles around a double bonded C are  $120^\circ$ ; and the shape is trigonal planar
- (iii) Bond angles around the triple bonded C found in an alkyne are  $180^\circ$ , shape is linear.

## Optical Isomers or Enantiomers

Optical isomers (like geometric isomers) are examples of stereoisomers. The enantiomer and its mirror image are non-identical. All amino acids, (except the simplest amino acid, glycine), are optically active. This means they contain an **asymmetric**, or **chiral**, carbon atom. This is a carbon atom, which has four different groups attached.

To show the different enantiomers of a molecule it is necessary to draw a 3-dimensional structure.

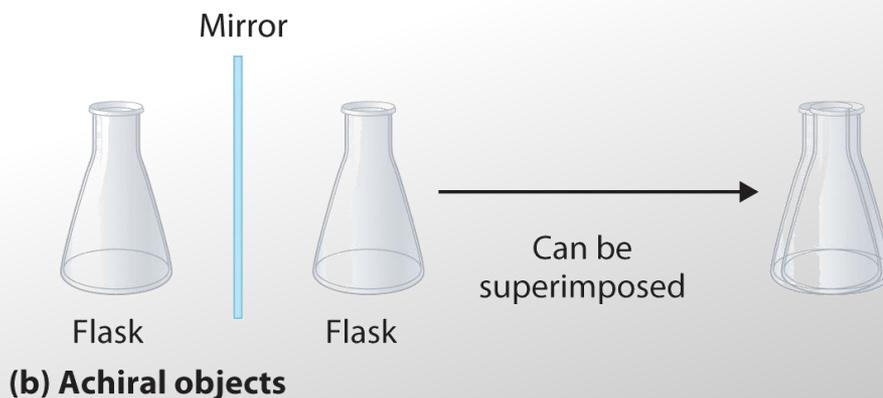
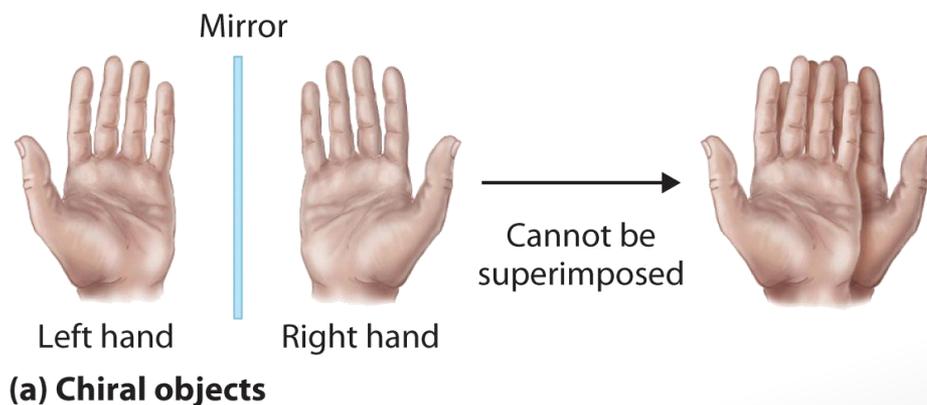
For any enantiomer, the structure of the mirror image can be drawn by swapping **any two** groups.



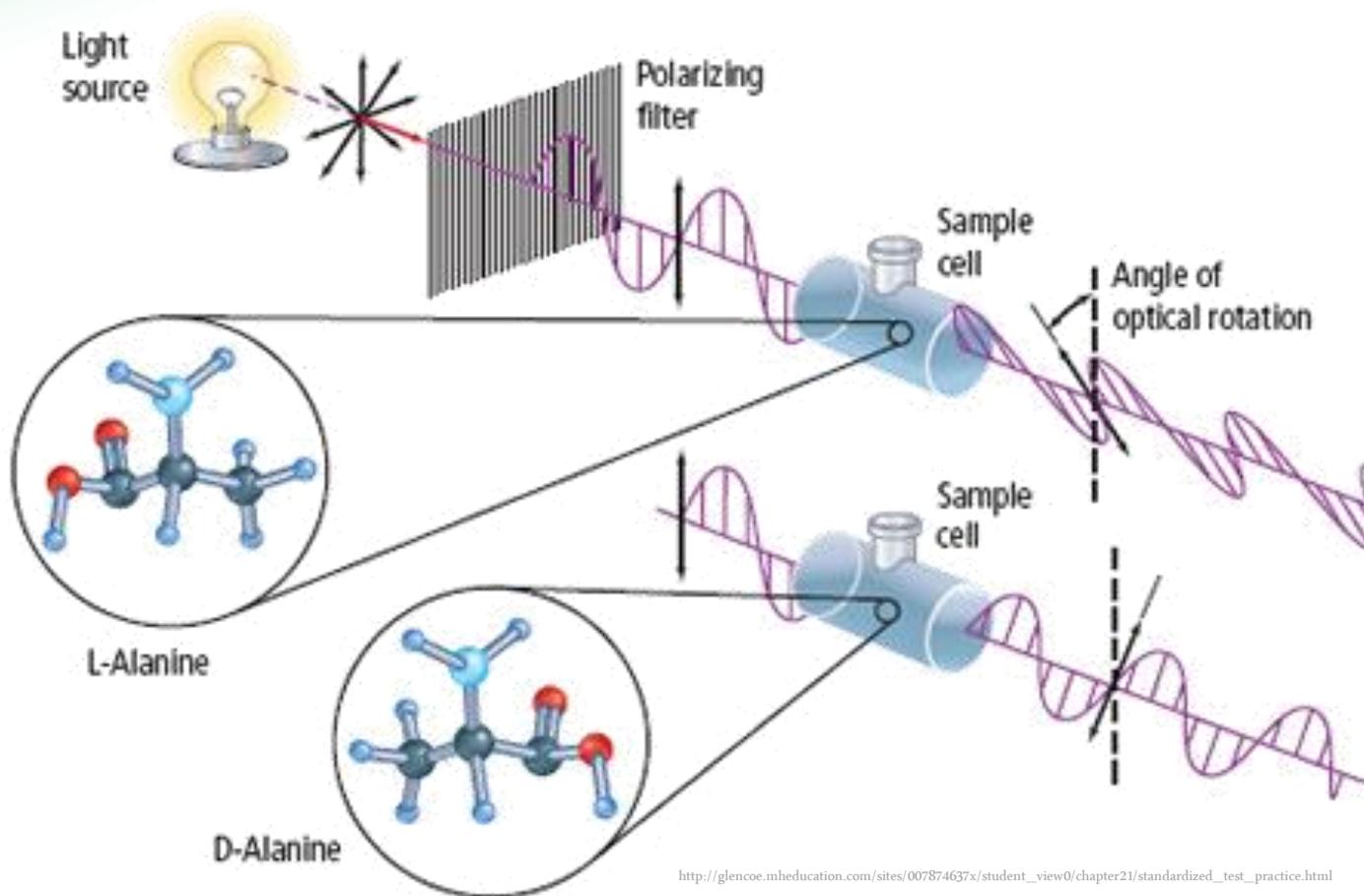
A chiral molecule is a type of molecule that lacks an internal plane of symmetry and has a non-superimposable mirror image. The feature that is most often the cause of chirality in molecules is the presence of an asymmetric carbon atom.

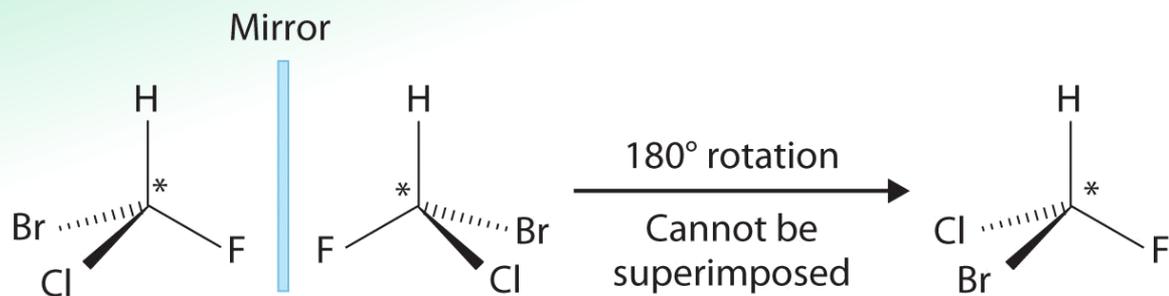
The term chiral (pronounced in general is used to describe an object that is non-super imposable on its mirror image.

Achiral (not chiral) objects are objects that are identical to their mirror image. In chemistry, chirality usually refers to molecules. Two mirror images of a chiral molecule are called enantiomers or optical isomers. Pairs of enantiomers are often designated as "right-" and "left-handed."

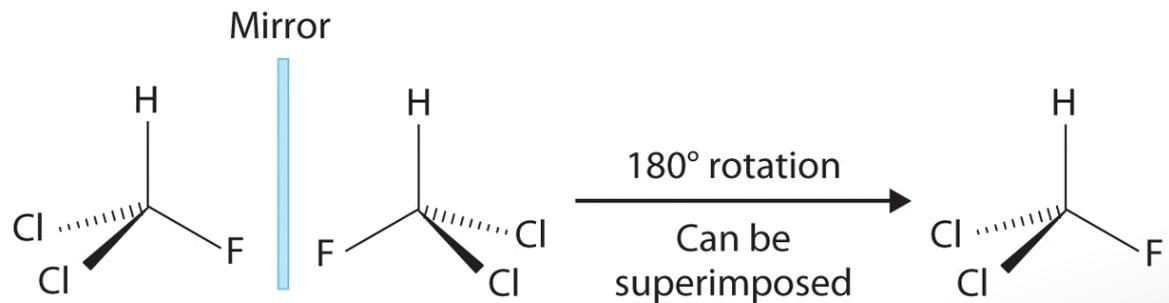


Enantiomers have identical physical properties (melting point, solubility etc.) BUT differ in that they **rotate** plane polarised light in opposite directions.





(a) Bromochlorofluoromethane



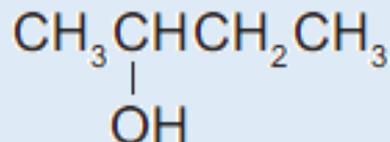
(b) Dichlorofluoromethane

Optical isomers cannot be superimposed. If two of the groups are the same around the chiral carbon then the molecule can be turned 180° and be superimposed therefore it is not an optical isomer.

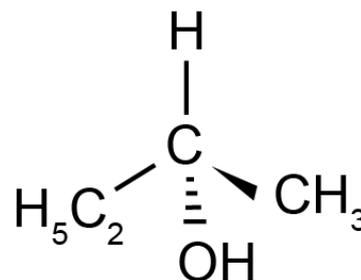
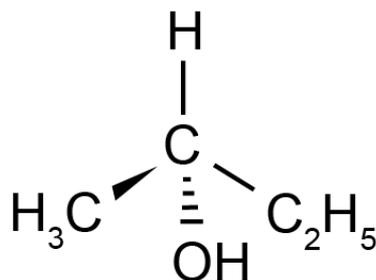
## NCEA 2013 Optical Isomers

Merit  
Question

**Question 1b:** (i) The alcohol below can exist as two enantiomers (optical isomers).



(i) Draw three-dimensional structures for the two enantiomers.



**Question 1b:** (ii) Link the structure of enantiomers to a physical property that can be used to distinguish them from non-optically active molecules.

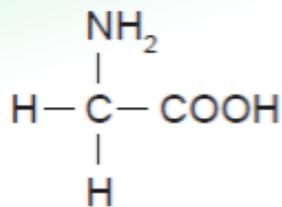
Enantiomers exist for atoms containing a carbon atom with 4 different groups attached / Non-optically active substances do not have any carbon with 4 different groups attached.

Enantiomers rotate (plane) polarised light in opposite directions.

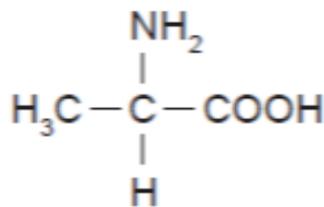
# NCEA 2016 Optical Isomers

Merit  
Question

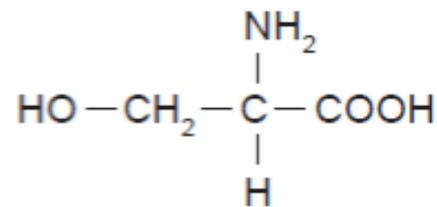
Question 1c: (i) Glycine, alanine, and serine are three amino acids shown below.



glycine

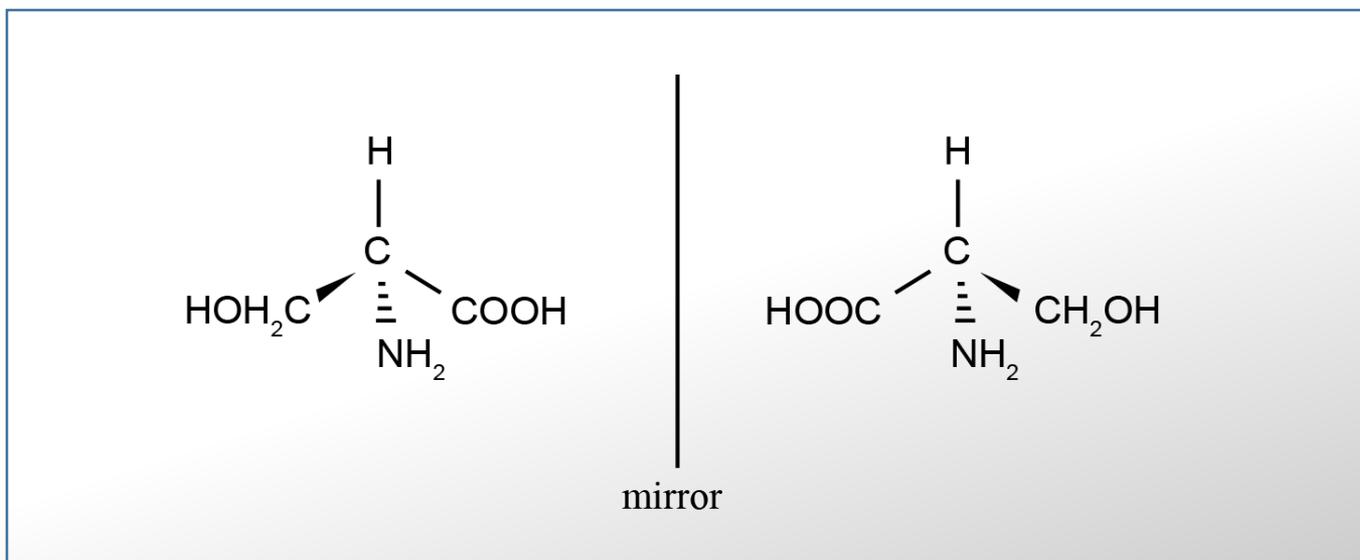


alanine



serine

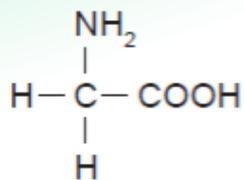
Draw the 3-D structures of the enantiomers (optical isomers) of **serine** in the boxes below.



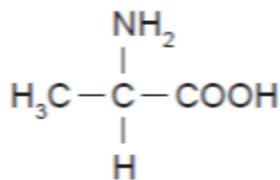
# NCEA 2016 Optical Isomers

Merit  
Question

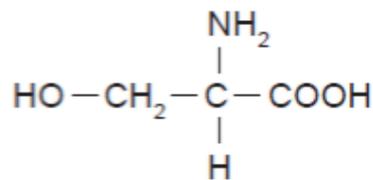
Question 1c: (ii) Which amino acid below which does NOT display optical isomerism: Explain your answer



glycine



alanine



serine

Glycine.

It does NOT have a chiral C, i.e. it needs four different groups around the central C atom, glycine only has three

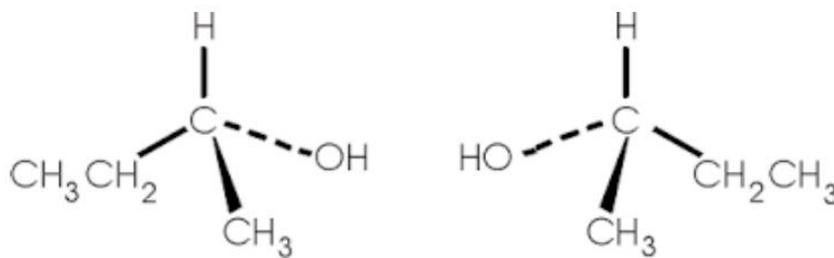


## NCEA 2017 Optical Isomers

Excellence  
Question

**Question 1c: (i)** Some organic compounds can exist as enantiomers (optical isomers). An example is a secondary alcohol with the molecular formula  $C_4H_9OH$ .

(i) Draw the enantiomers of  $C_4H_9OH$  below.



**Question 1c: (ii)** Explain what is meant by the term enantiomers (optical isomers). In your answer, you should:

- identify the structural requirement for a molecule, such as  $C_4H_9OH$ , to exist as enantiomers
- explain how enantiomers can be distinguished from each other.

There must be a carbon atom that has **four different species (groups)** attached to it. This creates two molecules that are **mirror images** of each other that are **nonsuperimposable**.

The different isomers will **rotate (plane)-polarised light in opposite directions**. This will distinguish the isomers.

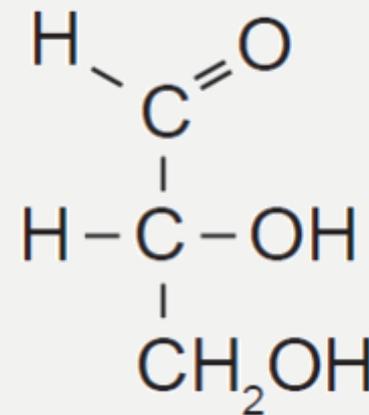
# NCEA 2018 Optical Isomers

Merit  
Question

**Question 2a:** The structural formula of 2,3-dihydroxypropanal, more commonly known as glyceraldehyde, is shown below.

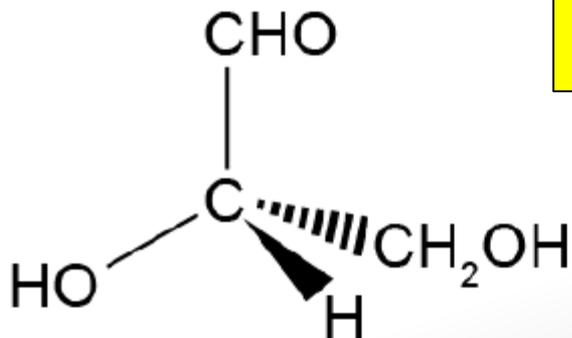
Glyceraldehyde can exist as enantiomers (optical isomers).

(i) Draw the enantiomers of glyceraldehyde

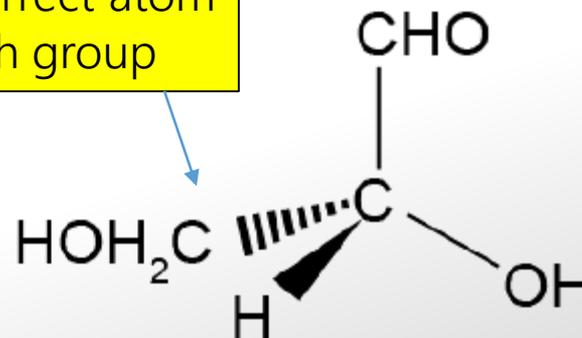


Names not  
required for  
correct answer

Note the chiral  
carbon  
connected to  
the correct atom  
in each group



L-Glyceraldehyde



D-Glyceraldehyde

# NCEA 2018 Optical Isomers

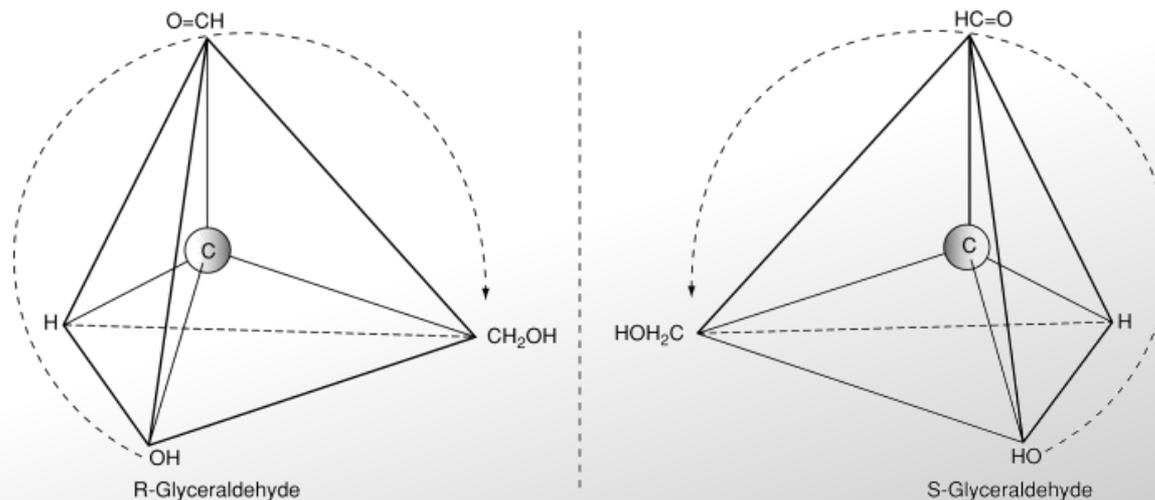
Merit  
Question

## Question 2a:

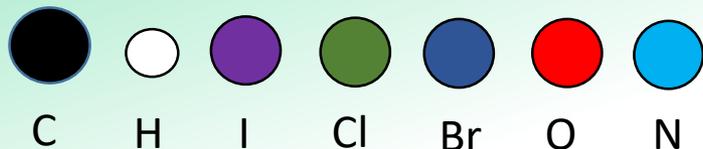
- (ii) Explain why glyceraldehyde can exist as enantiomers.  
(iii) How could the two enantiomers of glyceraldehyde be distinguished? Explain your answer.

(ii) Glyceraldehyde can exist as enantiomers because it has an asymmetric carbon atom, i.e. a carbon atom with four different groups attached.

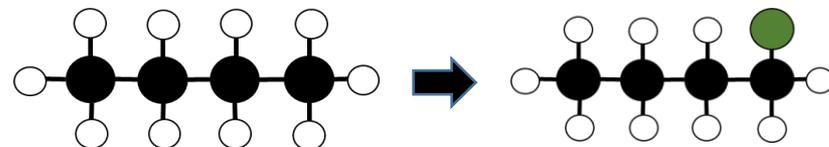
(iii) The enantiomers can be distinguished based upon their ability to rotate plane polarised light. One enantiomer will rotate the plane polarised light to the left while the other enantiomer will rotate the plane polarised light to the right.



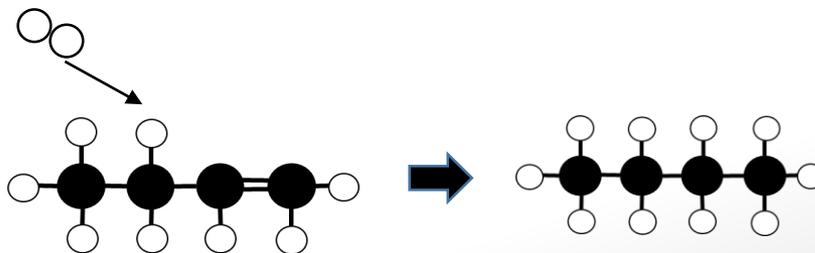
# Reaction types (1)



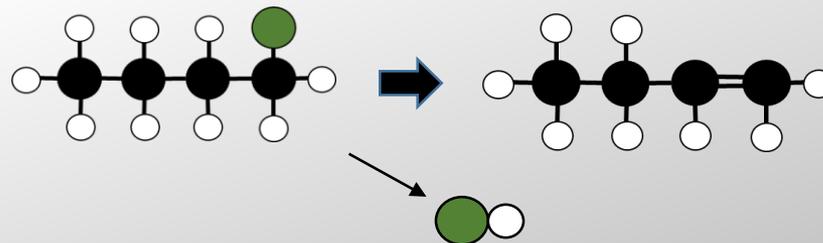
**Substitution** reactions are characterized by replacement of an atom or group (Y) by another atom or group (Z). Aside from these groups, the number of bonds does not change.



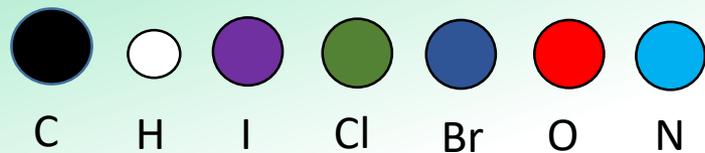
**Addition** reactions increase the number of bonds to the Carbon chain by bonding additional atoms, usually at the expense of one or more double bonds.



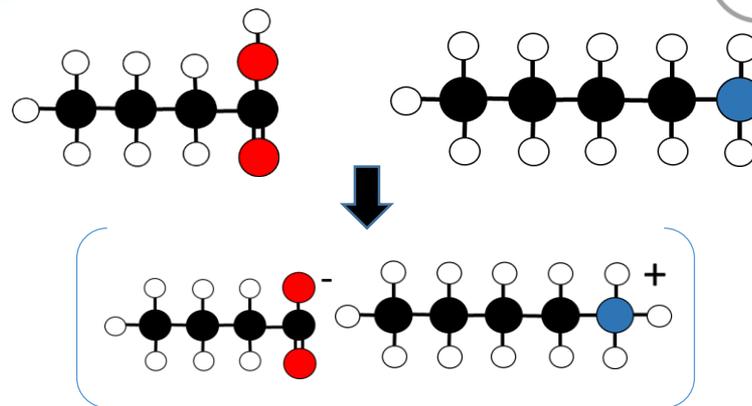
**Elimination** reactions decrease the number of single bonds by removing atoms and new double bonds are often formed.



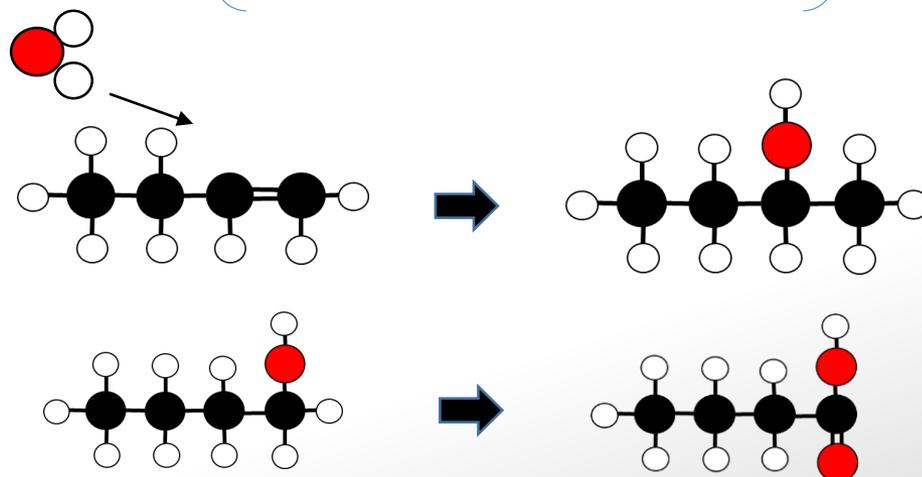
## Reaction types (2)



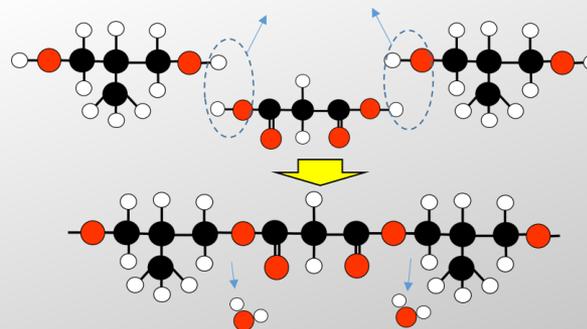
**Acid Base Reactions** involve the transfer of a proton from the acid to the base which produces a salt



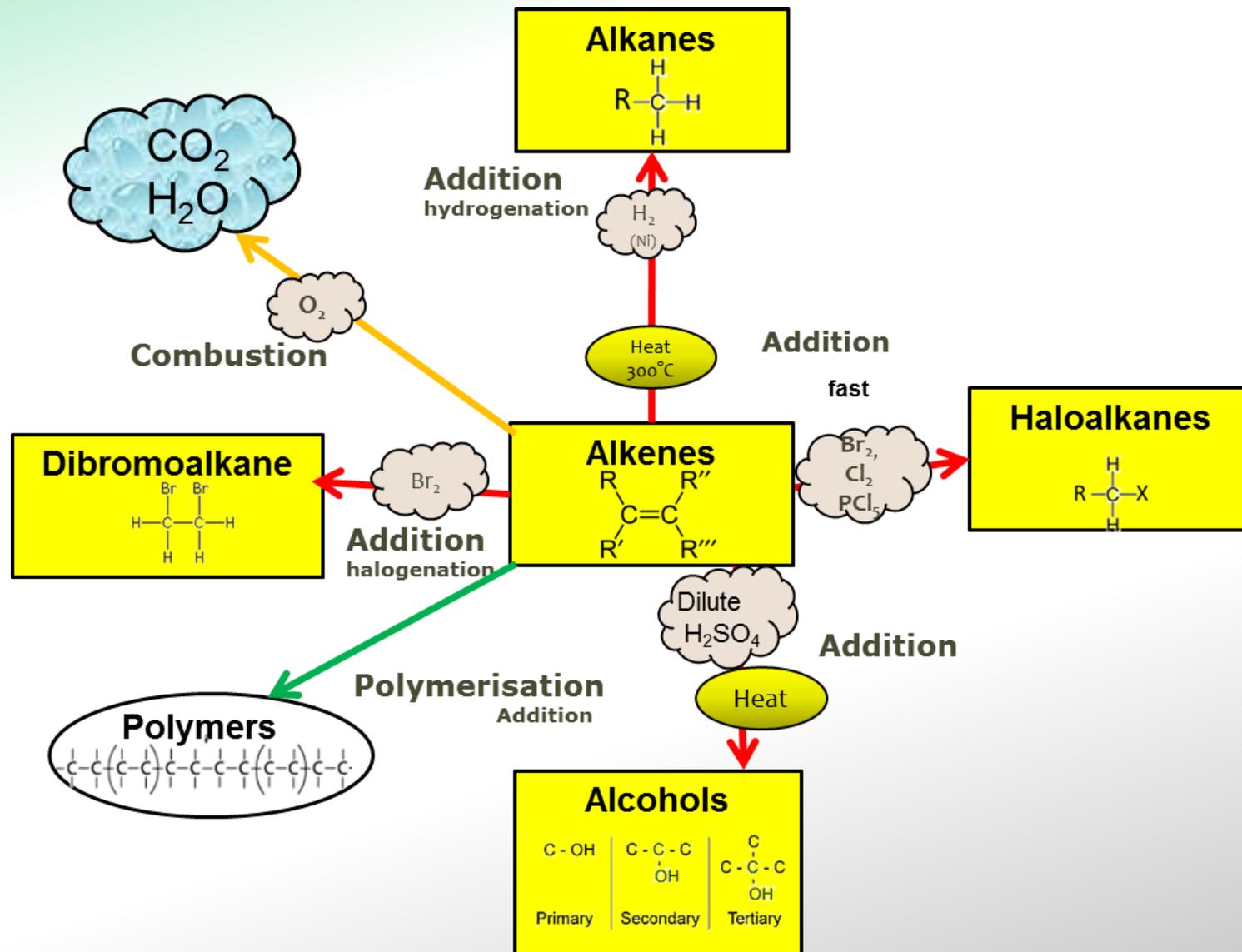
**Oxidation** reactions involve a loss of electrons from the organic molecule or a gain of oxygen. An oxidant such as dichromate or permanganate is used to make a diol (2 OH) or dilute acid to make an alcohol (1 OH)



**Polymerisation** reactions join monomers together to form a polymer. **Condensation polymerisation** removes a small molecule and joins monomers

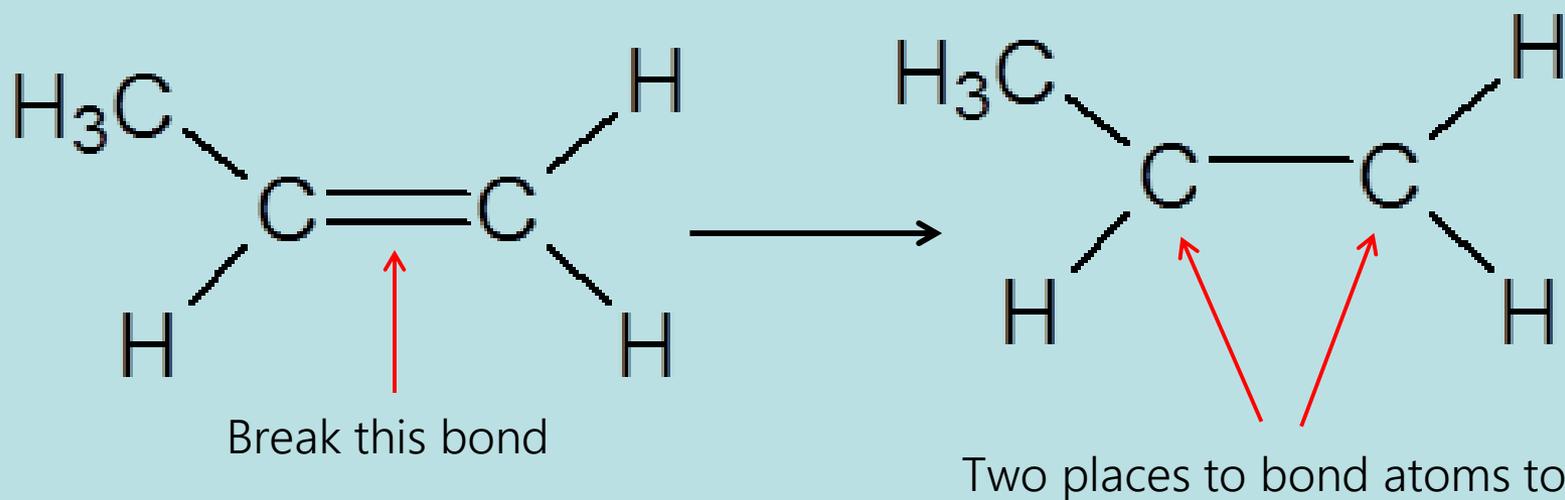


# Alkene reactions



Alkenes are **unsaturated** molecules, where not every carbon atom has the maximum amount of atoms bonded to it because it has one or more double bonds. If another atom is added to an alkene, the double bond can be broken down to a single bond and another atom can occupy the available site.

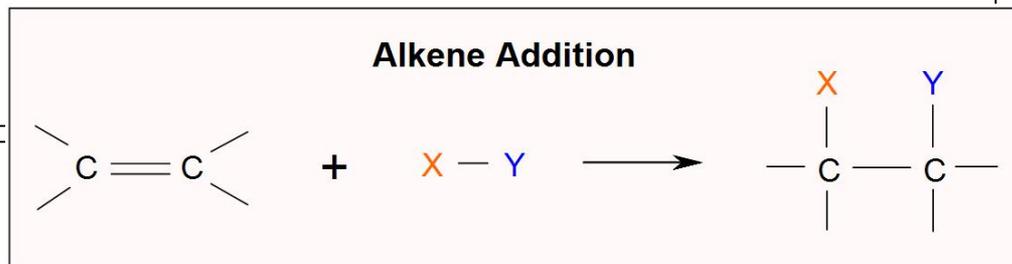
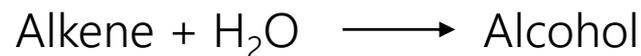
This reaction is known as an **addition** reaction. This reaction has a lower activation energy requirement than substitution, therefore it requires less energy to break a double bond than break a C-H bond, and it can proceed easier than a substitution reaction.



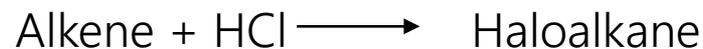
## 1. Hydrogenation



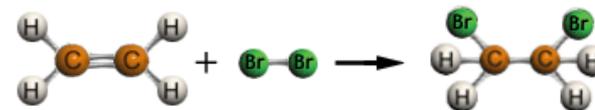
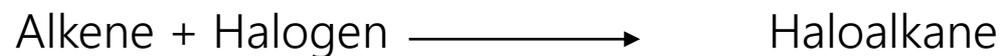
## 2. Hydration



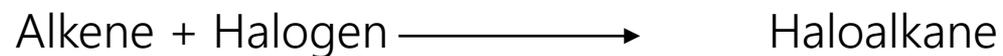
## 3. Reaction with HCl



## 4. Halogenation (Bromine/Chlorine)



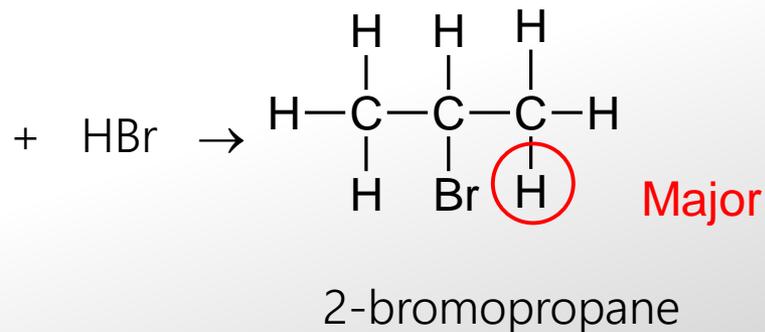
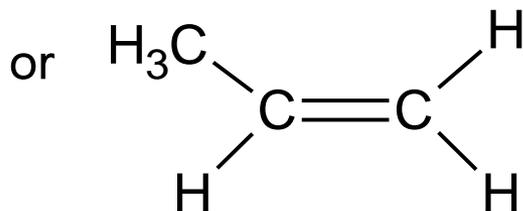
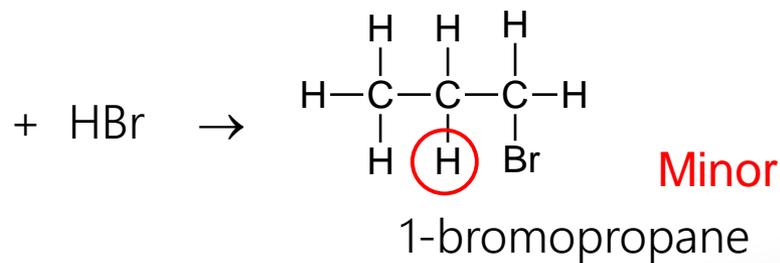
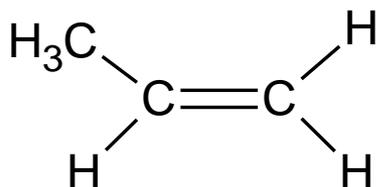
## 5. Oxidation (oxidant)



Markovnikov's rule - sometimes called the "rich get richer" rule

The **major** product is the one in which the H atom of HBr attaches to the C atom with the **most H atoms** already

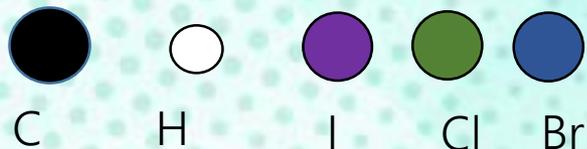
Asymmetric molecules such as HCl and H<sub>2</sub>O can also be added to alkenes resulting in the formation of **two** possible products.



As an easy way to remember:  
The Major is 2° product (larger)  
and minor is 1°

# Addition Reaction - HCl or HBr to unsymmetrical Alkenes to produce a haloalkane

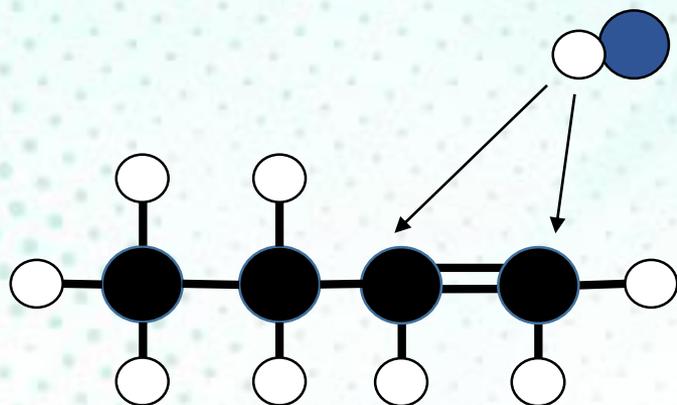
3



**Addition** reactions increase the number of bonds to the Carbon chain by bonding additional atoms, usually at the expense of one or more double bonds.

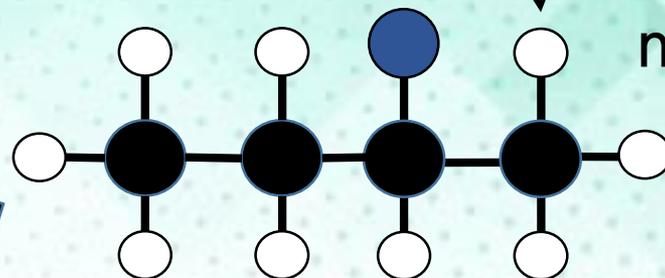
## Markovnikov's rule

The **major** product is the one in which the H atom of HBr attaches to the C atom with the **most H atoms** already.



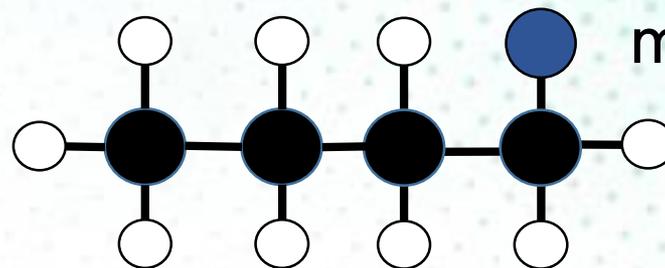
Prop-1-ene

An asymmetric molecules breaks apart into two different atoms. i.e. HCl into H and Cl atoms



major

2-bromo propane



minor

1-bromo propane

# Addition Reaction - H<sub>2</sub>O (acidified) to unsymmetrical Alkenes to produce an alcohol

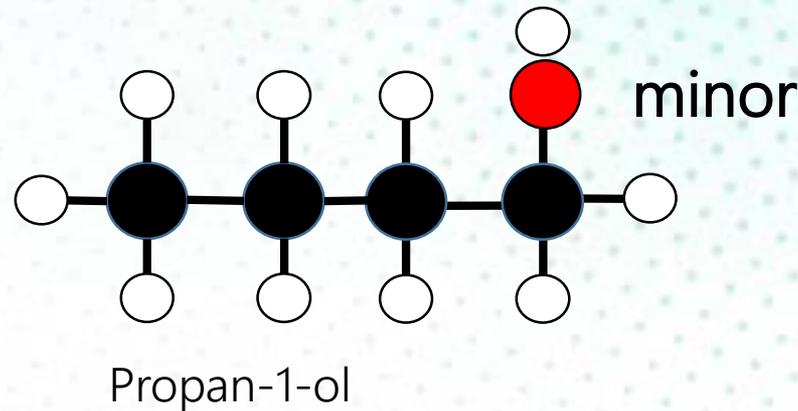
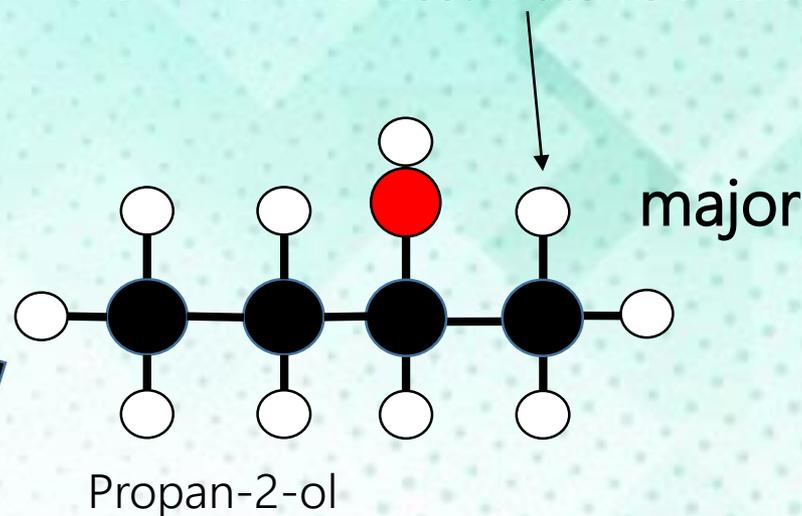
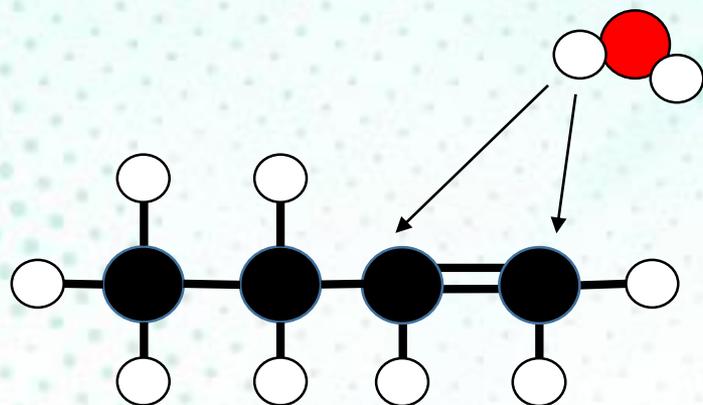
3



The asymmetric molecules of water H<sub>2</sub>O breaks apart into two different atoms. i.e. H and OH atoms

## Markovnikov's rule

The **major** product is the one in which the H atom of H<sub>2</sub>O attaches to the C atom with the **most H atoms** already.



A helpful reminder is that major is greater than minor, so 2 is greater than 1 (propan-2-ol vs propan-1-ol)

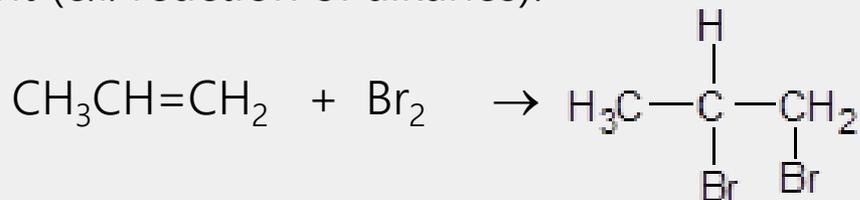
## Testing for alkanes and alkenes



Background  
Knowledge

Alkenes and alkynes undergo **addition** reactions - this means they can undergo addition of a halogen across the double (or triple) bond to form a di-haloalkane (or tetra-haloalkane).

The common test for an unsaturated hydrocarbon is therefore the **rapid** decolourisation of an orange solution of bromine. This occurs both in the presence or absence of sunlight (c.f. reaction of alkanes).

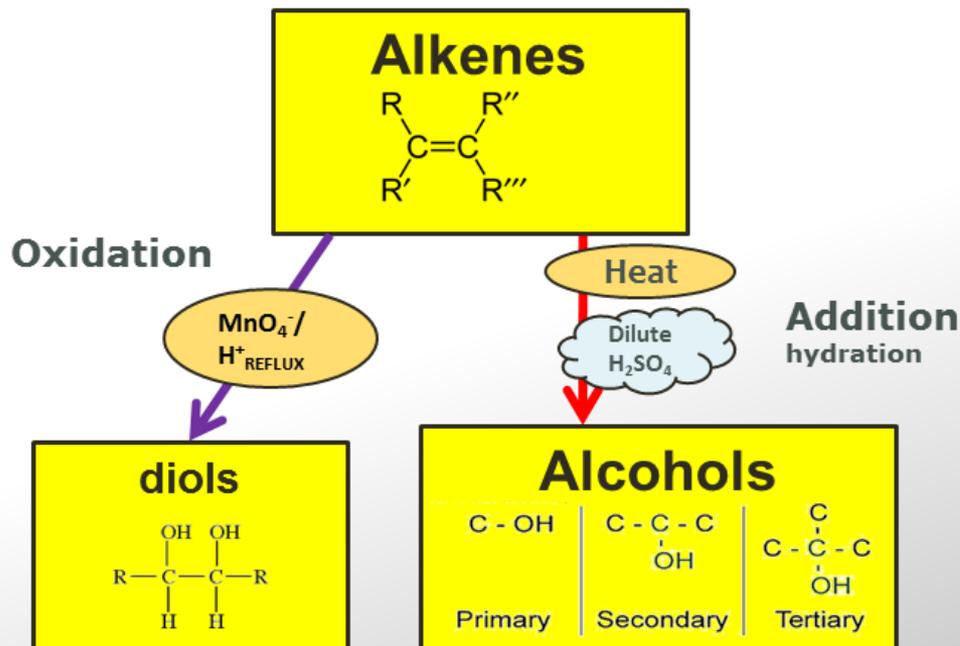


1,2-dibromopropane

An alternative test to distinguish alkenes from alkanes is the reaction of alkenes with potassium permanganate. In acid solution the purple permanganate ion,  $\text{MnO}_4^-$ , is reduced to colourless manganese ion,  $\text{Mn}^{2+}$ , while in neutral solution it is reduced to brown manganese dioxide,  $\text{MnO}_2$ . Alkanes have no reaction with potassium permanganate so the solution remains purple.

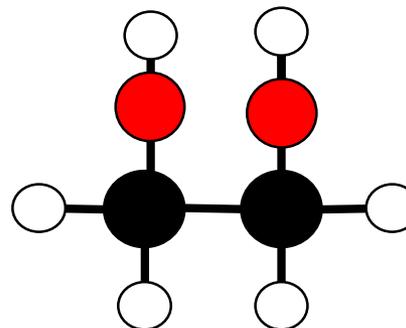
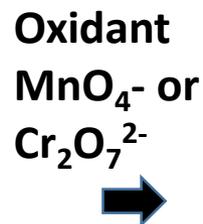
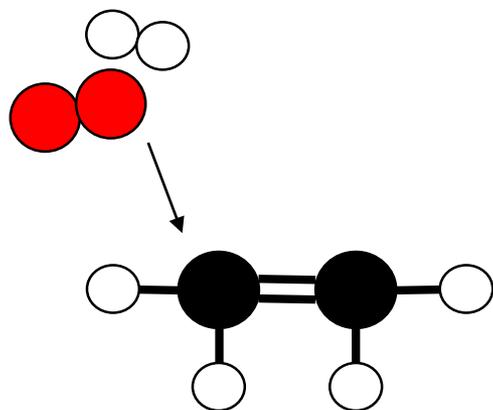
Alkenes can also undergo an **oxidation** reaction (this could also be classified as an addition reaction). The reagent is an oxidant, potassium permanganate (acidified),  $\text{MnO}_4^-/\text{H}^+$ , performed under reflux conditions. The reaction creates a diol. Two hydroxyl groups join onto the carbons on either end of the broken double bond.

Compare this to the addition reaction that which occurs with dilute acid added to an alkene. Only a single hydroxyl group is added to make an alcohol.

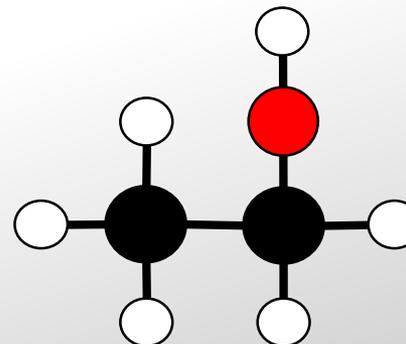
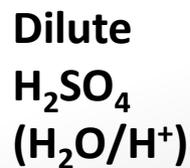
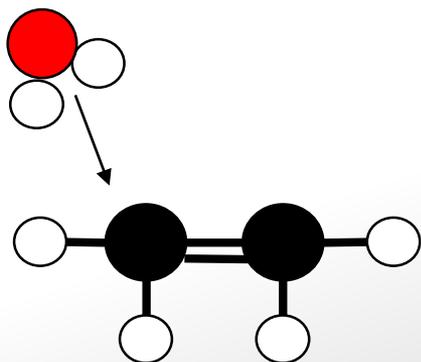




Oxidation reactions involve a loss of electrons from the organic molecule or a gain of oxygen. An oxidant such as dichromate or permanganate is used to make a diol (2 OH) or dilute acid to make an alcohol (1 OH)



diol



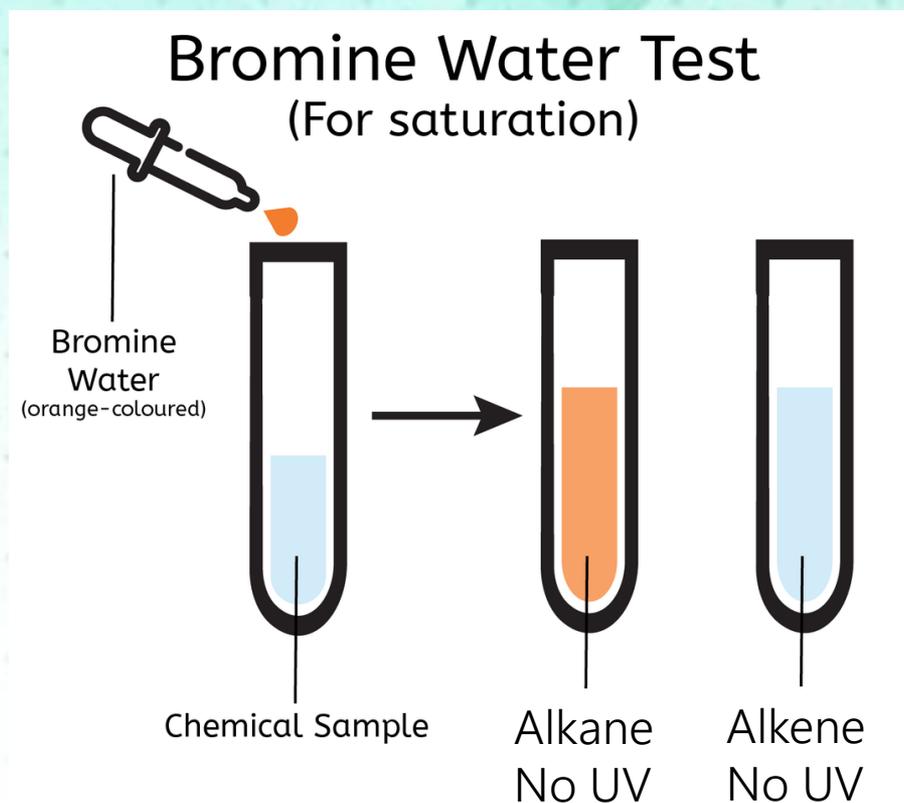
alcohol

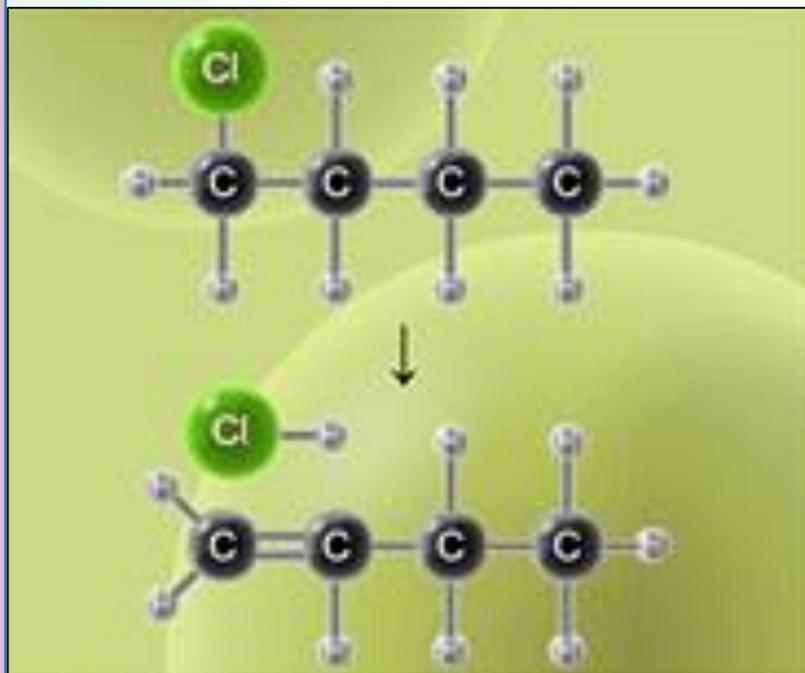
# Testing for Addition and Substitution reactions

Alkenes undergo **addition** reactions - this means they can undergo addition of a halogen atom (chlorine, bromine, iodine) across the double bond to form a haloalkane.

The common test for an unsaturated hydrocarbon (alkene) to distinguish it from a saturated hydrocarbon (alkane) is the **rapid** decolourisation of an orange solution of bromine in the **addition reaction of an alkene**.

This occurs much **slower** in the **substitution reaction of an alkane** and requires the presence of **UV light** (sunlight) to provide the activation energy to break the bond of the C-H





Elimination reactions decrease the number of single bonds by removing atoms and new double bonds are often formed.

In **alcohols** the elimination reaction, using concentrated  $\text{H}_2\text{SO}_4$  and heat, removes a  $\text{H}_2\text{O}$  molecule and forms an alkene.

In **haloalkanes** the Halogen atom is removed and a double bond forms between the two carbon atoms.

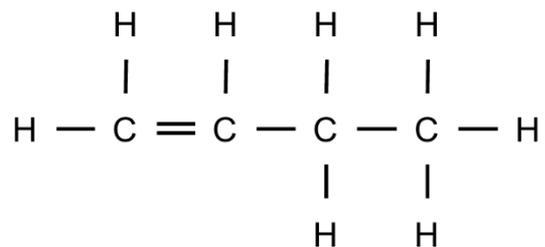
Elimination of Haloalkanes is favoured when the solvent used is less polar e.g. **alcoholic** (rather than aqueous) **KOH**. The reagent may be referred to as either ethanolic KOH,  $\text{KOH} / \text{CH}_3\text{CH}_2\text{OH}$  or  $\text{OH}^-$  in alcohol. The reaction also occurs more favourably with tertiary haloalkanes rather than primary.

# Haloalkane Elimination – major and minor products

## Saytzeff's rule (poor get poorer)

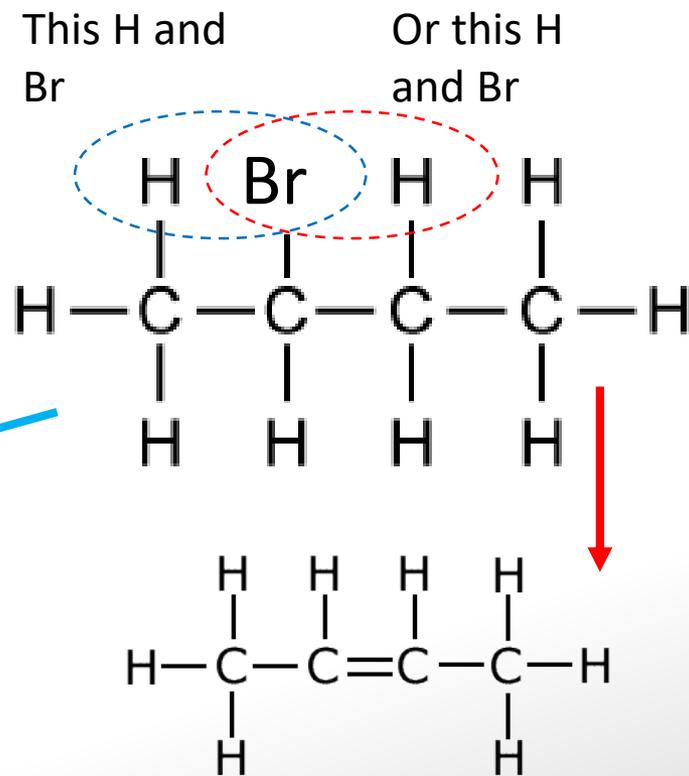
4

When an elimination reaction occurs on a **secondary haloalkane** (with more than 3 carbons in the longest chain) then the H removed along with the halogen (Cl/Br) can come from either side. This produces 2 types of products; major or minor.



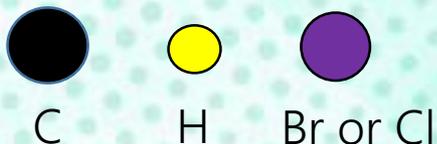
But-1-ene

**Minor product** as the H is taken from the Carbon with the most hydrogen atoms.

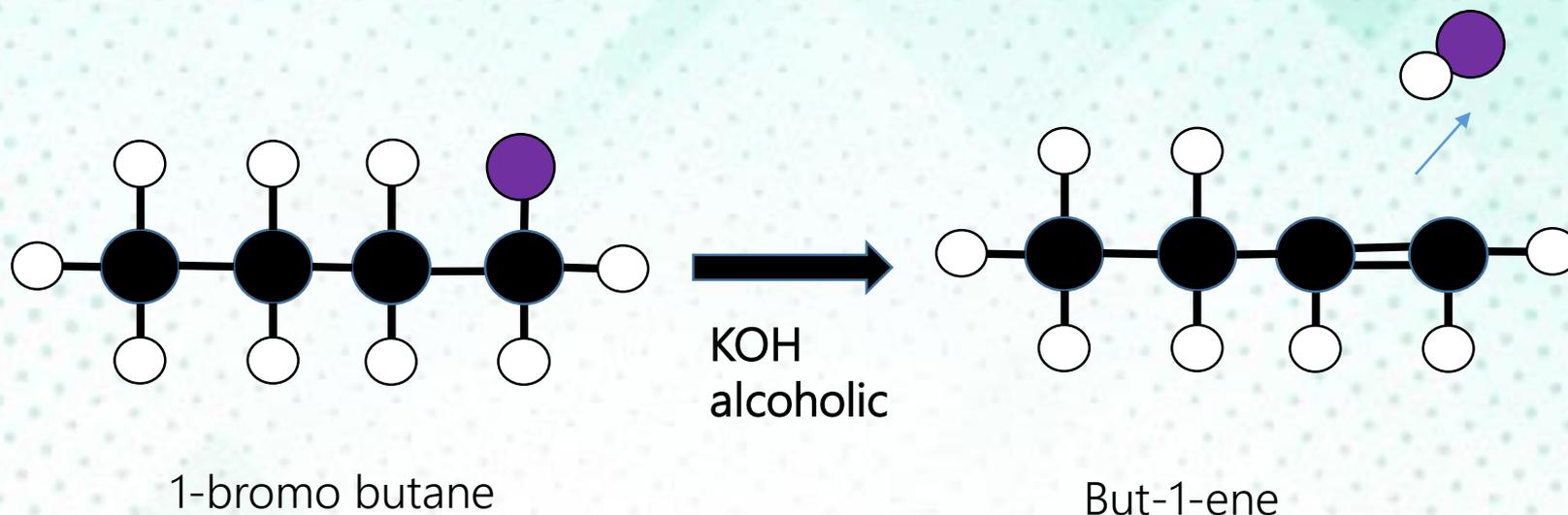


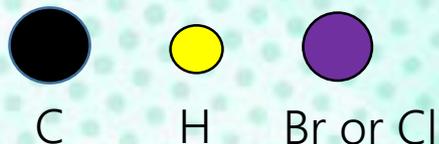
But-2-ene

**Major product** as the H is taken from the Carbon with the least hydrogen atoms (can be cis or trans)



Elimination reactions decrease the number of single bonds by removing atoms and new double bonds are often formed. The Halogen atom is removed and a double bond forms between the two carbon atoms.

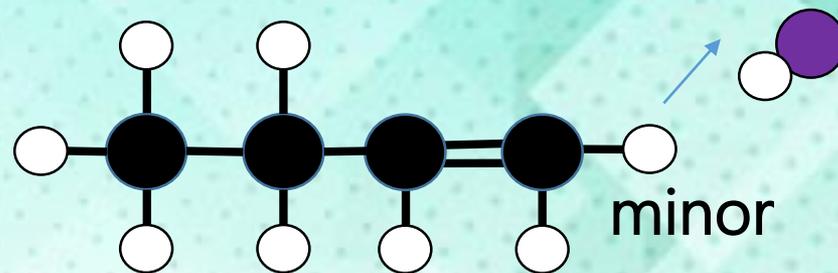




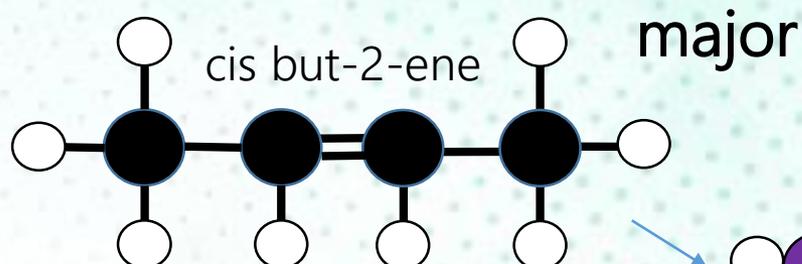
More than one product will be formed. The alkene will form a major and minor product. The newly formed (major) alkene may also form a cis and trans geometric isomer.

Another product, the removed halogen will join with a removed hydrogen atom to form a hydrogen halide i.e. HCl or HBr.

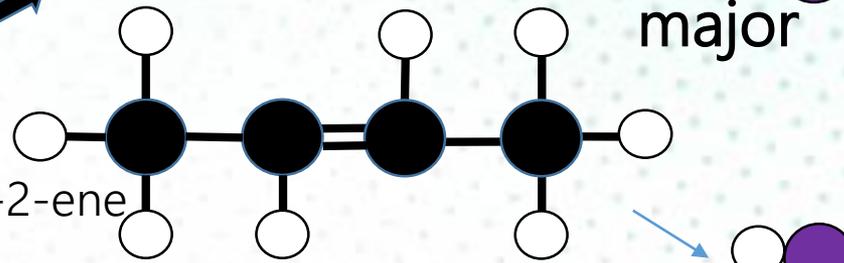
Elimination reactions decrease the number of single bonds by removing atoms and new double bonds are often formed.



But-1-ene

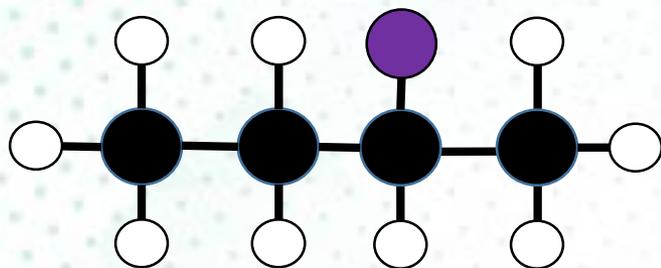


major



KOH  
alcoholic

trans but-2-ene



2-bromo butane

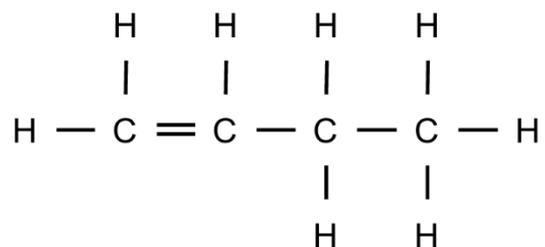
## Elimination – using conc. Sulfuric acid (catalyst)

Alcohol +  $\text{H}_2\text{SO}_4$  heated  $\longrightarrow$  Alkene



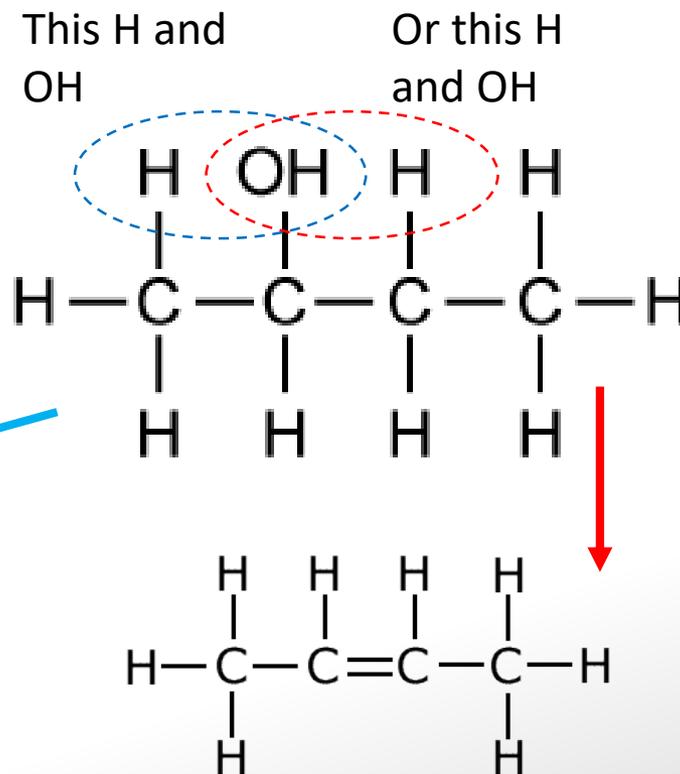
**Elimination** reactions occur when the hydroxyl group (OH) plus a hydrogen from an adjacent (beside) carbon atom is removed. The OH and the H removed form a water molecule. The two carbons with the OH and H taken off join to form a double one. A concentrated sulphuric acid is used as the reagent. This type of elimination reaction is also known as a dehydration reaction because water is removed.

When an elimination reaction occurs on an **asymmetrical secondary** alcohol (with more than 3 carbons in the longest chain) then the H removed along with the OH can come from either side. This produces 2 types of products; major or minor.



But-1-ene

**Minor product** as the H is taken from the Carbon with the most hydrogen atoms.

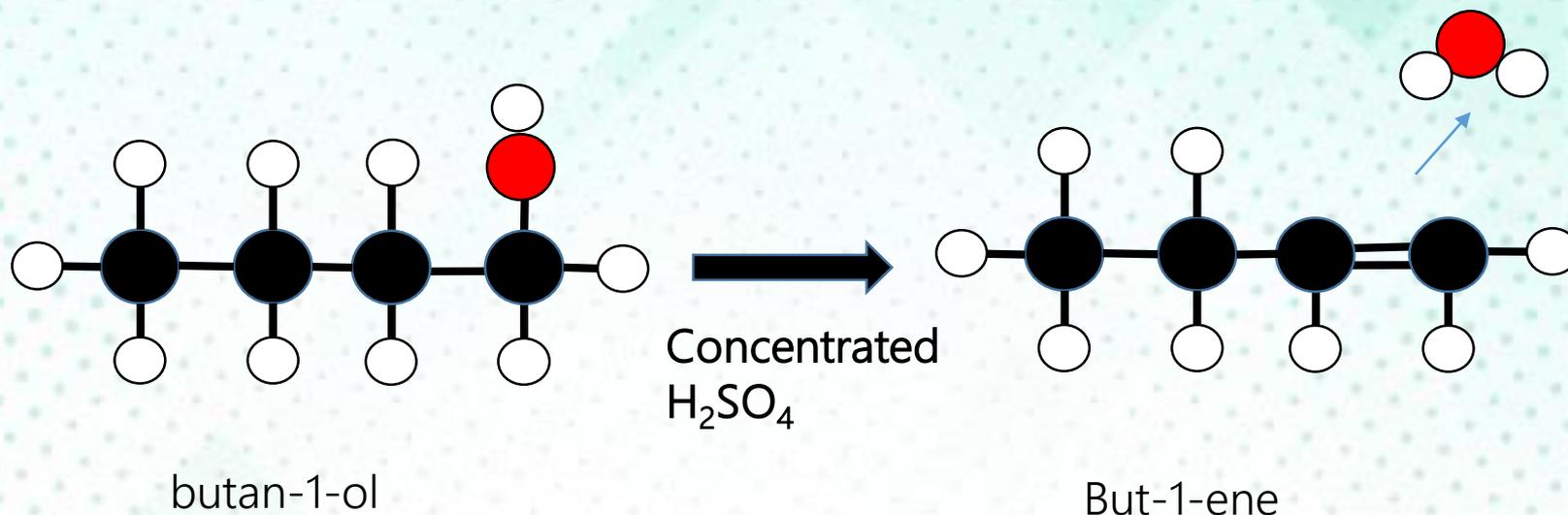


But-2-ene

**Major product** as the H is taken from the Carbon with the least hydrogens atoms (can be cis or trans)



Elimination reactions decrease the number of single bonds by removing atoms and new double bonds are often formed. The Halogen atom is removed and a double bond forms between the two carbon atoms.

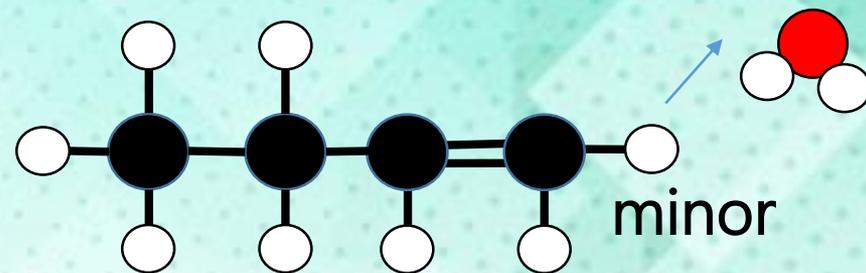




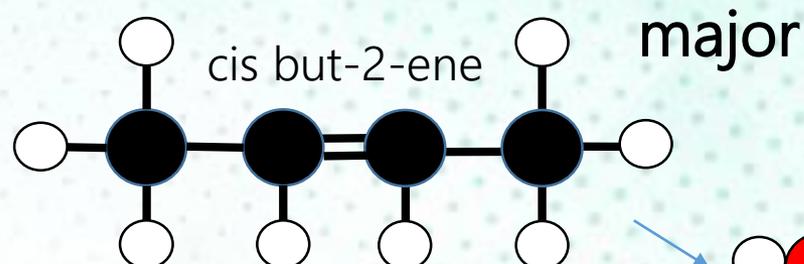
Elimination reactions decrease the number of single bonds by removing atoms and new double bonds are often formed.

More than one product will be formed. The alkene will form a major and minor product. The newly formed (major) alkene may also form a cis and trans geometric isomer.

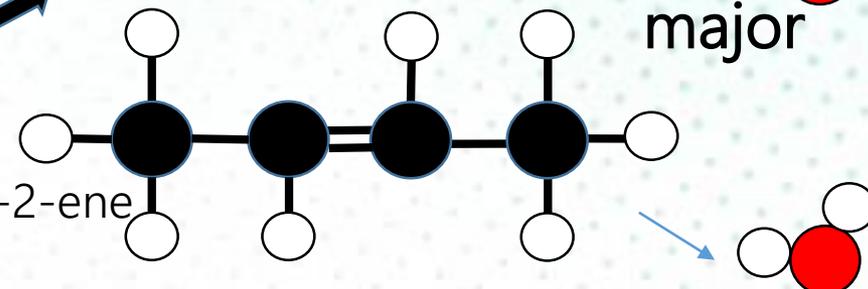
Another product, the removed OH will join with a removed hydrogen atom to form a water molecule



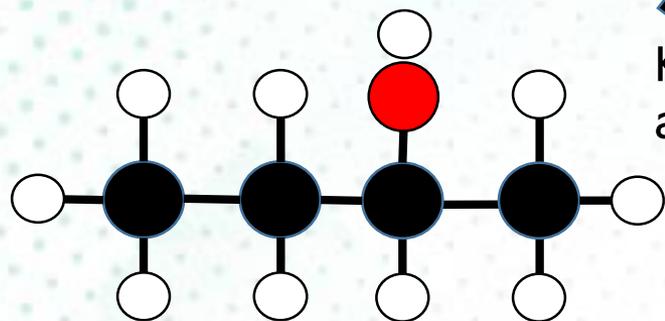
But-1-ene



cis but-2-ene



trans but-2-ene



2-bromo butane

KOH  
alcoholic

## NCEA 2013 Elimination Reactions (Alcohol)

Excellence  
Question

**Question 2a:** (ii) Butan-2-ol is converted to a mixture of but-1-ene and but-2-ene.

Reagent: conc  $\text{H}_2\text{SO}_4$  / conc  $\text{H}_3\text{PO}_4$  /  $\text{Al}_2\text{O}_3$

Type of reaction – elimination / dehydration / condensation

Discuss the reaction occurring in (ii) above, with reference to the structures of the organic reactant and products.

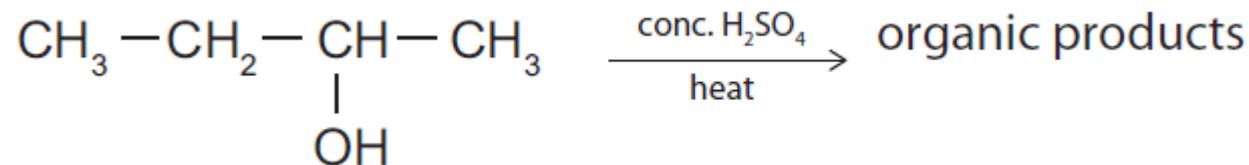
Explanation:

- An elimination reaction occurs because the molecule has changed from saturated to unsaturated / a (C=C) double bond forms.
- Because water is removed / H and OH have been removed (from adjacent C atoms).
- The but-2-ene is the major product / but-1-ene is the minor product.
- A mixture of products is formed, because the two carbons adjacent to the carbon-bearing OH have different numbers of H atoms attached / it is asymmetric.  
(Zaitsev's (Saytzeff's) rule – the major product has the more substituted double bond)

# NCEA 2014 Elimination Reactions (Alcohol)

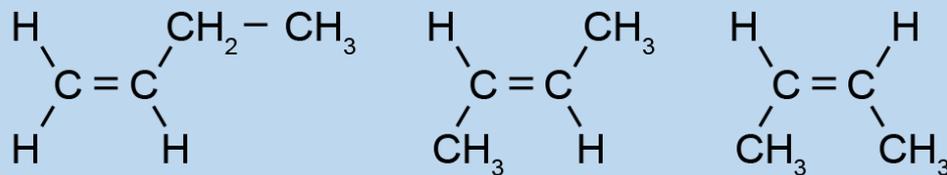
Excellence  
Question

**Question 1(b)** When butan-2-ol undergoes a reaction with concentrated  $\text{H}_2\text{SO}_4$ , three possible organic products form, which are isomers of each other.



- (i) Draw the three isomers formed during this reaction.  
 (ii) Which of the three isomers from part (i) will be formed in the smallest amount?

**Answer:**



in lowest concentration

**Answer:** The minor product is but-1-ene.

Saytzeff's rule: the minor product will have the least substituted double bond OR Saytzeff's rule is explained.

Eg: the minor product is formed by the removal of the OH group and a hydrogen atom is removed from the carbon adjacent to the C-OH that has the most hydrogens

**Question 1(c) (ii)** : Elaborate on the reactions occurring when each of the haloalkane isomers from (c)(i) reacts with KOH in alcohol.

In your answer you should include:

- the identification of ALL organic products formed
- an explanation of the type of reaction taking place
- reasons for the formation of any major and minor products.

**Answer:**  $\text{Cl-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 \rightarrow \text{H}_2\text{C}=\text{CH-CH}_2\text{-CH}_3$

$\text{H}_3\text{C-CH(Cl)-CH}_2\text{-CH}_3 \rightarrow$  two possibilities:

1. Minor  $\text{H}_2\text{C}=\text{CH-CH}_2\text{-CH}_3$  but-1-ene
2. Major  $\text{H}_3\text{C-CH}=\text{CH-CH}_3$  *cis* but-2-ene and *trans* but-2-ene (in equal quantities).

$\text{H}_3\text{C-CCl(CH}_3\text{)CH}_3 \rightarrow \text{C(CH}_3\text{)(CH}_3\text{)=CH}_2$

All reactions are **ELIMINATION** reactions as the Cl functional group and the hydrogen atom from the adjacent carbon atoms are removed.

(The molecule changes from saturated to unsaturated).

The secondary haloalkane produces major and minor products because the molecule is asymmetric OR it has two adjacent C atoms with different numbers of H atoms attached. The major product is formed when the H atom is removed from the adjacent C atom with the fewest H atoms attached,

OR the major product has the most substituted double bond.

## NCEA 2018 Elimination Reactions (part ONE)

Excellence  
Question

**Question 1c:** Unknown X has the molecular formula  $C_4H_8O_3$  and undergoes the following reactions:

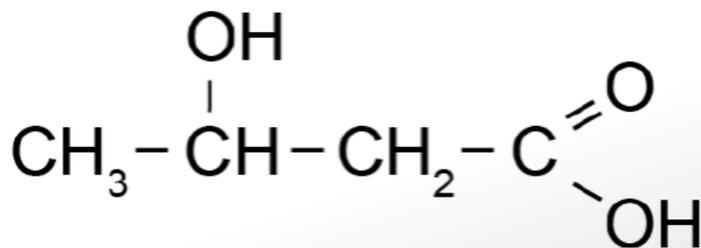
- It reacts with sodium carbonate solution to release carbon dioxide gas.
- When X is heated with acidified potassium dichromate, the colour changes from orange to green, but the product does not react with Benedict's solution.
- X undergoes an elimination reaction with concentrated sulfuric acid to produce two organic products.

Based on the information above, draw the structural formula of Unknown X.

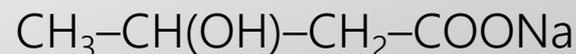
Justify your structural formula of X, including:

- structural formulae of any organic products
- an explanation of any major and minor products.

Unknown X has the structural formula below:



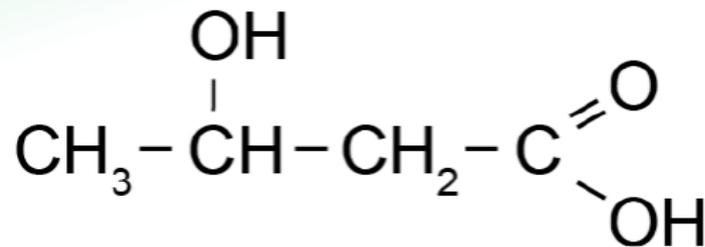
There must be a carboxylic acid group (on end of chain) since a carboxylic acid reacts with sodium carbonate to release bubbles of  $\text{CO}_2$ . The organic product is the salt below:



## NCEA 2018 Elimination Reactions (part TWO)

Excellence  
Question

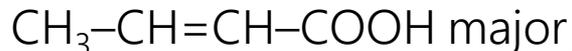
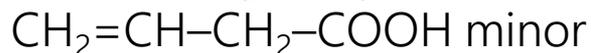
Unknown X has the structural formula below:



There must be a secondary alcohol group (not on end of chain) that can be oxidised by acidified potassium dichromate, because the product must be a ketone since it cannot be further oxidised by Benedicts' solution.  
 $\text{CH}_3 - \text{CO} - \text{CH}_2 - \text{COOH}$

For the elimination reaction to form both major and minor products, the  $-\text{OH}$  group must be on carbon 3 rather than carbon 2, since there would only be one product from elimination if the  $-\text{OH}$  was on carbon 2.

The two organic products are below:



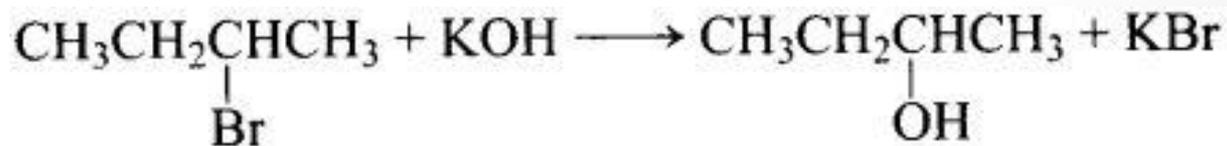
The major product forms when the H is removed from the C atom adjacent to the C-OH with the least number of H atoms already attached.

## Substitution Reactions

Substitution reactions do not change the number of single bonds.

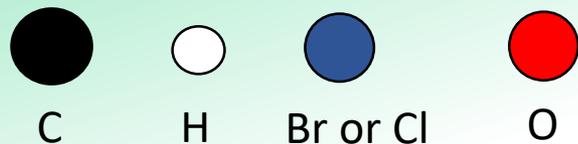
In **haloalkanes** the Halogen atom is removed and a hydroxyl (OH) group is substituted to form an alcohol. Substitution of Haloalkanes is favoured when the solvent used is polar eg. **aqueous** (rather than alcoholic) **KOH**.

The OH bonds with the **same** carbon that the halogen is removed from. A primary halogen will become a primary alcohol and a secondary halogen will become a secondary alcohol

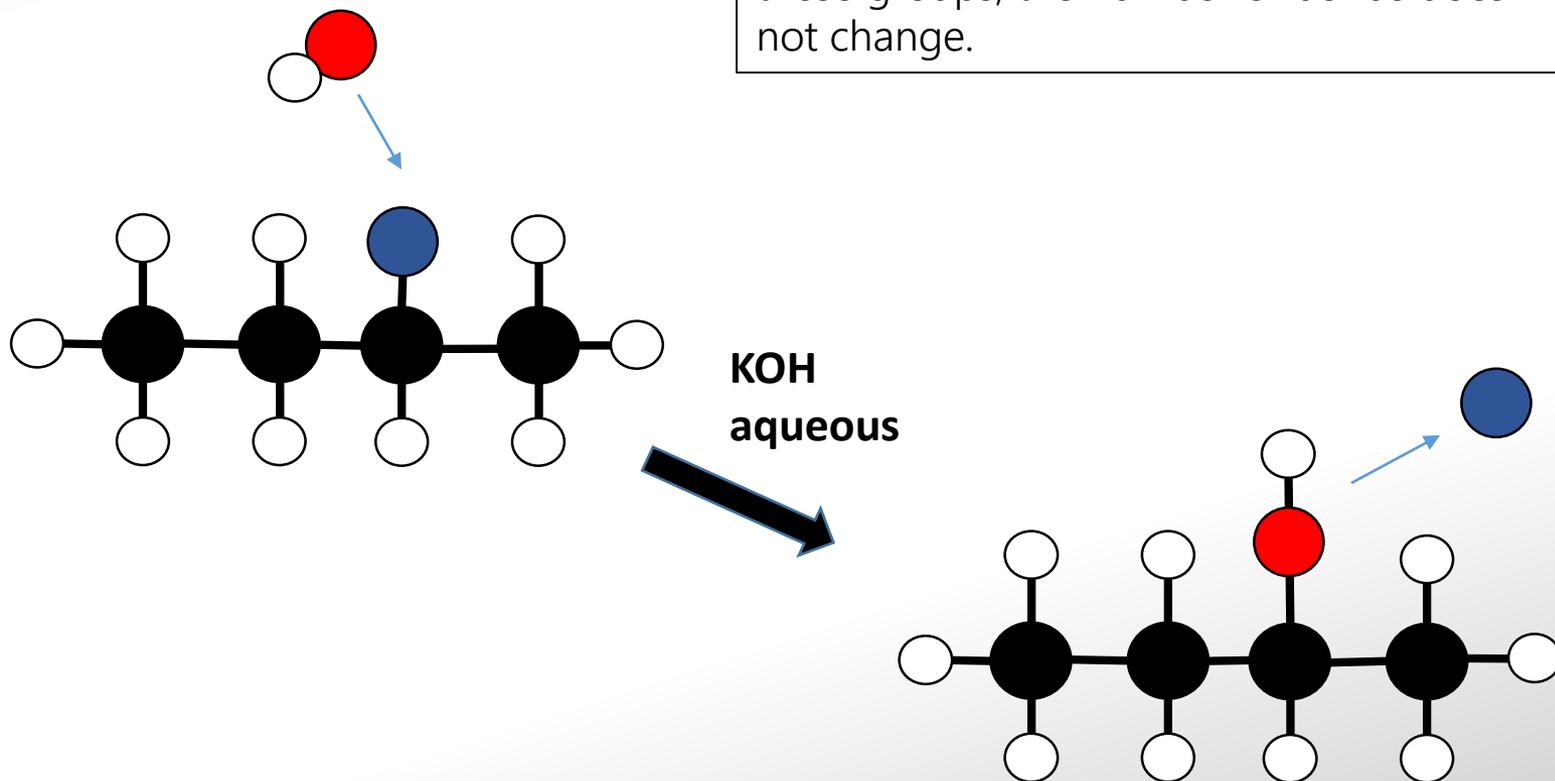


# Haloalkane Substitution to form alcohol

5



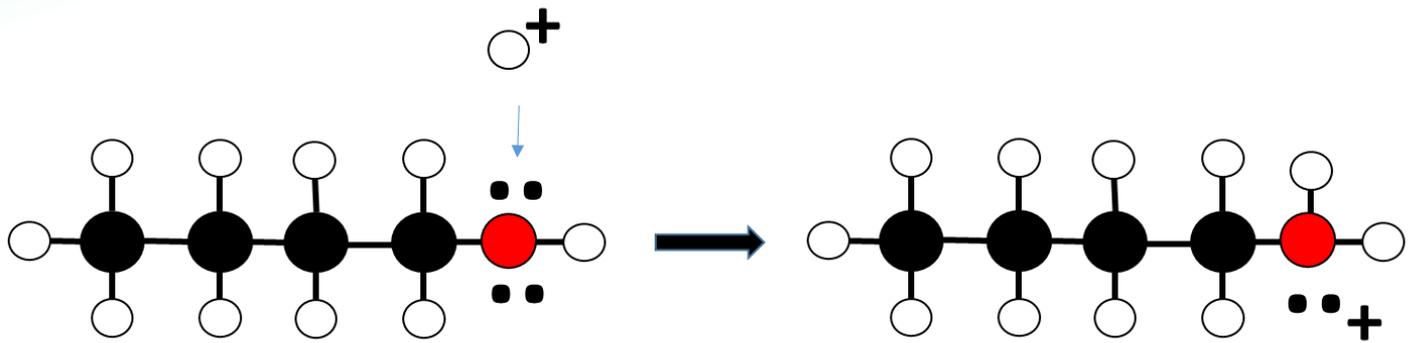
**Substitution** reactions are characterized by replacement of an atom or group (Y) by another atom or group (Z). Aside from these groups, the number of bonds does not change.



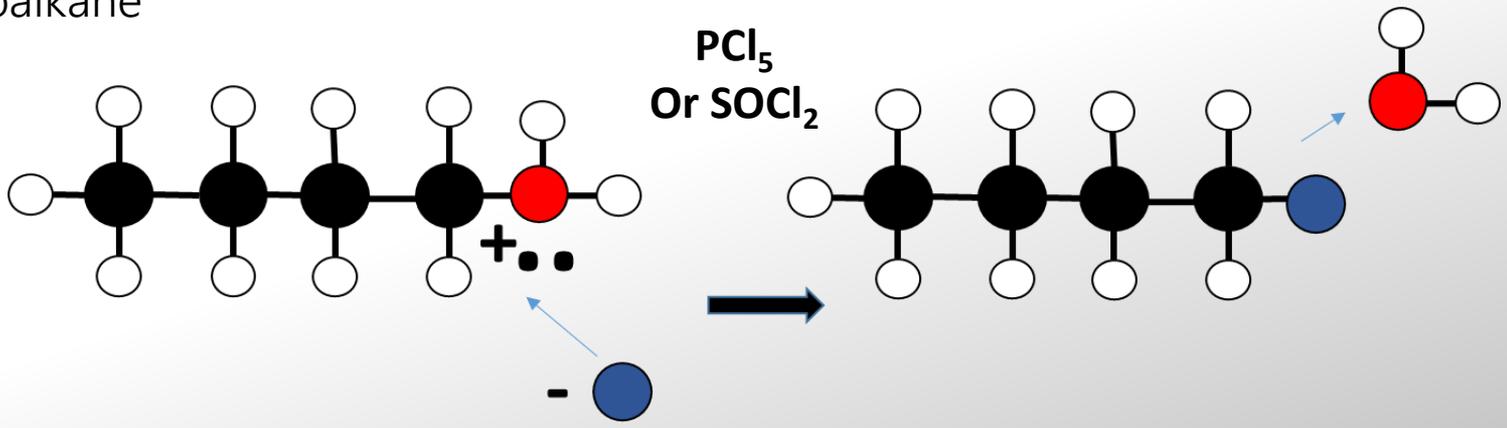
# Alcohol Substitution to form haloalkane (nucleophilic substitution)

Substitution Reactions

**Substitution** - of the OH by a Cl<sup>-</sup> or Br<sup>-</sup> to form a haloalkane. This substitution removes the hydroxyl group (plus one hydrogen to form water) and replaces the bonding sites on the carbon with a halogen. This is called a **nucleophilic** substitution as the Br/Cl is attracted to the nucleus of the carbon atom



An H<sup>+</sup> ion is attracted to the polar OH end to create a greater positive charge. The negative Br<sup>-</sup> or Cl<sup>-</sup> now attacks and replaces the H<sub>2</sub>O molecule removed forming a haloalkane



**Lucas' reagent** is a solution of zinc chloride in concentrated HCl, used to classify alcohols of low molecular weight. The reaction is a substitution in which the chlorine replaces the hydroxyl (OH) group.

The reagent dissolves the alcohol, removing the OH group, forming a carbocation. The speed of this reaction is proportional to the energy required to form the carbocation, so tertiary alcohols react quickly, while smaller, less substituted, alcohols react more slowly. The cloudiness observed is caused by the carbocation immediately reacting with the chloride ion creating an insoluble chloroalkane.

We can use these to identify whether an alcohol is primary, secondary or tertiary

The time taken for turbidity to appear is a measure of the reactivity of the class of alcohol with Lucas reagent, and this is used to differentiate between the three classes of alcohols:

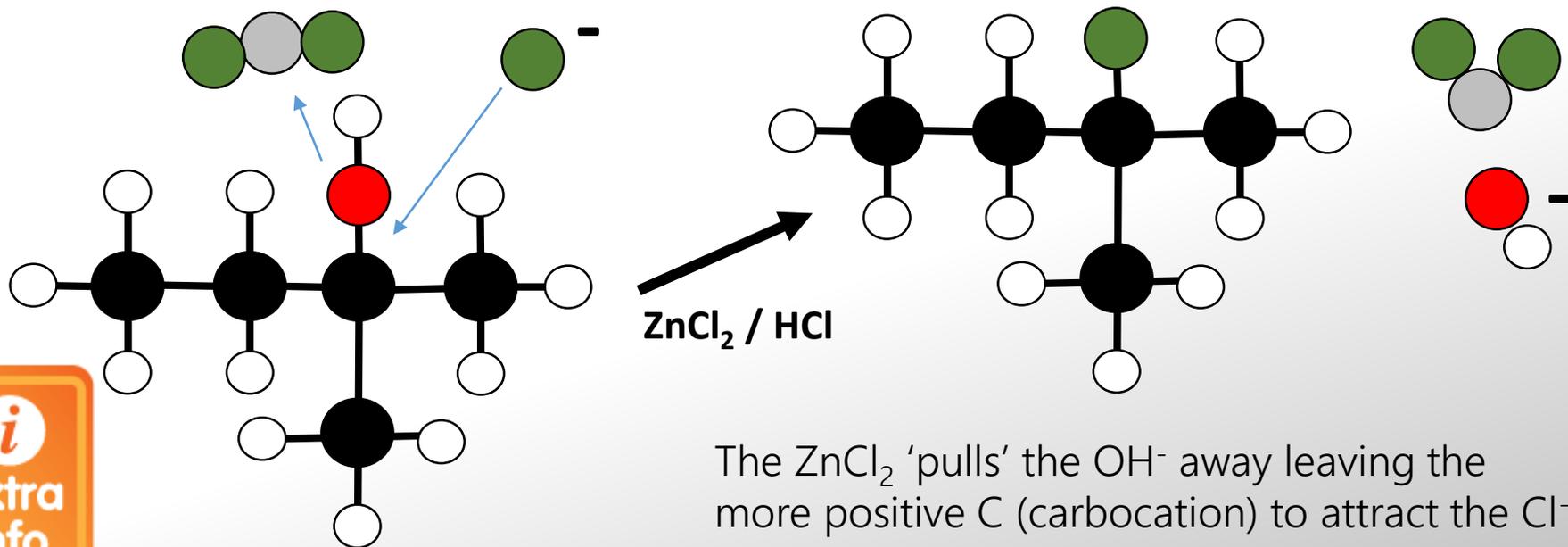
- no visible reaction: **primary alcohol**
- solution turns cloudy in 3-5 minutes: **secondary alcohol**
- solution turns cloudy immediately: **tertiary alcohol**

## Lucas Test observations



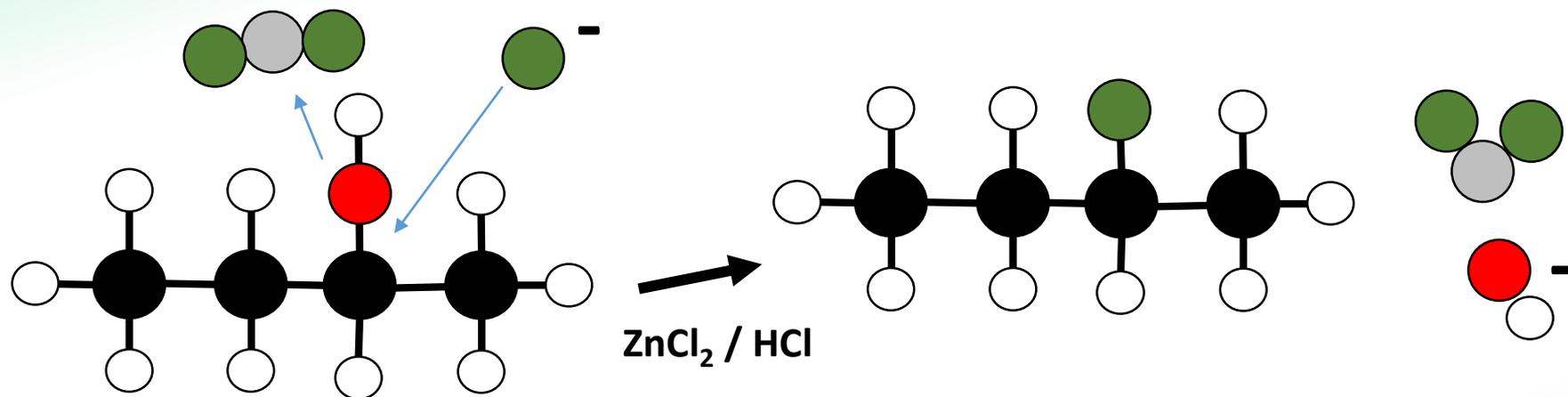
C H O Cl Zn

**Substitution (Nucleophilic)**- of the OH (hydroxyl) by a  $\text{Cl}^-$  to form a chloroalkane. This substitution is faster for tertiary alcohols than for secondary, and slowest for primary alcohols. It is the basis of the **Lucas test** for distinguishing between small molecules of primary, secondary and tertiary alcohols. The reagent used is conc HCl and anhydrous  $\text{ZnCl}_2$  (called Lucas Reagent), and it is shaken with alcohol in a test tube at room temperature. The haloalkane formed is nonpolar and insoluble in the aqueous solution so forms a cloudy emulsion that separates out as two layers. For **tertiary alcohols** - solution rapidly goes cloudy and two layers form.



The  $\text{ZnCl}_2$  'pulls' the  $\text{OH}^-$  away leaving the more positive C (carbocation) to attract the  $\text{Cl}^-$

For **secondary alcohols** - solution slowly goes cloudy as the chloroalkane slowly forms and separates.



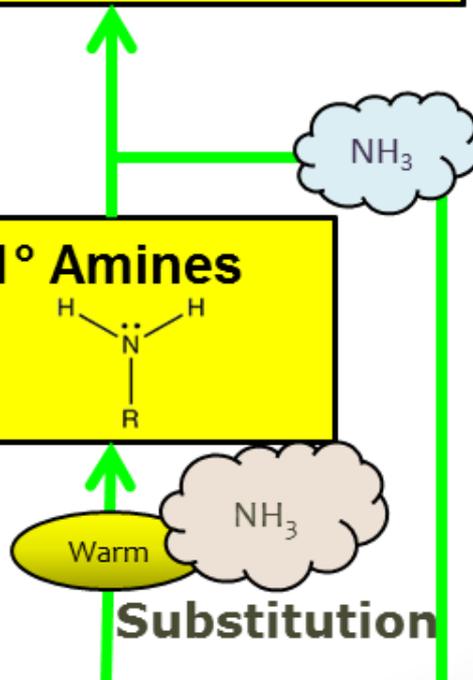
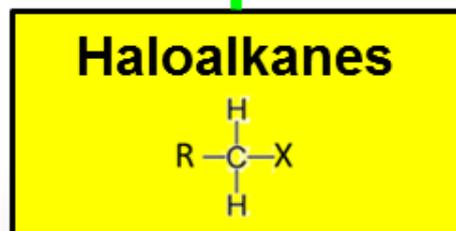
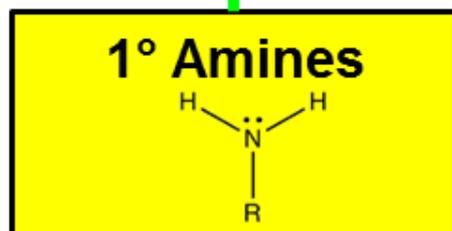
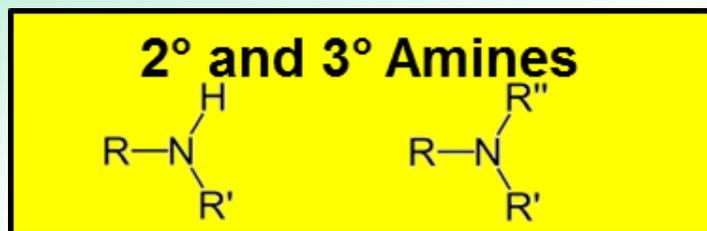
For **primary alcohols** - reaction is so slow a single layer containing unreacted alcohol remains.

Substitution of alcohols can also be carried out using  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{SOCl}_2$ .

The haloalkane formed is nonpolar and insoluble in the aqueous solution so forms a cloudy emulsion that separates out as two layers.



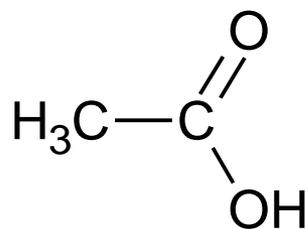
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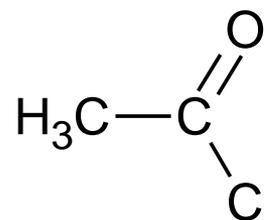
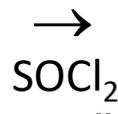
Substitution reactions are characterized by replacement of an atom or group (Y) by another atom or group (Z). Aside from these groups, the number of bonds does not change.

## Substitution reaction to form acid chlorides

Using  $\text{SOCl}_2$  (not conc HCl), carboxylic acids undergo a **substitution reaction** under reflux conditions.

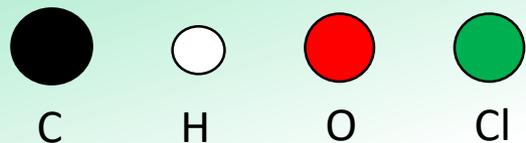


ethanoic acid

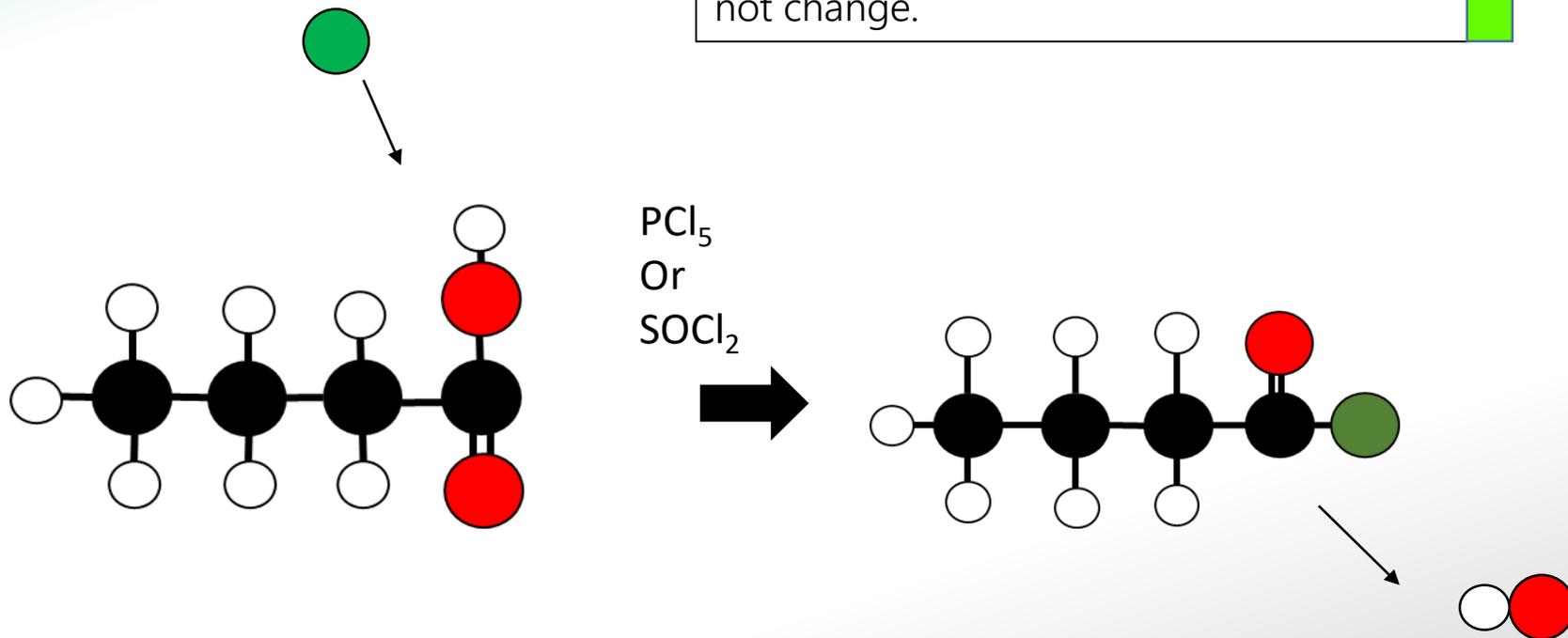


ethanoyl chloride

The acid chloride is named using the name of the parent alkane, but changing the final "-e" to "-oyl chloride". The acid chloride formed reacts violently with water to produce the corresponding carboxylic acid. It is for this reason that conc HCl cannot be used to make an acid chloride as the concentrated acid consists of at least 60% water.



Substitution reactions are characterized by replacement of an atom or group (Y) by another atom or group (Z). Aside from these groups, the number of bonds does not change.

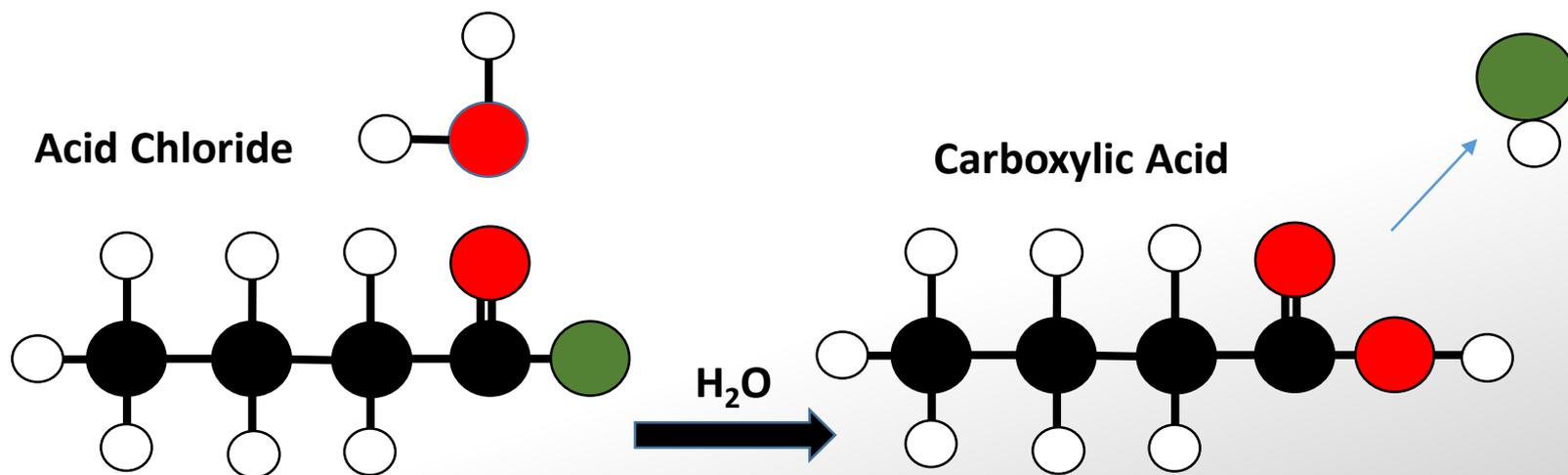


This reaction takes place under reflux conditions

## Reactivity

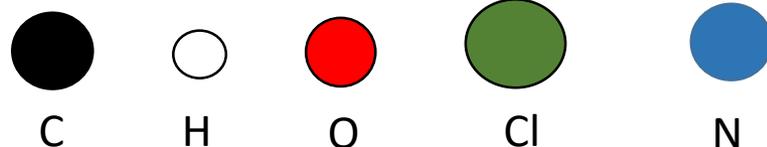
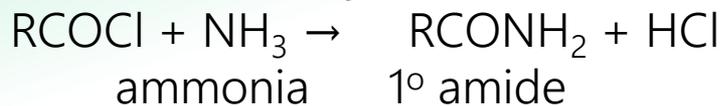
The C-Cl bond is highly polar. The carbon is  $\delta+$  and is readily attacked by nucleophiles causing substitution of the Cl. For this reason, acyl chlorides are useful for producing many chemicals.

Addition of water to acyl chlorides results in a vigorous exothermic reaction.

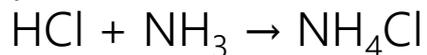


Acid chloride react readily with Ammonia to form Amides

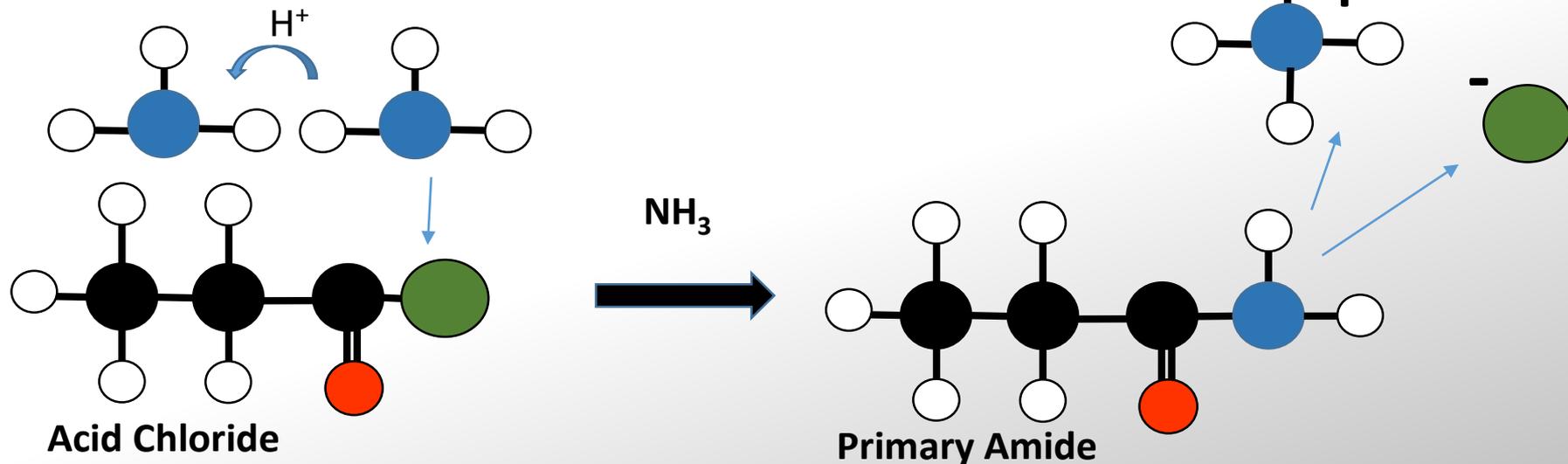
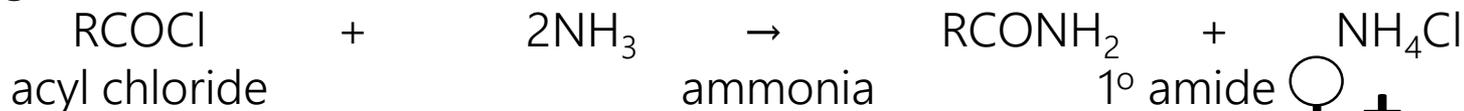
Acyl chlorides react readily with ammonia to form 1° amides.



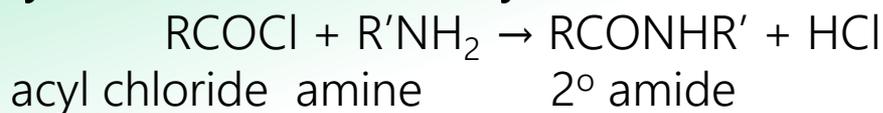
As HCl is produced in the reaction it reacts with unreacted NH<sub>3</sub>



Adding these two we find the overall reaction.



Acyl chlorides react readily with 1° amines to produce 2° amides



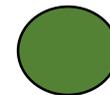
C



H



O



Cl

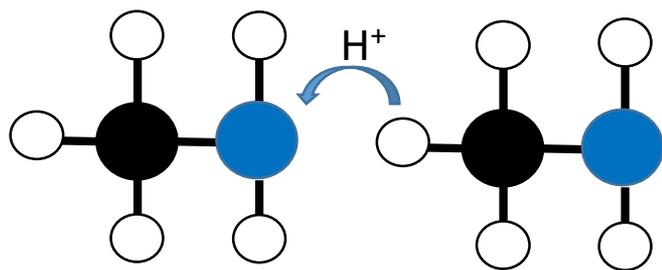
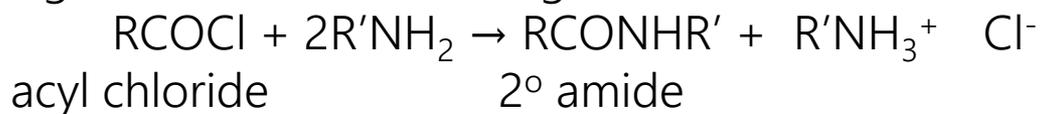


N

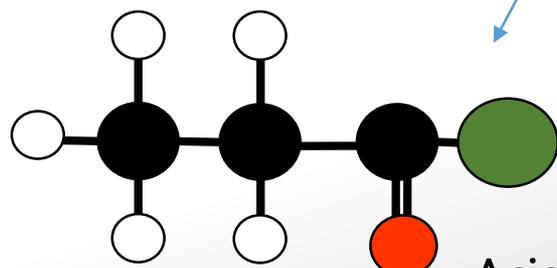
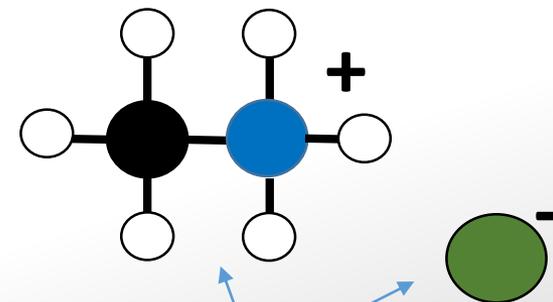
As HCl is produced in the reaction it reacts with unreacted amine.



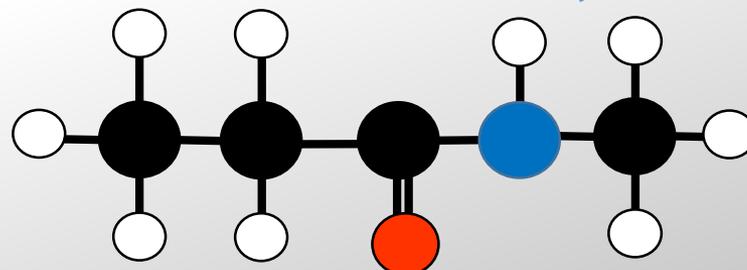
Adding these two reactions together we find the overall reaction.



Amine



Acid Chloride

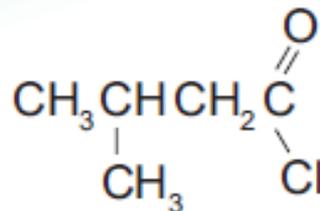


Secondary Amide

# NCEA 2013 Substitution Reactions (Acid Chlorides)

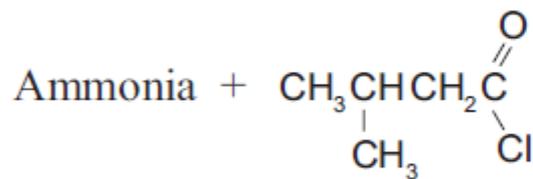
Excellence  
Question

Question 3c: When ammonia reacts with



two products are

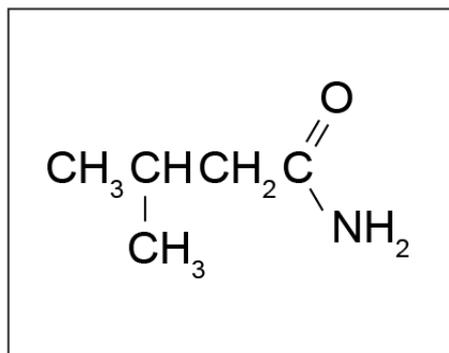
Complete the equation below by naming compounds or drawing the structure.



Name:

Name: 3 methyl butanoyl chloride.

Structural formula of  
organic product:



Name of inorganic  
product:

+ Hydrogen chloride / HCl /  
ammonium chloride /  
NH<sub>4</sub>Cl

## NCEA 2014 Substitution Reactions (Haloalkanes)

Achieved  
Question

**Question 2(b)** Instructions for the preparation of 2-chloro-2-methylpropane are given below.

Read the instructions carefully and answer the questions that follow.

1. Shake 10 mL of 2-methylpropan-2-ol with 30 mL of concentrated hydrochloric acid in a separating funnel for 10 minutes.
2. Run off the bottom acid layer and discard it. Add saturated sodium hydrogen carbonate to the organic product. Shake, releasing the tap every few seconds to relieve the pressure.
3. Run off the bottom aqueous layer and discard it. Transfer into a conical flask and add some anhydrous sodium sulfate, and stir thoroughly.
4. Transfer the organic product into a round-bottom flask, and collect the fraction boiling within 2°C of the boiling point of 2-chloro-2-methylpropane.

(i) Explain why the solution of sodium hydrogen carbonate is added in instruction 2.

Name the gas produced in this step.

**Answer:**

Gas = Carbon dioxide /  $\text{CO}_2$

$\text{NaHCO}_3$  is used to remove any remaining acid *mixed with the liquid product*.

## NCEA 2014 Substitution Reactions (Haloalkanes)

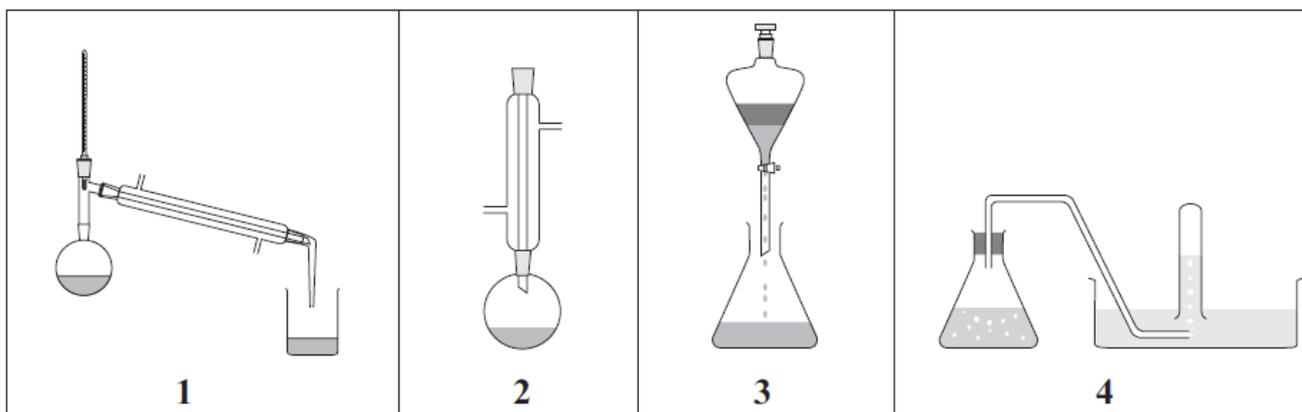
Excellence  
Question

Question 2(b) (ii) Explain why **anhydrous** sodium sulfate is added in instruction 3.

**Answer:**

$\text{Na}_2\text{SO}_4$  is added to remove any remaining water *mixed with the liquid product*.

Question 2(b) (iii – v) Name the process used in instruction 4 to purify the organic product. Identify which piece of the equipment that a student would use to perform this process from the diagrams below.

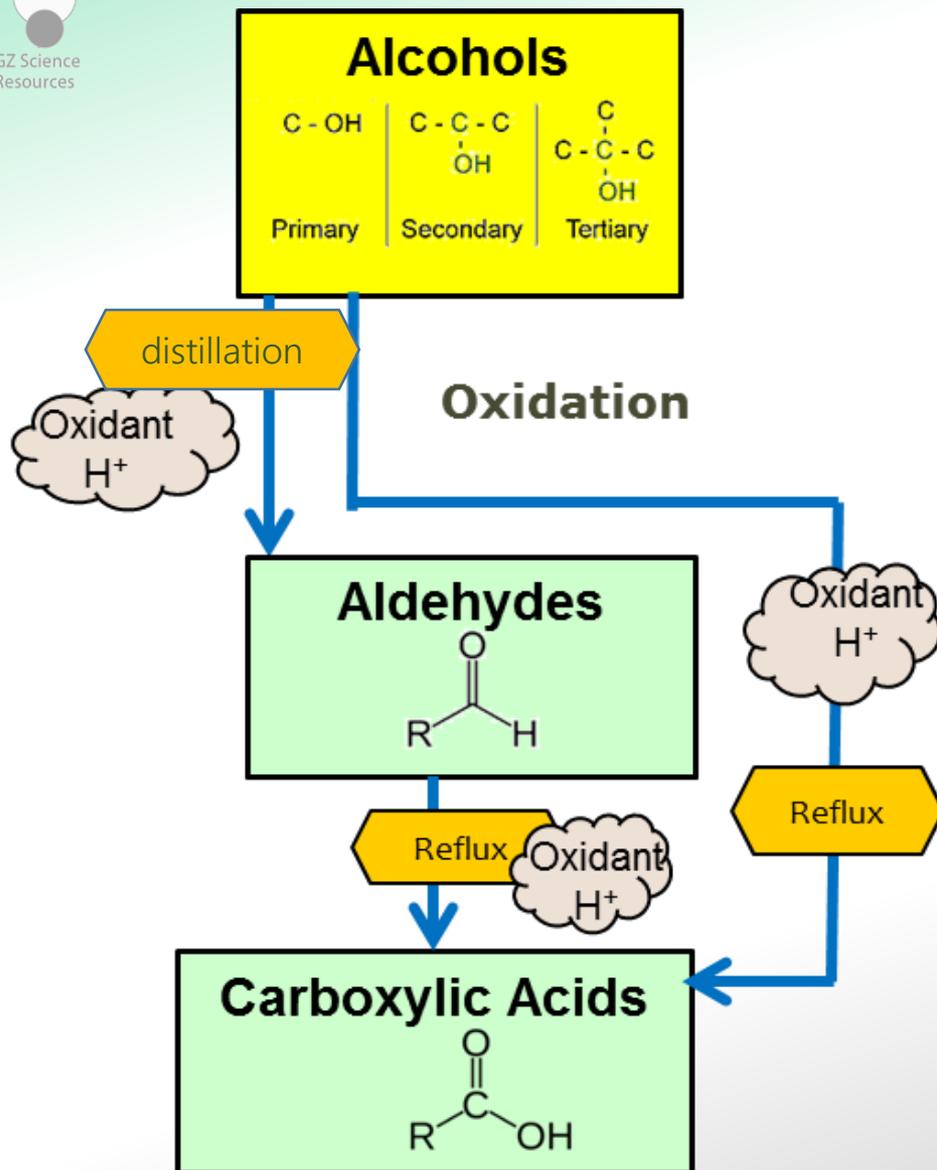


**Answer:** *Fractional* Distillation. Equipment 1.

The purpose of the process is to **purify** the chemical / **remove impurities** / **separate product**. This is achieved by separating liquids according to their **boiling points**.

Chemicals are boiled then condensed / liquid-gas then gas-liquid.

The fraction at the desired boiling point is kept / other fractions are discarded.



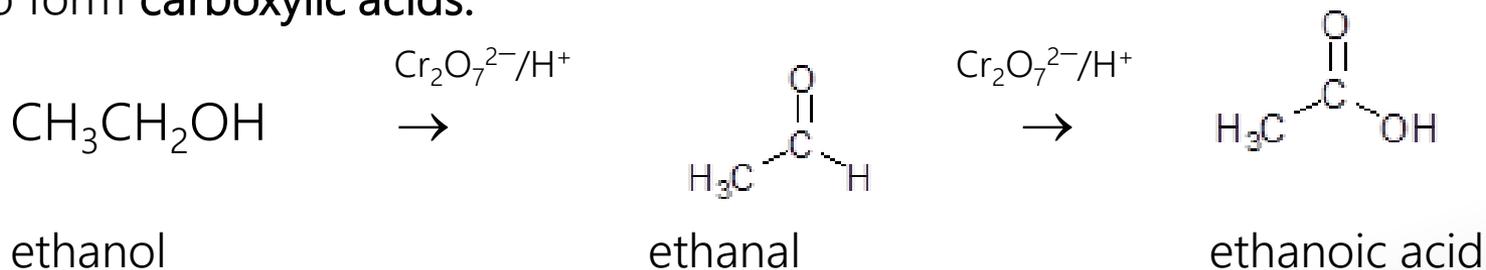
Aldehydes must always be prepared from Primary alcohols. Primary alcohols can be oxidized by mild oxidising agents, such as potassium dichromate ( $K_2Cr_2O_7$ ), or potassium permanganate ( $KMnO_4$ ) and distilled to yield aldehydes.

Further reacting with an oxidant under reflux conditions will yield a carboxylic acid.

**Oxidation** - using acidified  $\text{KMnO}_4$  or acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ . The type of product formed depends on whether the alcohol used in the oxidation reaction is primary or secondary.

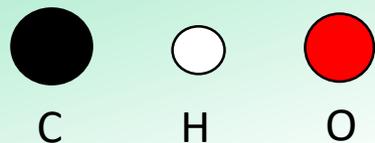
Conditions are warm only, with use of distillation to collect evaporated aldehyde, as it has a lower boiling point than the alcohol (which has hydrogen bonding)

**Primary alcohols** are oxidised to form **aldehydes**, which are then easily oxidised further to form **carboxylic acids**.

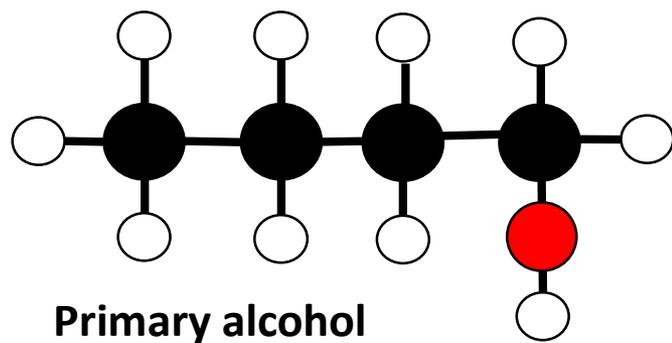


When using acidified dichromate in this redox reaction, the  $\text{Cr}_2\text{O}_7^{2-}$  is reduced to  $\text{Cr}^{3+}$ , and the colour changes from orange to green. This colour change was the basis for the chemical reaction in the old "blow in the bag" breathalyser test.

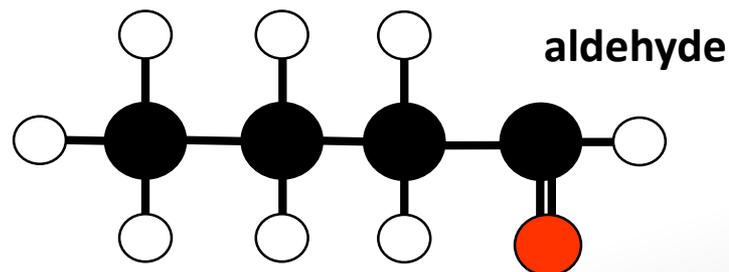
When using acidified permanganate in this redox reaction, the  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$ , and the colour changes from purple to colourless.



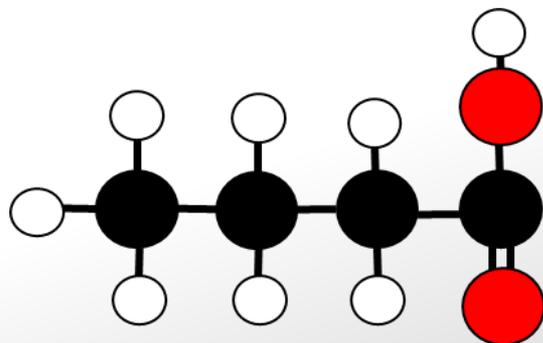
Oxidation reactions involve a loss of electrons from the organic molecule or a gain of oxygen. An oxidant such as dichromate or permanganate is used to make an aldehyde



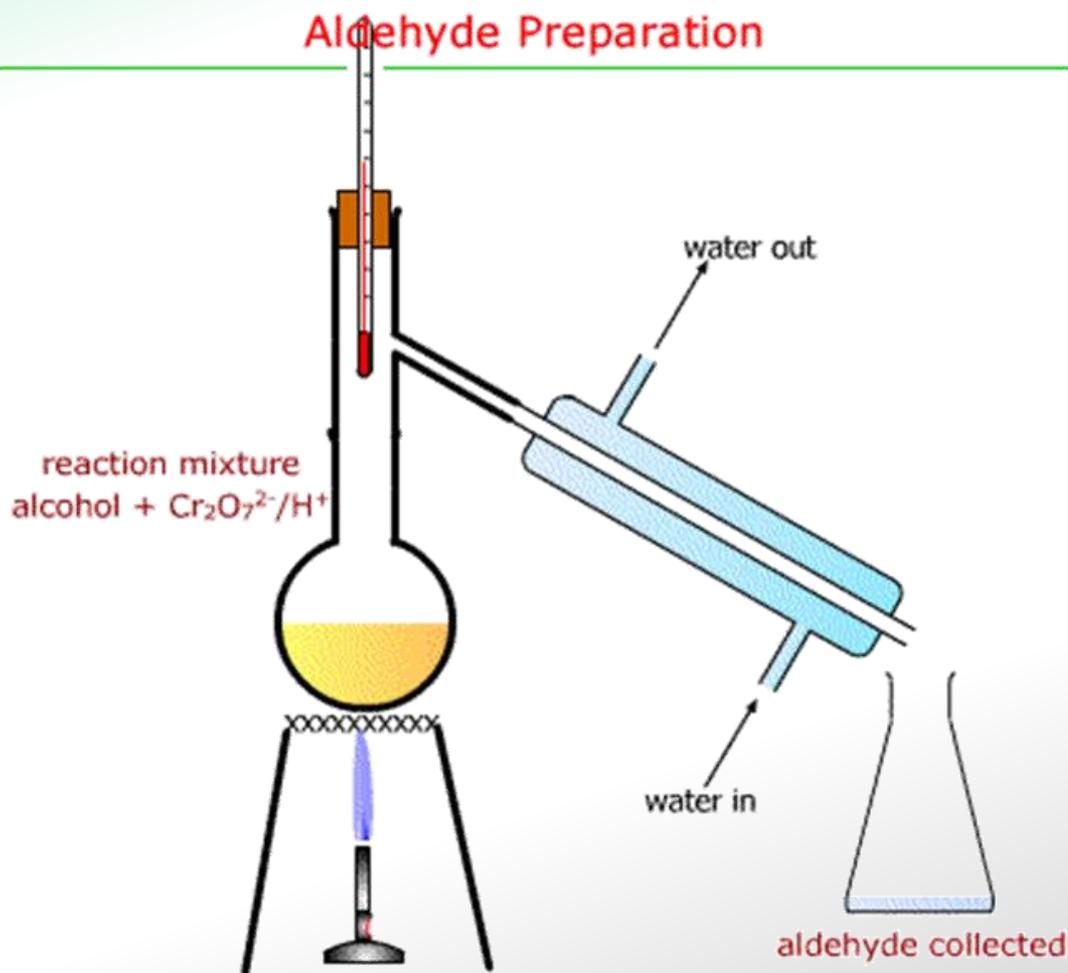
distillation  
 Oxidant  
 $\text{MnO}_4^-$



reflux  
 Oxidant  
 $\text{MnO}_4^-$

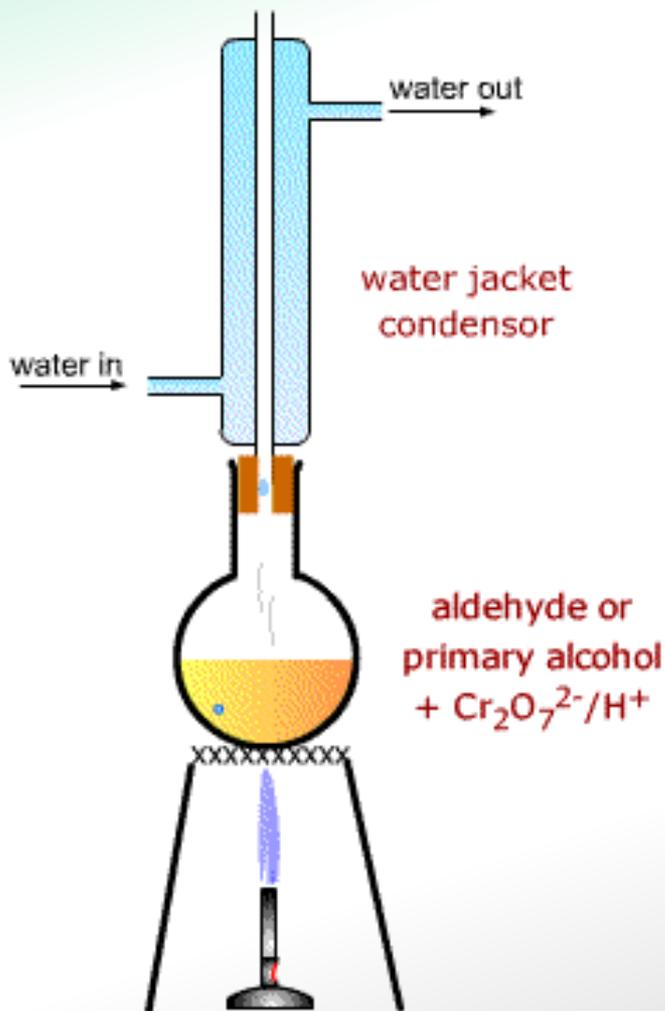


Carboxylic acid



A primary alcohol is oxidised to an aldehyde. The aldehyde can be further oxidised by exactly the same reagent to a carboxylic acid, so it is important to remove it from the reaction vessel immediately. This is possible as the aldehyde has a much lower boiling point than both the alcohol and carboxylic acid. The reaction is performed in a distillation flask above the boiling point of the aldehyde and below the boiling point of the other compounds and the aldehyde is allowed to distil off as it is formed.

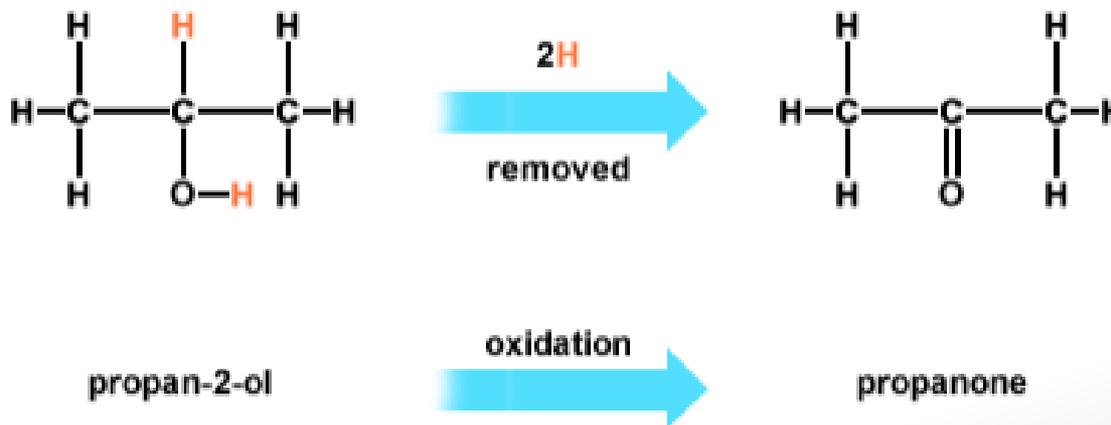
## Carboxylic acid preparation



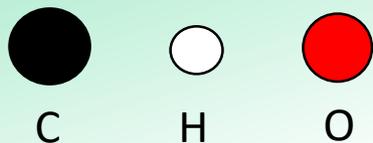
An Aldehyde can be further oxidised to produce Carboxylic acid. (the Carboxylic acid can also be prepared directly from the primary alcohol). The process requires the use of **reflux** apparatus. The aldehyde (or alcohol solution) is heated until it forms the carboxylic acid but the water jacket condenser prevents the aldehyde escaping as vapour – which has a lower boiling point than the Carboxylic acid that has Hydrogen bonding.

Oxidation - using acidified  $\text{KMnO}_4$  or acidified  $\text{K}_2\text{Cr}_2\text{O}_7$

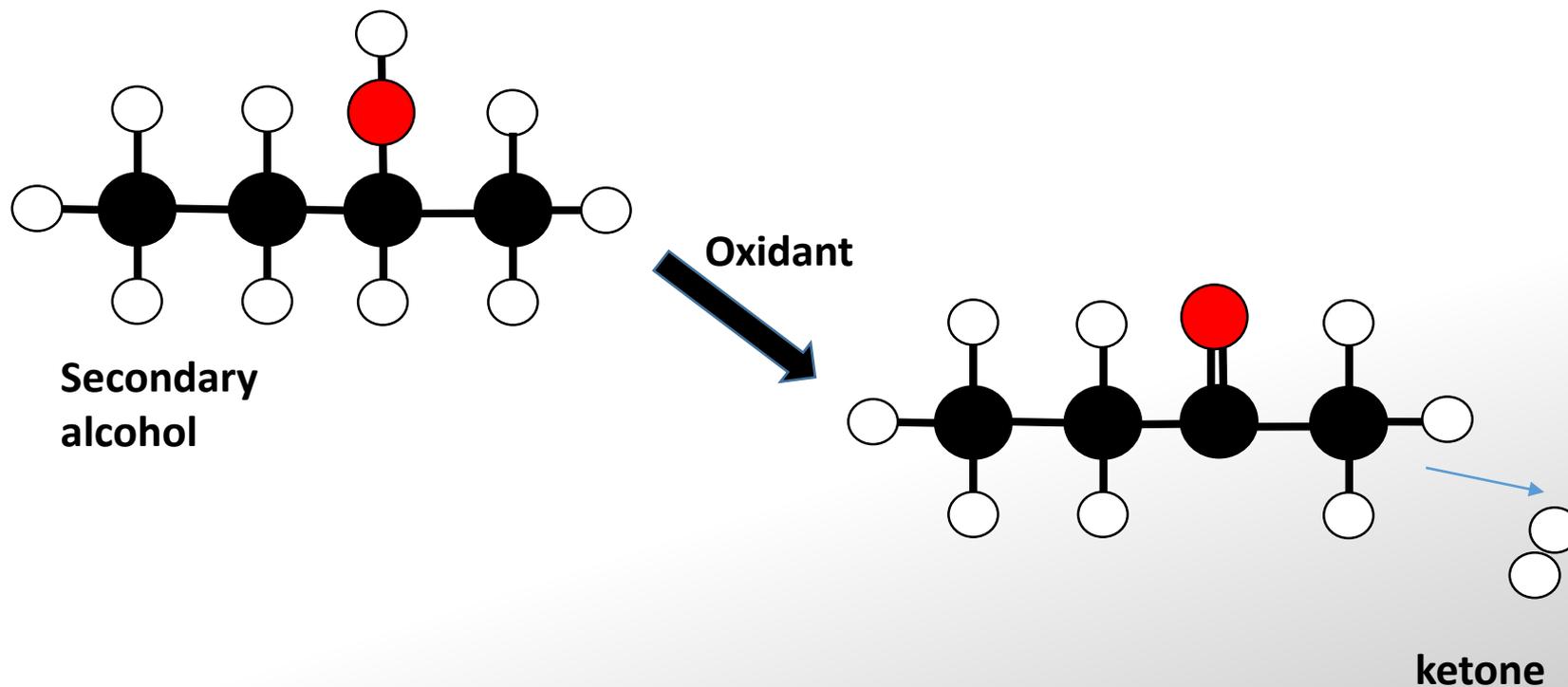
Secondary alcohols are oxidised to form **ketones**, which do not oxidise further



Tertiary alcohols do not oxidise



Oxidation reactions involve a loss of electrons from the organic molecule or a gain of oxygen. An oxidant such as dichromate or permanganate is used to make a ketone



## NCEA 2013 Oxidation Reactions (Alcohol)

Excellence  
Question

**Question 2b:** Discuss the laboratory procedures used to convert butan-1-ol into butanal, and butan-1-ol into butanoic acid.

In each discussion, you should:

- outline the process for each conversion
- state and justify the type of reaction occurring
- identify the reagents used, and explain any observations made.

Aldehyde (Butanal) is obtained by **distillation** of butan-1-ol with acidified (potassium) dichromate / (acidified potassium) permanganate solution.

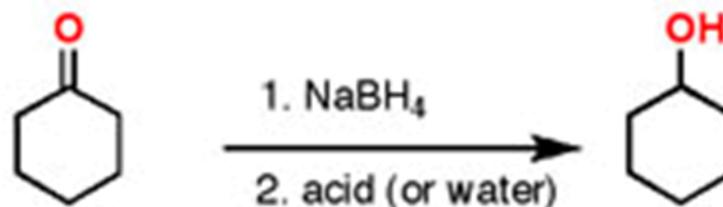
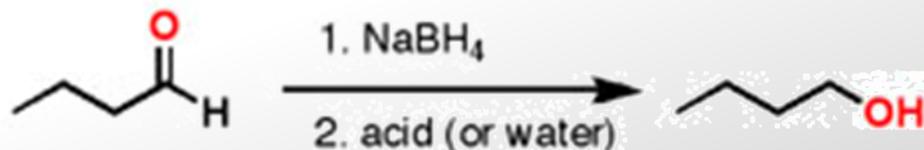
(Distillation) is used because the aldehyde has a lower boiling point (than butan-1-ol and the carboxylic acid formed) / to prevent it from being oxidised further.

(Both) reactions are oxidation–reduction because butan-1-ol has lost electrons/lost hydrogen/gained oxygen/oxidation number (of C) has increased.

Carboxylic acid (butanoic acid) is obtained by reacting a mixture of butan-1-ol with acidified potassium dichromate solution (under **reflux** conditions) until all of the reactant has been converted to butanoic acid.

Observations: orange  $\text{Cr}_2\text{O}_7^{2-}$  to green /, purple  $\text{MnO}_4^-$  to colourless / aldehyde condensed in the condenser.

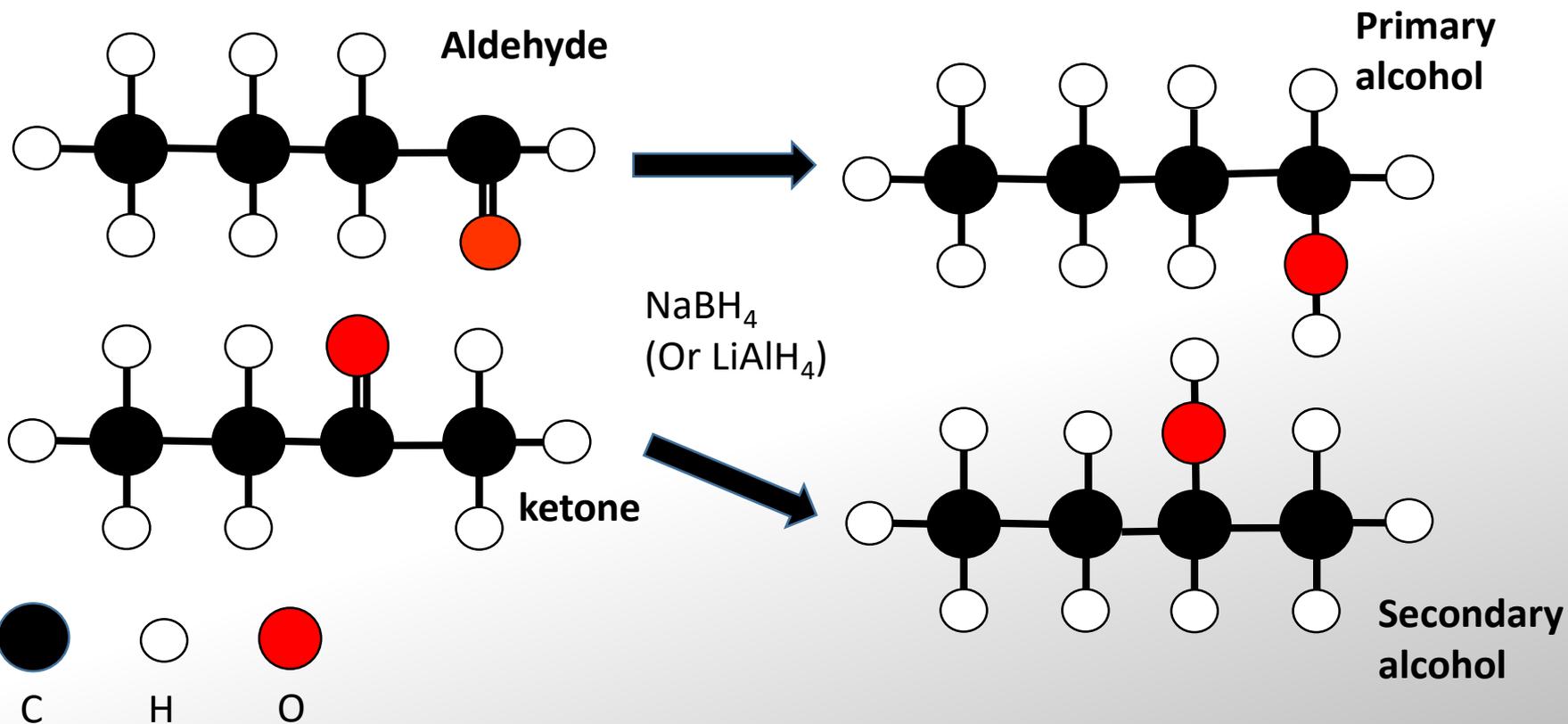
**Reduction of Aldehydes and Ketones-**  $\text{NaBH}_4$  (sodium borohydride)- reduce aldehydes to primary alcohols and ketones to secondary alcohols. This is considered a reduction reaction because the amount of Hydrogen increases. Sometimes  $\text{LiAlH}_4$  (lithium aluminium hydride) can also be used as a reductant

**Example 1: Reduction of ketones****Example 2: Reduction of aldehydes**

### Reduction of Aldehydes and Ketones with $\text{NaBH}_4$

In this Reduction reaction we are breaking a C-O bond and replacing it with a C-H bond. This is what helps us classify the reaction as a reduction.

Note that we also form an O-H bond. In order to make the alcohol, the oxygen needs to pick up a proton ( $\text{H}^+$ ) (called protonation) from either water or acid that is added after the reaction is complete.



# NCEA 2016 Reduction Reactions (Aldehydes and Ketones)

Merit  
Question

**Question 2a: (i)** What reagent can be used to reduce aldehydes and ketones?

Sodium borohydride /  $\text{NaBH}_4$  (accept  $\text{LiAlH}_4$ )

**Question 2a: (ii)**

For the reduction of pentanal and pentan-2-one, draw the structure of the organic product formed in each case.

Identify the functional group of each product formed.

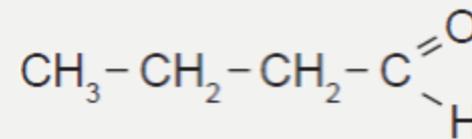
<b>pentanal</b>	<p>Structure of the product:</p> $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ <p>Pentanal will produce a primary alcohol / pentan-1-ol.</p> <p>Functional group: _____</p>
<b>pentan-2-one</b>	<p>Structure of the product:</p> $\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_3 \\   \\ \text{OH} \end{array}$ <p>Pentan-2-one will produce a secondary alcohol / pentan-2-ol.</p> <p>Functional group: _____</p>

# NCEA 2018 Reduction Reactions

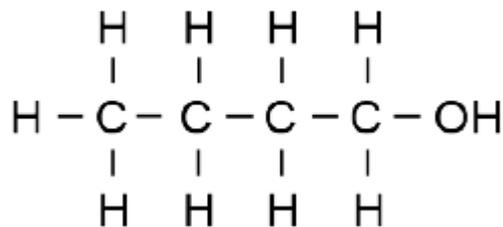
Excellence  
Question

**Question 2c:** The structural formula of butanal is:  
Devise a reaction scheme to convert butanal into butanone.  
For each step include:

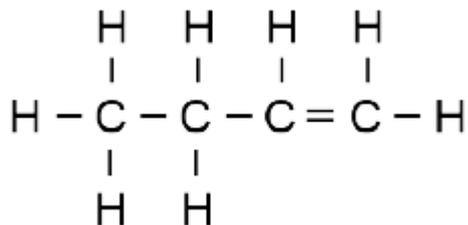
- the reagents and conditions
- structural formula of the organic product after each step.



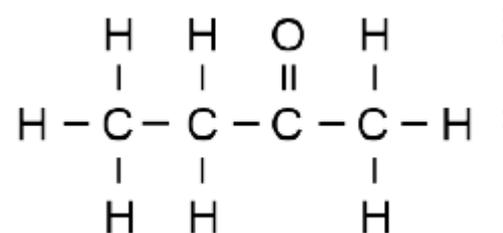
**Step 1:** Add  $\text{NaBH}_4$  /  $\text{LiAlH}_4$  /  $\text{LiBH}_4$  to reduce butanal to butan-1-ol:



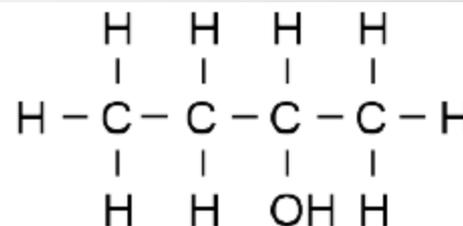
**Step 2:** Add concentrated  $\text{H}_2\text{SO}_4$  to the butan-1-ol, and heat. This will produce but-1-ene:



**Step 4:** Add  $\text{H}^+$  /  $\text{Cr}_2\text{O}_7^{2-}$  or  $(\text{H}^+) / \text{MnO}_4^-$ , and heat. The butan-2-ol will be oxidised to butanone:



**Step 3:** Add dilute  $\text{H}_2\text{SO}_4$  ( $\text{H}^+$  /  $\text{H}_2\text{O}$ ). This will produce butan-1-ol and butan-2-ol. It is the butan-2-ol that will be used in step 4:



## Oxidation of aldehydes

Aldehydes are readily oxidised by even mild oxidising agents such as  $\text{Ag}^+$  and  $\text{Cu}^{2+}$ , which are too weak to oxidise alcohols. Like alcohols they are also oxidised by acidified potassium dichromate and acidified potassium permanganate. In contrast, ketones are not oxidised, and this means that they can readily be distinguished by observing the reaction with an oxidising agent.

## Tollens' test

If Tollens' reagent (a colourless solution  $[\text{Ag}(\text{NH}_3)_2]^+$ ) is heated with an aldehyde a redox reaction occurs, which produces a silver mirror on the inner surface of the test tube. The aldehyde is oxidised to a carboxylic acid.

The reduction half-equation is



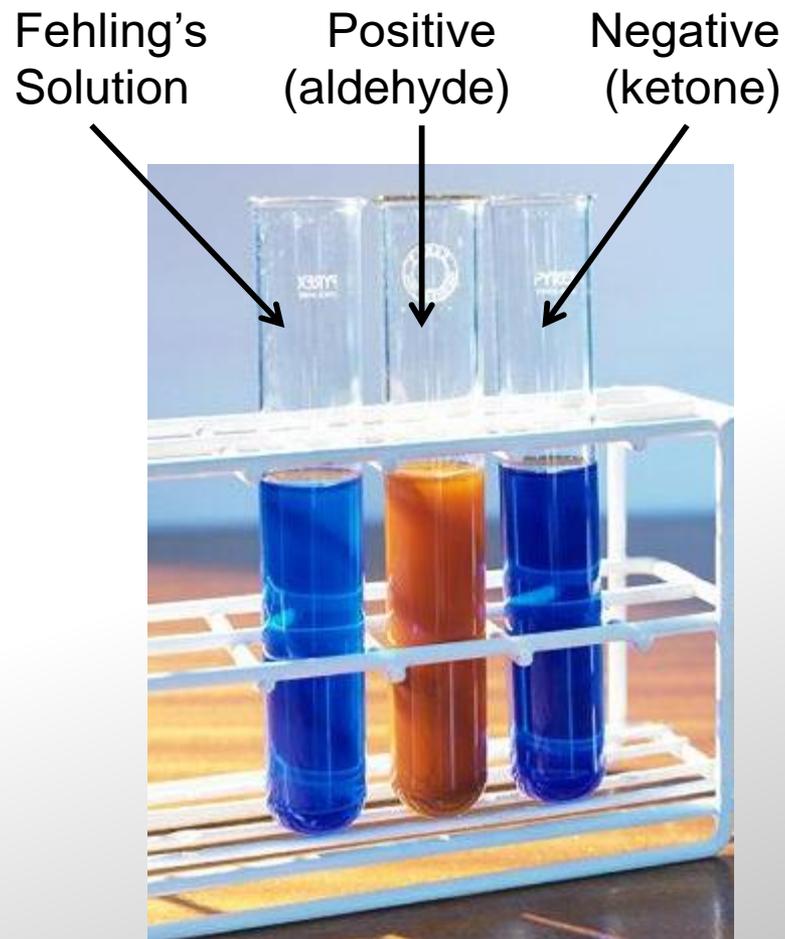
If Tollens' reagent is heated with a ketone or an alcohol no reaction occurs. This means there would be no observed colour change and no formation of a silver mirror.



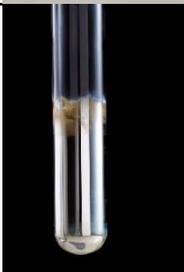
## Tests to distinguish between Aldehydes and Ketones

**Benedict's test** - Benedict's reagent is an alkaline solution containing a copper(II) citrate complex ion. When Benedict's solution is heated with an aldehyde, the  $\text{Cu}^{2+}$  complex ion acts as an oxidising agent, and the blue complex of  $\text{Cu}^{2+}$  is reduced to a **brick red precipitate of  $\text{Cu}_2\text{O}$** . When heated with a ketone (or an alcohol), Benedict's solution does not react and remains blue.

**Fehling's test** - Fehling's solution is an alkaline solution containing a deep blue complex ion of  $\text{Cu}^{2+}$  (copper(II) tartrate complex ion). It is also reduced to red  $\text{Cu}_2\text{O}$  when heated with an aldehyde, but has no reaction with ketones (or alcohols).



We can use these to identify whether the molecule is an Aldehyde or Ketone

Testing Reagent		observations	
		Aldehyde $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	Ketone $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$
<b>Potassium permanganate</b> $\text{MnO}_4^-$ to $\text{Mn}^{2+}$		Oxidises into carboxylic acid Purple to colourless	No reaction
<b>Tollens' reagent</b> $[\text{Ag}(\text{NH}_3)_2]^+$ to Ag		Oxidise aldehydes (but not alcohols) Silver 'mirror' forms	No reaction
<b>Benedict's solution</b> $\text{Cu}^{2+}$ ions to $\text{Cu}^+$		Oxidises aldehydes (but not alcohols) to form $\text{Cu}^+$ ions Red/brown ppt forms	No reaction

Identify whether each reactant is a **ketone** or **aldehyde** and the expected observations in each of the following reactions. In some cases there will be no reaction.

- (a) **Methanal** is heated with Tollen's reagent. *Aldehyde so Silver mirror forms around the outside of the test tube. (aldehyde oxidises to a Carboxylic acid)*
- (b) **Hexanan-2-one** is heated with Benedict's reagent. *Ketone so no reaction*
- (c) **Propanone** is reacted with acidified potassium permanganate. *Ketone so no reaction*
- (d) **2-methylpropanal** is heated with  $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ . *Aldehyde so solution reduces from Orange dichromate into green chromium ions ( $\text{Cr}^{3+}$ ). (aldehyde oxidises to a Carboxylic acid)*
- (e) **3-methylpentanal** is reacted with Benedict's reagent. *Aldehyde so blue solution turns orange. (aldehyde oxidises to a Carboxylic acid)*
- (f) **Butanone** is heated with Tollen's reagent. *Ketone so no reaction.*

## NCEA 2013 Distinguishing Tests

Merit  
Question

**Question 3a:**(ii) Describe how you could distinguish between the alcohols in (i) above, using chemical tests on the alcohols and / or their oxidation products.

- Butan-1-ol is oxidised using permanganate / acidified dichromate,  
EITHER  
forming an aldehyde which can be identified using Tollens', silver mirror forms / Benedict's or Fehling's solution.  
OR  
forms brick red precipitate / forming a carboxylic acid, which can be identified turning (moist) blue litmus paper red.
- Butan-2-ol is oxidised to a ketone with permanganate / acidified dichromate, but this does not give a positive test using Tollens' or Benedict's.
- Methyl propan-2-ol does not react with oxidising agents, permanganate remains purple / dichromate remains orange.

*Lucas test may be accepted with correct explanation. (anhydrous)  $ZnCl_2$  and conc HCl*

*Solution goes cloudy / layers form: Tertiary in seconds*

*:Secondary in minutes*

*:Primary in hours / no reaction.*

## NCEA 2013 Distinguishing tests

Merit  
Question

**Question 2c:** Devise a method for distinguishing between the three liquid compounds, butan-1-ol, butanoic acid, and butanoyl chloride, using only blue litmus paper and water.

Explain each of the observations in your method, with reference to the structure of the organic compounds.

Add to water then test with blue litmus paper

The butan-1-ol will not react with water nor change the colour of the moistened litmus paper.

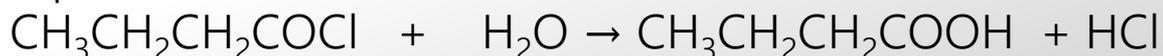
The butanoic acid will change the moistened blue litmus paper to red.

The butanoyl chloride will react violently with the water.

Carboxylic acids react with water to form hydronium ions / equation



Acyl chlorides react with water to form carboxylic acids and hydrogen chloride / equation



## NCEA 2014 Distinguishing Tests

**Question 2(a):** (iv) Explain why the equipment to the right is used for hydrolysis of the triglyceride.

(i) Aqueous solutions of propanamine and propanamide.

**Answer:** *Damp red* litmus.

Propanamine will change the colour of *red* litmus blue.

Propanamide will not change the colour of *red* litmus.

(ii) Propanone and propanal.

**Answer:** Tollens' reagent (Fehling's or Benedict's or  $\text{Cr}_2\text{O}_7^{2-} / \text{H}^+$  or  $\text{MnO}_4^- / \text{H}^+$ ).

Propanal will form a silver mirror when warmed with Tollens' reagent.

Propanone will not react with Tollens' reagent.

(iii) Propanoyl chloride and propyl propanoate.

**Answer:** Water.

Propanoyl chloride will react violently with water.

Propyl propanoate will not react with water / it will form layers.

## NCEA 2016 Distinguishing tests

Excellence  
Question

**Question 2b:** Explain how you would identify each of the organic substances, **A** to **D**, from the table in (b)(i), using only moist litmus paper, water, and Benedict's solution.

In your answer, you should include:

- a description of any tests carried out and any observations you would make
- equations to show the organic products formed, if applicable.

**A:** Propan-1-amine. (1-propanamine)

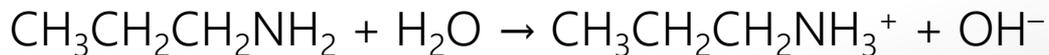
**B:** Propanal.

**C:** Propanoyl chloride.

**D:** Propan-2-one. (propanone)

**A:** *Propan-1-amine (a primary amine)*

$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  (propan-1-amine) will turn moist red litmus paper blue as it is basic.



Water: Dissolves in water.

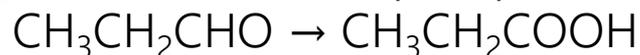
Benedict's solution will stay blue as primary amines do not react with Benedict's reagent.

**B:** *Propanal (An aldehyde)*

Damp Litmus: No colour change.

Water: Dissolves in water.

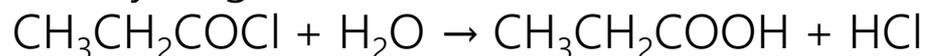
Propanal will react with Benedict's reagent, with the blue solution forming a (copper mirror) / brick red precipitate. Propanoic acid is formed.



**C:** *Propanoyl chloride (An acyl chloride)*

Damp Litmus: Turn blue litmus red

Water: Propanoyl chloride will react vigorously with water to produce propanoic acid and hydrogen chloride.



Benedict's solution will stay blue as the acyl chloride does not react with the Benedict's, but instead reacts with the water present in the Benedict's solution.

**D:** *Propan-2-one (A ketone)*



Damp Litmus: No colour change.

Water: Dissolves in water.

Benedict's solution: No reaction, so stays blue.

**Question 2b (i)** : Adding an acidified potassium dichromate solution to propan-1-ol can produce either propanal or propanoic acid.

Explain the laboratory procedure used to convert propan-1-ol to **propanal**.

In your answer, you should:

- outline the procedure for the conversion, and describe any colour changes linked to the species involved
- state the type of reaction occurring
- explain how the procedure ensures only **propanal** is collected.

Aldehyde (propanal) is obtained by distillation of propan-1-ol with acidified (potassium) dichromate ( $\text{Cr}_2\text{O}_7^{2-} / \text{H}^+$ ). The orange colour of the  $\text{Cr}_2\text{O}_7^{2-} / \text{H}^+$  changes to (blue) green ( $\text{Cr}^{3+}$  ions). The reaction is an oxidation reaction.

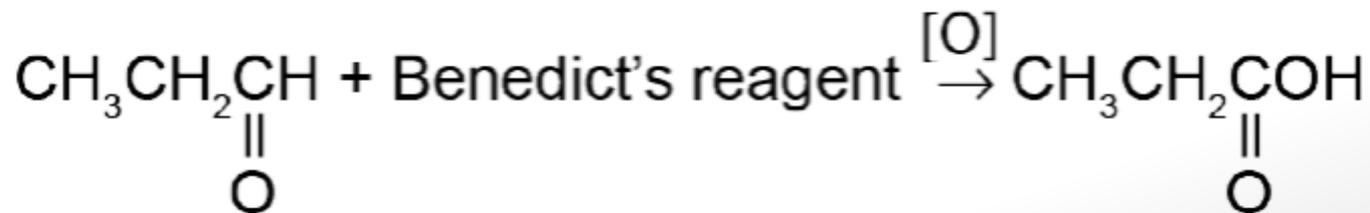
Distillation is a way to separate the aldehyde (propanal) from the reactant alcohol (propan-1-ol) which has a higher boiling point. The aldehyde (propanal) can react further to form a carboxylic acid (propanoic acid). This reaction is prevented if the **aldehyde is removed as it is formed** – distillation achieves this by evaporating the aldehyde and then allowing it to condense for collection.

**Question 2b (ii)** : Explain how Benedict's solution can be used to distinguish between propanone and propanal.

In your answer, you should include:

- any observations made linked to the organic compounds involved
- the type of reaction occurring
- relevant equations showing any organic reactants and products involved.

Adding blue Benedict's solution to a **warmed / heated** sample of propanal will cause a (brick) red colour to form. This happens because the propanal has been oxidised to propanoic acid / carboxylic acid (red colour is copper(I) oxide).



No change will occur when blue Benedict's solution is added to propanone, as it cannot be further oxidised / won't react.

## NCEA 2018 Distinguishing Tests

Achieved  
Question

**Question 1b:** Three bottles, each containing a different colourless liquid, have been incorrectly labelled. The three colourless liquids are known to be:

pentanal  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$

pentan-1-ol  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

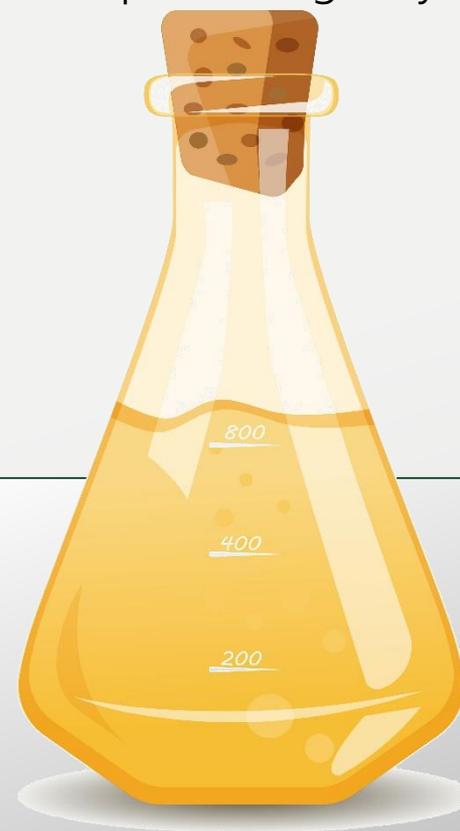
pentanoyl chloride  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COCl}$

Develop a procedure to identify each of the three colourless liquids using only the following reagents:

- water
- Tollens' reagent
- acidified potassium dichromate,  $\text{H}^+ / \text{K}_2\text{Cr}_2\text{O}_7$ .

Your procedure should include:

- observations linked to the species involved
- the type of reaction occurring
- structural formulae of any organic products.



## NCEA 2018 Distinguishing Tests

Excellence  
Question

**Question 1b:** Three bottles, each containing a different colourless liquid, have been incorrectly labelled. The three colourless liquids are known to be:

pentanal  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$

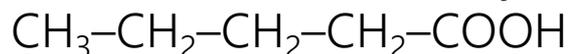
pentan-1-ol  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

pentanoyl chloride  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COCl}$

Add water to all three liquids:

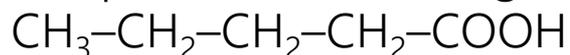
The water with pentanoyl chloride vigorously / to produce steamy fumes / heat.

This is a substitution / hydrolysis reaction to form the carboxylic acid below:



Add Tollens' reagent to the remaining two liquids:

The pentanal will undergo an oxidation reaction to form pentanoic acid:



A silver mirror / black precipitate forms.

Add acidified potassium dichromate to the remaining liquid. The pentan-1-ol will be oxidised to form pentanoic acid:  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ . The solution will change colour from orange to green.



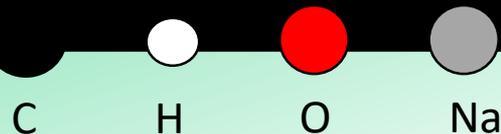


The formation of an ionic salt increases the solubility of the amine in acidic solutions (compared to their solubility in water). This change in solubility can be used to separate amines from other organic compounds. The formation of the salt also results in the disappearance of the obnoxious smell of the amine, which explains why lemon juice is often provided with fish meals.

Amines are made by the substitution reaction between  $\text{NH}_3$  and haloalkanes, but the reaction is carried out using alcohol as a solvent rather than water.

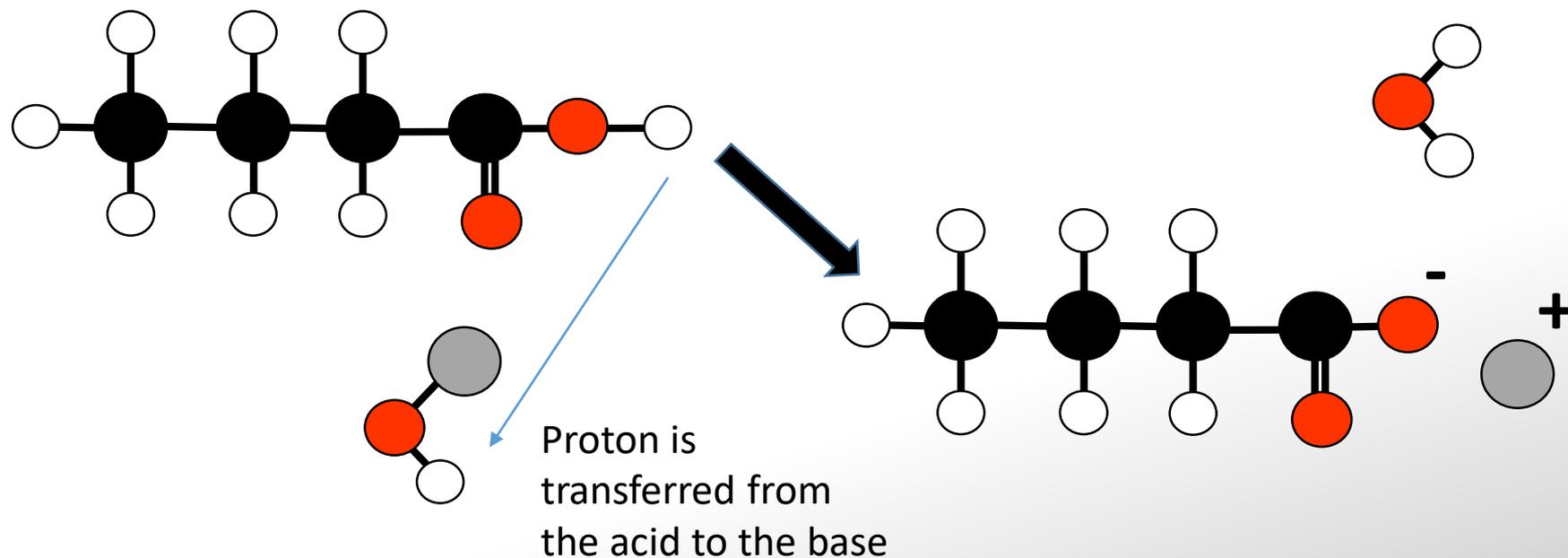
This reaction can occur in solution, or in the air as vapours given off solutions of both chemicals meet and combine to form a smoke. This smoke is made of the salt in solid form.





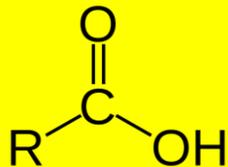
Carboxylic Acids are Weak Acids and are **proton donors** in water  
Carboxylic acids act as a weak acid by partially dissociating and **neutralising** bases:

For example



**acid + base → salt + water**

## Carboxylic Acids

Acid-Base  
reactionNH<sub>3</sub>

## Carboxylic ion

Acid + Base → Carboxylic salt + NH<sub>4</sub><sup>+</sup>

Carboxylic acid also have similar reactions to other acids

carboxylic acid + carbonate → carboxylic salt + water + carbon dioxide

carboxylic acid + metal → carboxylic salt + hydrogen gas

carboxylic acid + oxide → carboxylic salt + water

React with **magnesium** to give hydrogen gas (a useful test)React with calcium **carbonate** to give CO<sub>2</sub>(g) (a useful test)

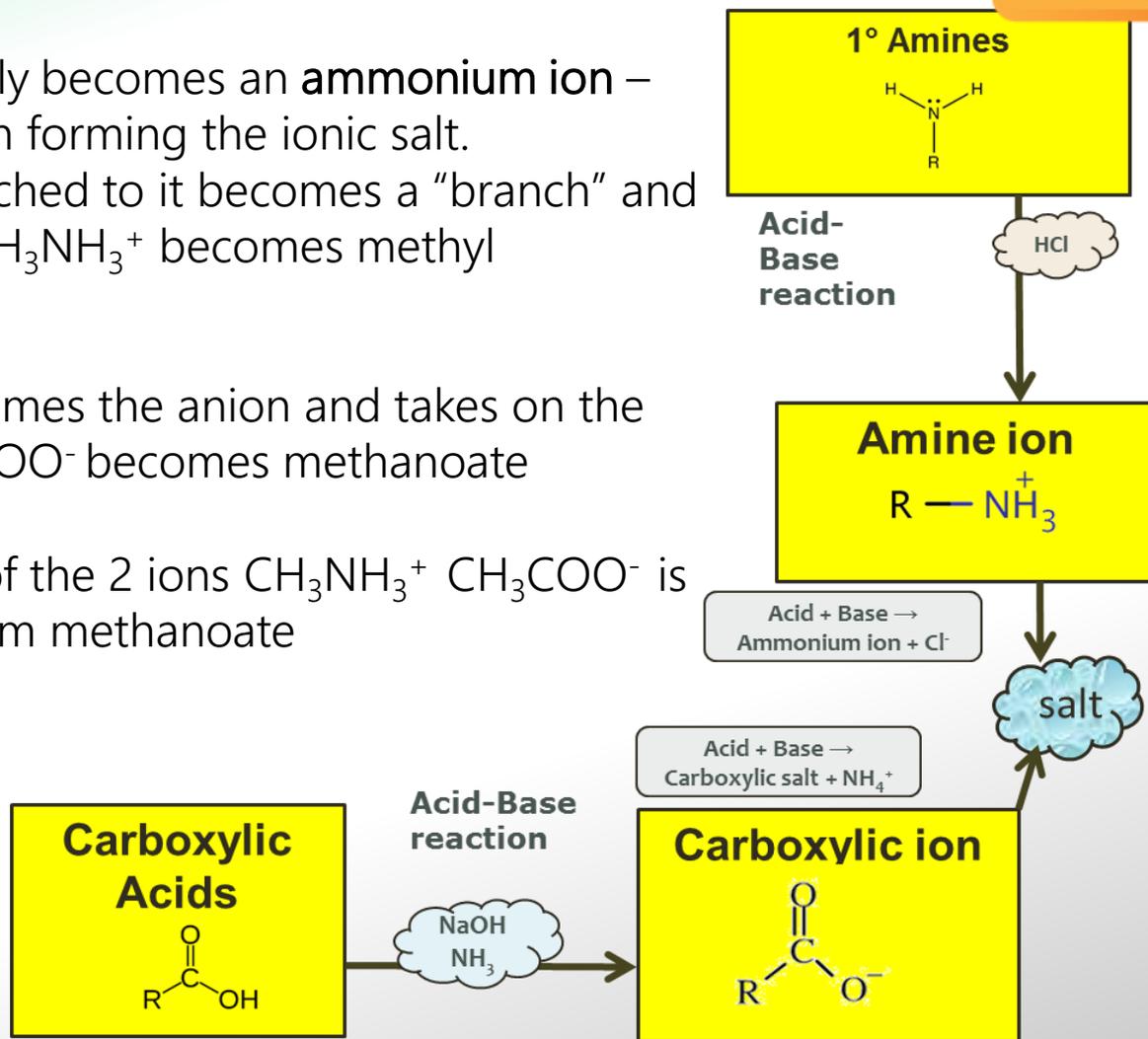
## Naming salts.

The amine ion effectively becomes an **ammonium ion** – and acts as the cation in forming the ionic salt.

The organic group attached to it becomes a “branch” and is named as such. i.e.  $\text{CH}_3\text{NH}_3^+$  becomes methyl ammonium

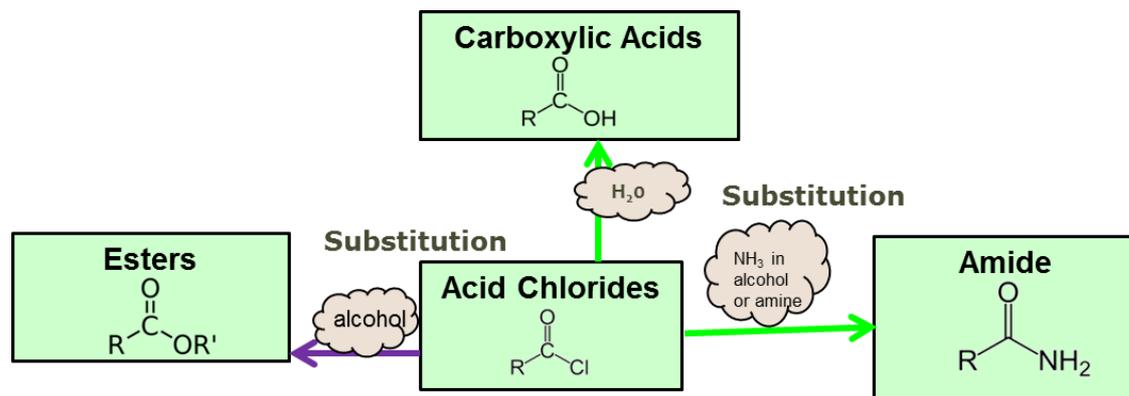
The **carboxylic ion** becomes the anion and takes on the suffix –anoate. i.e  $\text{CH}_3\text{COO}^-$  becomes methanoate

Therefore a salt made of the 2 ions  $\text{CH}_3\text{NH}_3^+$   $\text{CH}_3\text{COO}^-$  is called methyl ammonium methanoate



## Acid Chloride reactions

**Choice of chlorinating agent.** By choosing the correct chlorinating agent, the products will be easier to separate by fractional distillation. e.g. If  $\text{PCl}_5$  was used to chlorinate butanoic acid, the products butanoyl chloride (B.P.  $102^\circ\text{C}$ ) and phosphorous oxychloride  $\text{POCl}_3$  (B.P.  $103^\circ\text{C}$ ) would be difficult to separate



**Condensation** (or dehydration) reactions are a type of elimination reaction where a molecule of water is removed) – in **esterification** OH is removed from alcohol and O from a carboxylic acid and they are joined to form an ester

**Substitution** reactions are characterized by replacement of an atom or group (Y) by another atom or group (Z). Aside from these groups, the number of bonds does not change.

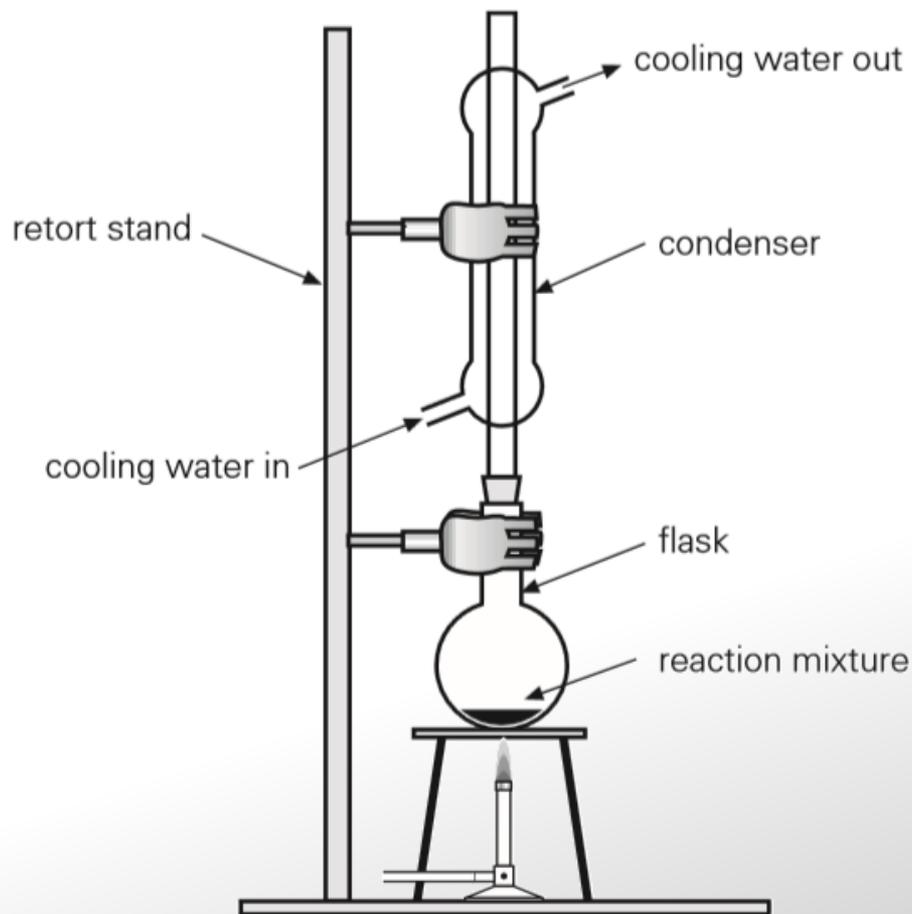


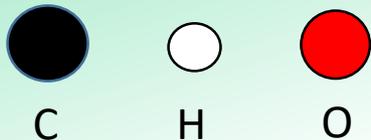
Esterification is a **condensation** reaction that combines a carboxylic acid and an alcohol, where a water molecule is removed.

The carboxylic acid and alcohol are **refluxed** with concentrated sulphuric acid.

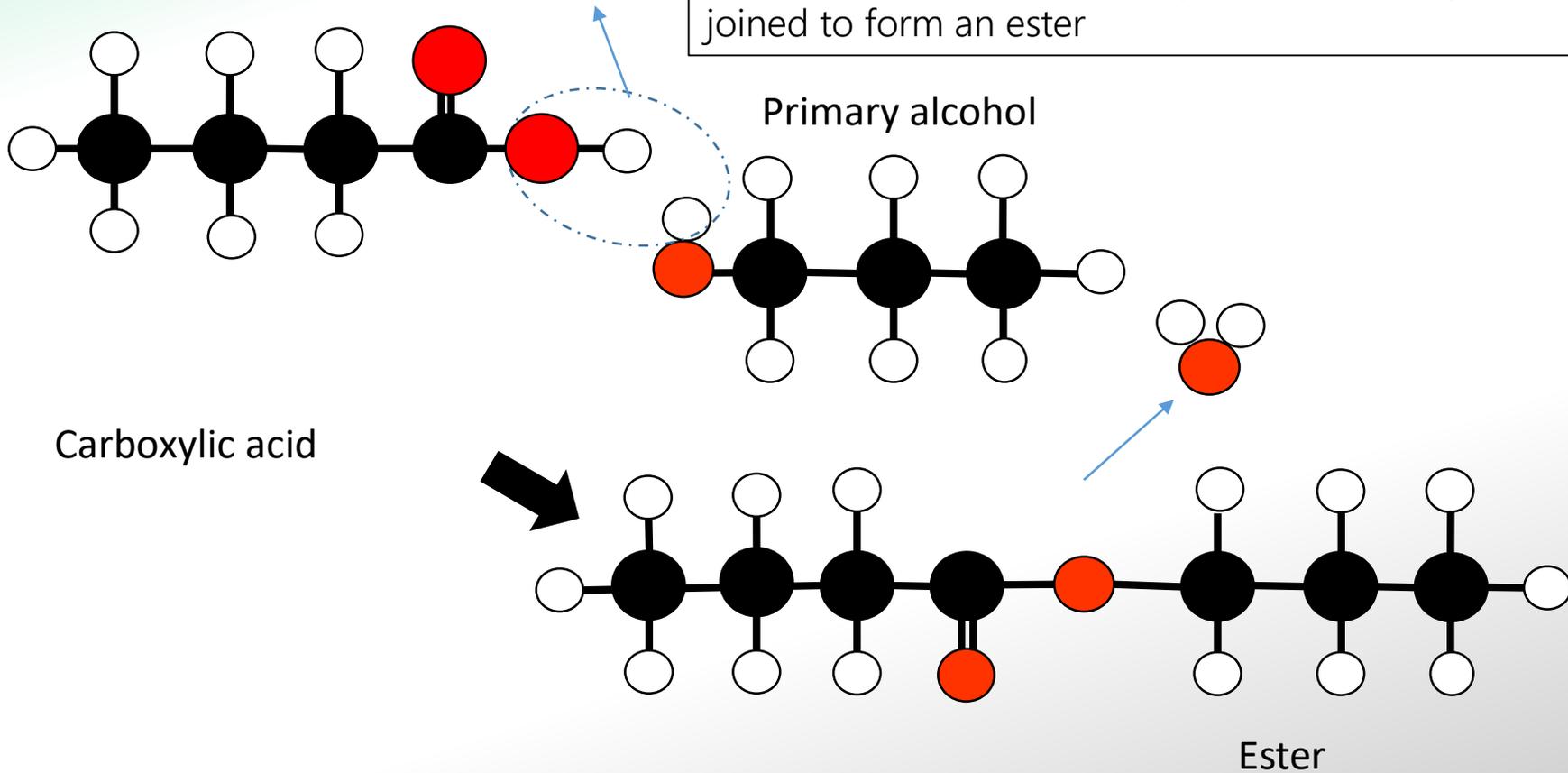
After reflux, **sodium carbonate** is added to neutralise any excess acid and **anhydrous magnesium sulfate**  $\text{MgSO}_4$  is added to remove water.

Because of the volatility of esters, they are then readily separated from the reaction mixture by fractional distillation.





Condensation (or dehydration) reactions are a type of elimination reaction where a molecule of water is removed) – in **esterification** OH is removed from alcohol and O from a carboxylic acid and they are joined to form an ester

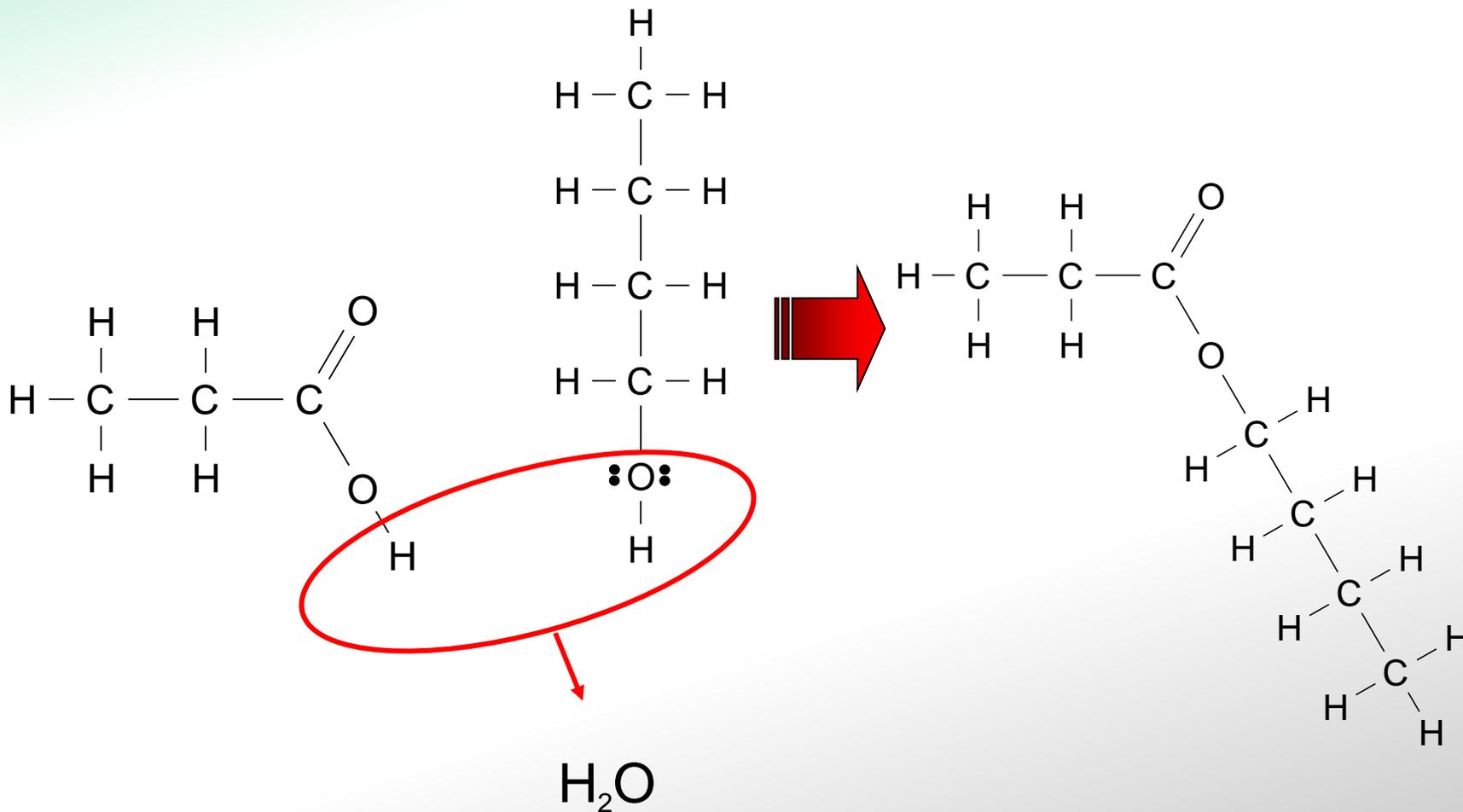


This reaction takes place under reflux conditions

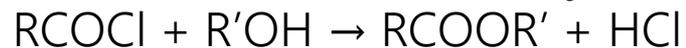
Carboxylic Acid + alcohol

Heating and H<sub>2</sub>SO<sub>4</sub>

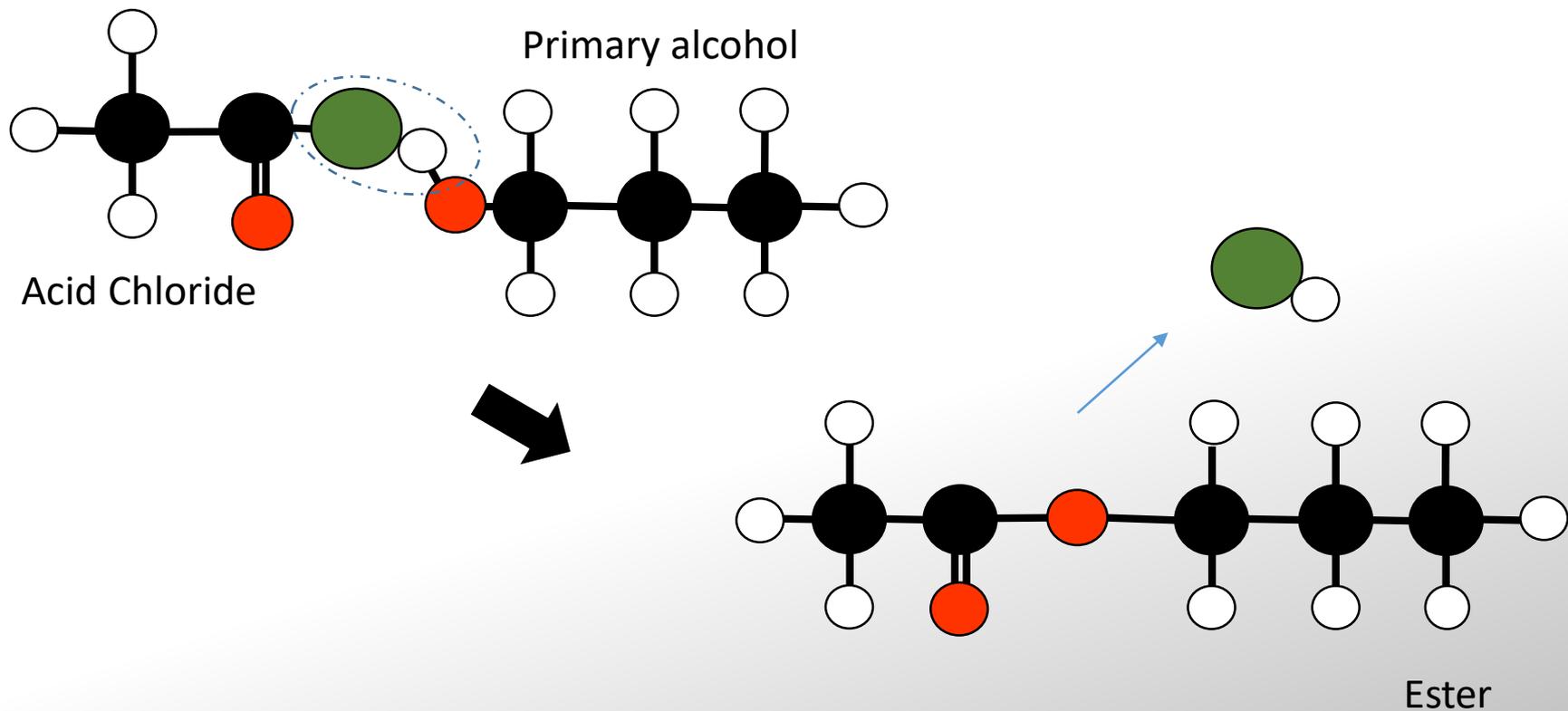
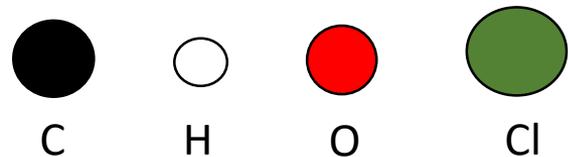
Ester + water



Acid Chlorides React readily with alcohols to produce esters



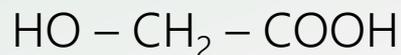
The acid chloride is dropped into pure alcohol, (in fume cupboard, because  $\text{HCl}_{(g)}$  is produced). Reaction is fast, yield is high, no heat or catalyst required.



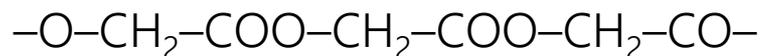
## NCEA 2018 Esterification Reactions

Excellence  
Question

**Question 3a :** Glycolic acid can be used to make polyglycolic acid (PGA), a polyester used to make dissolvable stitches. The structure of glycolic acid is shown below:

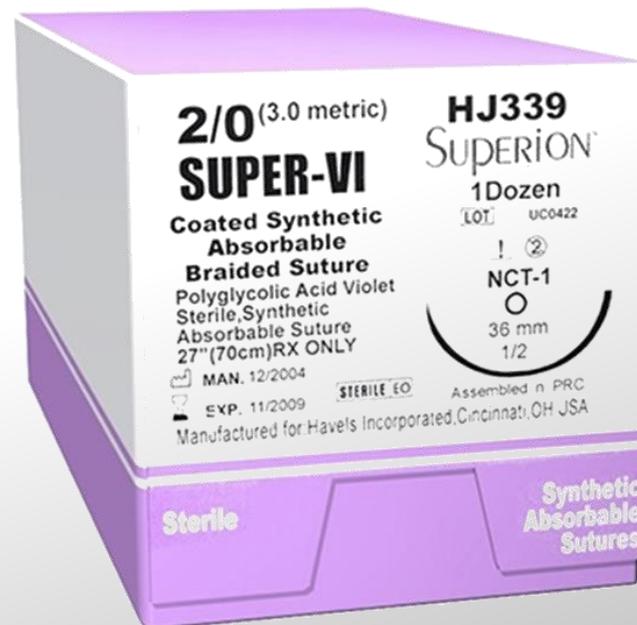


- In the box below, draw a section of the PGA polymer chain to show THREE repeating units.
- Identify and explain the type of reaction occurring in the formation of PGA.



The formation of PGA is a condensation polymerisation reaction. In a condensation reaction, small monomers join together releasing water.

Water is released for each ester linkage formed / because the monomers have two functional groups they react at both ends



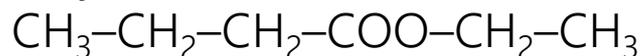
# NCEA 2018 Esterification Reactions

Merit  
Question

**Question 3b :** Many organic synthesis reactions are heated under reflux.

(i) Draw the structural formula and name the ester formed from heating ethanol and butanoic acid under reflux in the presence of concentrated sulfuric acid.

ethyl butanoate



Increases rate because it is able to be heated

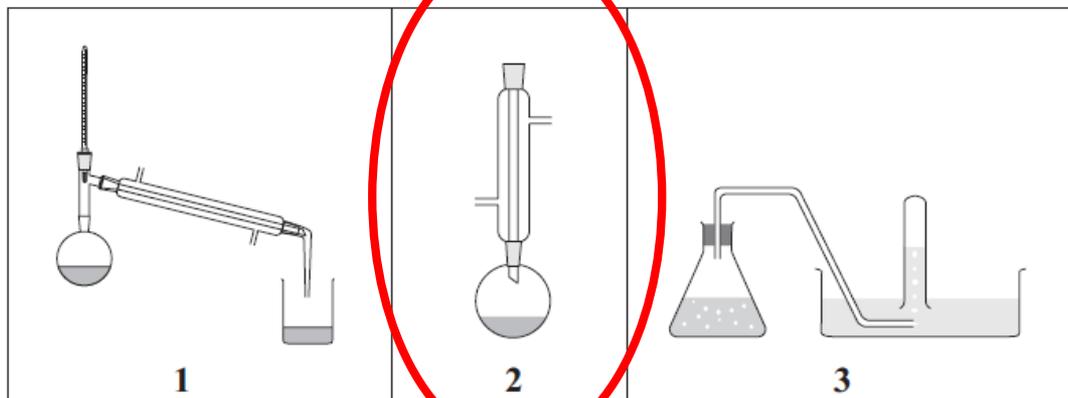
No loss of products / reactants because they are condensed back into the mixture

Increases the amount of products / yield because reactants

/ products are prevented from escaping

**Question 3b :** (ii) From the diagrams below, give the number of the apparatus used for heating under reflux.

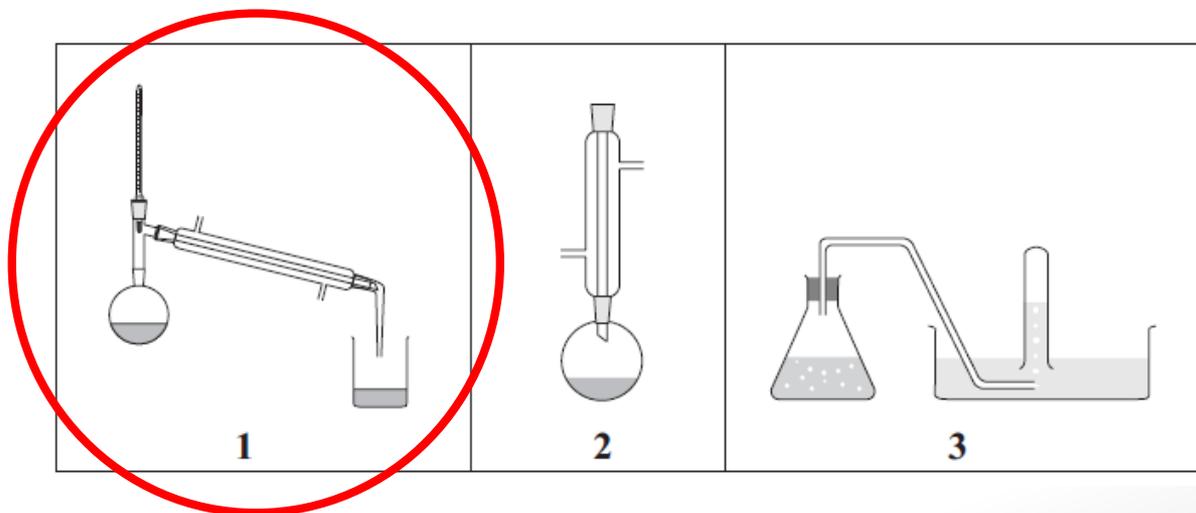
(iii) Outline the advantages of heating under reflux in the preparation of the ester in part (i).



## NCEA 2018 Esterification Reactions

Excellence  
Question  
with v

**Question 3b :** (iv) From the diagrams below, give the number of the apparatus and explain the process that could be used to purify (separate) the ester in part (i) from the reaction mixture.



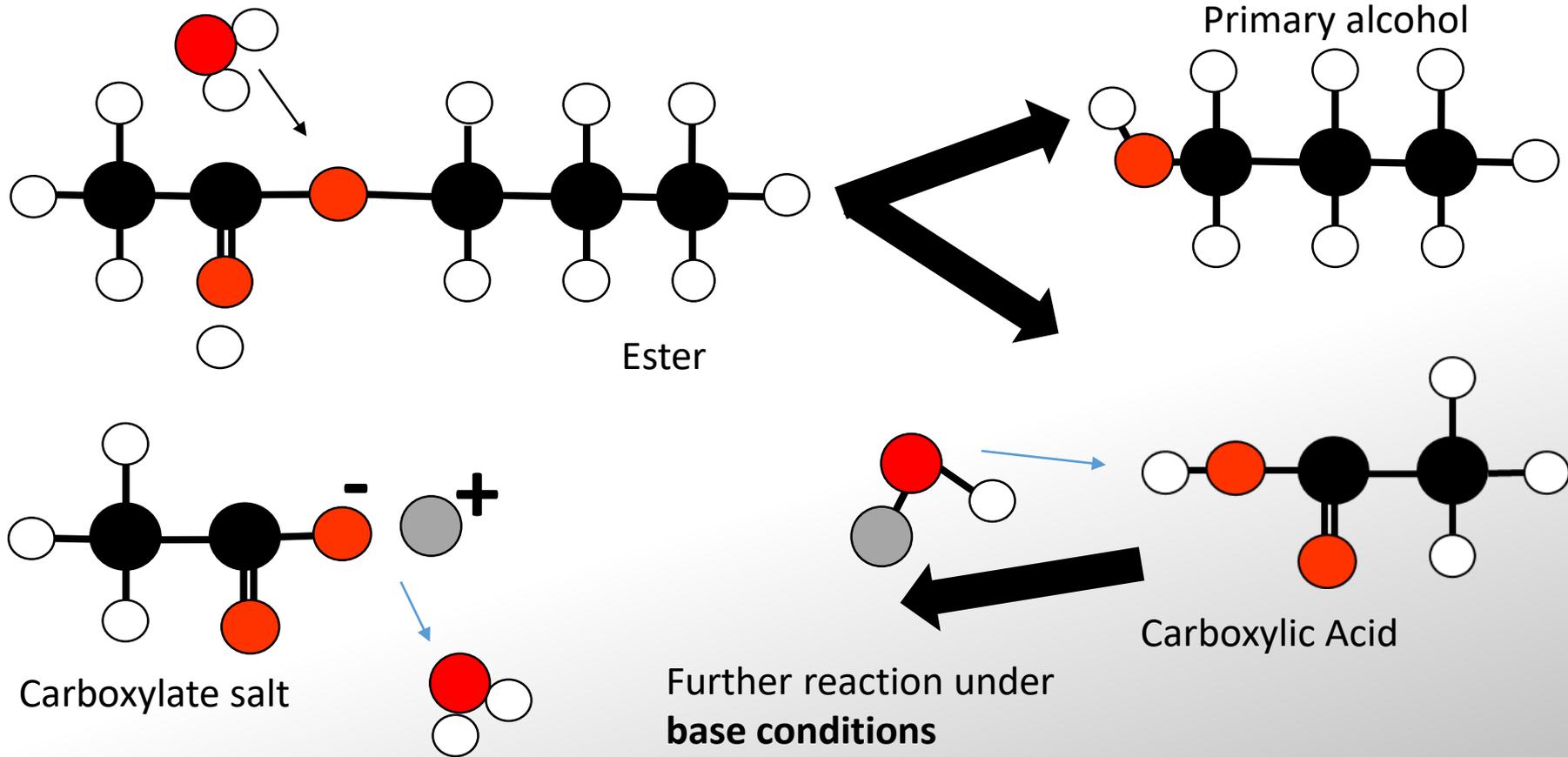
Distillation could be used to purify the ester (diagram 1).

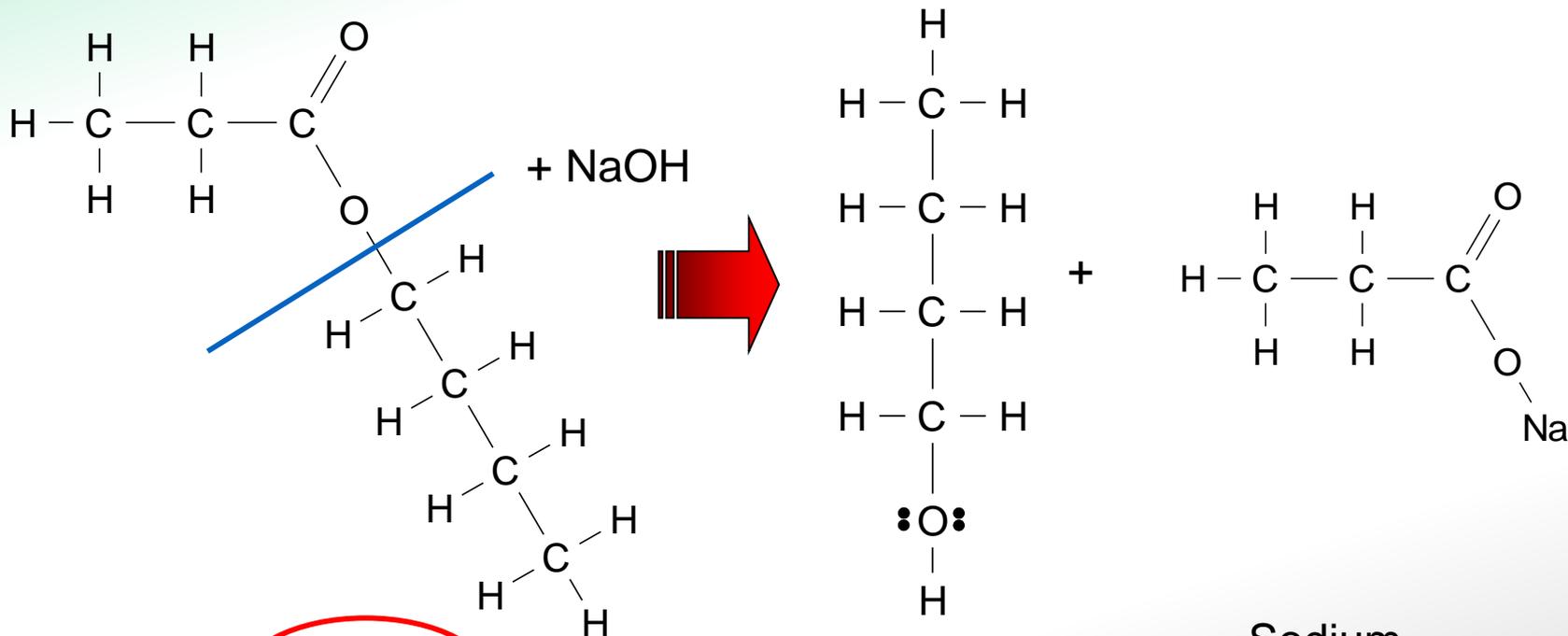
The reaction mixture is heated to the boiling point of the ester which is different from both the alcohol and carboxylic acid reactants. The ester will evaporate from the mixture and enter the condenser where it is cooled back to the liquid to be collected. The ester has therefore been separated from the reaction mixture.

## Hydrolysis with Esters



Hydrolysis reactions involve water as a reactant and becomes part of the reaction product. Hydrolysis 'splits' the ester bond (C-O-C) and the ester breaks into the 'original' alcohol and the carboxylic acid. These two products will remain if under acid conditions. When under base conditions then the carboxylic undergoes a further reaction with the base to form a salt (+water)





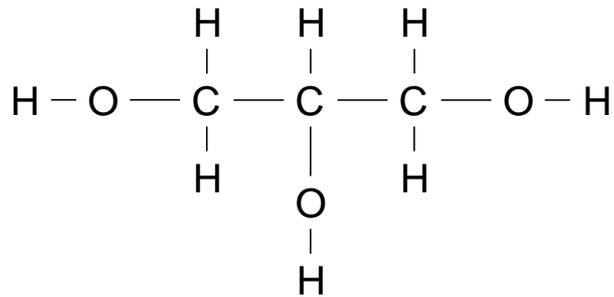
Butyl propanoate

butanol

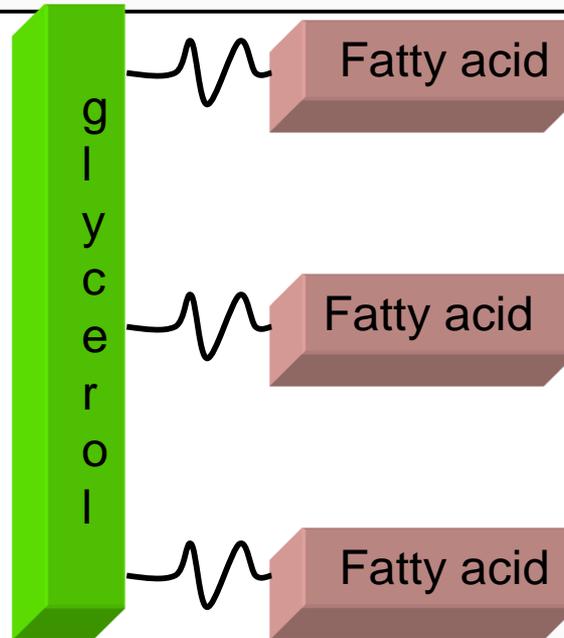
Sodium propanoate

Glycerol (triol) + 3 long carboxylic acids (fatty acids)  $\longrightarrow$   
triglyceride

## GLYCEROL



propan,-1,2,3-triol

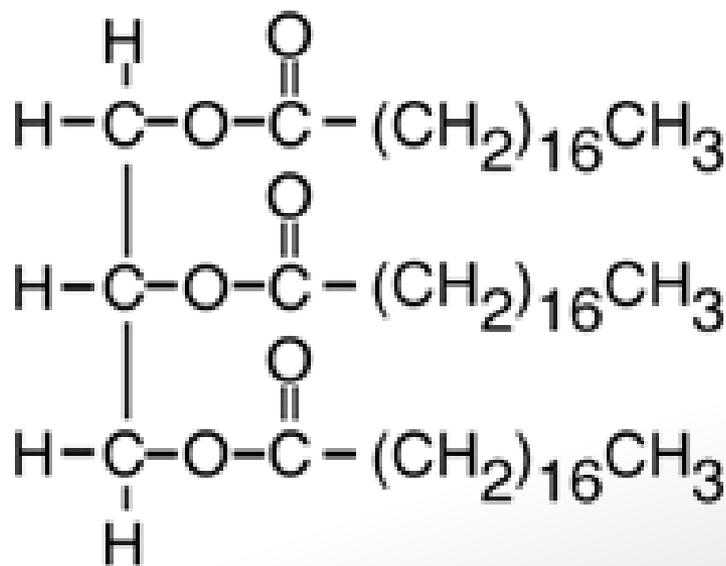


Triglycerides are naturally found in animal fats and seed and nut oils

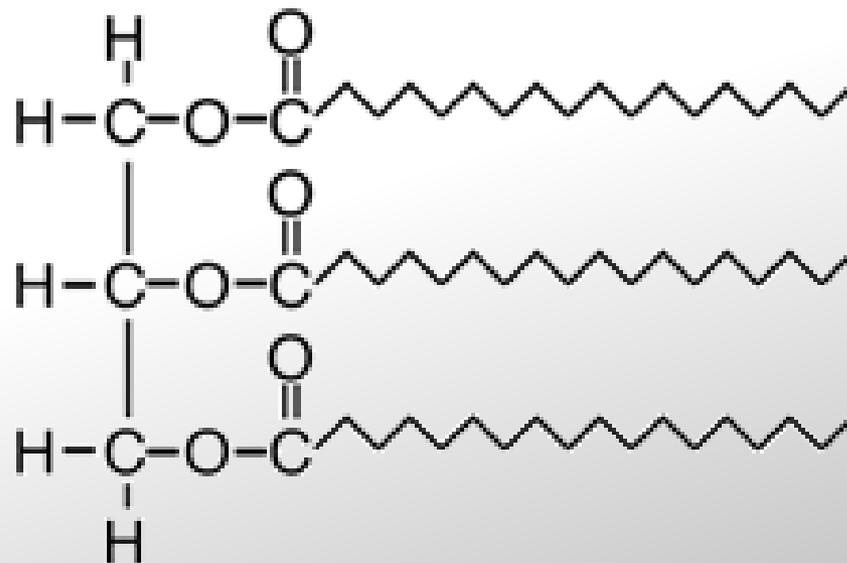
## Saponification

Triglycerides heated with NaOH produce soap + glycerol

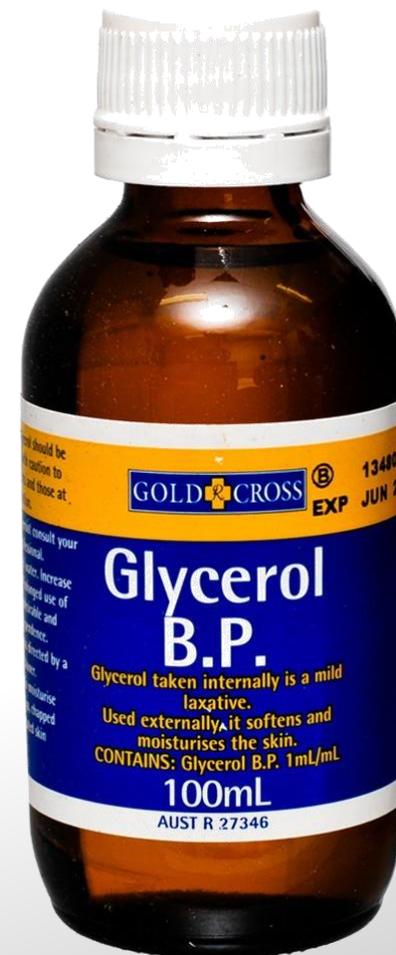
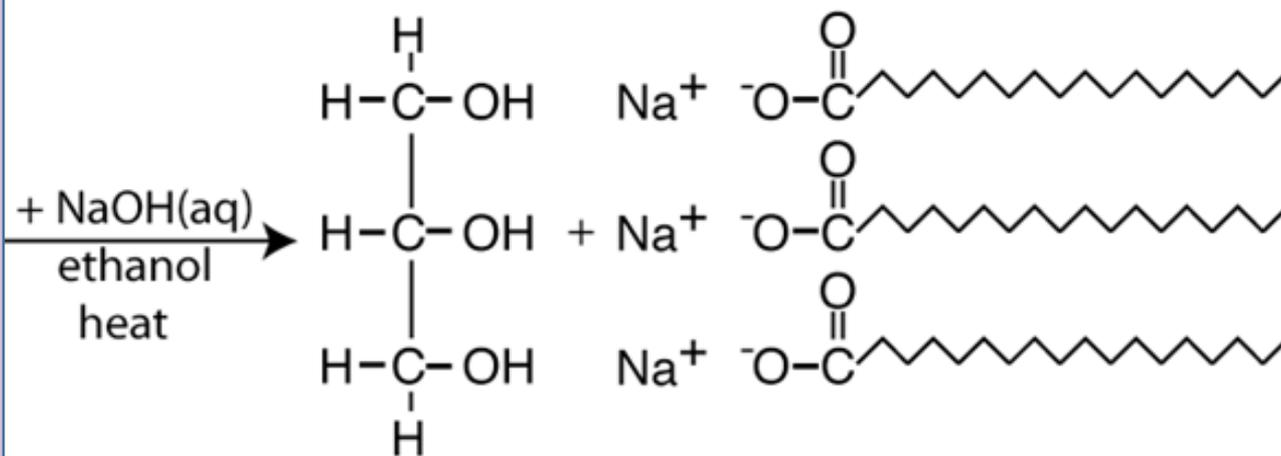
Fats and oils are "triesters"  
 e.g. glycerol tristearate  
 a saturated fat found in many  
 animal and vegetable fats such as  
 tallow (animal fat).



OR

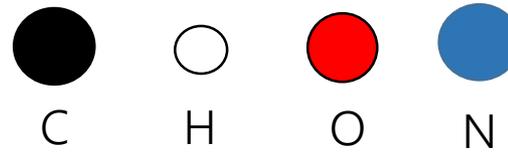
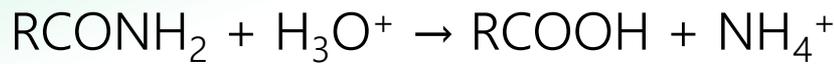


Hydrolysis of fats or oils with ethanolic aqueous sodium hydroxide produces glycerol and the sodium salt of the fatty acid.

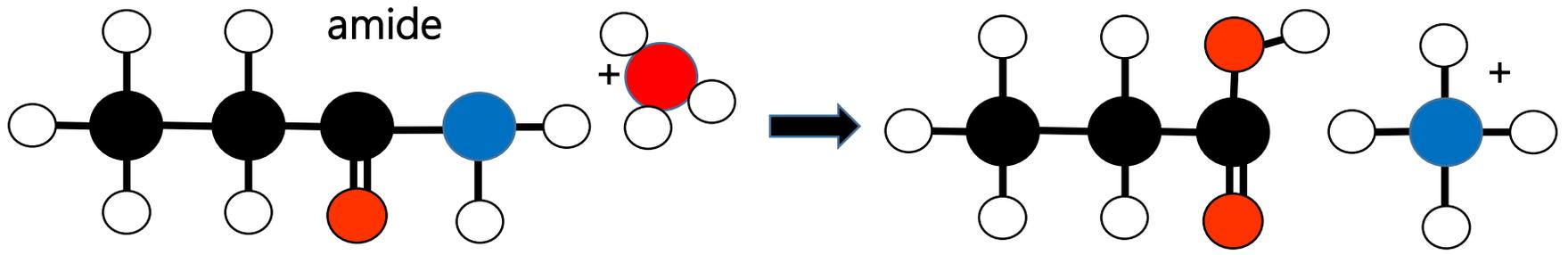


## Hydrolysis Reactions of Amides

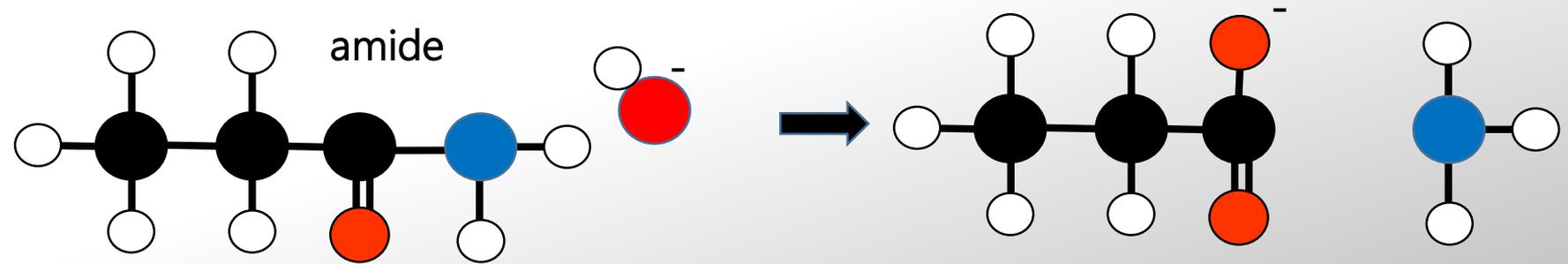
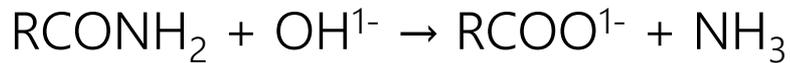
Acid hydrolysis produces the carboxylic acid and ammonium ions.



You distinguish an amide from an amine by adding NaOH. Only the amide releases NH<sub>3</sub>.



Base hydrolysis produces the carboxylate ion and ammonia

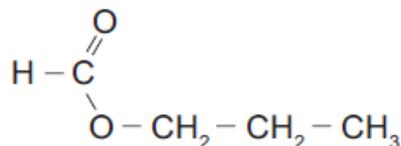


# NCEA 2013 Hydrolysis reactions (PART ONE)

Merit  
Question

**Question 1d:** Give the structures and names of the products of the reactions below. These reactions are carried out by heating in either:

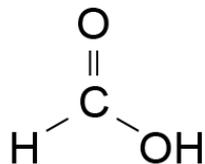
- dilute hydrochloric acid solution, or
- dilute sodium hydroxide solution.



dilute hydrochloric  
acid solution

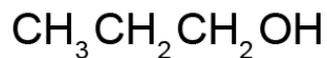
dilute sodium  
hydroxide solution

In acidic conditions the products are:



Name: \_\_\_\_\_

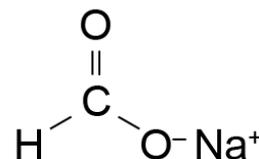
methanoic acid



Name: \_\_\_\_\_

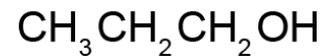
propan-1-ol

In basic conditions the products are:



Name: \_\_\_\_\_

sodium methanoate  
/ methanoate ion



Name: \_\_\_\_\_

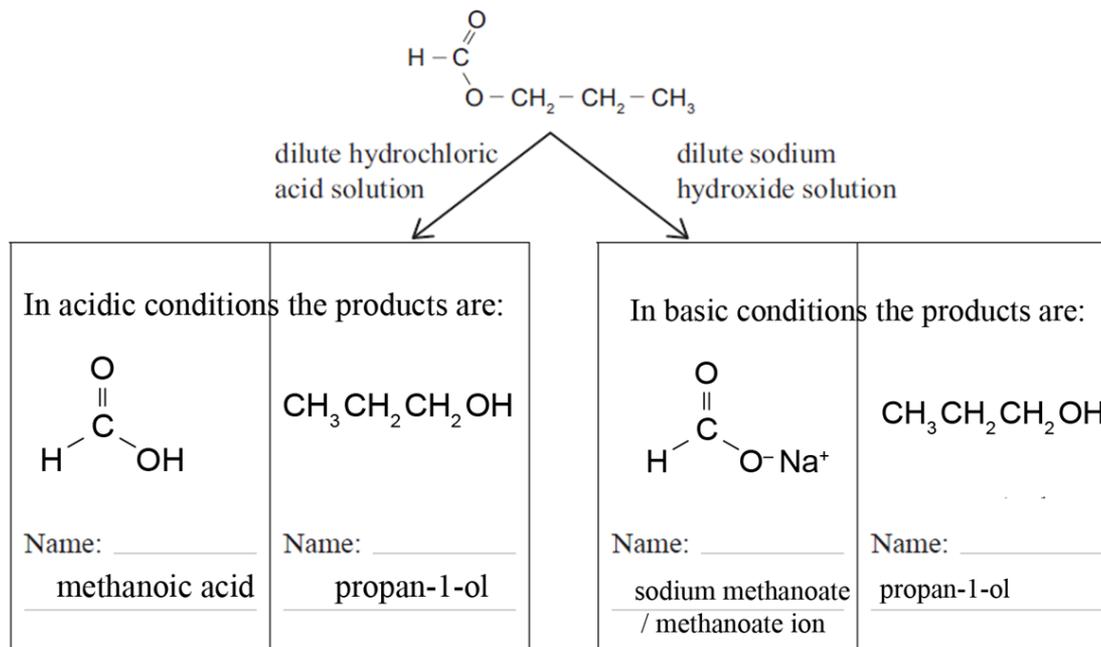
propan-1-ol

# NCEA 2013 Hydrolysis reactions - (PART TWO)

Excellence  
Question

**Question 1d:** Compare and contrast the reactions below.

In your answer, you should include the type of reaction(s) taking place.



The ester link is hydrolysed in both acid and basic conditions.

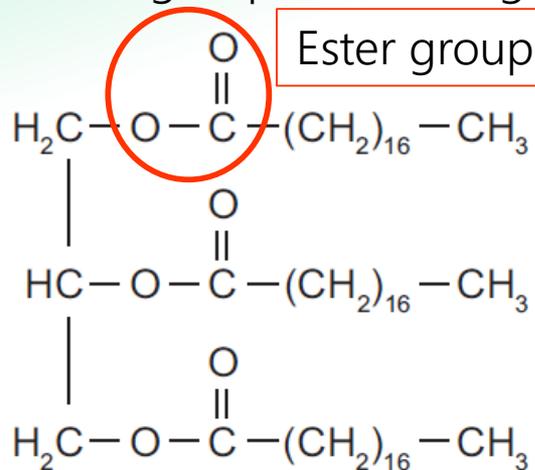
Both produce an alcohol.

Acidic hydrolysis produces an acid and basic hydrolysis produces a base or salt / following hydrolysis in sodium hydroxide, an acid-base reaction occurs to form the sodium salt and water. (No further reaction occurs in acid.)

# NCEA 2014 Hydrolysis Reactions

Merit  
Question

**Question 1(c):** (i) The triglyceride below is shown in condensed form. Circle a functional group on the diagram above and give its name.



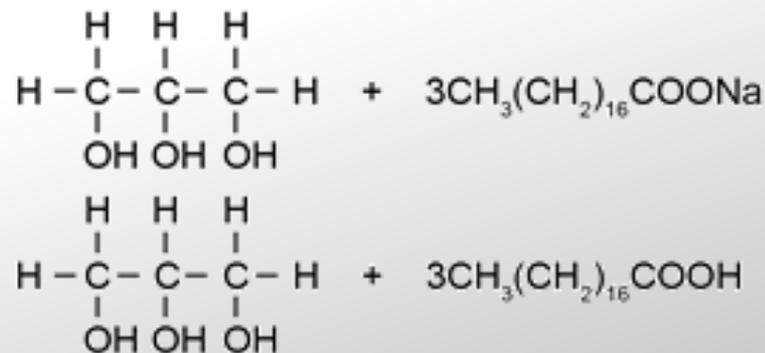
Ester group

(ii) Compare and contrast the reaction of the triglyceride when it undergoes both acidic and basic hydrolysis.

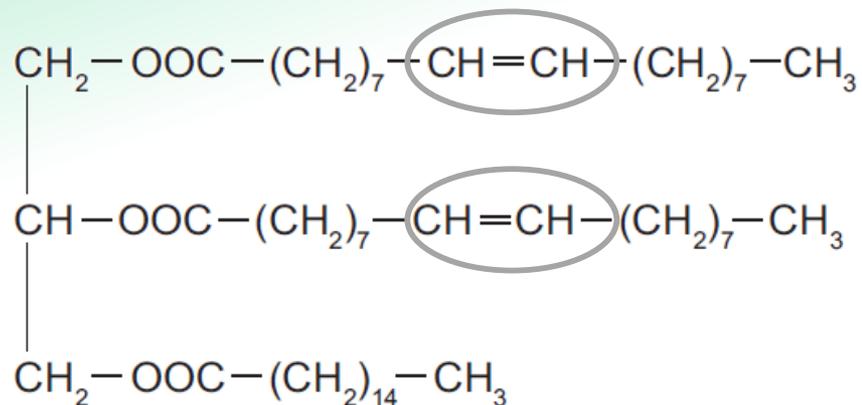
In your answer you should include:

- drawings of condensed structures of the organic products
- any reagents and conditions required for the reaction to proceed.

**Answer:** Both acidic and basic hydrolysis produce the same alcohol *propan-1,2,3-triol*. In addition, they both require heat / reflux. In contrast, acidic hydrolysis requires  $\text{H}_2\text{O}$  /  $\text{H}^+$  or  $\text{HCl(aq)}$  and produces the carboxylic acid, whereas basic hydrolysis requires  $\text{H}_2\text{O}$  /  $\text{OH}^-$  or  $\text{NaOH(aq)}$  and produces the carboxylate ion/salt.



Question 3(a): (a) A triglyceride has the following structure:



(i) Circle one of the alkene groups in the triglyceride molecule.

This triglyceride is described as unsaturated.

(ii) Describe a chemical test that can be used to show that the molecule is unsaturated.

Give any observations, and state the type of reaction occurring.

**Answer:**

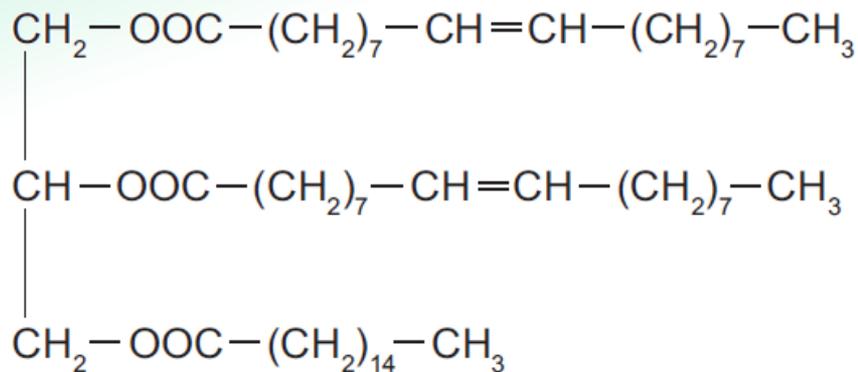
Bromine water rapidly decolourised from red or orange to colourless in an addition reaction.

OR

Acidified permanganate rapidly decolourised from purple to colourless in a redox or oxidation or reduction reaction.

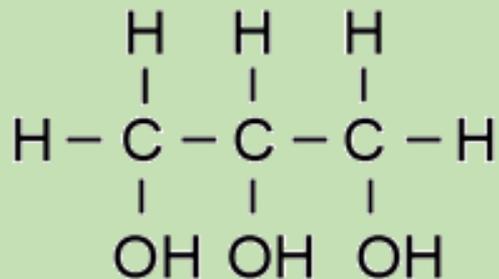
# NCEA 2015 Hydrolysis Reactions

Merit  
Question



**Question 3(a):** (iii) Draw the structural formulae of the organic products formed by hydrolysis of this triglyceride using aqueous sodium hydroxide.:

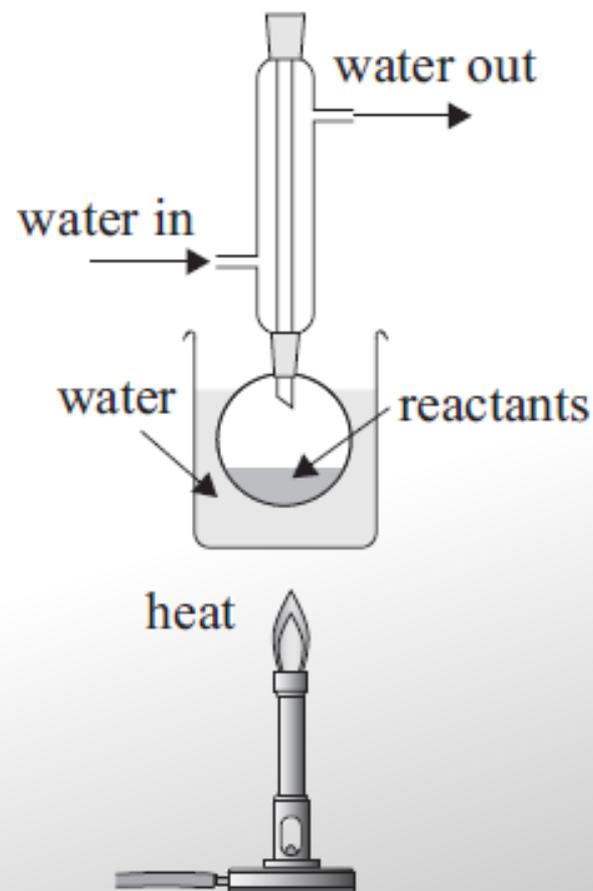
Answer:



**Question 3(a):** (iv) Explain why the equipment to the right is used for hydrolysis of the triglyceride.

**Answer:**

**Reflux** - Increases the rate of reaction;  
(Condensing) prevents volatile chemicals from being lost to the environment,  
(The mixture refluxed to increase reaction rate without loss of product through evaporation).



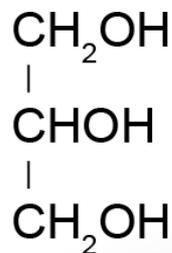
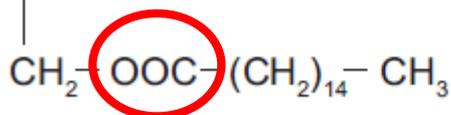
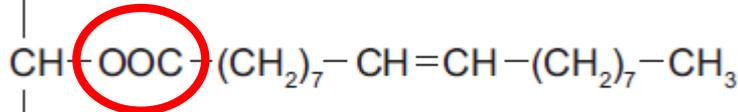
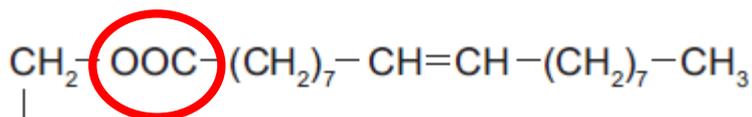
# NCEA 2016 Hydrolysis Reactions

Merit  
Question

**Question 3c:** A triglyceride found in olive oil has the following structure below.

(i) Put a **circle** around one of the ester groups in the triglyceride molecule shown above.

(ii) Draw the structural formulae of the products produced by the hydrolysis of this triglyceride in basic conditions, using aqueous sodium hydroxide, NaOH.



and



# NCEA 2018 Hydrolysis Reactions

Excellence  
Question

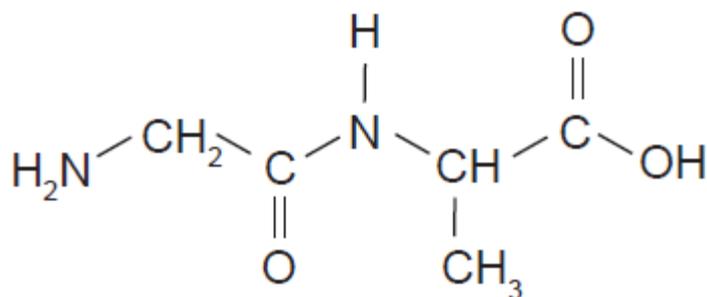
**Question 2b:** Dipeptides are made from two amino acids joined by an amide (peptide) bond. The dipeptide shown below is made from glycine and alanine:

(i) Circle the amide (peptide) bond.

(ii) Compare and contrast the acidic and basic hydrolysis of the above dipeptide.

Your answer should include: • an explanation of the hydrolysis reaction

• structural formulae of the products formed when the dipeptide undergoes acidic and basic hydrolysis

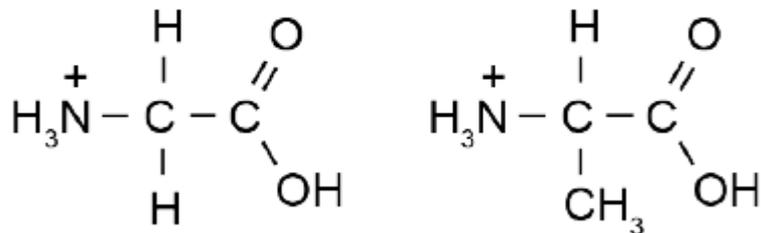


Water is used to break the amide (peptide) bond. H is added to one molecule and OH to the other.

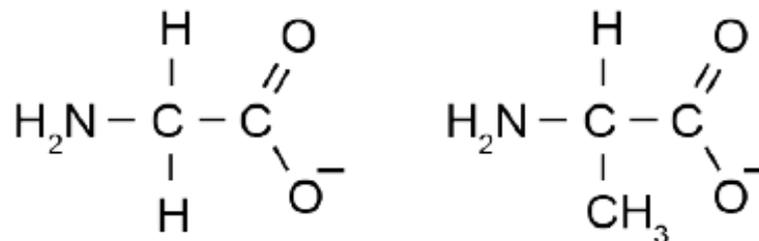
The  $\text{NH}_2$  group gains a proton ( $\text{H}^+$ ) in acidic conditions / forms  $\text{NH}_3^+$ .

The  $\text{COOH}$  group loses a proton ( $\text{H}^+$ ) in basic conditions / forms  $\text{COO}^-$ .

Acidic conditions:



Basic conditions:

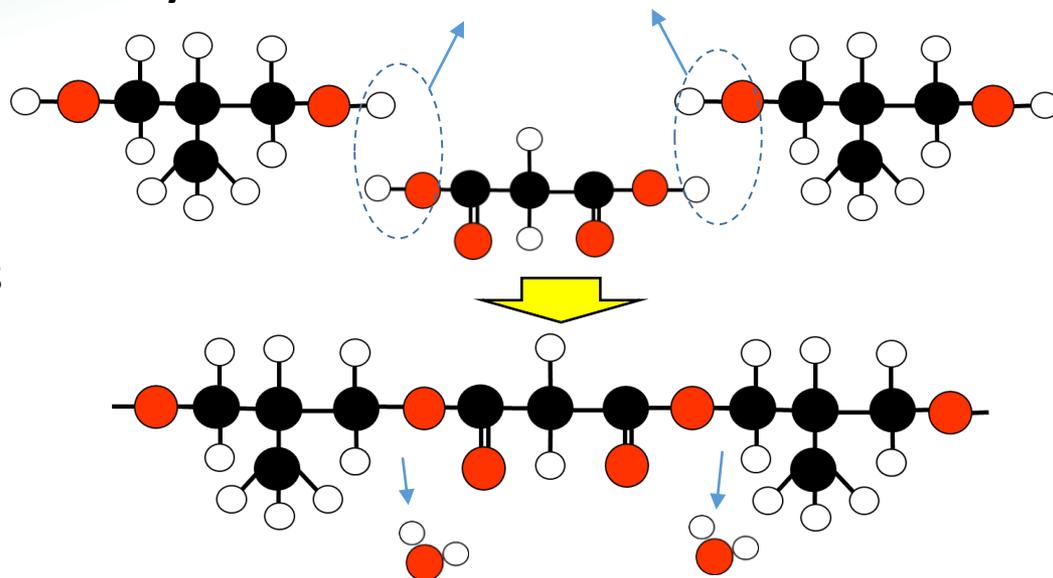


Condensation reactions involve the elimination of water. Polymerisation involves smaller units called monomers joining together to form larger molecules or chains called polymers.

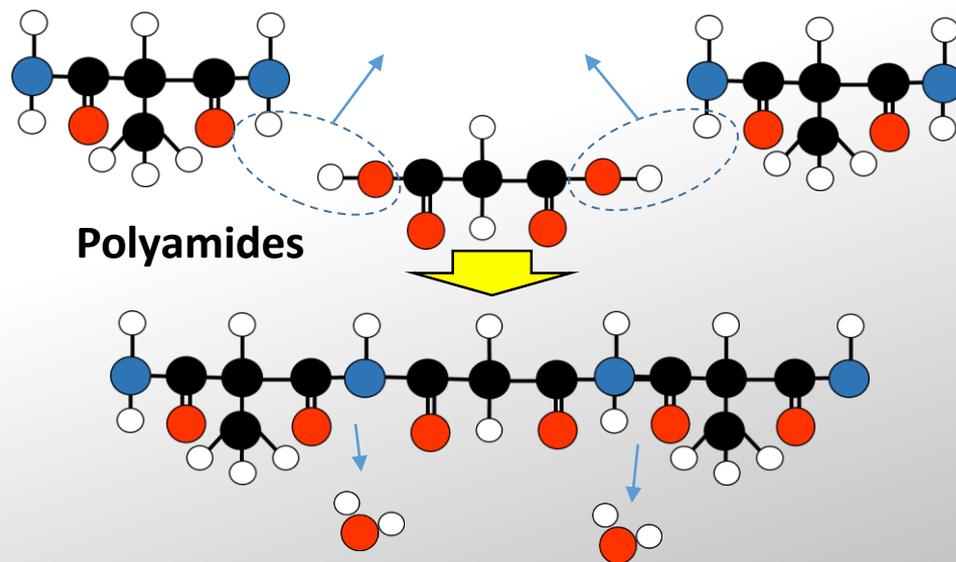
There are two main types of condensation polymers – **Polyesters** - the monomers consist of a di-carboxylic acid (a COOH at each end) and a diol (an -OH at each end). These monomers join together at each end to form an ester bond. The CA and the alcohol then continue joining in repeating patterns.

**Polyamide** – the monomers consist of an amide and a di-carboxylic acid.

## Polyesters



## Polyamides

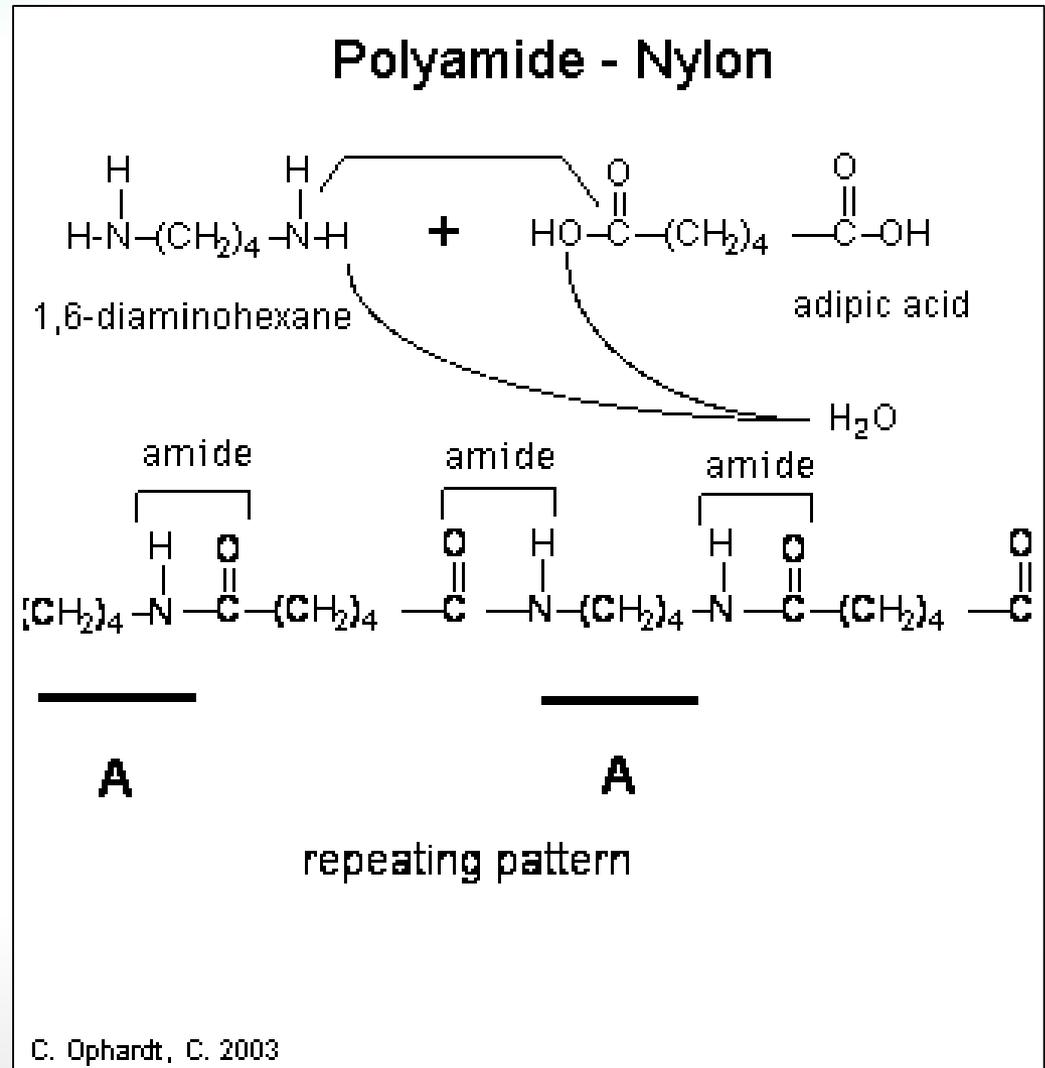


A carboxyl group (carbon with a double bonded oxygen such as carboxylic acid) and an amino group (with a  $\text{NH}_2$  attached to the carbon chain such as an amide or amine) can react together to form an amide or **peptide** link ( $-\text{CONH}$ ) through condensation polymerisation – as a water molecule is released to form each link.

e.g. Nylon-6,6

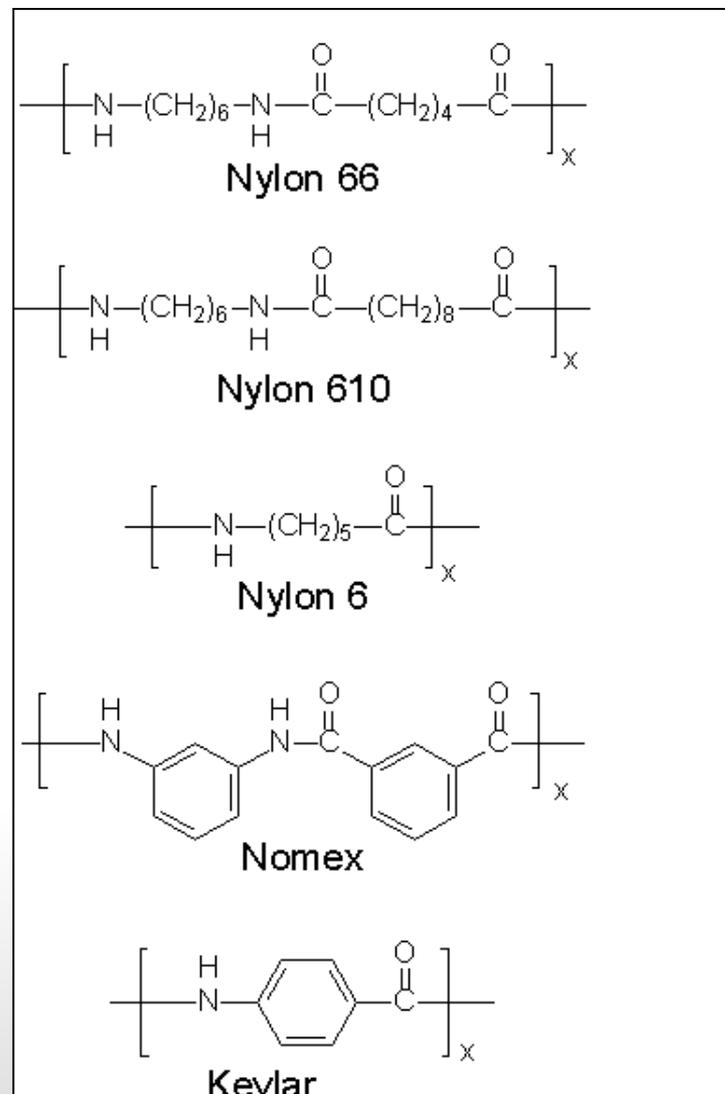
**Preparation:**

Condensation polymerisation of a diamine and a dicarboxylic acid

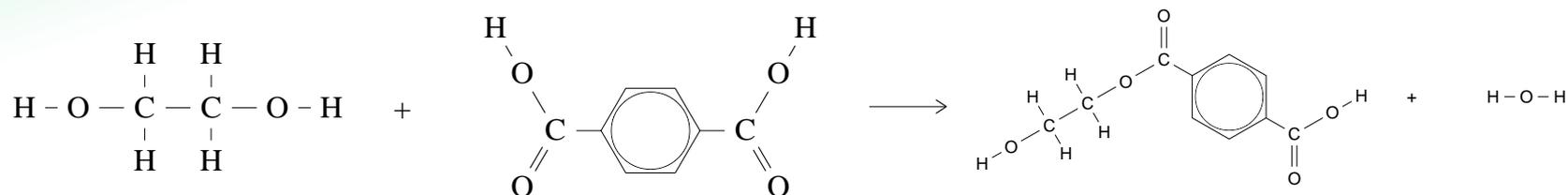




A polyamide is a polymer containing monomers of amides joined by peptide bonds. They can occur both naturally and artificially, examples being proteins, such as wool and silk, and can be made artificially through step-growth polymerization or solid-phase synthesis, examples being nylons, aramids, and sodium poly(aspartate). Polyamides are commonly used in textiles, automotives, carpet and sportswear due to their extreme durability and strength



These are formed by repeated condensation of a di-acid and a di-alcohol.  
e.g. Preparation of Terylene



1,2-ethanediol

benzene-1,4-dicarboxylic acid

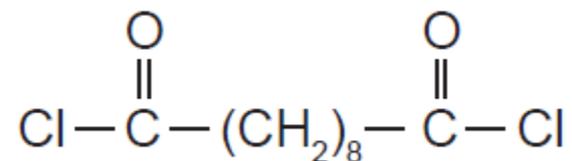
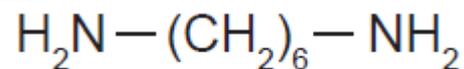
Repeated condensation reactions at either end produces the polymer Terylene.



**Question 2(c):** A form of the polymer nylon can be made from the two monomers below.

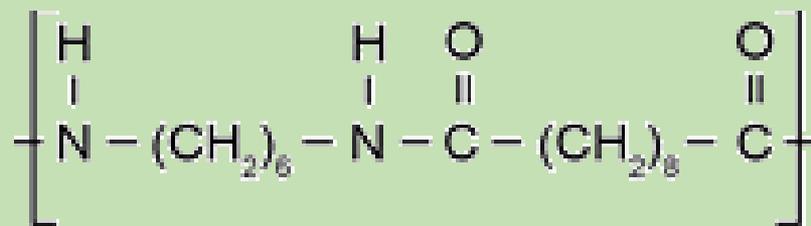
1,6-diaminohexane

Sebacoyl chloride (decanedioyl dichloride)



(i) draw the repeating unit of the polymer formed if these two monomers are used.

**Answer:**





**Question 2(c):** (iv) Elaborate on the reaction that will occur if a dilute aqueous solution of acid is mixed with the newly formed polymer.

**Answer:**

Dilute acid will cause hydrolysis of the amide linkage.

The products formed would be (di)ammonium salt or  $^+H_3N(CH_2)_6NH_3^+$  and the (di)oic acid.  $HOOC(CH_2)_8COOH$

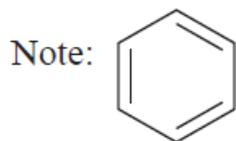
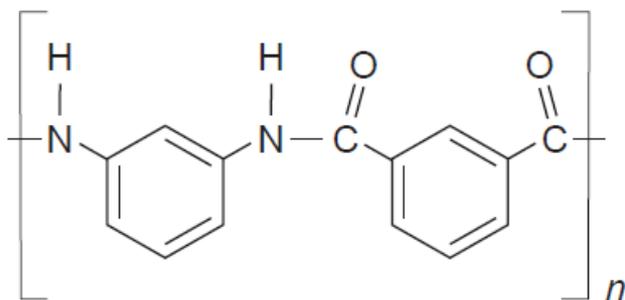
(Names not required)



## NCEA 2017 Polymerisation

Excellence  
Question

**Question 3b:** Nomex<sup>®</sup> is a polymer used in firefighters' suits. Nomex<sup>®</sup> is made up of two different monomers bonded together to form the polymer chain. A small portion of the structure of Nomex<sup>®</sup> is shown below.



is a benzene ring and does not change when the monomers bond together to form the polymer.

Explain the structure of the polymer, Nomex<sup>®</sup>.

In your answer, you should include:

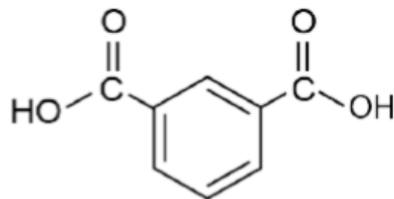
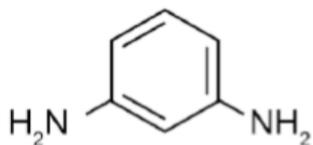
- the name of the functional group linking the monomers
- a drawing of both monomers
- a classification of the type of polymer formed, with an explanation to justify your choice. (see next slide)

Explain the structure of the polymer, Nomex®.

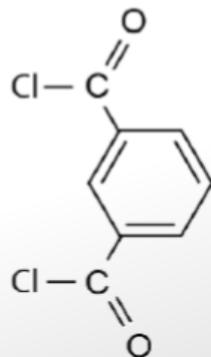
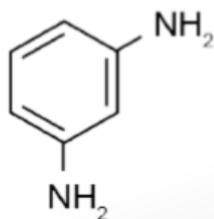
In your answer, you should include:

- the name of the functional group linking the monomers
- a drawing of both monomers
- a classification of the type of polymer formed, with an explanation to justify your choice.

Monomers:



OR



Nomex® has an amide linkage  
This is a condensation polymer /  
polyamide, as monomers join /  
amide link  
forms and a molecule of water or  
HCl is released during the  
reaction.

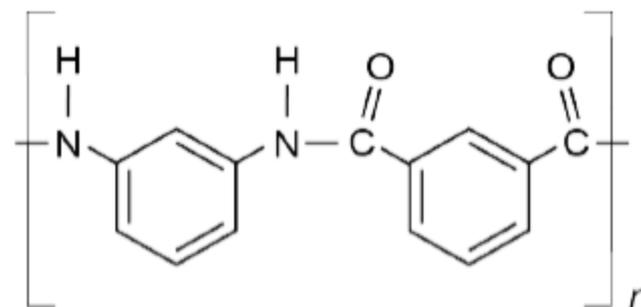
### Question 3c:

Polymers such as Nomex® can be hydrolysed by either aqueous acid or base.

Show the products of the hydrolysis of Nomex® using:

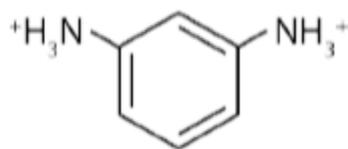
(i) aqueous acid

(ii) aqueous base.

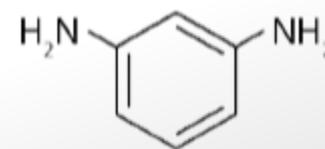
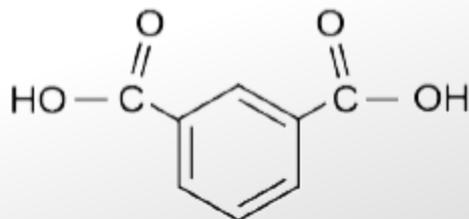


HCl/heat

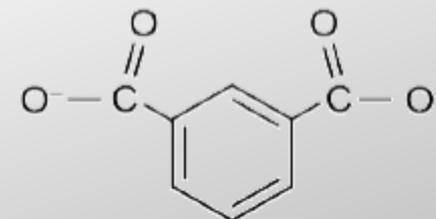
NaOH/heat



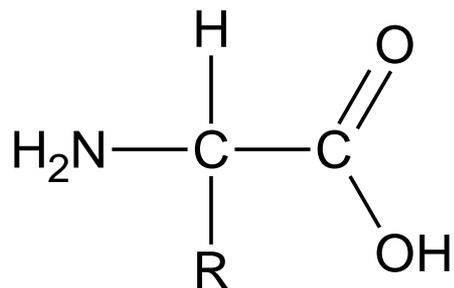
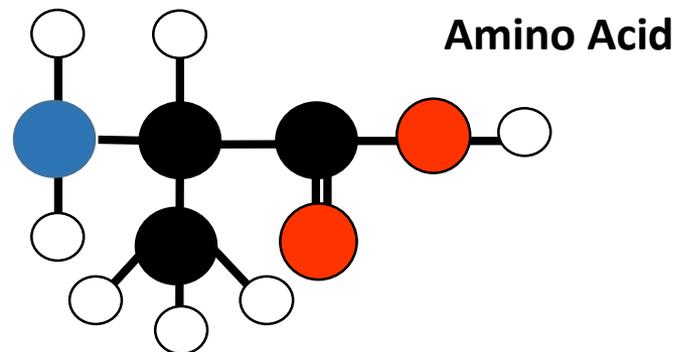
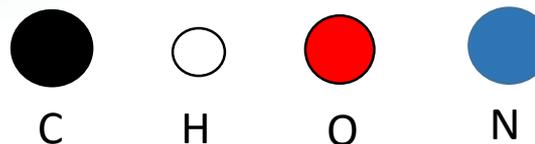
+



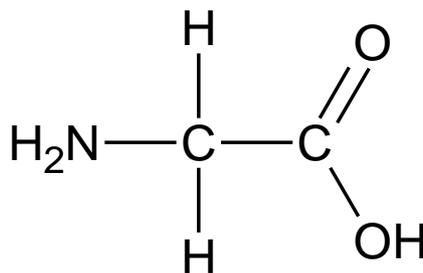
+



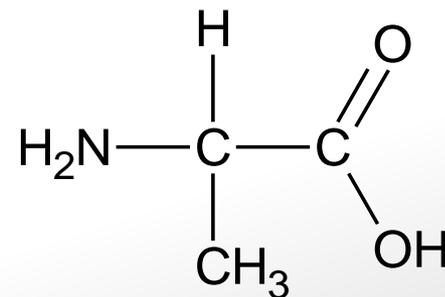
Amino acids have both the basic amino,  $\text{NH}_2$ , and acidic carboxylic acid,  $\text{CO}_2\text{H}$ , groups. In acidic solutions, the basic  $\text{NH}_2$  group is protonated to form a positively charged amino acid.



General formula



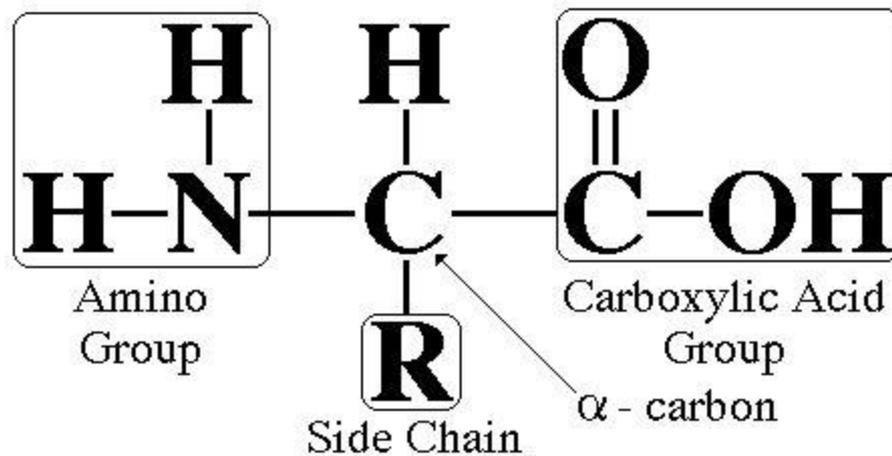
aminoethanoic acid



2-aminopropanoic acid

Most Amino Acids form optical isomers (or enantiomers) because they have a chiral carbon with four different groups off it. Our bodies only use one type of optical isomer for each amino acid.

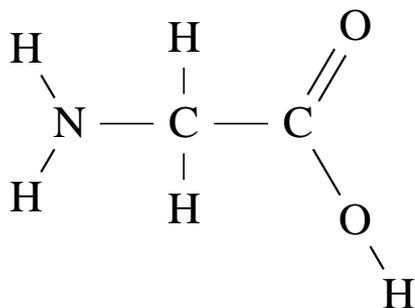
## Amino Acid Structure



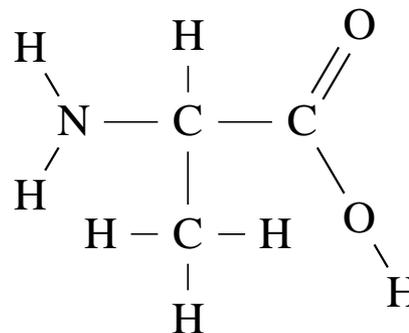
Polypeptide chains can be made from condensation polymerisation of amino acids.

Two simple amino acids that can form polymers are glycine and alanine.

Alanine has optical isomers.



glycine

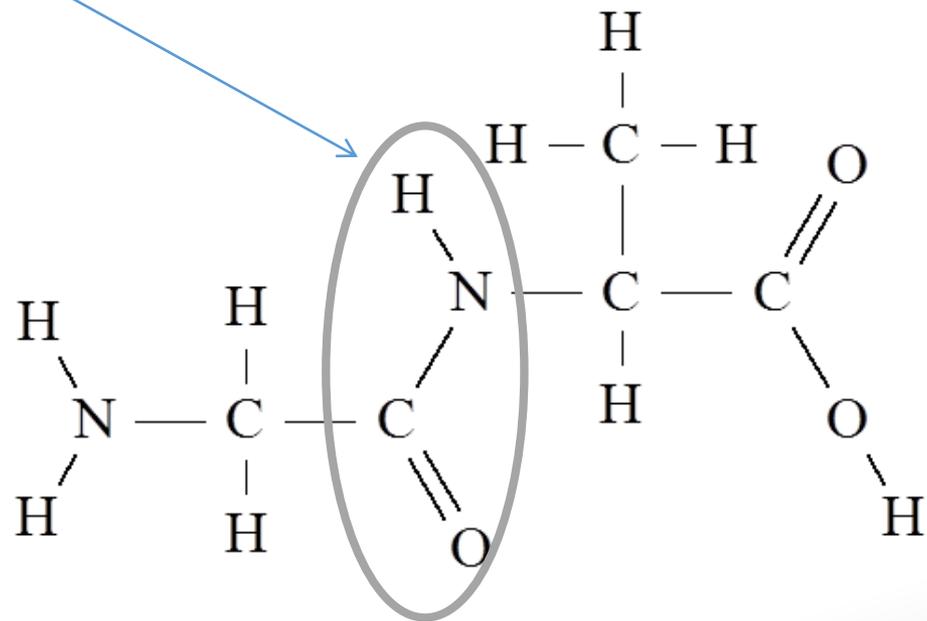


alanine

Human protein is made from about 20 different amino acids.

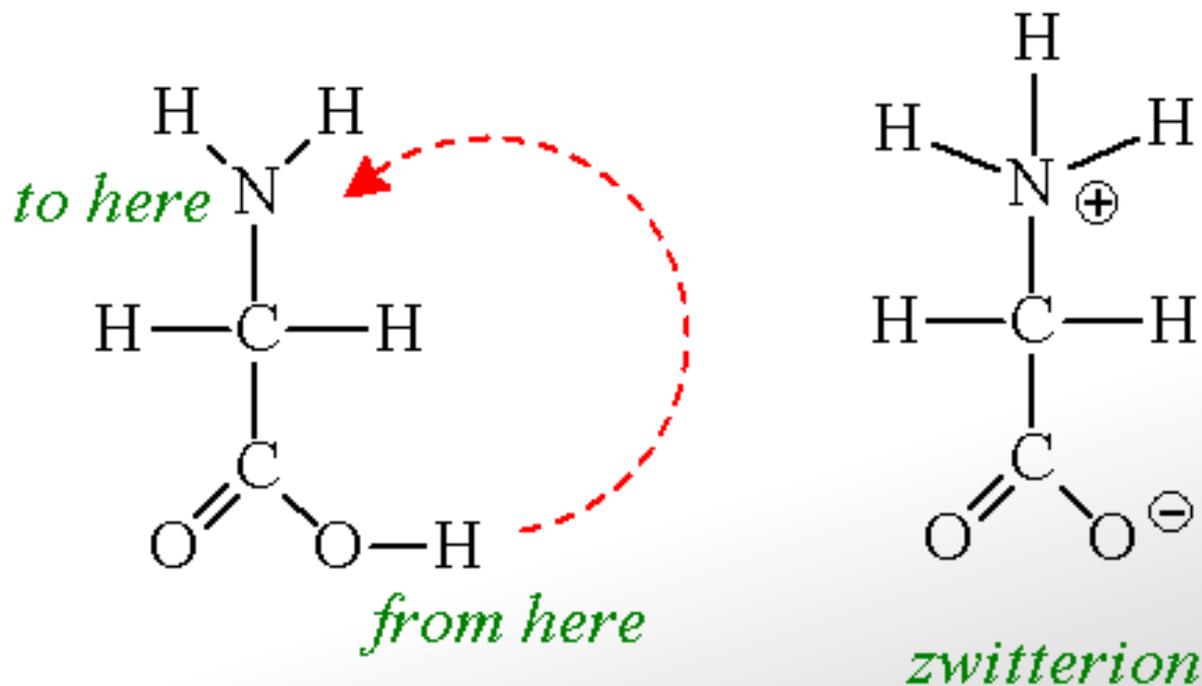
**peptide link:** The linking bond between two amino acids.  $-\text{CONH}-$  (same as an amide link)

Peptide bond



**dipeptide:** A dimer formed by two amino acids.

In solution the carboxylic acid can donate a proton to the amine, and form a zwitterion. (zwei = 2 in German) There are two separate charges on the ion.

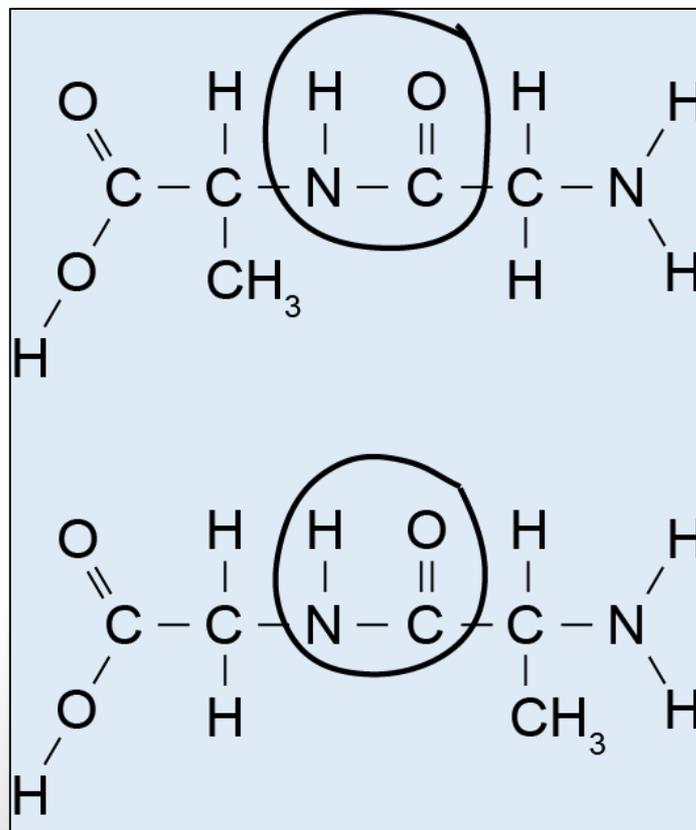
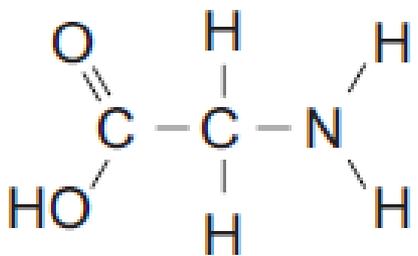
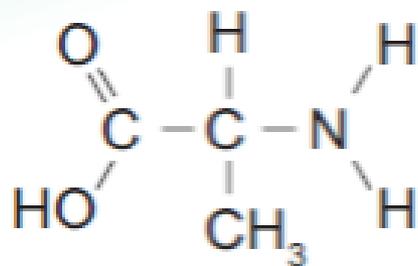


# NCEA 2013 Amino Acids

Merit  
Question

**Question 2d:** Peptides are formed when amino acids combine.

(i) In the boxes below, show two possible dipeptides that can be formed by combining the amino acids:

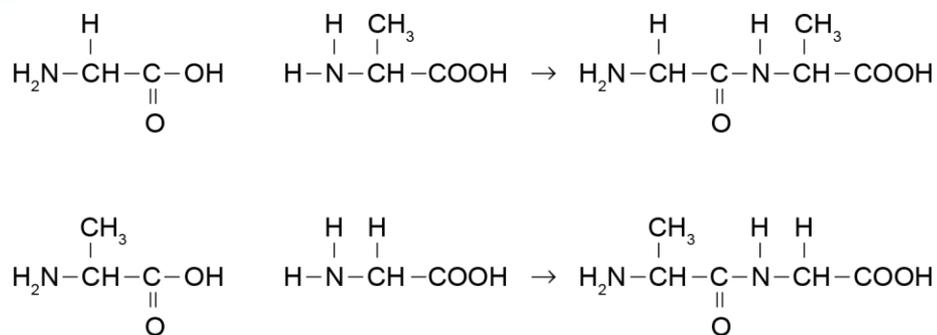




## NCEA 2016 Amino Acids

Merit  
Question

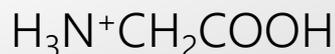
**Question 1c: (iv)** Name the type of reaction that occurred when the dipeptides formed in (iii) above. Explain your Answer



Condensation.  
Two larger molecules are joined together with the elimination of a smaller molecule.

**(v)** Draw the products of an **acidic hydrolysis** for ONE of the dipeptides from (iii) above. Explain why these products are formed.

Acidic hydrolysis leaves COOH group intact and NH<sub>2</sub> group becomes protonated to form NH<sub>3</sub><sup>+</sup>.

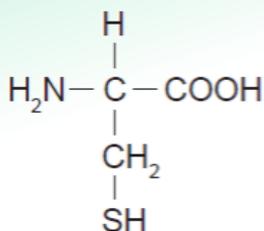


Excellence  
Question

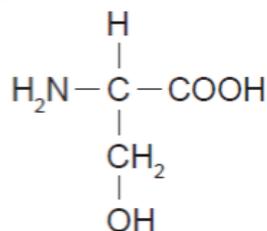
# NCEA 2017 Amino Acids

Merit  
Question

**Question 3a:** Peptides are molecules that form when amino acids combine. The following structures show the amino acids cysteine and serine.



cysteine



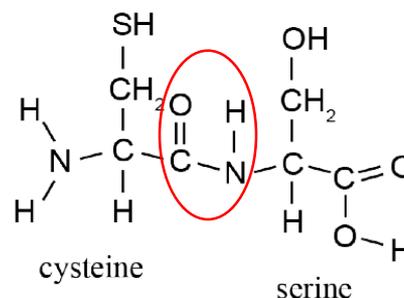
serine

Amide linkage group circled on one of the dipeptides.

(i) In the boxes to the left, show two possible dipeptides that can be formed by combining the two amino acids shown above.

(ii) Circle the amide functional group on ONE of the dipeptides drawn in part (i).

Dipeptide 1:



Dipeptide 2:

Second dipeptide the same structure above, with the  $\text{CH}_2\text{SH}$  swapped with  $\text{CH}_2\text{OH}$ .

# Reaction types

<p><b>Substitution</b> reactions are characterized by replacement of an atom or group (Y) by another atom or group (Z). Aside from these groups, the number of bonds does not change.</p>	
<p><b>Polymerisation</b> reactions join monomers together to form a polymer. <b>Condensation polymerisation</b> removes a molecule of water (H from one monomer and OH from another) and joins the two ends of the monomers together</p>	
<p><b>Oxidation</b> reactions involve a loss of electrons from the organic molecule or a gain of oxygen. An oxidant such as dichromate or permanganate is used.</p>	
<p><b>Condensation</b> (or dehydration) reactions are a type of elimination reaction where a molecule of water is removed) – in <b>esterification</b> OH is removed from alcohol and O from a carboxylic acid and they are joined to form an ester</p>	
<p><b>Addition</b> reactions increase the number of bonds to the Carbon chain by bonding additional atoms, usually at the expense of one or more double bonds.</p>	
<p><b>Hydrolysis</b> reactions involve water as a reactant and becomes part of the reaction product.</p>	
<p><b>Elimination</b> reactions decrease the number of single bonds by removing atoms and new double bonds are often formed.</p>	
<p><b>Reduction</b> reactions involve a gain of electrons from the organic molecule or a loss of oxygen. A reductant such as <math>\text{NaBH}_4</math> is used.</p>	

# C3.5 Reaction Scheme



**Substitution reactions** are characterized by replacement of an atom or group (Y) by another atom or group (Z). Aside from these groups, the number of bonds does not change.

**Polymerisation reactions** join monomers together to form a polymer.  
**Condensation polymerisation** removes a molecule of water (H from one monomer and OH from another) and joins the two ends of the monomers together.

**Oxidation reactions** involve a loss of electrons from the organic molecule or a gain of oxygen. An oxidant such as dichromate or permanganate is used.

**Condensation (or dehydration) reactions** are a type of elimination reaction where a molecule of water is removed – in esterification OH is removed from alcohol and O from a carboxylic acid and they are joined to form an ester.

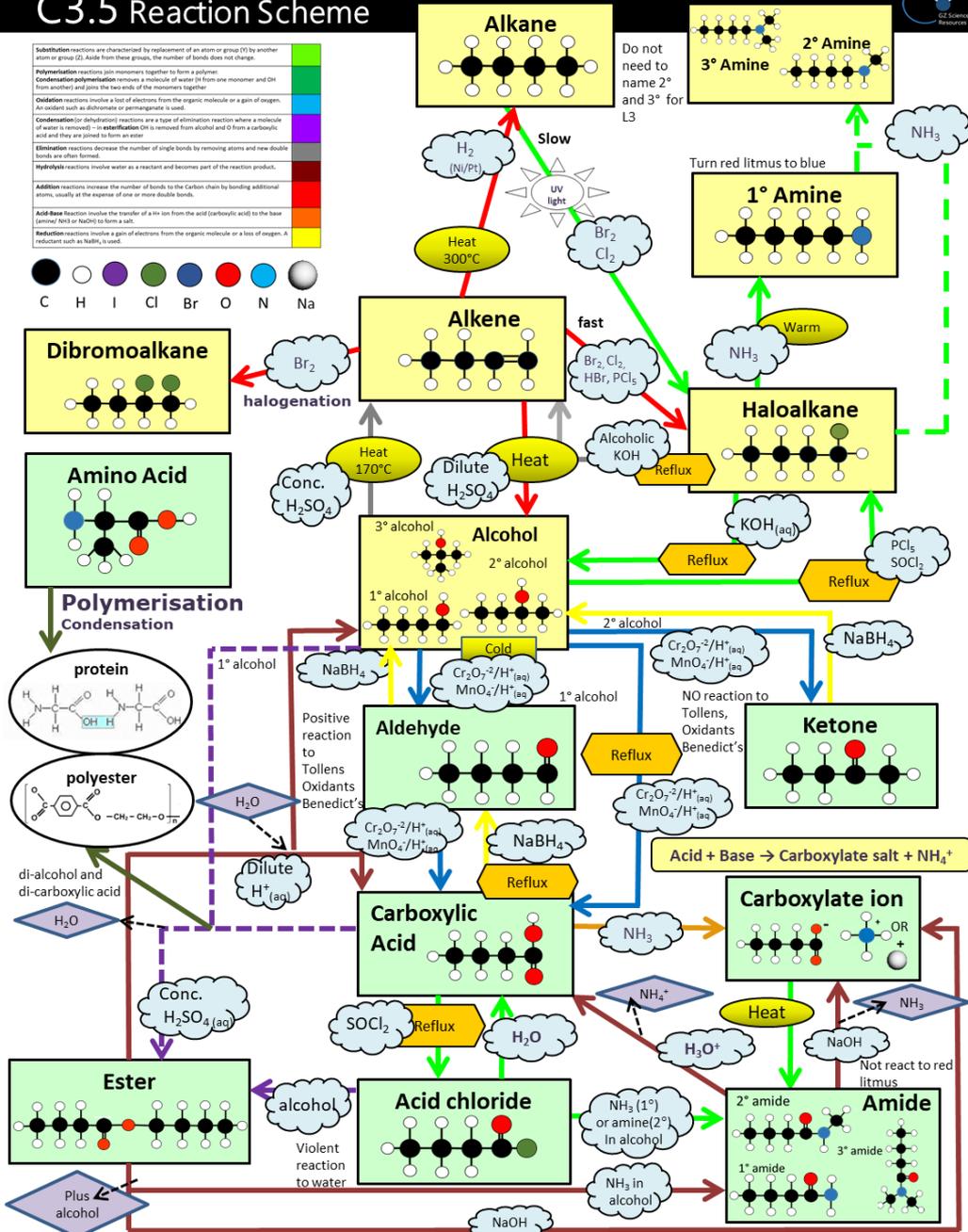
**Elimination reactions** decrease the number of single bonds by removing atoms and new double bonds are often formed.

**Hydrolysis reactions** involve water as a reactant and becomes part of the reaction product.

**Addition reactions** increase the number of bonds to the Carbon chain by bonding additional atoms, usually at the expense of one or more double bonds.

**Acid-Base Reaction** involve the transfer of a H<sup>+</sup> ion from the acid (carboxylic acid) to the base (amine/ NH<sub>3</sub> or NaOH) to form a salt.

**Reduction reactions** involve a gain of electrons from the organic molecule or a loss of oxygen. A reductant such as NaBH<sub>4</sub> is used.



**Question 2a:** For the following conversions, identify the reagent required, and state the type of reaction occurring.

(i) Pentan-2-one is converted to pentan-2-ol.

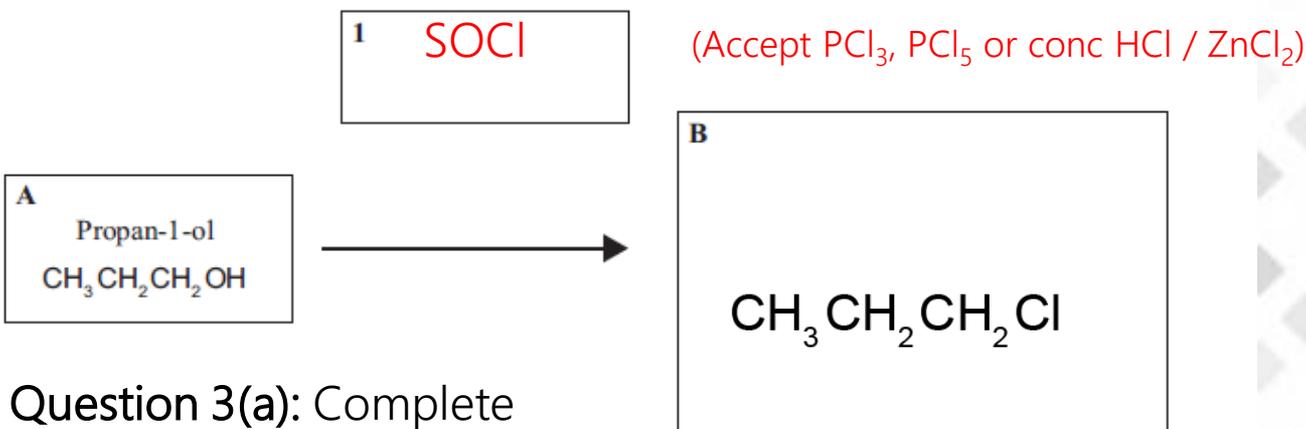
Reagent:  $\text{NaBH}_4$  /  $\text{LiAlH}_4$

Type of reaction – reduction / redox

(ii) Butan-2-ol is converted to a mixture of but-1-ene and but-2-ene.

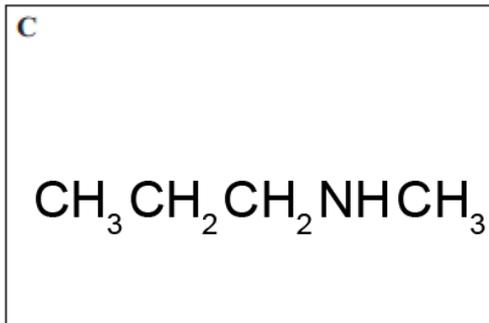
Reagent: conc  $\text{H}_2\text{SO}_4$  / conc  $\text{H}_3\text{PO}_4$  /  $\text{Al}_2\text{O}_3$

Type of reaction – elimination / dehydration /  
condensation



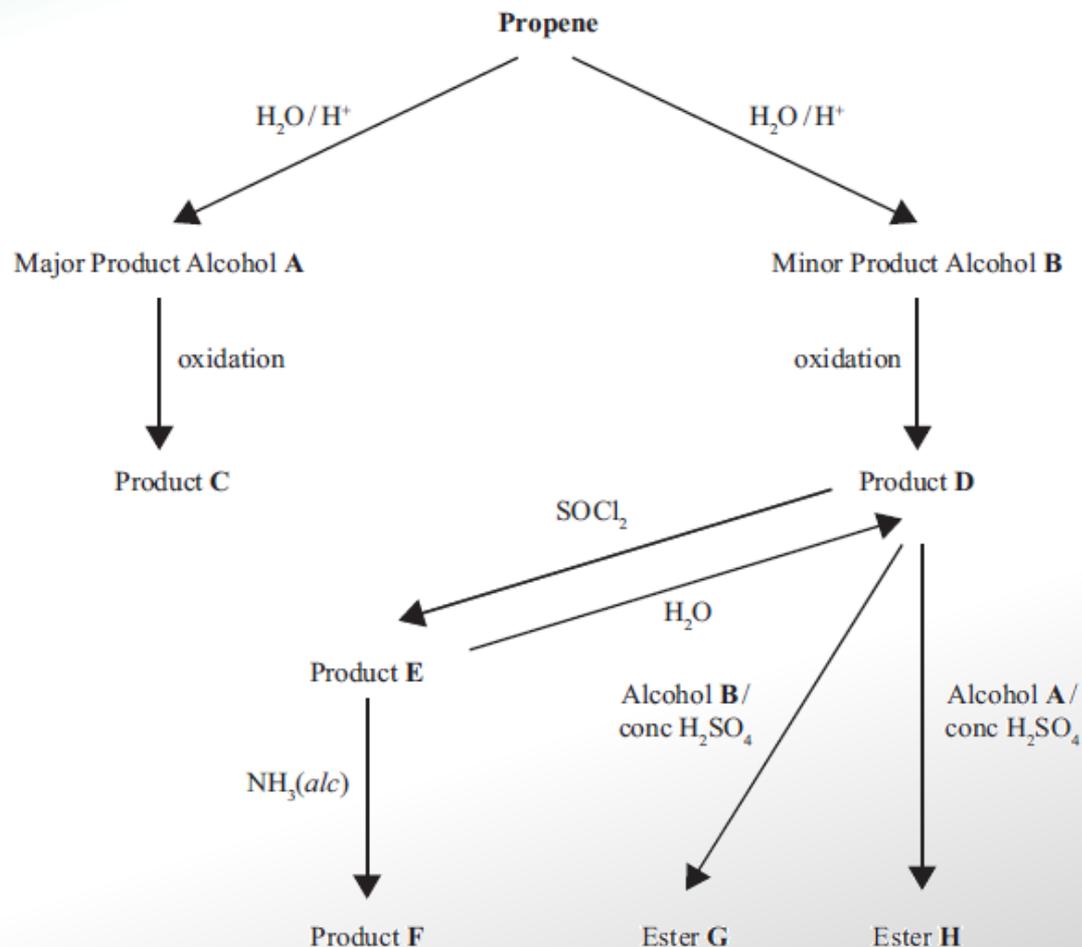
**Question 3(a):** Complete the following reaction scheme by drawing the structural formulae of the organic compounds **B** and **C**, and identifying reagent **1**.

Include any necessary conditions, needed to bring about the transformation from reactant **A** to the organic compound **C**, which is a base.



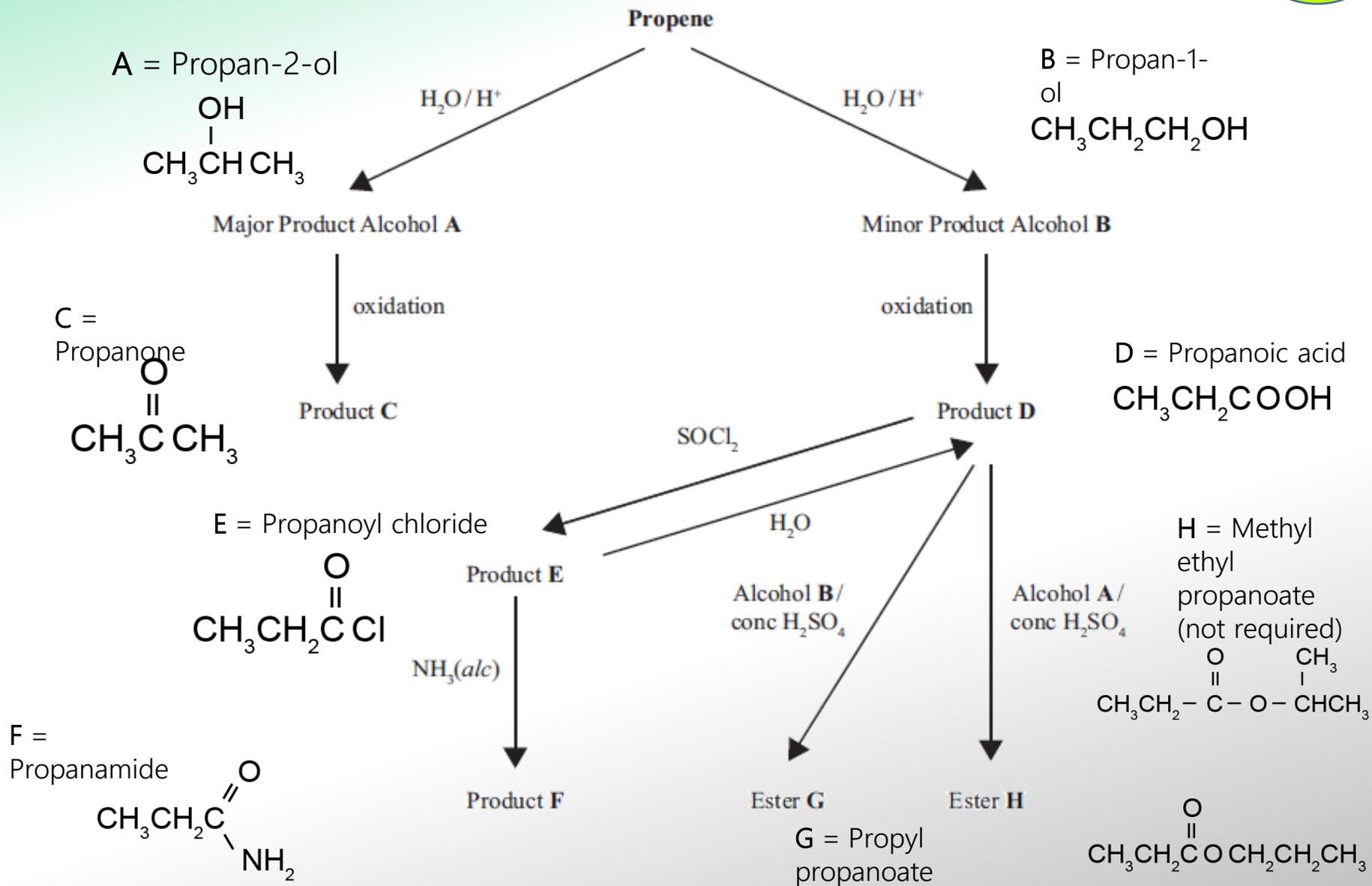
**Question 3(a):** Propene can be reacted with water in the presence of acid to form a major product (**A**) and a minor product (**B**).

- **A** is oxidised to form product **C**.
- **B** is oxidised to form product **D**.
- When **D** is reacted with  $\text{SOCl}_2$ , it forms product **E**.
- When **D** is reacted with alcohol **B**, it forms an **ester G**.
- When **D** is reacted with alcohol **A**, it forms **ester H**, which is an isomer of **G**.
- When **E** is reacted with alcoholic ammonia, it forms product **F**.
- When **E** is reacted with water, it forms product **D**.



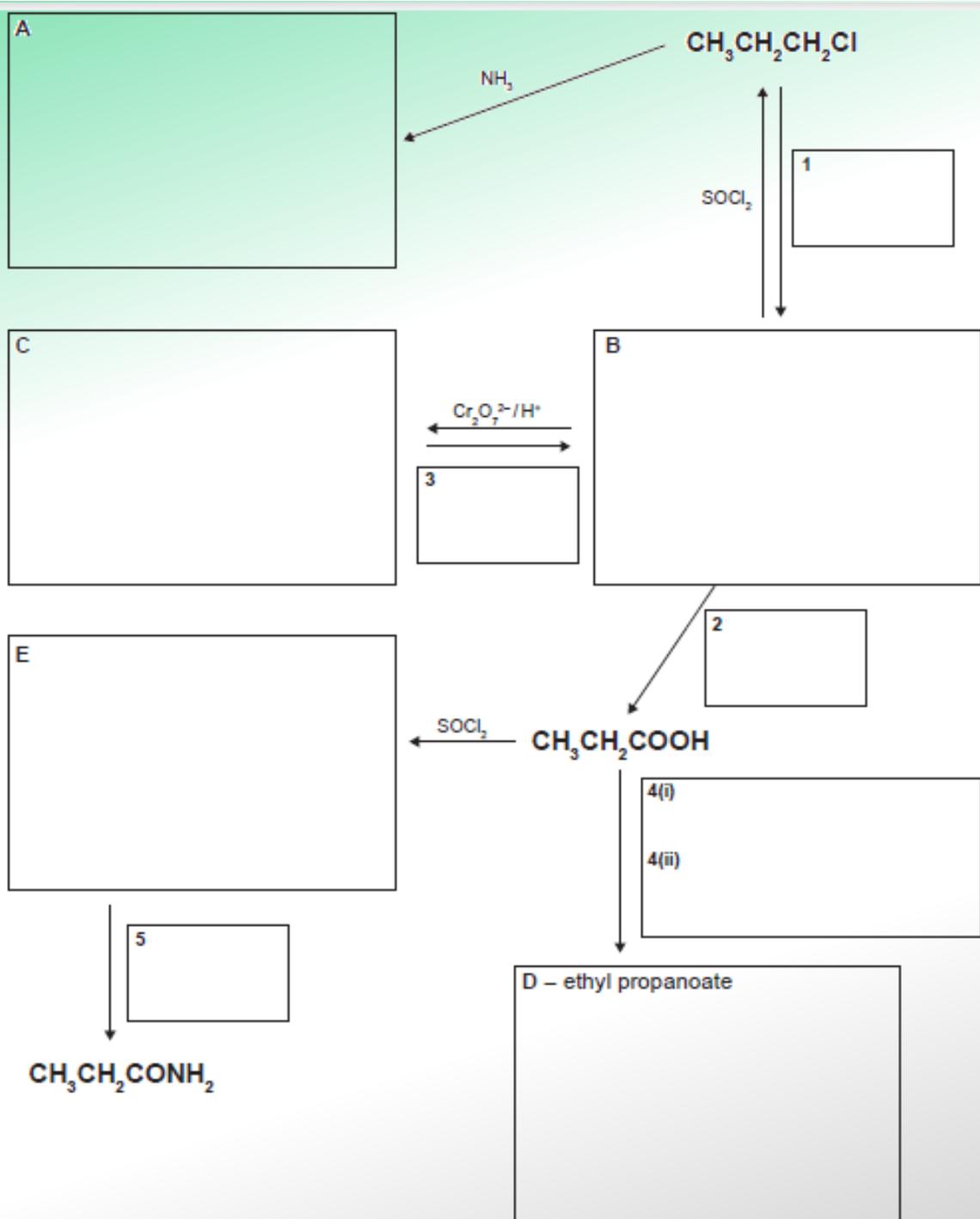
# NCEA 2014 Reaction Scheme

Excellence Question



# NCEA 2015 Reaction Scheme

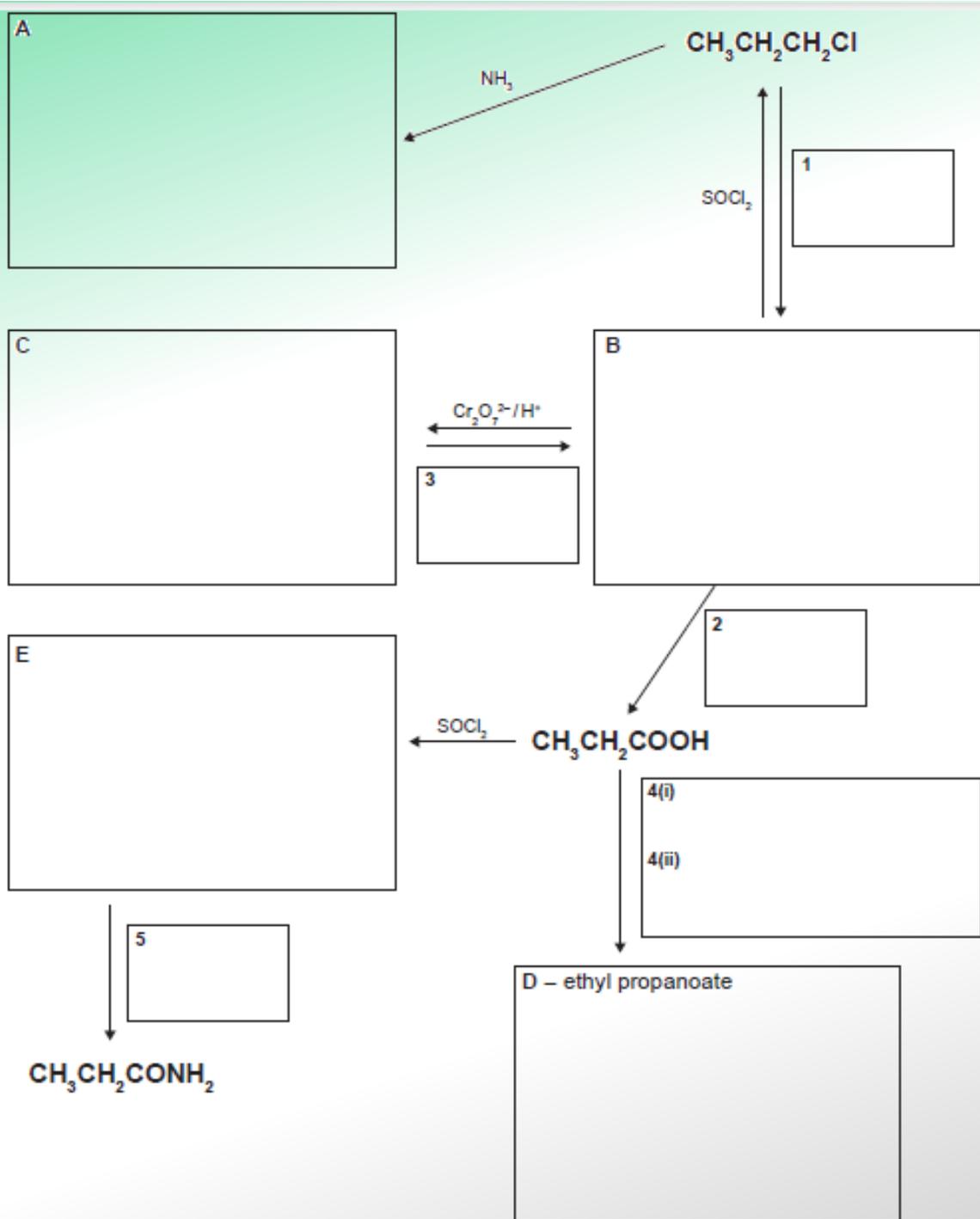
Excellence Question



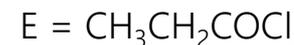
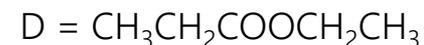
**Question 3(b):**  
Complete the following reaction scheme by drawing the structural formulae of the organic compounds A to E, and identifying reagents 1 to 5.

# NCEA 2015 Reaction Scheme

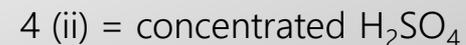
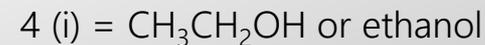
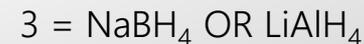
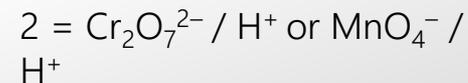
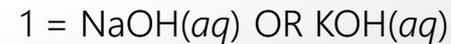
Excellence Question



## Structures

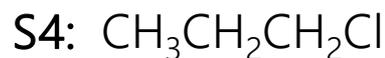
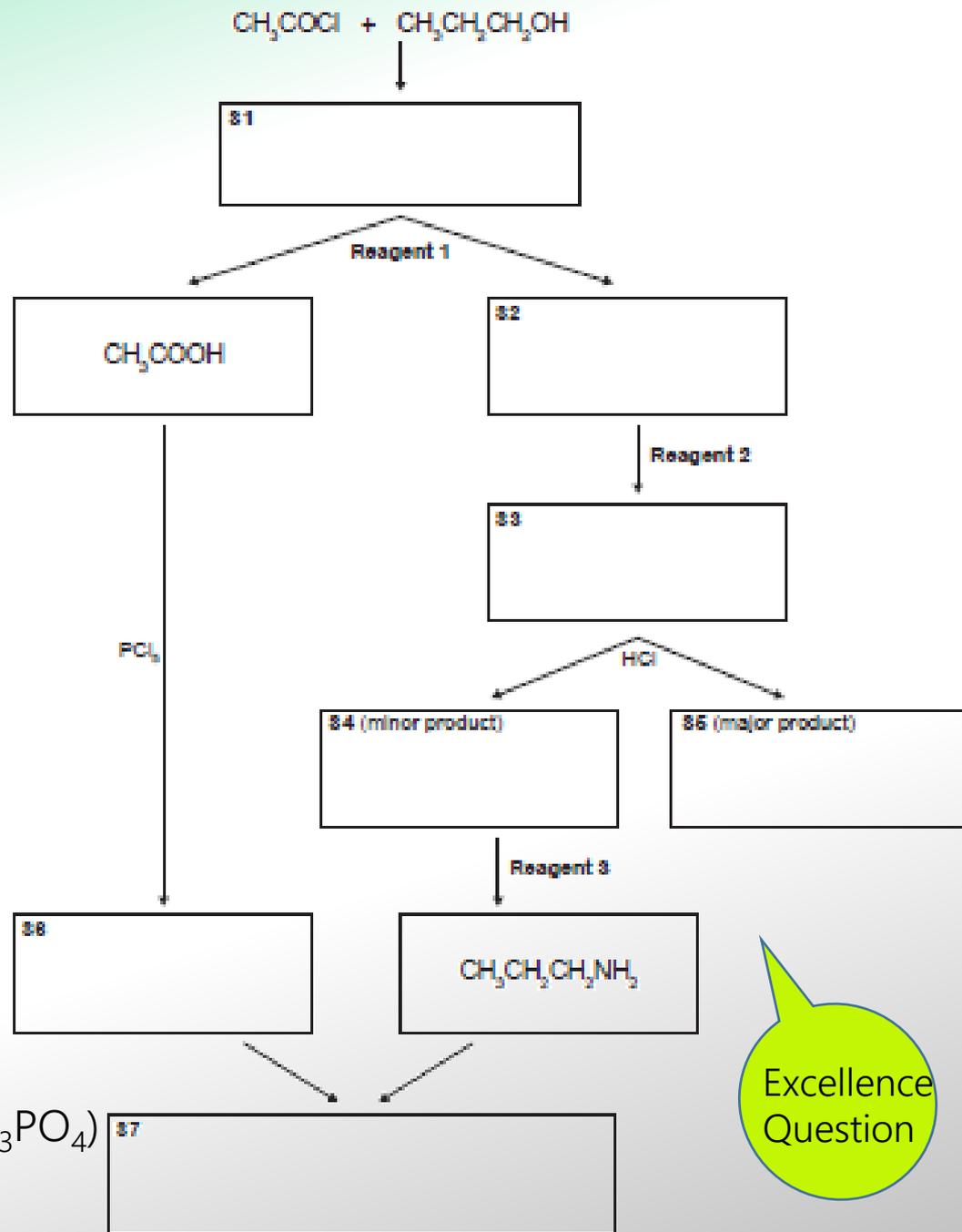


## Reagents



# NCEA 2016 Reaction Scheme

**Question 3a:** Complete the following reaction scheme by drawing organic structures for **S1** to **S7**, and identifying reagents **1** to **3**.



Reagent 1 =  $\text{H}_2\text{O} / \text{H}^+$  (dilute acid)

Reagent 2 = conc.  $\text{H}^+$  ( $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ )

Reagent 3 =  $\text{NH}_3$  (alc) or conc.



# NCEA 2016 Reaction Scheme

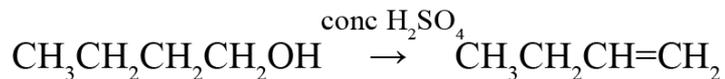
Excellence  
Question

**Question 3b:** Draw a reaction scheme to show the conversion of **butan-1-ol** to **butan-2-one**.

You should include any relevant reagents, conditions required, and the structures of all organic substances involved.

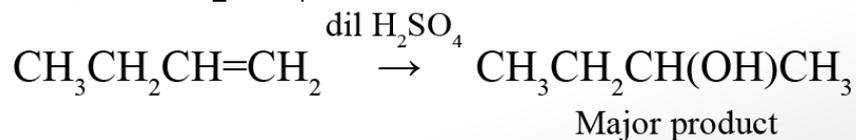
**Step 1: Butan-1-ol to but-1-ene.**

Dehydration reaction (elimination reaction) using conc  $\text{H}_2\text{SO}_4$ .



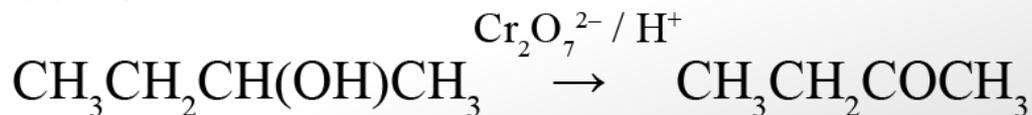
**Step 2: But-1-ene to butan-2-ol.**

Hydration reaction (addition reaction) using dil.  $\text{H}_2\text{SO}_4$   
( $\text{H}^+/\text{H}_2\text{O}$ )



**Step 3: Butan-2-ol (Major product) to butan-2-one.**

Oxidation reaction of secondary alcohol to form a ketone using  $\text{Cr}_2\text{O}_7^{2-} / \text{H}^+$   
under reflux.

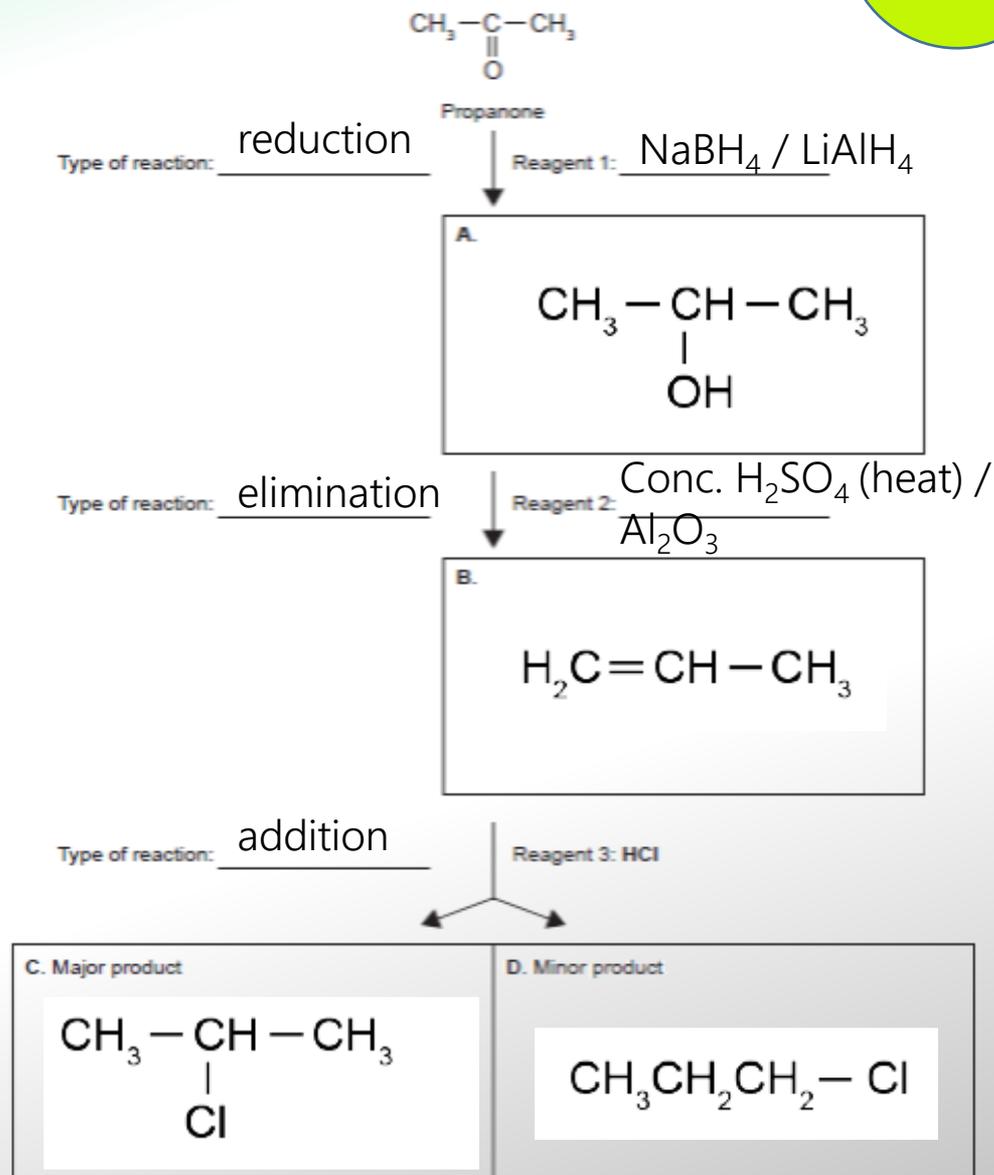


# NCEA 2017 Reaction Scheme

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## Question 1b:

Complete the following reaction scheme by drawing the structural formulae of both organic compounds **A** and **B**, as well as the major and minor products **C** and **D**. Identify both reagents 1 and 2, and indicate the type of reaction occurring at each step.



**Question 2a:**

Compound **P** and compound **Q** are straight-chain constitutional (structural) isomers with the molecular formula  $C_5H_{12}O$ . Compound **P** can form optical isomers, whereas compound **Q** cannot.

When reacted with concentrated sulfuric acid, compound **P** forms two products, compounds **R** and **S**; compound **Q** forms only one product, compound **S**.

When compound **Q** is reacted with *Reagent 1*, it forms a chloroalkane, compound **T**.

Compound **T** reacts with concentrated  $NH_3$  to form compound **U**.

Compound **Q** can also be oxidised to form compound **V**, which will turn moist blue litmus paper red.

Compound **V** can also be reacted with compound **Q** and *Reagent 2*, to form a sweet-smelling liquid, compound **W**.

Use the information above to identify compounds **P** to **W**, and *reagents 1* and *2*.

# NCEA 2017 Reaction Scheme

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**Question 2a:** Complete the following tables using the information found on the previous page.

Compound	Structure
P	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_3 \\   \\ \text{OH} \end{array}$
Q	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 - \text{OH}$
R	$\text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_3$
S	$\text{CH}_2 = \text{CHCH}_2\text{CH}_2\text{CH}_3$
T	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 - \text{Cl}$
U	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 - \text{NH}_2$
V	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C} - \text{OH} \\    \\ \text{O} \end{array}$
W	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C} - \text{O} - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\    \\ \text{O} \end{array}$

<i>Reagent 1</i>	$\text{SOCl}_2 / \text{PCl}_3 / \text{PCl}_5$
<i>Reagent 2</i>	conc. $\text{H}_2\text{SO}_4$