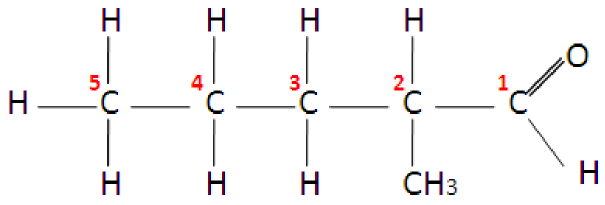
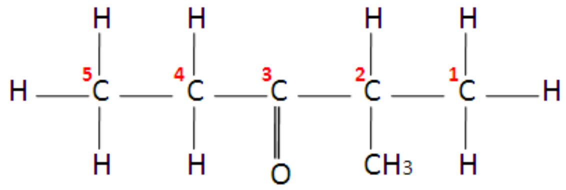
An introduction to carbonyl compounds

Aldehydes and ketones:



Aldehyde

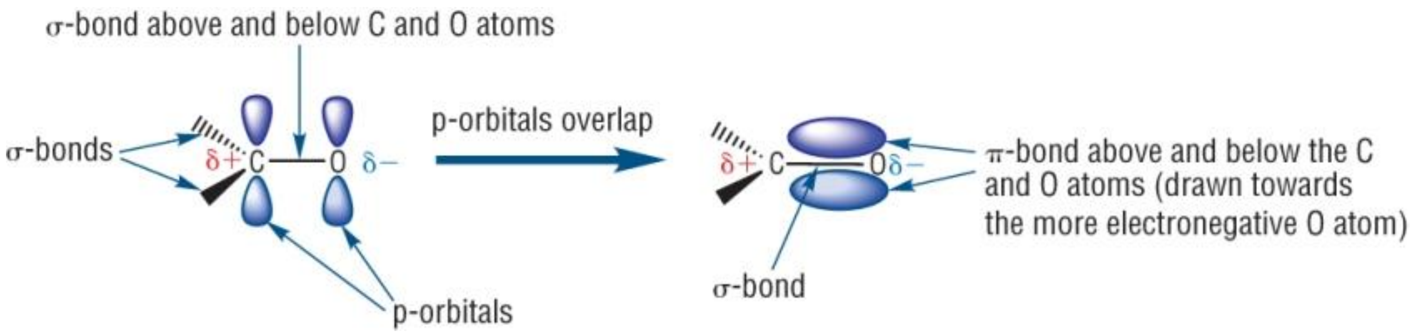


Ketone

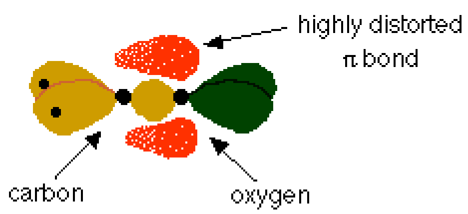
- **Aldehydes** end in **'al'** and have a **carbonyl group (C = O) with 1 hydrogen and 1 Alkyl group** attached
- **Ketones** end in '**one**' and have a **carbonyl group (C = O) with 2 alkyl groups** attached.

p's to π's

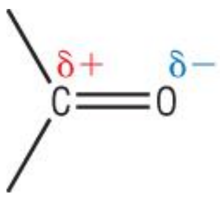
- Like the alkenes, the carbonyl group consists of a **σ bond** and a **π bond** between the carbon and oxygen:



- The difference in this set up is the difference in electronegativities of the carbon and oxygen atom.
- Oxygen is much more electronegative than carbon meaning that the π electrons will be highly distorted towards the oxygen atom as shown above.

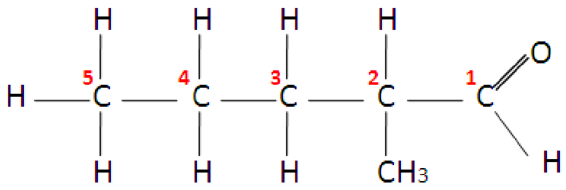


- This sets up a permanent dipole across the C=O bond:

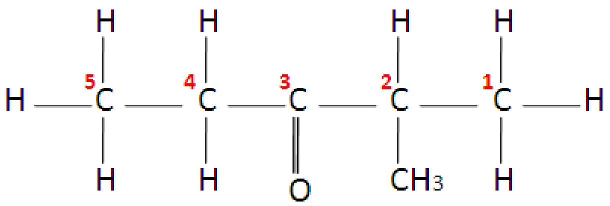


Naming aldehydes and ketones:

- Aldehydes and ketones are named in the same way as in AS:



2-Methylpentanal

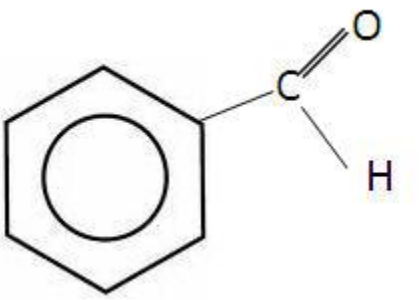


2-methylpentan-3-one

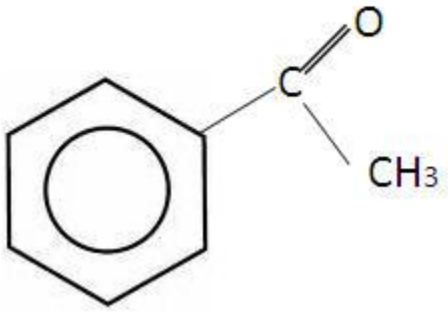
- In aldehydes, the aldehyde carbon always starts at 1.
- In ketones, the ketone (or carbonyl group) is always counted to give it the smallest possible number.

Aromatic aldehydes and ketones:

- The simplest aldehyde is benzaldehyde and the simplest ketone is phenylethanone:



Benzaldehyde



Phenylethanone

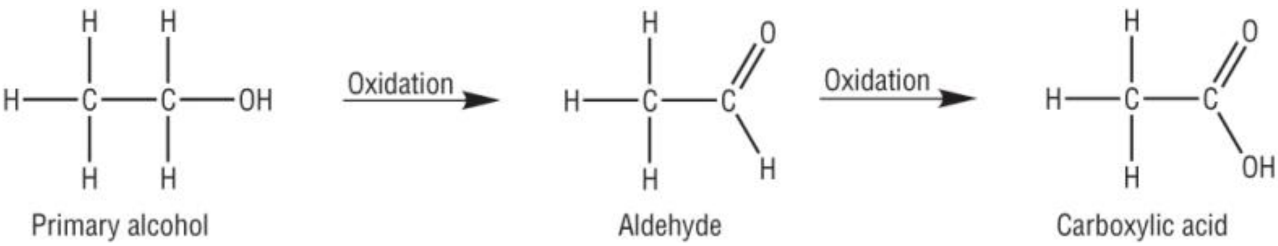
- These aromatic aldehydes and ketones have a fragrant smell, often found naturally in foods.

Qu 1 - 4 P21

<u>Oxidation of alcohols and aldehydes</u>

- In unit 2, module 2 we oxidised primary, secondary alcohols and aldehydes further.
- Tertiary alcohols however could not be oxidised further.
- We used acidified dichromate, H^+ / $Cr_2O_7^{2-}$ to oxidise (usually as sulphuric acid and potassium dichromate).
- We noticed that if we oxidise alcohols:

Primary alcohols:



- The oxidation reaction is complex so we use [O] to show oxidation and balance them accordingly:

$$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$$
$$CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$$

- Distilling to collect the adehyde and refluxing (then distilling) for the carboxylic acid.

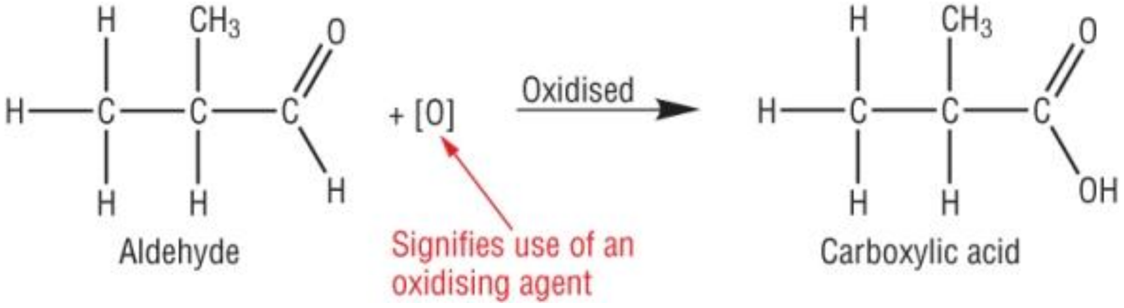
Secondary alcohols:

- The oxidation reaction:

$$CH_3CHOHCH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$$

- Refluxing is used. Distilling is not necessary as the product cannot oxidise further.

Aldehydes:



- The oxidation reaction:

$$CH_3CHO + [O] \rightarrow CH_3COOH + H_2O$$

- Refluxing is used. Distilling is not necessary as the product cannot oxidise further.

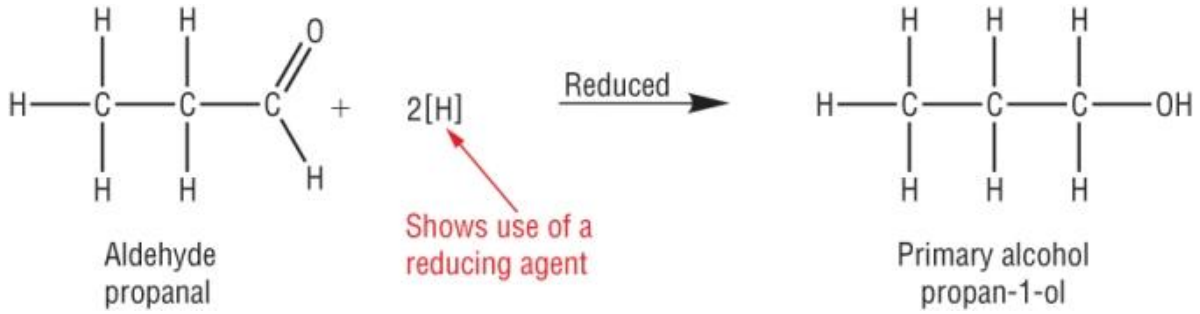
Qu 1 - 3 P23

Reactions of aldehydes and ketones

Reducing aldehydes and ketones

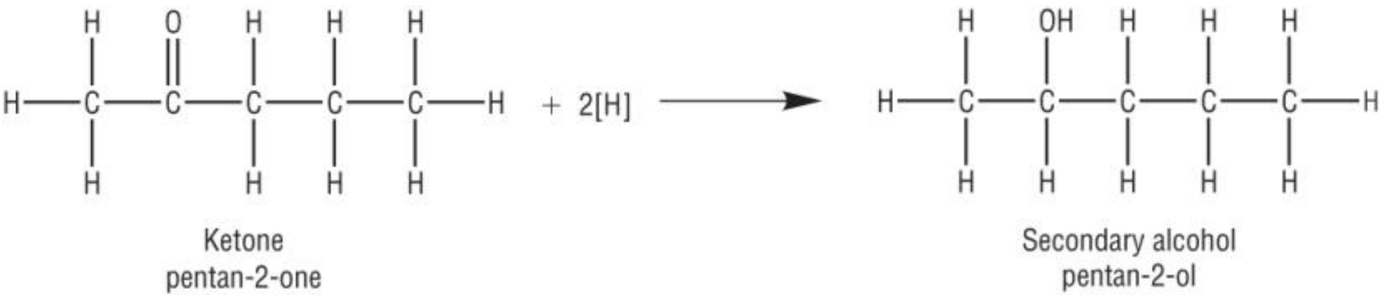
- Alcohols can be oxidised to aldehydes and ketones by using an oxidising agent (earlier)
- This means that aldehydes and ketones can be reduced to form the corresponding primary or secondary alcohols.
- The reducing agent used is sodium tetrahydidoborate (III), $NaBH_4$ sometimes called sodium borohydride.
- The reaction(s) are complex so we use [H] in the equation (as we used [O] in the oxidation reactions).

Reduction of aldehydes:



CH_3CHO + 2[H] → CH_3CH_2OH

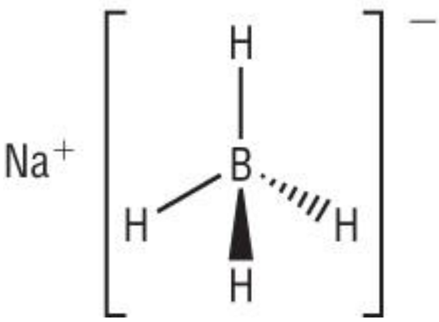
Reduction of ketones:



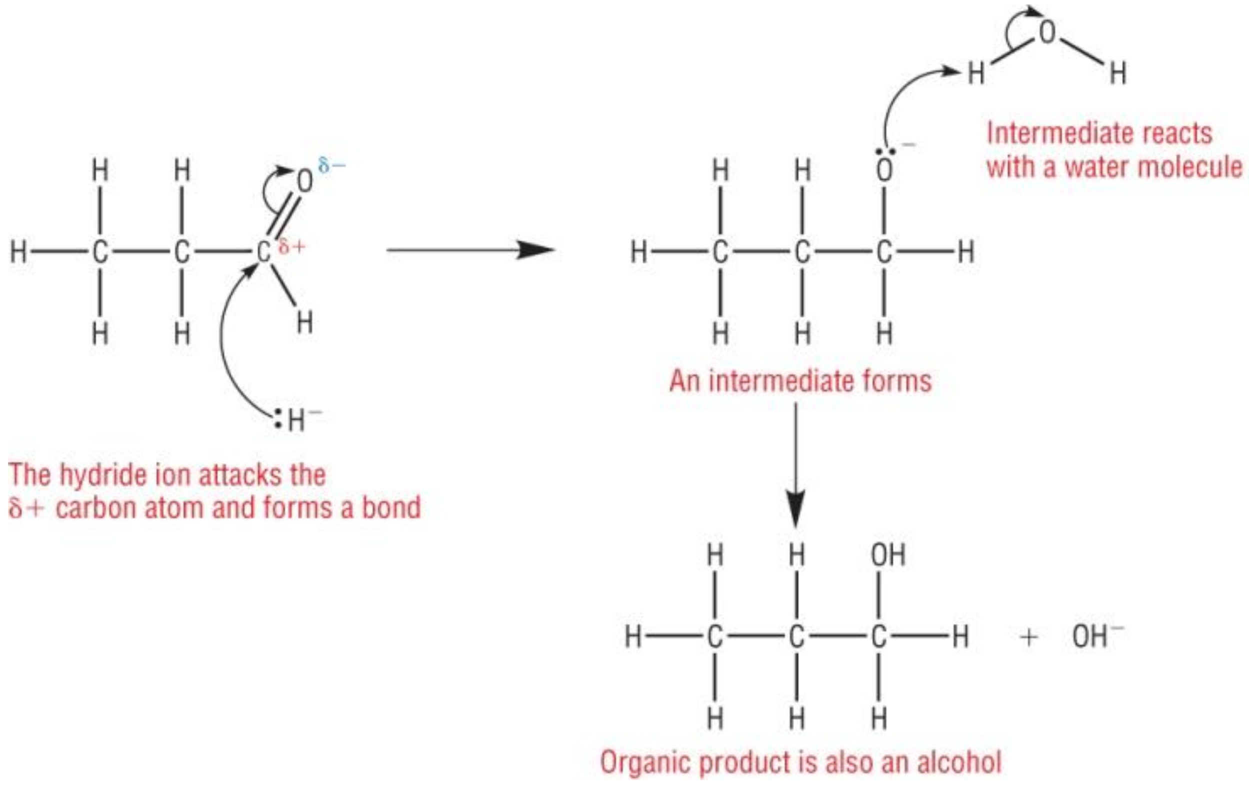
CH_3COCH_3 + 2[H] → $CH_3CH(OH)CH_3$

Nucleophilic addition reactions:

- $NaBH_4$ reacts with aldehydes and ketones by nucleophilic addition.
- $NaBH_4$ is a source of hydride ions, H^-.
- This is the nucleophile and is attracted to the δ**+** carbon in the carbonyl group.



The Mechanism:

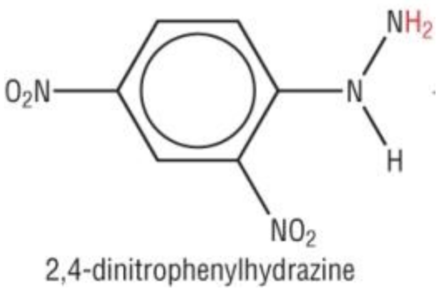


Qu 1 - 4 P 25

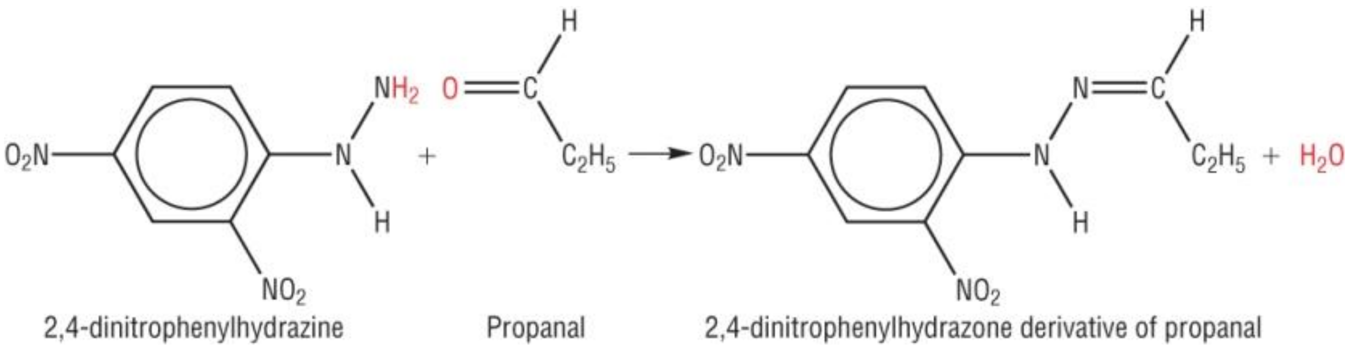
Chemical tests on carbonyl compounds

1) Detecting the presence of a carbonyl group:

- **Brady's reagent – 2,4-dinitrophenylhydrazine in methanol and sulphuric acid:**



- This reaction produces a **yellow/orange precipitate** specifically with the carbonyl group of an aldehyde or a ketone **only**:



Yellow / Orange crystals

- This is followed by elimination of water and is often described as a condensation reaction.
- **The crystalline product can be separated and purified.**
- **Determining the melting point of the product allows you to find out which aldehyde or ketone was present.**

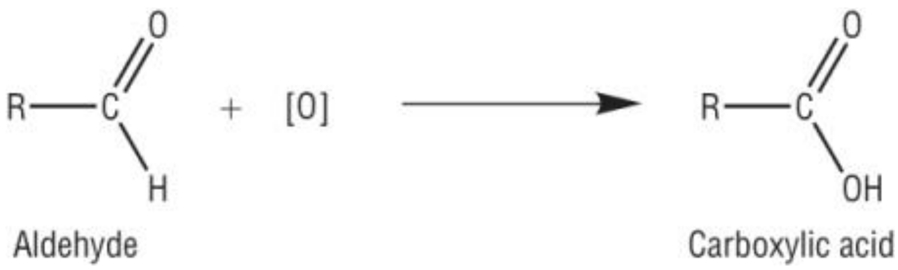
Aldehyde or ketone?

2) Tollens' reagent

- This is used to identify whether the molecule is an aldehyde or ketone.
- Often referred to as the 'silver mirror' test or 'ammoniacal silver nitrate'
- This is a solution of silver nitrate in an excess of ammonia and is a weak oxidising agent.
- Silver nitrate contains Ag^+ ions.
- They can be reduced to silver by a reducing agent / something that will itself be oxidised:

$$Ag^+_{(aq)} \quad + \quad e^- \quad \rightarrow \quad Ag_{(s)}$$

- Only aldehydes can be oxidised further which means that only aldehydes will produce a silver mirror with Tollens' reagent:



Summary – how to test / distinguish for aldehydes and ketones:

Reaction	**Aldehyde**	**Ketone**
2.4-DNPH	A yellow / orange crystalline solid is formed	A yellow / orange crystalline solid is formed
Tollen's reagent	A silver mirror is formed as Ag^+ is reduced to Ag	No reaction
Oxidation with acidified sodium dichromate (VI) (from AS)	Orange to green, as Cr^{6+} is reduced to Cr^{3+}	No reaction

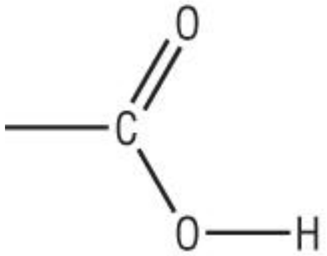
The orange crystals from 2,4-DNPH can be filtered, recrystallised and melting point determination. Once you know whether it is an aldehyde or ketone from Tollen's reagent, look up the MPt of the derivative in a table to identify the crystals and hence the aldehyde / ketone.

Qu 1 - 3 P27

Carboxylic acids

Introduction to carboxylic acids

- Carboxylic acids have the general formula:



Has carbonyl group C = O

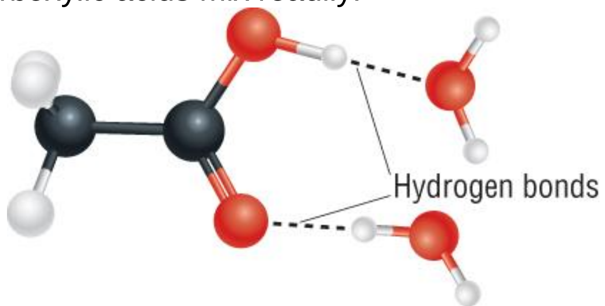
and hydroxyl group C – OH

- These are present in many foods:

  Ethanoic acid – vinegar
  Benzoic acid – used as flavouring in lemonade
  Citric acid – Used as flavouring in citrus drinks

1) Solubility and pH

- Solubility – C_1 - C_4 carboxylic acids mix readily:



- C_5 → solubility reduces due to length of insoluble R chain.
- All carboxylic acids H - bond to each other and with water.

Acid reactions of carboxylic acids:

- Carboxylic acids are weak acids as they partially dissociate in water.
- They react as acids to form salts called carboxylates.
- Less than 1% ionised:-

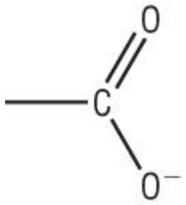
$$RCO_2H_{(aq)} \rightarrow H^+_{(aq)} + RCO_2^-{}_{(aq)}$$

2. Formation of salts:

- Carboxylic acids are acidic enough to react with:

Metals Metal hydroxides Metal carbonates

- They react in the usually acidic way making **salts**, hydrogen, water or water and carbon dioxide.



- The salt is a carboxylate ion.

a) With magnesium

$$\mathbf{2CH_3CO_2H + Mg \rightarrow \underset{\text{Magnesium ethanoate}}{(CH_3CO_2)_2Mg} + H_2}$$

b) With sodium hydroxide

$$CH_3CO_2H \quad + \quad NaOH \rightarrow CH_3CO_2Na \quad + \quad H_2O$$

Sodium ethanoate

c) With sodium carbonate

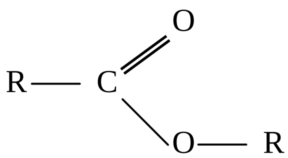
$$2CH_3CO_2H \quad + \quad Na_2CO_3 \rightarrow 2CH_3CO_2Na \quad + \quad H_2O \quad + CO_2$$

Sodium ethanoate

In each case the carboxylic acid has donated a proton, H^+
A salt is formed each time

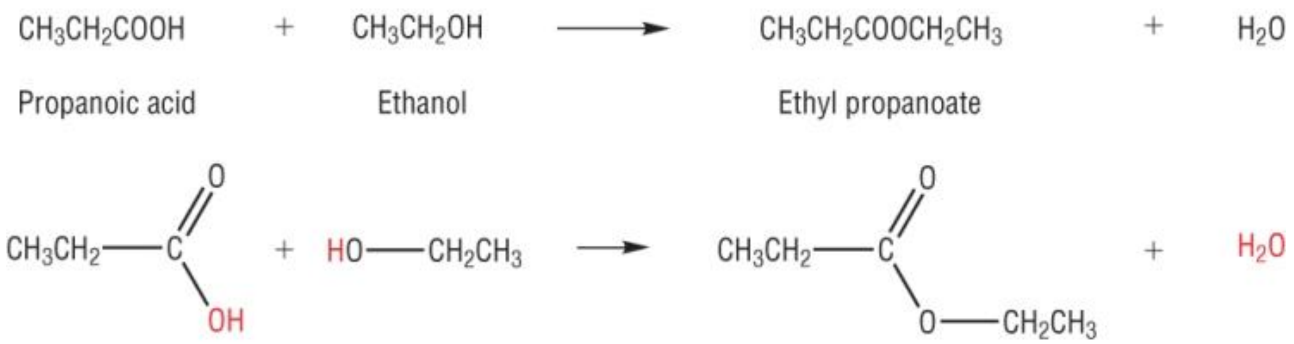
Qu 1 - 2 P29

<u>Esters</u>
Esters have the general formula:



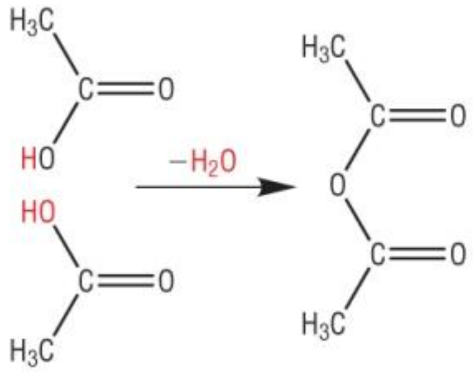
- Esters are referred to as a derivative of carboxylic acids due to the easy substitution of the hydrogen in the hydroxyl group with an alkyl group. They are derived from carboxylic acids.
- Again these are found in foods and have a fruity aroma.

Making esters:
- From AS you made esters from carboxylic acids and alcohols using an acid catalyst and heat.
- The reaction is known as esterification. It is a reversible reaction (later) and the yield of ester was low:

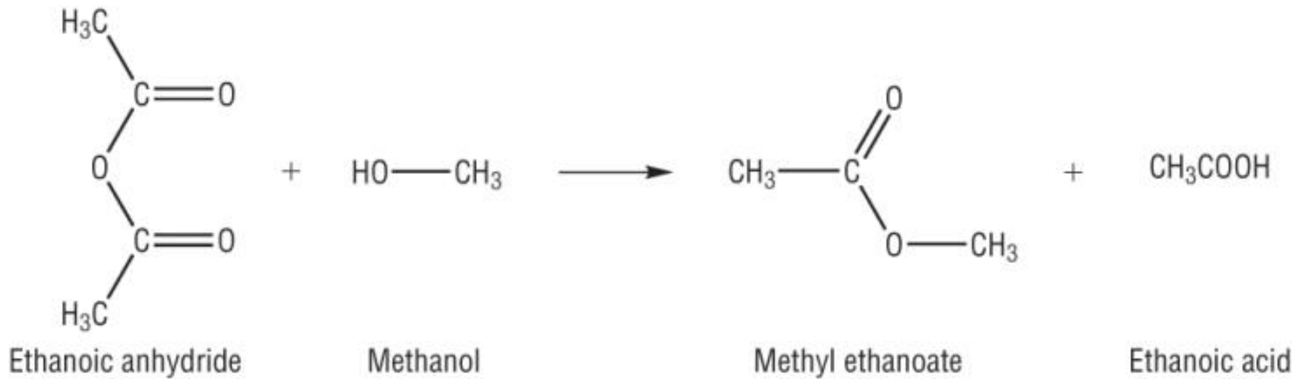


Esters from acid anhydrides

- Esters can be produced from acid anhydrides with gentle heating.
- This gives a better yield of ester as acid anyhdrides are a lot more reactive than carboxylic acids:



The reaction:



Ester hydrolysis:

- This is the break down of esters with the reaction with water.

  Ester + water → Carboxylic acid + Alcohol

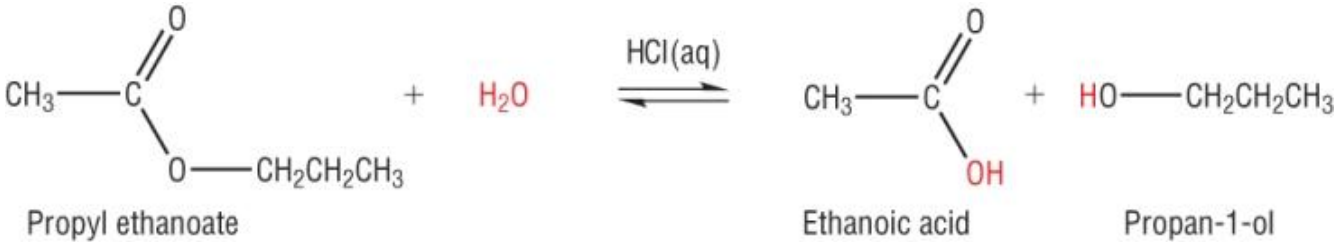
- It is the reverse reaction of the esterification reaction.

  Carboxylic acid + Alcohol → Ester + water

- It can be done using an acid or alkaline catalyst. The products formed are slightly different:

1) Acid hydrolysis:

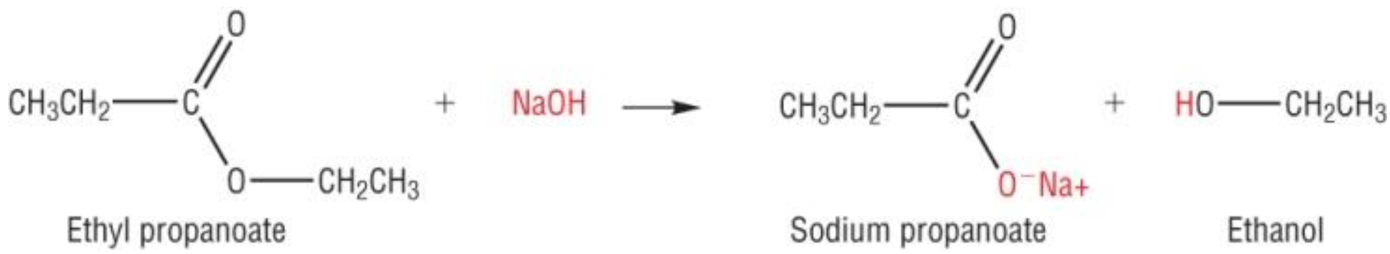
- The **hydrolysis** of any carboxylic acid **derivative** results in the **carboxylic acid**.



- The reaction is in equilibrium which means molecules of reactants and products are present in the reaction mixture.

2) Alkaline hydrolysis:

- When a base is used, the product is the sodium salt of the carboxylic acid:



- The reaction is non reversible which means that only products are present in the final reaction mixture.
- This reaction is also called 'saponification' as soaps are made in this way by the hydrolysis of fats (later).

Esters as perfumes and flavourings:

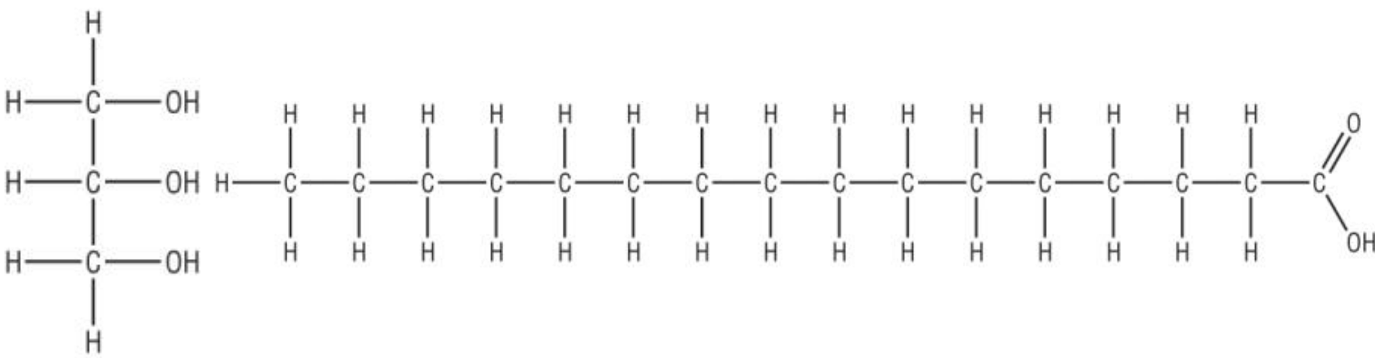
- Esters occur naturally in foods and flowers so can be used as perfumes.
- Esters are also found in essential oils, 'oil of wintergreen' used as deep heat.
- Benzyl ethanoate gives and apple and pear flavour / smell.

Qu 1 - 3 P31

<u>Fats and oils - building triglycerides</u>

Fats and oils:

- Fats and oils are basically esters made from propan-1,2,3-triol or glycerol (a triol) and long chain carboxylic acids, fatty acids:



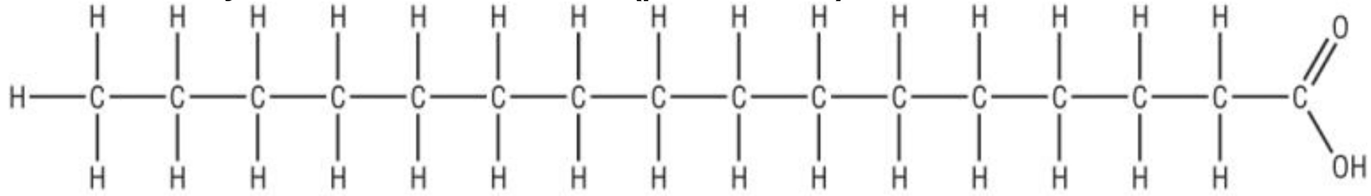
Glycerol **Long chain carboxylic acid, fatty acid - hexadecanoic acid**

- Its melting point determines whether it is a fat or oil.
- If its melting point is above room temperature it is a solid which makes it a fat, eg margarine and butter.
- If its melting point is below room temperature it is a solid which makes it an oil, eg olive oil.

Triglycerides - the building blocks:

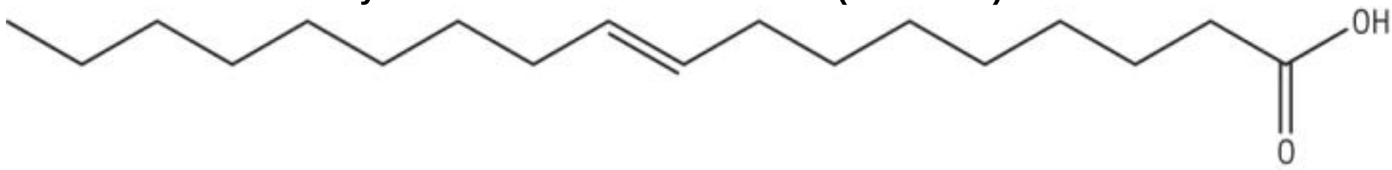
- Triglycerides are naturally occurring fats. They are triesters of propan - 1,2,3 - triol, glycerol and fatty acids.
- Glycerol has 3 alcohol groups which can react with a carboxylic acid (stearic acid) to form an ester.
- If all 3 join we make a **tri**glyceride (an ester).
- The carboxylic acids occur naturally and because they make fats (upon esterification) we call them fatty acids.
- Fatty acids are saturated if they contain only C - C and unsaturated if they contain C=C.
- Fatty acids contain an even number of carbon atoms due to their synthesis in nature.

A saturated fatty acid: Hexadecanoic acid (palmitic acid)



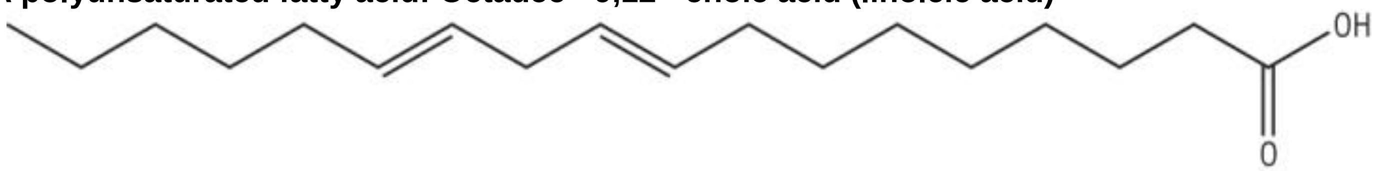
- Has no C = C

A monounsaturated fatty acid: Octadec - 9 - enoic acid (oleic acid)



- Has 1 C = C between Carbon 9 and 10 (common)

A polyunsaturated fatty acid: Octadec - 9,12 - enoic acid (linoleic acid)

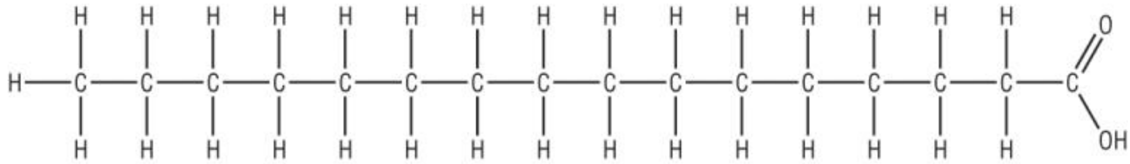


- Has 2 C = C between Carbon 9 and 10 / 12 and 13

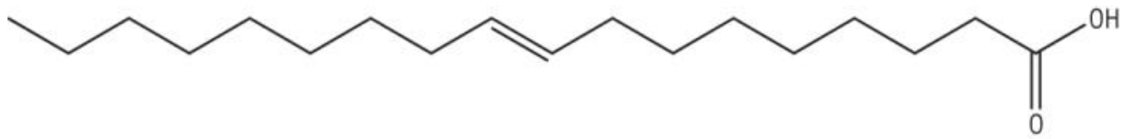
Fatty acid - shorthand:

- Fatty acids can be written in shorthand:

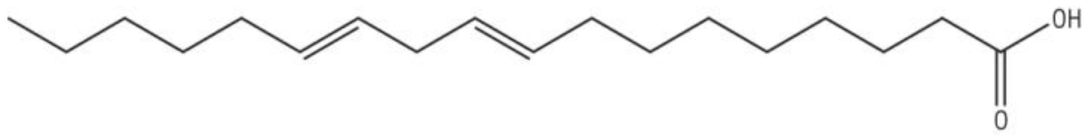
Number of carbon atoms		Number of double bonds	Position of double bonds
18	**:**	**1**	**(9)**



16:0



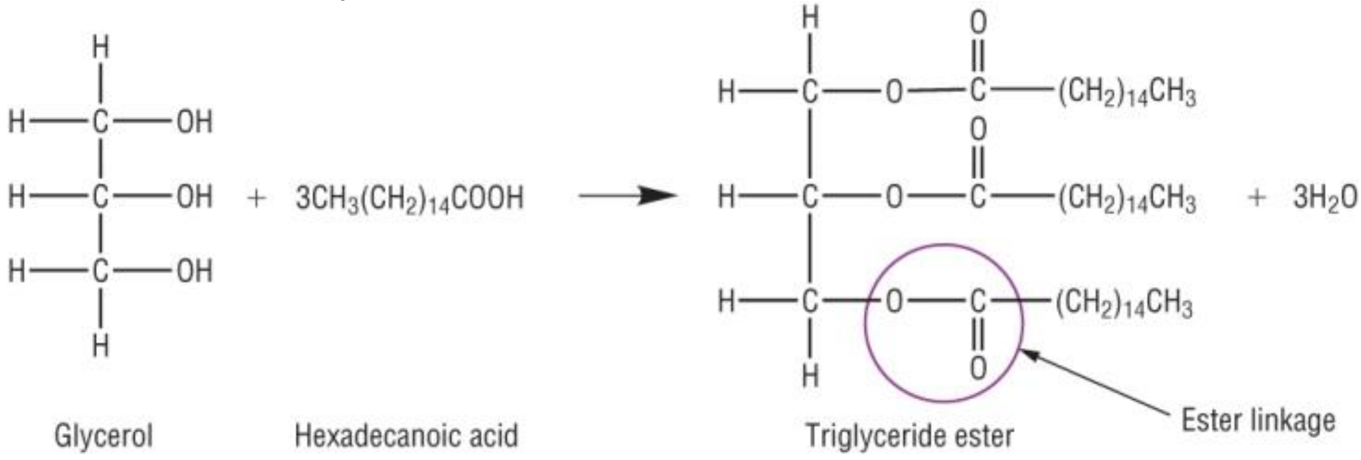
18:1 (9)



18:2 (9.12)

Forming triglycerides:

- These are basically esters:



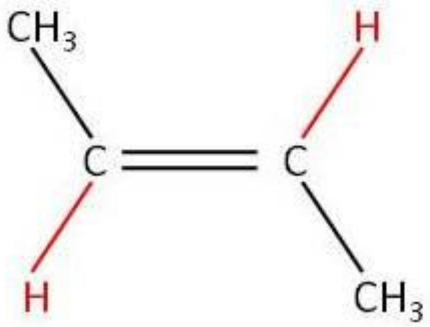
- Most triglycerides (fats) actually form using different fatty acids
- Triglycerides (fats) can be saturated or unsaturated depending on whether the fatty acids they are made of are saturated or not

Qu 1 - 4 P33

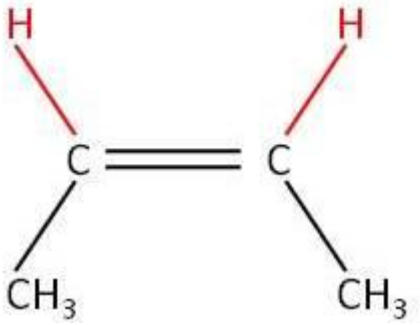
<u>Triglycerides, diet and health</u>

Isomerism in unsaturated fatty acids:

- In **AS** we covered the **Cis Tranz (E/Z)** isomerism involving a **C=C**:



No free rotation around the C=C



Trans but-2-ene

(E-but-2-ene)

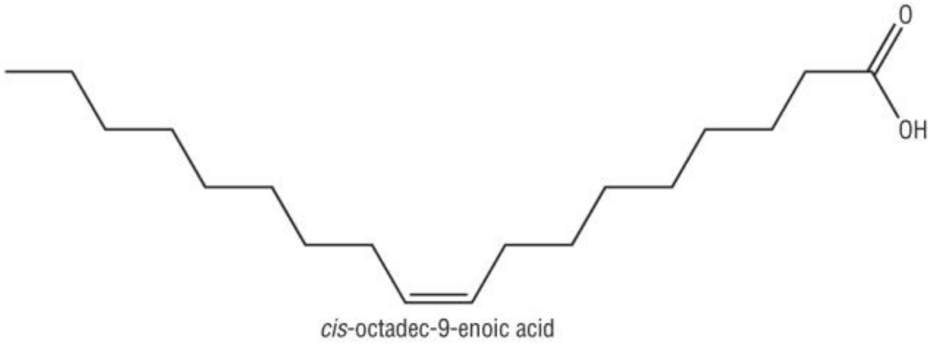
Cis but-2-ene

(Z-but-2-ene)

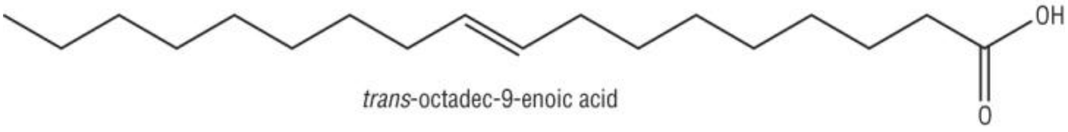
- Remember the C=C stops free rotation around the C=C.
- Fats and oils come from saturated and unsaturated fatty acids:

Fatty Acid		**Risk**	**Reason**	**Packing**	**State**	**Cause**
Saturated		Heart disease	Raises blood cholesterol	Close	Solid	Blocks arteries
Unsaturated	**Trans**	Coronary heart disease	Raises blood cholesterol	Close	Solid	Blocks arteries
	Cis	No Health risk		Cannot pack close together	Liquid	No effect

Unsaturated packing:



Non linear - inefficient packing - liquid

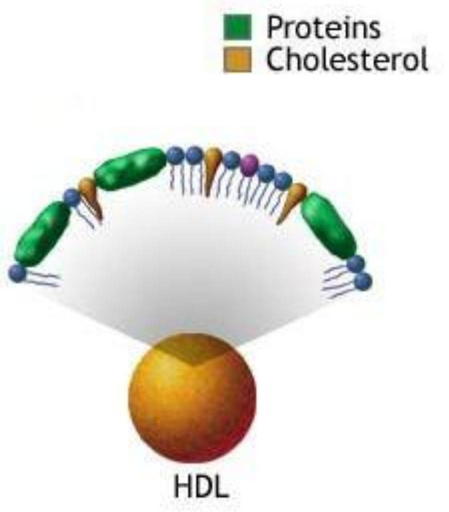


Linear - efficient packing - solid

- The food industry often removes some of the C=C by hydrogenation (adding H_2 across the C=C)
- This makes them more solid = margarine manufacture.
- A side effect of this is that the structure of the fat is changed from a liquid (little health risk) to a solid (Heart risk)

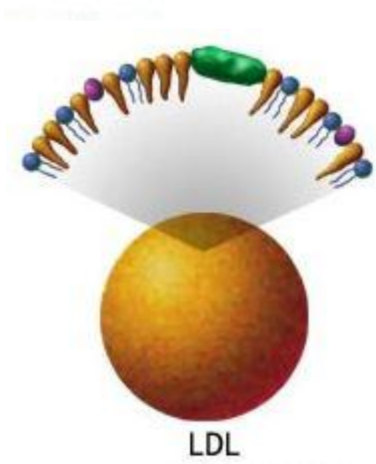
Trans fats cholesterol:

High Density Lipoproteins



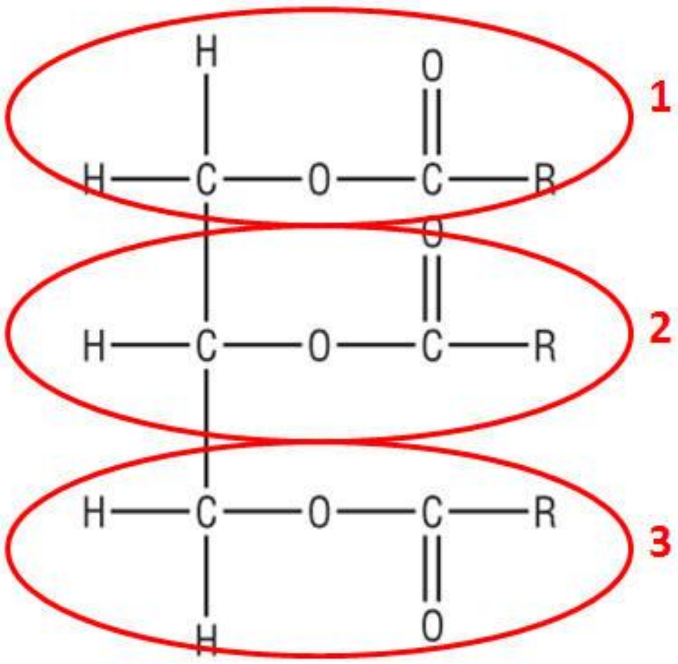
- These carry cholesterol out of the blood and out of the body.
- Good

Low Density Lipoproteins



- These carry about 65% of cholesterol around the blood
- End up depositing lipids (fats) onto artery walls
- This restricts blood flow
- Bad

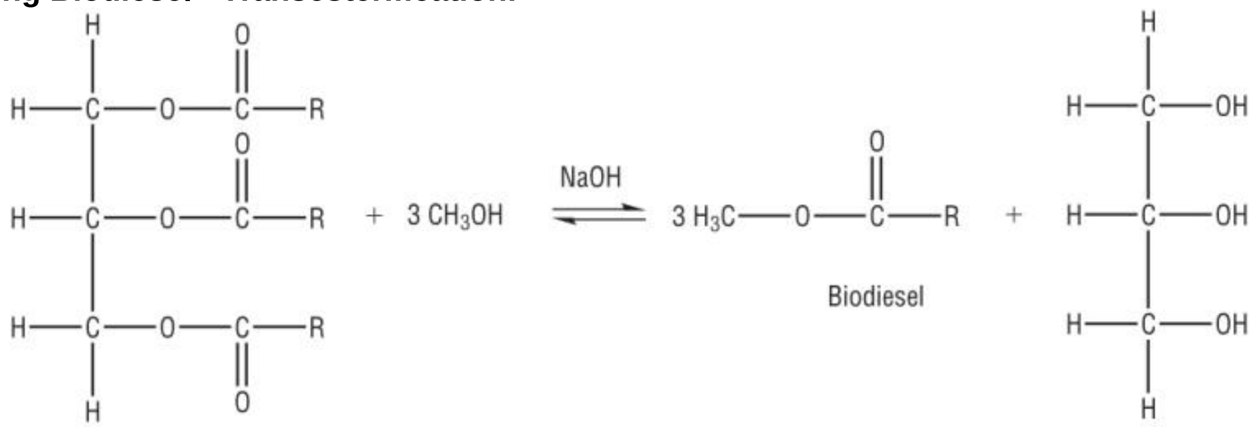
Fatty Acids as Biodiesel:



- Biodiesel is in fact a methyl or ethyl ester.
- Fats are essentially 3 methyl esters joined together.
- This can be made by using waste cooking oil and using a procedure called:

TRANSESTERIFICATION

Making Biodiesel - Transesterification:



- The waste oil is filtered then reacted with methanol and sodium hydroxide (catalyst) to form biodiesel.
- This also increases the atom economy of fats.

Qu 1 - 4 P35
Qu 5 - 8 P41 / 4 - 10, 14 P42 - 45