Introduction to Organic Chemistry

Theory Manual

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An Introduction to Organic Chemistry

Organic chemistry is the study of carbon containing compounds and their properties**.** This includes the great majority of chemical compounds on the planet, but **some substances** such as **carbonates** and **oxides of carbon** are considered to be **inorganic** substances even though they contain carbon.

Organic chemicals are continually released into the environment in large quantities. For example, global production of mineral oil exceeds 3 billion tonnes a year and the amount of new organic chemicals made each year in research laboratories and industry is increasing exponentially. There is a need to understand how these organic molecules will interact with the environment in order to minimise their impact. To achieve this the type of reactions that organic molecules undergo needs to be understood.

How do you tell the difference between an Organic and an Inorganic Compound?

Probably the best way is to compare the chemical and physical properties of substances to the table below. If they concur with those properties on the left column of the table then the substance is probably organic, whilst if they compare to the properties listed in the right column then the substance is most likely inorganic.

Organic Compounds	Inorganic Compounds
Use mostly covalent bonding	Mostly ionic bonding
Are gases, liquids or solids with low melting points	Are generally solids with high melting points
Mostly insoluble in water	Many are water soluble
Many are soluble in organic solvents such as petroleum, benzene and hexane	Most are not soluble in organic solvents
Solution in water generally do not conduct electricity	When dissolved in water conducts electrical current
Almost all burn	Most not combustible
Slow to react with other chemicals	Often undergo fast chemical reactions

Table 1: **Comparison of the properties of organic and inorganic compounds**

The vast majority of organic compounds are typically chains or rings of carbon atoms that contain other elements such as O, N, P, S, Cl, Br and I. There are over five million of these compounds known today and an almost infinite number of new compounds could possibly be synthesized. This can be compared to the total number of inorganic compounds, which is approximately half a million.

Why does carbon form so many compounds?

Carbon has the ability to bond with itself to form long chains and ring structures; hence it can form molecules that contain from one to an infinite number of C atoms.

Additionally C atoms may:

- be bonded by multiple bonds (i.e. double and triple) as well as single

- contain branches of other carbon chains

- need additional atoms attached to them to make them stable. The most common of these is H, but, N, O, X, P and S also commonly occurs attached to C and may even be attached in several different ways.

Note X is the symbol for any of the halides – F, Cl, Br or I

The Rules for Drawing Organic Molecules

1. C always has four bonds. This may consist of:

- 4 single
- 1 double and 2 single
- 1 triple and 1 single
- 2 double

2. H always has one bond.

3. O always has two bonds. This may consist of:

- 2 single
- 1 double

4. X always has one bond. X = F, Cl, Br or I

5. N always has three bonds. This may consist of:

- 3 single
- 1 single and 1 double
- 1 triple

6. S may have 2, 4 or 6 bonds, but for this course it has 2 bonds.

Class exercise:

Given 2 carbon atoms and as many hydrogen atoms as required construct 3 possible organic molecules which contain

(i) 1 oxygen atom   (iv) 1 nitrogen atom

(ii) 2 different halogen atoms   (v) 1 sulfur, 1 nitrogen, 1 halogen and 1 oxygen.

(iii)   1 sulfur atom

Conclusion –

The number of different design possibilities for organic molecules is endless.
In order to enable classification of such a large number of molecules, organic chemists have employed the principle of classifying all organic compounds into families according to their *functional groups*.

This greatly simplifies the study of organic compounds as molecules with the same functional groups behave the same in most chemical reactions.

Functional Groups

The behavior of any molecule in a particular chemical environment is determined by the stability or reactivity of its bonds. Each different type of bond shows different levels of reactivity.

Generally in a molecule there is **a group of bonds that are more reactive than all the others** and this group tends to determine how the whole molecule behaves in a particular chemical environment regardless of the structure of the rest of the molecule.

Chemists call these dominant groups of atoms and bonds **functional groups** and these are used to classify organic compounds into families.

Understanding the types of reactions that functional groups undergo will enable an understanding of how an organic molecule interacts with the environment.

A carbon-carbon double bond is an example of a functional group. Organic compounds that contain a carbon-carbon double bond and no other functional group are called alkenes (a family name used to classify these compounds). All alkenes react with bromine to yield dibromoalkanes**.**

Hence if you know a functional group reacts in one molecule you can predict how it will react in almost all other molecules.

It is possible to get more than one functional group in a single molecule, but the generalisation stated above still applies.

Table 2 (below) contains a list of all the functional groups you are expected to know for this course.

Type of Functional Group	General Formula
Alkane	$\begin{array}{c} \;\,\vert\;\,\vert \\ \text{-C-C-} \\ \;\,\vert\;\,\vert \end{array}$
Alkene	$\begin{array}{c} \;\,\vert\;\,\vert \\ \text{-C=C-} \end{array}$
Alkyne	$-\text{C}\equiv\text{C}-$
Alkanol (old name alcohol)	$\begin{array}{c} \vert \\ -\text{C-OH} \\ \vert \end{array}$
Amine (Primary)	$\begin{array}{c} \vert \\ \text{-C-NH}_2 \\ \vert \end{array}$
Amine (Secondary)	$\begin{array}{c} \vert \\ \text{-C-NH-R} \\ \vert \end{array}$
Amine (Tertiary)	$\begin{array}{c} \text{-C-N-R} \\ \vert \\ \text{R} \end{array}$
Alkanal (old name aldehyde)	$\begin{array}{c} -\text{C}-\text{C}-\text{H} \\ \;\;\;\;\;\;\Vert \\ \;\;\;\;\;\;\text{O} \end{array}$
Alkanone (old name ketone)	$\begin{array}{c} \;\;\;\;\;\;\;\;\;\;\vert \\ -\text{C}-\text{C}-\text{C}- \\ \;\;\;\;\Vert\;\;\;\vert \\ \;\;\;\;\text{O} \end{array}$
Amide	$\begin{array}{c} -\text{N}-\text{C}-\text{R} \\ \;\;\;\;\;\;\Vert \\ \;\;\;\;\;\;\text{O} \end{array}$
Ester	$\begin{array}{c} \;\;\;\;\vert \\ -\text{C}-\text{C}-\text{O}-\text{R} \\ \;\;\vert\;\;\Vert \\ \;\;\;\;\;\;\text{O} \end{array}$
Alkanoic acid (also called carboxylic acid)	$\begin{array}{c} -\text{C}-\text{OH} \\ \;\;\Vert \\ \;\;\text{O} \end{array}$

Table 2 – **Some common functional groups and their general formula.**

Note 1: R is the symbol for any hydrocarbon chain.

Note 2: There are many other functional groups besides those listed in Table 1, but these will not be studied in this course.

Chemical Formulae and the Structures of Organic Compounds

How does the chemist know the structure or composition of a particular chemical substance?

- Physical properties enable identification, but give no clues as to the composition or structure.

- Chemical reactivity gives clues as to the functional groups present, but does not tell the complete structure or chemical composition.

Elemental analysis (through chemical tests and combustion analysis) allows the determination of the **empirical formula** of the substance. This expresses the **simplest ratio of the elements present**.

For example if there were 6 carbons, 12 hydrogen and 6 oxygen in a compound then the ratio of each is 6C:12H:6O, but the simplest ratio (read empirical formula) is C:2H:O, which is obtained by dividing by 6 (the lowest common denominator).

This means that the empirical formula will be CH_2O.

Class Exercise:

Calculate the empirical formula for each of the substances shown below.

(i)   A substance containing 5C's, 10H's and 5O's.

(ii)   A substance containing 5C's, 10H's and 2O's.

(iii)   A substance containing 6C's, 12H's and 2O's.

Another formula, the **molecular formula** expresses the **total number of each atom present** and is always a multiple of the empirical formula (it may also be the same as the empirical formula).

To determine the molecular formula we need to know the molecular mass of the substance. This is done by dividing the molecular mass by the mass of the empirical formula to obtain a multiplication factor. The empirical formula is then multiplied by this factor.

e.g. Given a molecular mass of 180 and an empirical formula of CH_2O calculate the molecular formula.   Data atomic mass of C = 12.00, H = 1 and O = 16.00.

Mass of empirical formula = 12.00 + (2 x 1) + 16 = 30

Molecular mass   = 180

Multiplier = 180 / 30 = 6

Molecular formula   = empirical formula x multiplier

                      = CH_2O x 6

                      = $C_6H_{12}O_6$

Once the molecular formula is determined the next step is to determine the **molecular structure** that is **a representation of how the atoms are bonded to each other**. It is possible to have several different organic compounds with the same molecular formula, but different molecular structures.

For example given that the molecular formula of a substance was C_2H_6O, it is possible to draw the structure of this molecular formula in two ways (which are shown below). Hence this formula represents two different organic compounds, with different physical properties. Ethanol is a liquid at room temperature while methoxy methane is a gas.

CH_3CH_2-OH CH_3-O-CH_3
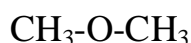
    ethanol   **methoxy methane**

Compounds that have the same molecular formula, but different structural formulas are known as **isomers**.
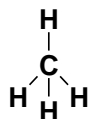
Class Exercise.

Give as many structures as you can for the molecular formula $C_4H_{10}O$.

Class Exercise. Representing 3D Organic Structures on Paper

Using the models provided complete the following class exercises:

Shown below is a 2D representation of methane. Study this and the molecular model of methane provided.

$$\begin{array}{c} H \\ | \\ C \\ H \diagup \, | \, \diagdown H \\ H \end{array}$$

(i)   Comment on how the "on page" representation differs from the model, paying particular attention to the angles of the bonds.
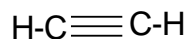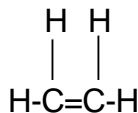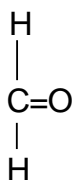
(ii)   What do you think the bond angle is in the model?

(iii)   Study the model of methane and draw a pictorial representation of the molecule in 3D using a pencil.

(iv)   Use models to build the following molecules:

$$\begin{array}{c} CH_3 \\ | \\ CH_3CH_2CH_2CH_3 \qquad\qquad CH_3CH_2CH_2 \end{array}$$
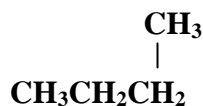
What do you notice about these molecules?

(v) Use models to build the following molecules.

$$\begin{array}{c} H \\ | \\ C=O \\ | \\ H \end{array} \qquad \begin{array}{c} H \;\; H \\ | \;\; | \\ H\text{-}C=C\text{-}H \end{array} \qquad H\text{-}C \equiv C\text{-}H$$

Comment on how the shape of these molecules differs from that of methane. Is it possible to rotate the double bonds in the same fashion as the single bonds in methane can be rotated?
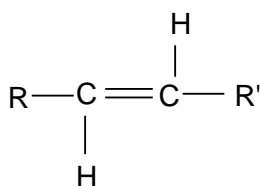
Isomers

Structural Isomers (sometimes called constitutional)

These have the same molecular formulae but differ in the order of connection of atoms.
e.g.

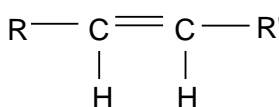CH_3CH_2-OH CH_3- O-CH_3
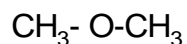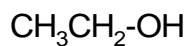
Geometric isomers

They have the atoms bonded in the same order but differ in arrangement of atoms in space.
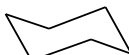e.g.   cis and trans in alkenes. (Z and E)

trans   **cis**

Conformational isomers

Due to rotation about C-C bonds.
e.g. Chair and boat formation of cyclohexane.

boat formation   chair formation

The IUPAC Naming (nomenclature) System - How to Name Organic Compounds

We will use the nomenclature (systematic) system for alkanes and cycloalkanes as a demonstration of how to systematically name organic compounds. The system used to name alkanes forms the basis for naming all organic compounds.
The general approach is as follows:

The name given to any compound containing a chain of carbon atoms consists of three parts;

- The **root** of the name which appears in the middle (this is further divided into the carbon chain designation and the infix),
- The **prefix** which appears at the start; and
- The **suffix** which appears at the end.

Each part will be described, and then some examples examined to show how organic compound nomenclature works.

1. The Root

This is divided into two sections – the **chain designation** and the **infix**.
The **chain designation** tells us the number of carbon atoms contained in the **longest continuous carbon chain** in the molecule. This is based upon the Table given below.

For example if the longest continuous C chain is four the chain designation is but-, if it is eight it is oct-

Chain Designation	No. of C Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Table 3. **Table of chain designation and corresponding number of carbons. The prefix cyclo- is added to these chain designations if the carbons exist in ring formation.**

The **infix** tells us the **nature of the carbon bonds.** This is based on the system shown in the table below.

Infix	Nature of Carbon-Carbon Bonds
-an-	only single bonds
-en-	one or more double bonds
-yn-	one or more triple bonds
-yl	attached group (not part of main carbon chain)

Table 4: **The infix and corresponding nature of carbon-carbon bonds.**

2. The Suffix

This tells us the class of compound to which the substance belongs. It is derived from the most important functional group in the molecule. The suffixes listed in the table below are given in their order of importance, the most important at the top, the least at the bottom. If more than one functional group is in the molecule, it is assigned to that class which has the more important functional group. In organic chemistry this is based upon the amount of oxygen and hydrogen in the functional group. **Essentially the more oxygen and the less hydrogen the more important the functional group.**

Suffix	Class of Compound	
-oic acid	alkanoic acid	$R - \overset{\overset{\textstyle O}{\|\|}}{C} - O - H$
-oate	ester	$R - \overset{\overset{\textstyle O}{\|\|}}{C} - O - R$
-al	alkanal	$\overset{\overset{\textstyle O}{\|\|}}{C} - C - C$
-one	alkanone	$C - \overset{\overset{\textstyle O}{\|\|}}{C} - C$
-ol	alkanol	$R - C - OH$
-e	hydrocarbon	$C - C - C^{\cdot}$

Table 5: **The suffix and the corresponding class of organic compound.**

3. The Prefix

This **tells us the other atoms and groups of atoms attached to the main carbon chain**. It may be single species such as halogen atoms, carbon chains smaller than the main carbon chain, or even rings of carbon atoms.

The three parts of the name are linked together as shown below:

PREFIX---ROOT---SUFFIX

Note: In naming, **dashes** are used to separate numbers and letters; **commas** are only used to separate numbers from other numbers. Names are given in **one piece**; there are no gaps between the pieces except when specifically stated in the naming system.

Some examples of the naming system are given below.

Example 1

$$CH_3$$
$$|$$
$$CH_3CHCH_2CHCH_3$$
$$|$$
$$CH_3$$
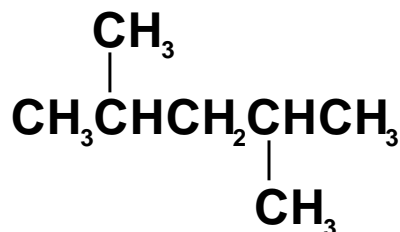
To name this compound

   1a. First count the longest continuous carbon chain – in this case 5.

Therefore the chain designation is **pent-.**

   1b. As the molecule contains only single bonds to the carbon and hydrogen atoms the infix is **an**-.

Therefore the root of the name is **pentan-**.

   2. Next add the suffix. As this molecule is a hydrocarbon the suffix is just **-e**.

Therefore the root plus suffix is **pentane**.

Finally we must list the attached groups as prefixes. In this case there are two groups attached to the main carbon chain. They are both single carbon groups. When naming carbon chains that are attached to the main carbon chain, the same naming conventions are used as in determining the root of the name for carbon designation, but the infix **-yl** is employed to distinguish attached chains from the main carbon chain.

In this case the attached groups have only one carbon atom so the chain designation is **meth**-, whilst the infix is -**yl**.

Therefore the attached groups are referred to as **methyl** groups.

3. If there is any ambiguity as to the position of the attached groups they must be numbered. The numbering and listing system has the following rules.

- the longest continuous carbon chain is numbered such that the most important functional group is given the lowest number.

- the attached groups are listed in alphabetical order.

- the number of the carbon atom from the main chain to which the group is attached is placed in front of the name for the group and a hyphen placed between them.

- if there is more than one type of group attached then the pre-prefixes listed below are used to state how many of each attached group is present.

Pre-Prefix	Number of Attached Groups
di-	two
tri-	three
tetra-	four
penta-	five
hexa-	six

Table 6: **The pre-prefix and the corresponding number of attached groups.**

Using the above conventions the attached groups in our example would be 2,4-dimethyl-, because the one carbon groups are attached to carbons two and four of the main chain and the pre-prefix **di-** is used as there are two of them.

So the full name is **2,4-dimethylpentane.**

Note: There are no gaps between the parts of the name, only commas to separate the numbers and hyphens to separate the numbers from the words.

Example 2.

For the structure

$$CH_3$$
$$|$$
$$CH_3CHCH_2CH_2$$
$$|$$
$$OH$$

the number 1 tells us which C
the –OH group is attached to

four C in the main chain

single carbon group attached at
C number 3

3-methyl-1-butanol

the most important functional group is
alkanol

the main C chain contains only
single bonds
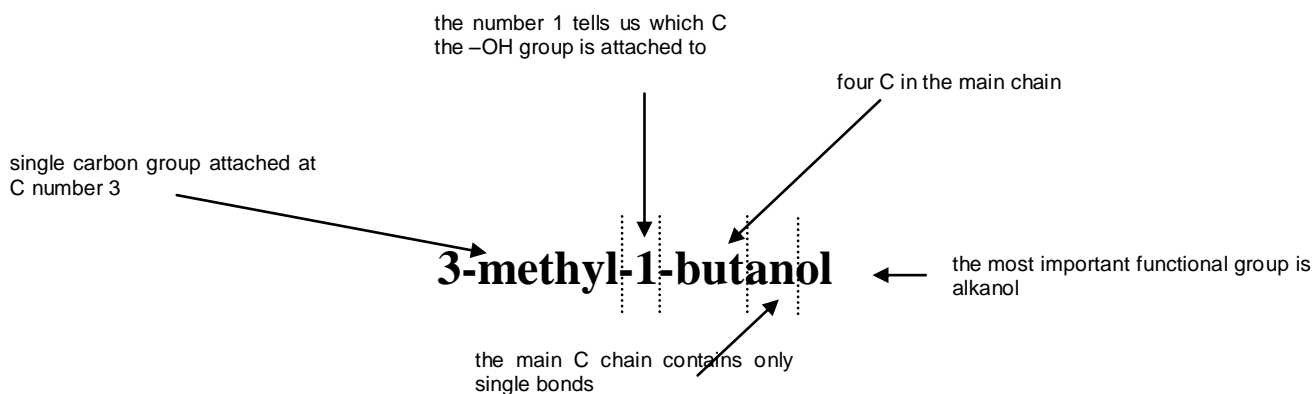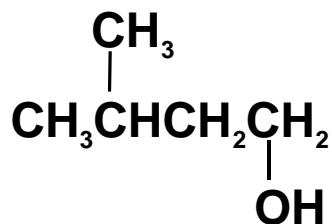
Example 3.

For the structure

6C atoms in a ring

main C chain has only single bonds

3-ethylcyclohexanone

2 C group attached to C number 3

*most important functional group is
alkanone*
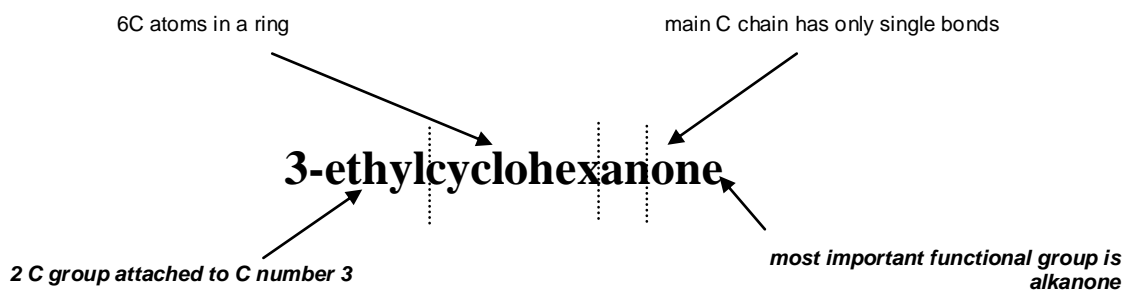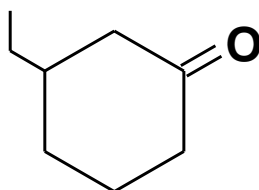
Shorthand Notation for Drawing Organic Structures

Organic molecules often appear to have large and complex structures, but in reality they consist of many simple repeating patterns of CH_3-, CH_2-, and CH- groups plus a few others. Rather than draw oodles (a technical term) of CH_3 and CH_2 groups organic chemists use a shorthand notation to allow these structures to be drawn very rapidly and simply.

Individual carbon atoms are represented by inflections (read kinks) in a line and the hydrogen are left out completely. Double and triple bonds are drawn in as required.

For example, $CH_3CH_2CH_3$ is represented as ⌃ The start, end, and each point of inflection represent a C atom.

The structure for $CH_3CH_2CH=CH_2$ is
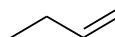
Class Exercise.

Draw structures for each of the following molecules

(a) pentane

(b) 2 -methylpropane

(c) 3-methylheptane

(d) 2,2,3-trimethyloctane

(e) 3,5-dimethylheptane

(f) 1-ethyl-3-propylcyclohexane

Write correct systematic names for each of the structures (alkanes) given-

(a)
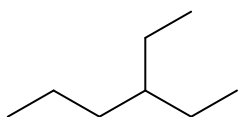
(b)
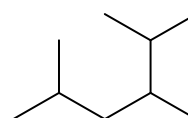
(c)
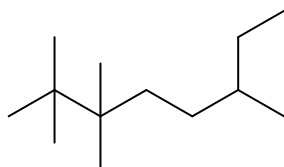
(d)

(e)
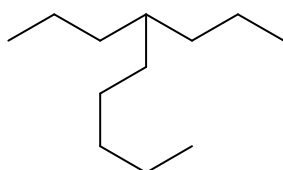
(f)
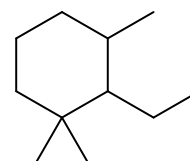
Hydrocarbons

These are compounds **composed of carbon and hydrogen.** They are generally insoluble in water although those with lighter molecular masses are gases and are slightly soluble. Examples of hydrocarbons include methane - the gas we burn as natural gas, propane (also called liquid petroleum gas) and petroleum jelly.

Hydrocarbons with single carbon-carbon bonds are referred to as being **saturated** whilst any hydrocarbon that contains a double bond is said to be **unsaturated.**

$$CH_3CH_2CH_2CH_3$$
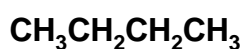
a saturated hydrocarbn

```
     H   H
     |   |
H  - C = C H
```
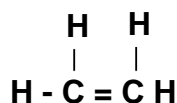
an unsaturated hydrocarbon

Saturated hydrocarbons are also called the **alkanes**, whilst the unsaturated hydrocarbons include both those molecules that contain carbon-carbon double bonds (referred to as the **alkenes**) and those that contain carbon-carbon triple bonds (referred to as the **alkynes**).

Alkanes and alkenes are natural products that have resulted from the decay of organic compounds from plants and animals that lived millions of years ago. They are found today as petroleum, which are mixtures of hydrocarbons containing up to 30 or 40 carbon atoms. Different components of petroleum can be isolated by fractional distillation.

These hydrocarbons are good sources of fuels, the so-called 'fossil fuels'. As mentioned previously, the global production of such fossil fuels is 3 billion tonnes. As they are produced in such large quantities, pollution of the environment with these fossil fuels is of concern. The major route of entry into the environment isn't through spectacular disasters such as the oil spills from ships, but rather through our daily activities. Pumping fuel into cars, and oil spilled onto the road as a result of old faulty cars are major contributors.

The Alkanes

This family of compounds consists of substances that contain only carbon and hydrogen joined by **single bonds**. They obey the general formula

$$C_nH_{2n+2}$$

Thus if an alkane has six carbons, its formula will be C_6H_{14}. The simplest alkane is methane, CH_4. Methane is also the most abundant organic species in the atmosphere. It is produced mainly by organisms breaking down organic material in places such as marshes, lake bottoms, land fills and the stomach of ruminant animals.

Reactions of Alkanes

Because they are saturated compounds and because the C-C and C-H bonds are relatively strong, the alkanes are fairly unreactive, (e.g. at room temperature they do not react with acids, bases, or strong oxidising agents) which makes them invaluable as lubricants and the backbone of plastics.

At sufficiently high temperatures, **alkanes react vigorously with oxygen.** This is known as a **combustion** reaction and is the basis for their widespread use as fuels. An example is the reaction of butane with oxygen.

Class Exercise.
See if you can write the correct equation for the combustion of butane in oxygen to give water plus carbon dioxide.

The production of carbon dioxide in the environment is of concern because it has been implicated in the green house effect. **Animals and plants produce carbon dioxide.** Recently there has been an increase in carbon dioxide production brought about by a combination of deforestation and the burning of fossil fuels. (Plants use up carbon dioxide in photosynthesis, so removing vegetation is a good way to increase the amounts of carbon dioxide in the atmosphere). Carbon dioxide is thought to act like a blanket placed over the earth, it captures infrared radiation and transforms it into heat (The so-called "Green House Effect"). This may lead to an increase in the earth's temperature, which may cause a melting of the earth's ice caps. This could have potentially devastating effects, particularly for people who live in seaside cities.

Alkanes also under-go reactions induced by UV light. Examples include the slow breakdown of plastics in the sun, and halogenation reactions (reactions where halogen atoms such as Cl, Br, or I replace H in the molecule).

Alkenes and Alkynes

When hydrogen is removed from an alkane multiple carbon-carbon bonds result. Hydrocarbons that contain a carbon-carbon **double bond** are called **alkenes,** and have the general formula

$$C_nH_{2n}$$

The simplest alkene is ethene (also known as ethylene) (C_2H_4). Ethylene is emitted by green plants in substantial quantities. It has hormonal activity and has been implicated in the control of many physiological processes in plants. The natural atmospheric concentration of ethylene is low due to its high reactivity with ozone and other atmospheric chemicals, but in polluted environments concentrations can be much higher. It is a product of the combustion of wood, coal, oil, natural gas and petroleum.

Hydrocarbons that contain a carbon-carbon triple bond are called **alkynes.** These compounds have the general formula

$$C_nH_{2n-2}$$
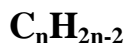
The simplest alkyne is ethyne (which is also known as acetylene) which has the formula C_2H_2. Ethyne is a flammable and explosive gas, when burnt in the presence of oxygen enough heat is produced to cut and weld metals (the basis of the oxyacetylene welding torch). Alkynes are not normally found in the environment because they are highly reactive.

Nomenclature of Alkenes and Alkynes

The systematic nomenclature for alkenes is quite similar to that for alkanes. Important differences are listed below.

- The root hydrocarbon name ends in -**ene** rather than -**ane**.

- In alkenes with more than three carbon atoms, the **lowest numbered carbon atom involved in the double bond indicates the location of the double bond.**

Thus $CH_2=CHCH_2CH_3$ is called 1- butene, and $CH_3CH=CHCH_3$ is called 2 - butene.

The restricted rotation around a double bond means that alkenes exhibit **cis-trans isomerism** (they have the same molecular formula but different structural formula). For example in the case of 2 - butene we can draw structures (a) and (b) below. Identical substituents in the **same side** of the double bond are referred to as **cis- (or Z)**, whilst identical substituents on the **opposite side** of the double bond are designated **trans- (or E).** Hence structure (a) is called cis-2-butene, whilst structure (b) is called trans-2-butene. Cis-trans isomers have different physical properties.
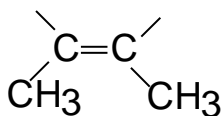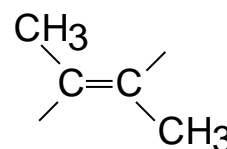
(a) bp = 4°C, mp = -113°C   (b) bp = 1°C, mp = -106°C

The nomenclature for alkynes involves the use of -**yne** as a **suffix** to replace the **-ane** of the parent alkane. Thus the molecule $CH_3CH_2C=CCH_3$ has the name 2-pentyne.

Physical and Chemical Properties of Alkenes and Alkynes

Physical Properties

The physical properties of alkenes and alkynes are **very similar to alkanes** with the same number of carbon atoms and branching pattern.

Chemical Properties

Unlike alkanes, which are fairly inert, **alkenes** and **alkynes undergo many chemical reactions.** These reactions take place at the multiple carbon-carbon bonds and are called addition reactions.
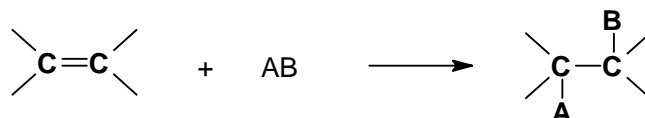
An example of an addition reaction to an alkene.

ADDITION REACTIONS OF ALKENES

HYDROGENATION

H_2 / Pt

```
H   H
C – C
H   H
alkane
```

HYDRATION

H^+ / H_2O

```
H   H
C – C -
H   OH
alkanol
```

HALOGENATION

X_2

```
X   H
C – C -
H   X
dihaloalkane
```

HYDROHALOGENATION

HX

```
H   H
C – C -
X   H
haloalkane
```

TRANS (E) ADDITION.

HYDROXYLATION

$KMnO_4$ / H_2O

```
H    H
C – C -
HO   OH
diol
```

HYPOHALOGENATION

HOX

```
H   H
C – C -
HO  X
haloalkanol
```

CIS (Z) ADDITION.

$C=C$
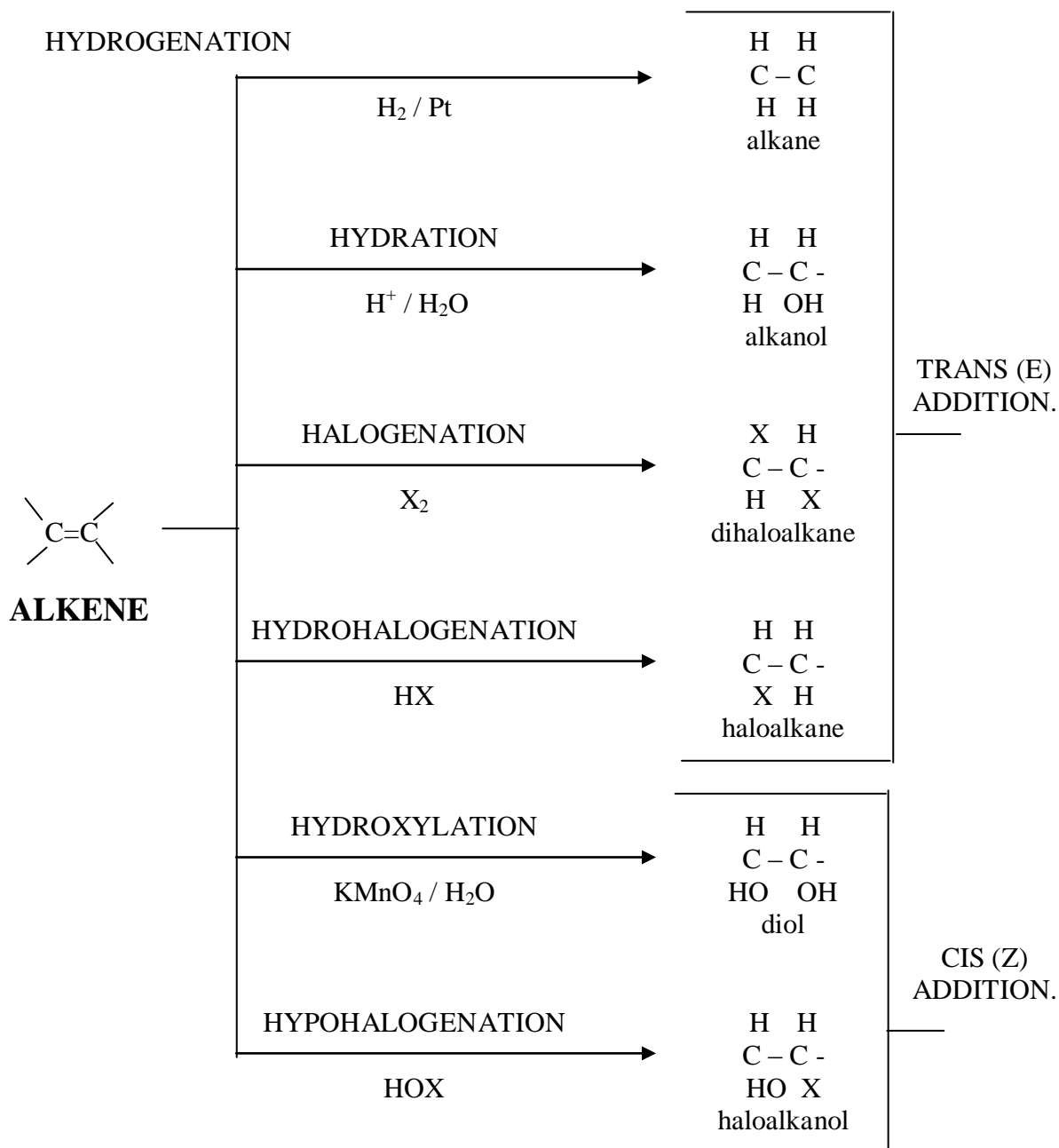
ALKENE

POINTS TO NOTE.

a. Trans (E) and Cis (Z) addition.

b. Markovnikov addition to unsymmetrical alkenes by unsymmetrical reagents i.e. the non-hydrogen part adds to the more substituted carbon (with HO the OH adds to the more substituted carbon)

MARKOVNIKOV'S RULE.

In an addition reaction, where the reagent being added to the double bonds is unsymmetrical (e.g. HCl), there can be two possible products, depending on which end of the double bond is attacked by the two components of the reagent.

Markovnikov's rule states that the negative part of the reagent bonds to the end of the C=C, which has the LEAST number of hydrogens.

The negative component is normally the non-H part, except in HOX, where it is OH.

Types of Organic Reactions

1. Addition
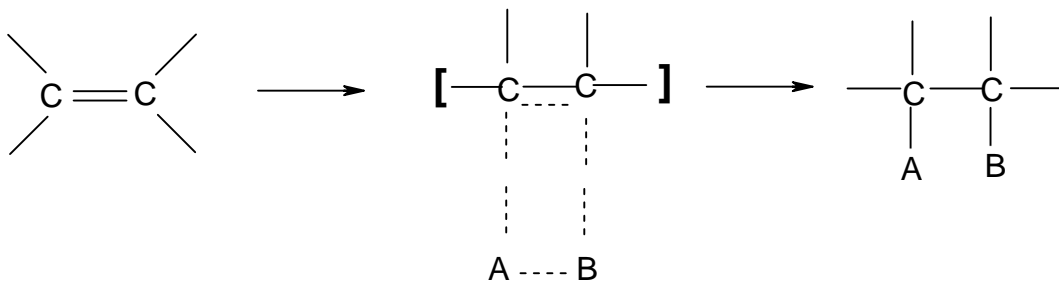
The double bond dissolves back to single bond and new bonds reach out to A and B whose bond is also dissolving

A – B can be.

H-H	H-OH	H-X	X-X	OH-OH	OH-X

Draw the product of each of these examples of A-B when they add to 1-propene.
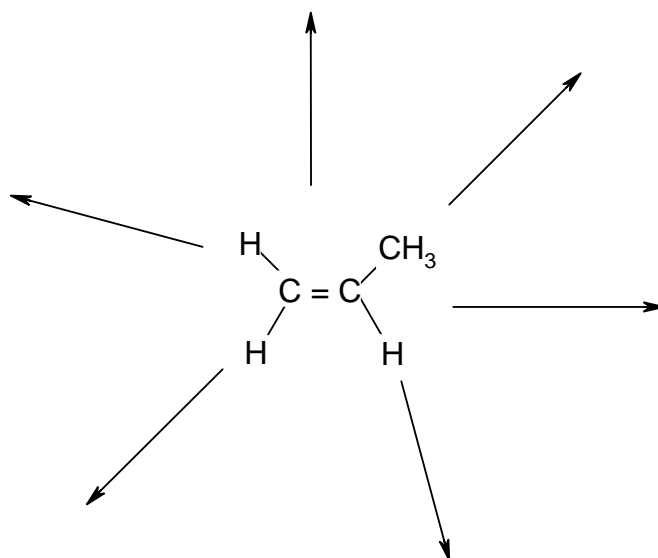
2. Elimination

This is the opposite of addition i.e. a double bond is created when two groups on adjacent carbons are rejected by the molecule. The groups are just those groups which were added in the first place. The only one we cannot do is the elimination of H-H bond.

3. Substitution

One non-carbon group is replaced by another group. Usually only occurs at a singly bonded site. The only example so far is halogen/UV on alkanes but alkanols and haloalkanes love a bit of substitution as well.

4. Condensation and Hydrolysis

Are reversals of one another. Condensation is where two molecules join together and lose a simple molecule. **e.g.** water or carbon dioxide. Hydrolysis is the reverse.

5. Oxidation and Reduction

Are opposite of each other. Oxidation is either adding **O** or making it have a double bond or removing **H** or both. Reduction is the opposite.

Alkanols (alcohols)

Any molecule which contains the functional group **-C-OH** is a member of the alkanol family. Usually it is restricted to cases where the C atom attached to the -OH has no other heteroatom (atom other than C or H) attached to it.

The simplest alkanol is methanol (CH_3OH). Its common name wood alcohol comes from the fact that it was first obtained by heating wood in the absence of air. Methanol is very poisonous; consumption of less than two teaspoons can cause blindness. Of all the alkanols, methanol is produced in the greatest quantities in industry.

Ethanol (CH_3CH_2OH) or simply, alcohol in layman's terms has been prepared since antiquity by fermentation of sugars and starches, catalyzed by yeast. Sugars for fermentation come from a variety of sources, including grains, grape juice, various vegetables and agricultural wastes. The immediate product of fermentation is a water solution containing up to 15% ethanol (its not surprising that home brew can be so potent!). This value can be increased by distillation.

Nomenclature of alkanols

The systematic name for an alkanol is obtained by following the rules listed below:

1. Find **the longest chain that contains the -OH group.** The stem of the alkanols name is obtained from the parent alkane, with the -e **being replaced by the suffix -ol.**

2. The **position of the -OH group is specified by a number** chosen so that it is the smallest of the substituent numbers.

Physical Properties of Alkanols

Boiling Point

Alkanols usually have **much higher boiling points than might be expected from their molecular weights.** For example, both ethanol and ethane have a molecular weight of 30, but the boiling point for methanol is 65°C whilst that for ethane is -8°C. This difference can be understood if we consider the types of intermolecular attractions (attractions between molecules) that occur in these liquids.

Ethane molecules are non-polar and exhibit only weak London dispersion forces. However, the polar -OH group of methanol produces extensive hydrogen bonding similar to that found in water (see Figure 1) which results in the relatively high boiling point. The boiling point for the homologous series of alkanols is proportional to the number of C atoms, as in the alkanes.

$$\delta\text{-} \qquad \delta\text{+}$$

$$\text{O} \longrightarrow \text{H} \qquad \qquad \text{Hydrogen bond between O and H}$$

$$\text{H} \longrightarrow \text{O}$$

$$\delta\text{+} \qquad \delta\text{-}$$

Means that the atom is slightly positively charged
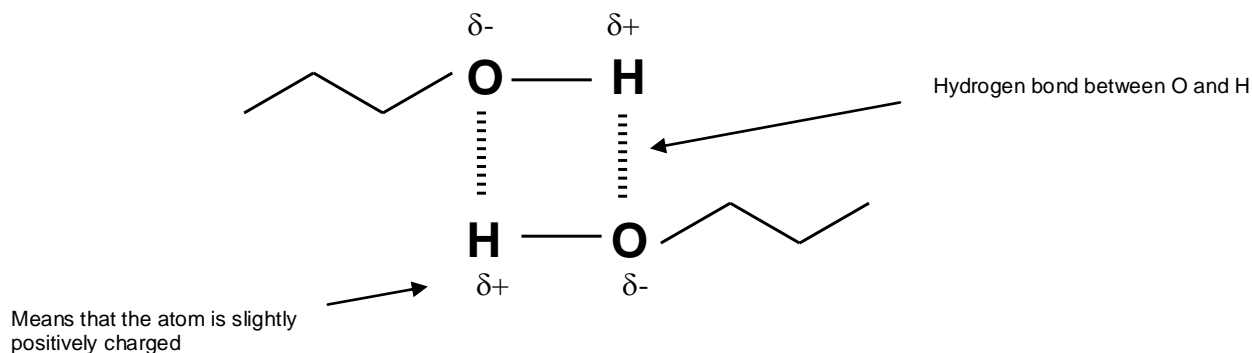
Figure 1 – Hydrogen bonding in an alkanol

Water Solubility

Due to the presence of the polar -OH group the alkanols **up to C4 is all water-soluble.**
Those alkanols from C4-C8 have slight water solubility**.**
Most physical properties (e.g. refractive index, density, melting point, etc.) change gradually for the homologous series as the number of C increases.

Preparation of Alkanols

Methanol and ethanol are of the greatest commercial value, and have been prepared from natural sources for centuries (methanol from wood and ethanol from fermentation of sugars).

OXIDATION OF ALKANOLS

Alkanols are classified according to the number of hydrocarbon fragments attached to the C where the –OH group is bonded.

    R – CH$_2$OH   is known as a **primary alkanol**.
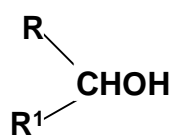
R
   CHOH
R^1   is known as a **secondary alkanol**
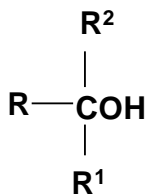
    R^2
    |
R—COH
    |
    R^1   is known as a tertiary **alkanol.**

Where **R, R^1, R^2** (which may be the same or different) represent hydrocarbon groups.

The three classes of alkanols behave differently towards oxidizing agents.

Primary alkanols - general reaction.

R-CH$_2$-OH $\xrightarrow{\text{[O]}}$ **R-C-H** $\xrightarrow{\text{[O]}}$ **R-C-OH**
            ‖   ‖
            O   **O**

primary alkanol   **alkanal**   **alkanoic acid**

Secondary alkanols – general reaction.

R-CH-R $\xrightarrow{\text{[O]}}$ **R-C-R**
 | ‖
 OH   **O**
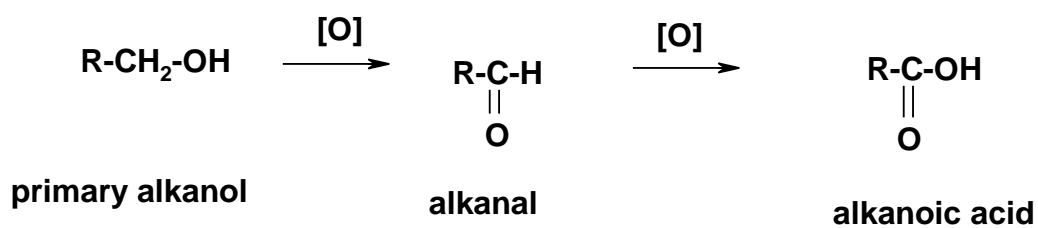
secondary alkanol   **alkanone**
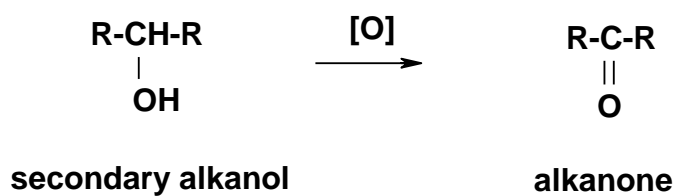
Tertiary alkanols – general reaction.

 R
 |
R-C-R $\xrightarrow{\text{[O]}}$ **No Reaction**
 |
 OH
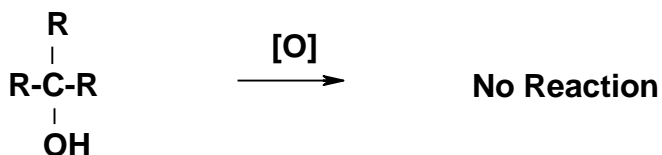
As tertiary alkanols do not have an H atom on the OH bearing C, they do not react with oxidizing agents.

Haloalkanes

These are simply alkanes that have one or more of the **H** replaced by a halogen (F, Cl, Br, I) that is often designated by the symbol **X**.

e.g. CH_3Cl or CH_2ClBr or $CHCl_3$ etc is written as CH_nX.

Nomenclature

The names for haloalkanes are derived according to the rules that have previously been discussed for naming alkanes. The parent C chain is numbered in the direction that gives the substituent encountered first (regardless of whether it is a halogen or an alkyl group) the lowest number. Halogen substituents are denoted by the prefixes fluoro, bromo, chloro and iodo.

e.g.

$$CH_3CHCH_2CH$$

Cl   is referred to as 2-chlorobutane.

Cl

$$CH_3CHCHCH_2CH_3$$

Br   is referred to as 3-bromo-2-chloropentane.

Class Exercise

Name the following compounds:

a

F

$$CH_3CHCHCH_2CH_3$$

CH_2

CH_3

b

Br

c

$CHCl_3$

d

H

F—C—Br

Cl
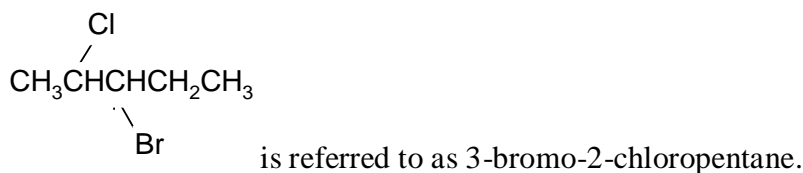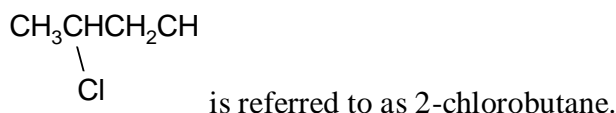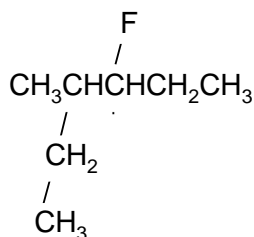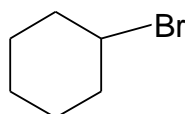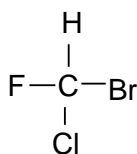
Preparation of Haloalkanes

There are a number of different procedures described for the preparation of haloalkanes, but the most important are the derivation from alkenes, alkanols and alkanes.

1. Synthesis from alkanes (substitution)

If a mixture of an alkane and a halogen are kept in the dark no reaction occurs, but if the mixture is exposed to visible or UV light a reaction occurs quite quickly with heat being evolved. This reaction is referred to as a substitution reaction because one or more of the Hydrogen atoms (randomly) on the alkane is replaced by a halogen.

e.g.
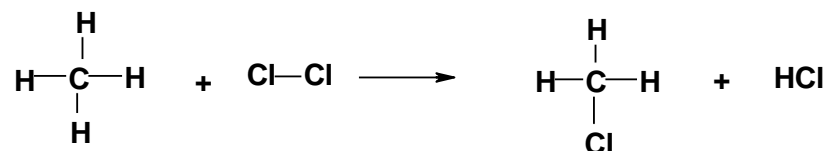
2. Synthesis from alkenes (addition reaction).

Halogens (and HX compounds) add readily to alkenes to form single covalent carbon halogen bonds on adjacent carbons in a reaction called halogenation. This reaction is also referred to as an addition reaction because the halogen atoms simply add on to the alkene.

e.g.

$$CH_3CH=CHCH_3 \quad + \quad Br_2 \longrightarrow$$
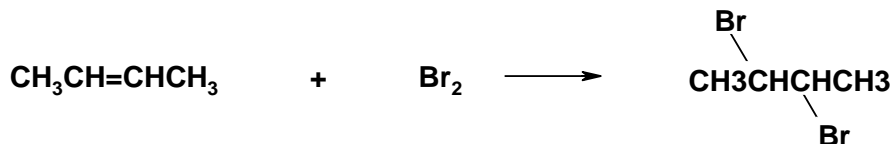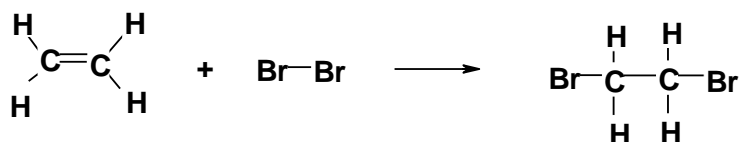
Alkanals and Alkanones

(Previously known as aldehydes and ketones)

These compounds contain a functional group known as the carbonyl group – $\textbf{-C=O}$

This is one of the most important functional groups in organic chemistry and biochemistry, as it undergoes a wide variety of reactions. This group is present in all alkanals (which are also commonly called aldehydes) and alkanones (which are commonly called ketones).
The C atom of the carbonyl group must be connected to two other atoms or groups.

Natural Occurrence

Both alkanals and alkanones occur in natural and man-made products very frequently. All naturally occurring plant sugars (such as glucose) are alkanals, alkanones, or their products. These compounds are also often responsible for the smell component of many natural body substances. e.g. the strange smelling breath of a diabetic is due to the presence of propanone (also called acetone). Propanone is an important solvent in the chemical industry.

If methanol is ingested into the body, it is converted in the liver to methanal (also known as formaldehyde or formalin), which is known to attack the optic nerve and cause blindness (hence the old expression 'blind drunk').

A great variety of combustion processes produce alkanals, they are particularly abundant in wood smoke, and have also been identified in the products of combustion of natural gas, fuel oil and engine exhaust samples. Alkanals are also produced in the atmosphere from hydrocarbons as a result of a complicated process called photo-oxidation. These alkanals contribute to smog, ethanal is the alkanal most commonly identified in smog. Methanal is fairly ubiquitous in all air samples tested. Alkanals produced by plants such as 2-hexenal have been found in forested atmospheres, in addition to methanal and ethanal.
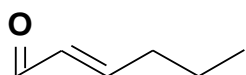
2-hexenal

Nomenclature of alkanals and alkanones

The naming system for both alkanals and alkanones is **very similar to that for the alkanes.** The root name of the compound **is** derived from the parent alkane, but in the case of alkanals the **suffix -al replaces the –e.**
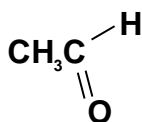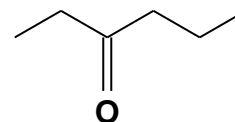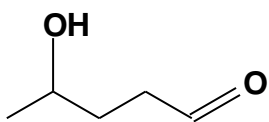
For example $CH_3C \overset{H}{\underset{O}{}}$ is called ethanal.

In the case of alkanones the suffix -one replaces the -e.
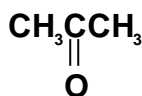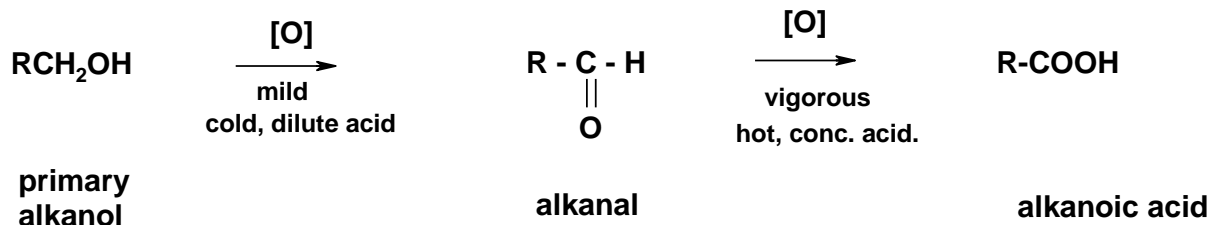
For example $CH_3CCH_3 \; (O)$ is called propanone.

Class Exercise.

Name the following compounds.

(a)
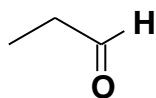
(b)

(c)

(d)
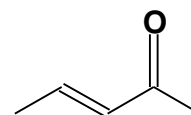
Draw the following compounds.

(a) 3-pentanone.

(b) cyclohexanone.

(c) 4-chloro-4-hydroxybutanal.
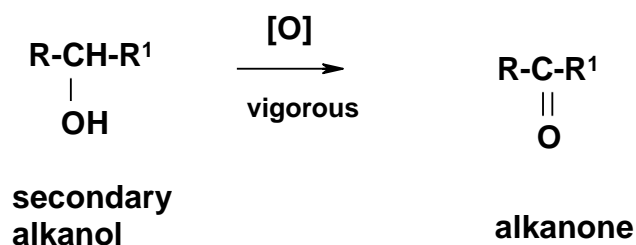
(d) cyclopentanone

Preparation of alkanals and alkanones

Alkanals and alkanones are most commonly made by the **oxidation of primary and secondary** alkanols respectively. **i.e.**

1.

$$RCH_2OH \xrightarrow[\substack{\textbf{mild} \\ \textbf{cold, dilute acid}}]{\textbf{[O]}} R-\underset{\substack{\| \\ O}}{C}-H \xrightarrow[\substack{\textbf{vigorous} \\ \textbf{hot, conc. acid.}}]{\textbf{[O]}} R\text{-}COOH$$

primary   **alkanal**   **alkanoic acid**
alkanol

2.

$$\underset{\substack{| \\ OH}}{R\text{-}CH\text{-}R^1} \xrightarrow[\textbf{vigorous}]{\textbf{[O]}} R\text{-}\underset{\substack{\| \\ O}}{C}\text{-}R^1$$

secondary
alkanol   **alkanone**

Tollen's Test – a test for alkanals

Tollen's reagent (a mixture of $AgNO_3$ and NH_3 in H_2O which forms the complex ion $Ag(NH_3)^{2+}$) **reacts specifically with alkanals** to form silver metal - which is deposited as a silver mirror around the inside of a test tube in which the reaction is contained.

Alkanones do not react with these reagents

Fehling's and Benedict's test – a test for alkanals

These tests are similar to Tollen's test in that a metal ion is reduced by reaction with an alkanal. A positive test is indicated by a colour change from blue to reveal a red precipitate of Cu_2O.

Alkanones do not react with these reagents.

2,4-dinitrophenylhydrazine (2,4-DNP) – a test for both alkanals and alkanones.

The presence of either an alkanol or an alkanone functional group in a molecule is indicated by reaction with 2,4-DNP (a positive test is indicated by the formation of an orange-yellow precipitate). Generally in functional group testing this test is carried out first if the presence of a carbonyl group is suspected. If this test is positive, then it is followed by the Tollen's or Fehling's tests to distinguish between alkanol and alkanone.

Hydrogen Bonding, Polar Functional Groups and Physical Properties

If you study the physical properties of the alkanes, alkenes and alkynes you will notice that there is relatively little attraction between the molecules (i.e. they are all gases at room temperature). This property has led chemists to refer to these families of compounds as being **non-polar**.

Many other organic functional groups are referred to as being **polar** because:
- their molecules are attracted to each other
- they have high melting points and boiling points
- they exhibit enhanced water solubility.

Consider the table below:

Number of Carbon atoms	alkene	alkanal	alkanone	alkanol
2	-103	21	-	78
3	- 47	49	56	97
5	30	103	102	138
Water Solubility	insoluble	soluble	soluble	soluble

Table 7: **Boiling Pts (^{o}C) and water solubility of some organic compounds.**

Why does this occur?

The explanation lies in the charge distribution of the functional group.

Non-polar groups such as an alkene have an equal distribution of electrons throughout, with no regions of positive or negative charge. Polar groups have regions of slight positive or negative charge that allow them to attract each other and mix with water (which is also slightly charged).

It is important to understand how functional groups and chemical structure affect a compound's physical properties. With this knowledge, it is possible to predict how a molecule will interact with the environment, for example whether it will evaporate and become part of the atmosphere, or if it will dissolve in water and become part of the water ways.

Many of the fundamental physical properties of organic compounds are related to their formula weights. Examples are density, boiling points and melting points. These are shown for the hydrocarbons in the following table (table 8).

Physical Properties of alkenes and alkynes

Name	Mol. Wt	Formula	Boiling Point	Density at 20^oC
The 1- alkenes,	C_nH_{2n}			
ethene	28	$CH_2=CH_2$	-102	
propene	42	$CH_2=CHCH_3$	-48	
butene	56	$CH_2=CHCH_2CH_3$	-6.5	
pentene	70	$CH_2=CH(CH_2)_2CH_3$	30	0.643
hexane	84	$CH_2=CH(CH_2)_3CH_3$	63.5	0.675
heptene	98	$CH_2=CH(CH_2)_4CH_3$	93	0.698
octane	112	$CH_2=CH(CH_2)_5CH_3$	122.5	0.716
nonene	126	$CH_2=CH(CH_2)_6CH_3$	146	0.731
decene	140	$CH_2=CH(CH_2)_7CH_3$	171	0.743
The 1-alkynes,	C_nH_{2n-2}			
ethyne	26	$CH\equiv CH$	-75	
propyne	40	$CH\equiv CCH_3$	-23	
butyne	54	$CH\equiv CCH_2CH_3$	9	
pentyne	68	$CH\equiv C(CH_2)_2CH_3$	40	0.695
hexyne	82	$CH\equiv C(CH_2)_3CH_3$	72	0.719
heptyne	96	$CH\equiv C(CH_2)_4CH_3$	100	0.733
octyne	110	$CH\equiv C(CH_2)_5CH_3$	126	0.747
nonyne	124	$CH\equiv C(CH_2)_6CH_3$	151	0.763
decyne	138	$CH\equiv C(CH_2)_7CH_3$	182	0.770

Table 8: **Physical properties of alkenes and alkynes.**

Physical Properties of alkanals and alkanoic acids

Name	Mol Wt	Formula	Boiling Pt (0^oC)	Sol in H_2O (g/100mL)
The alkanals	**CHO**			
methanal	30	HCHO	-21	v. soluble
ethanal	44	CH_3CHO	20	v. soluble
propanal	58	CH_3CH_2CHO	49	16
butanal	72	$CH_3(CH_2)_2CHO$	76	7
pentanal	86	$CH_3(CH_2)_3CHO$	103	s. soluble
hexanal	100	$CH_3(CH_2)_4CHO$	131	s. soluble
heptanal	114	$CH_3(CH_2)_5CHO$	155	0.1
The alkanoic acids	**COOH**			
methanoic	46	HCOOH	100.5	v. soluble
ethanoic	60	CH_3COOH	117.6	v. soluble
propanoic	74	CH_3CH_2COOH	141	v. soluble
butanoic	88	$CH_3(CH_2)_2COOH$	164	3.7
pentanoic	102	$CH_3(CH_2)_3COOH$	187	1.0
hexanoic	116	$CH_3(CH_2)_4COOH$	205	0.7
octanoic	144	$CH_3(CH_2)_6COOH$	239	0.2
decanoic	172	$CH_3(CH_2)_8COOH$	269	Insoluble

Table 9: **Physical properties of alkanals and alkanoic acids.**

Many of the functional groups result in the organic molecules being polar. The inter-molecular attractive forces resulting from this polarity produce a greater density and higher boiling point than might be expected from the molecular weight. Such a difference can be seen by comparing the boiling points in the above tables.

The solubility of compounds in water is an indicator of their polarity. The more polar the compound the greater its solubility in water which is a polar solvent.

If the boiling points of the various simple homologous series are plotted on a graph against the number of carbon atoms in the molecule, the overall effect of the various functional groups can be seen. From the graph below we can see that the substitution of a functional group for a hydrogen atom will result in an increase in the boiling point. Further more, the most polar compounds, the carboxylic acids, have the highest boiling points.
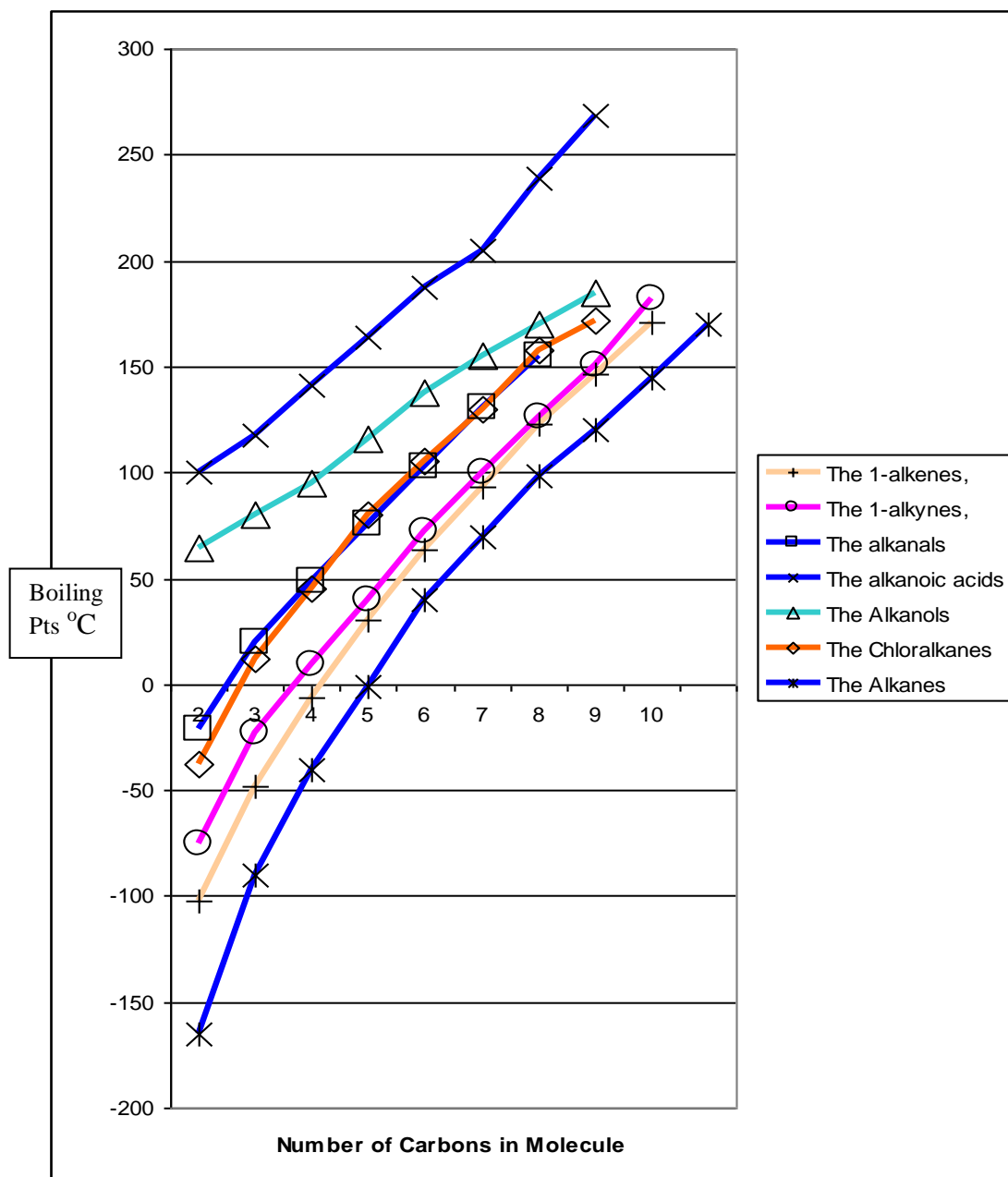
Graph 1: **A graph of the boiling pts of some organic compounds.**

Alkanoic (carboxylic) Acids

This refers to molecules containing -
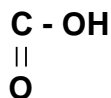
C - OH
||
O   This is referred to as the carboxyl group.

These molecules are of great importance biologically as they serve as building blocks for **amides** (important in proteins) and **esters** (the main functional group in lipids and many of the substances responsible for pleasant odors).

Most of the simpler saturated carboxylic acids are found in nature. For example ethanoic acid (also referred to as acetic acid) is commonly found in vinegar and wine. Butanoic acid is found in cheeses, rancid butter, and under your armpit; whilst hexanoic acid is the odour associated with goats and goat cheeses.

Ethanoic acid is an important industrial chemical with as much as 1.5 billion Kgs per annum being used. Benzoic acid and sorbic acid are important food preservatives especially in soft drinks and beverages.

Alkanoic acids are produced in major quantities by the combustion of coal and wood. Long chain carboxylic acids (C8-C34) have also been found in the atmosphere, the major source of the compounds being pollens and other plant products.

Salts of carboxylic acids are commonly used to produce soaps. The general structure of these types of molecules is shown below.

$$R-CH_2-\overset{\overset{\displaystyle O}{||}}{C}-O^-Na^+$$
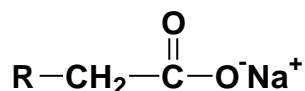
Where R = C10-16. These types of molecules are examples of surfactants.

A surfactant has a non-polar portion and a polar portion. The non-polar portion (in this case the long carbon chain) is hydrophobic (meaning water hating) while the polar portion (the carboxylic acid salt) is hydrophilic (meaning water loving). When a surfactant is placed in water, the molecules arrange themselves into spherical clusters called micelles. In this arrangement, the polar groups are in contact with water, whilst the non-polar chains are hidden away from the water.

According to the principle of like dissolves like, polar water molecules will dissolve any polar substances. To remove non-polar substances such as greases and oils, soap is used. The grease dissolves in the non-polar portion of the micelle, removing it from the surface being cleaned (see diagram below).

Diagram of a micelle encapsulating dirt

The O represents the polar group

the lines represent the non-polar carbon chain.
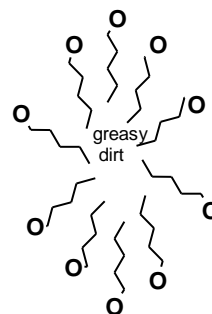
Because of their direct use in water, a large portion of the annual world production of over three million tonnes of surfactants is discharged into municipal and industrial wastewaters. Since these compounds often constitute a significant part of the organic carbon loading of wastewater, a lot of research has gone into understanding how they break down. Soap is biodegradable; it can be broken down into simple molecules such as carbon dioxide and water by bacteria in the environment.

Nomenclature

Alkanoic acids are systematically named by replacing the terminal -e of the corresponding alkane name with -oic acid. Note that the carboxyl carbon atom is always numbered as carbon number 1.
e.g.

$CH_3CH_2CH_2COOH$

butanoic acid

$CH_3CHCH_2CH_2COOH$
|
CH_3
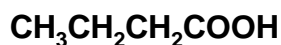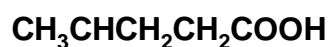
4-methylpentanoic acid

Alkanoic acids can also be named using the suffix carboxylic acid for ring systems. Here, the carboxyl group is attached to carbon 1.

e.g.
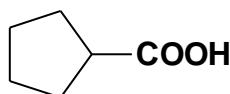
cyclopentylmethanoic acid

Class Exercise:
Give correct IUPAC names for the compounds listed below:

(i)

(ii)

(iii)

(iv)
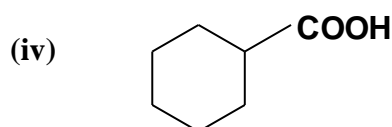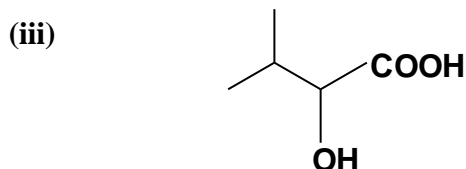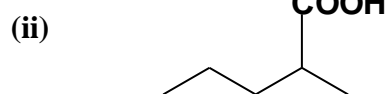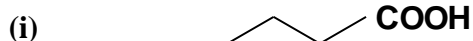
The table below shows some common saturated alkanoic acids along with their correct IUPAC and common names.

Structure	IUPAC name	Common name
$HCOOH$	methanoic acid	formic acid
CH_3COOH	ethanoic acid	acetic acid
CH_3CH_2COOH	propanoic acid	propionic acid
$CH_3(CH_2)_2COOH$	butanoic acid	butyric acid
$CH_3(CH_2)_3COOH$	pentanoic acid	valeric acid
$CH_3(CH_2)_4COOH$	hexanoic acid	caproic acid
$CH_3(CH_2)_6COOH$	octanoic acid	capryllic acid
$CH_3(CH_2)_8COOH$	decanoic acid	capric acid
$CH_3(CH_2)_{10}COOH$	dodecanoic acid	lauric acid
$CH_3(CH_2)_{12}COOH$	tetradecanoic acid	myristic acid
$CH_3(CH_2)_{14}COOH$	hexadecanoic acid	palmitic acid
$CH_3(CH_2)_{16}COOH$	octadecanoic acid	stearic acid

Table 10: **Short chain free fatty acids found in aromas**

The structures and names of several other alkanoic acids (and derivatives) important in the food industry are given below.

benzoic acid – a common preservative used in beverages
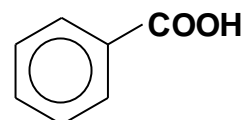
sodium propanoate – used to preserve breads and cereals

citric acid – used to provide a sour taste in fruit and vegetables
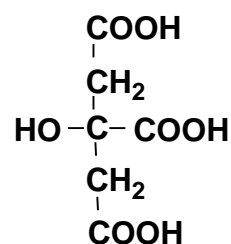
sorbic acid – used as an acidic anti-microbial agent
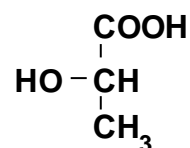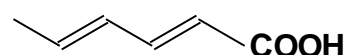
lactic acid – commonly found in cultured dairy products

malic acid – commonly found in fruits

$$
\begin{array}{l}
\qquad\quad \text{COOH} \\
\qquad\quad | \\
\text{HO}-\text{CH} \\
\qquad\quad | \\
\qquad\quad \text{CH}_2 \\
\qquad\quad | \\
\qquad\quad \text{COOH}
\end{array}
$$
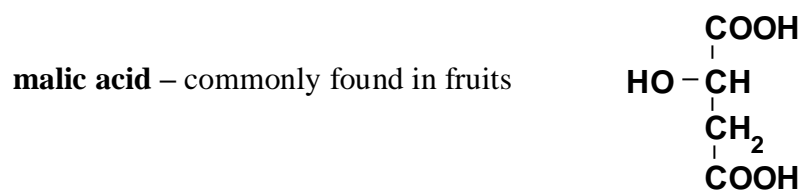
tartaric acid – used extensively in cooking processes (called cream of tartar)

$$
\begin{array}{l}
\qquad\quad \text{COOH} \\
\qquad\quad | \\
\text{HO}-\text{CH} \\
\qquad\quad | \\
\text{HO}-\text{CH} \\
\qquad\quad | \\
\qquad\quad \text{COOH}
\end{array}
$$
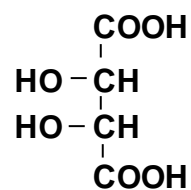
Class Exercise.

The names given to all the acids above are common names. See if you can deduce their correct systematic name.

Physical Properties

Carboxylic acid groups can participate in hydrogen bonding through both the –C=O and the -OH groups, thus their **boiling points are high.** e.g. the boiling points of alkanoic acids are higher than their equivalent chain length alkanols (ethanol b.p. = 78°C and ethanoic acid b.p. 118°C).

The hydrogen bonding properties of the carboxyl group also makes the alkanoic acids **quite water soluble up to a chain length of 6 carbons.**
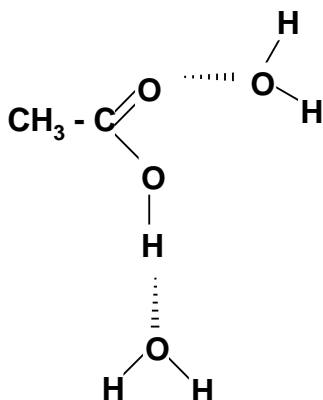
Preparation of Alkanoic Acids

There are many methods for preparing alkanoic acids, but we will only consider two of them in this course:

A.   Oxidation of Primary Alkanols:

Primary alkanols are oxidised to alkanoic acids (via alkanals) by reagents such as $KMnO_4$ and K_2CrO_7/H^+.
e.g.

$$CH_3CH_2CH_2OH \xrightarrow{\quad MnO_4^- \quad} CH_3CH_2COOH$$
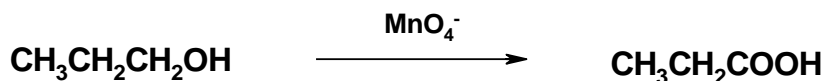
Reactions of Alkanoic acids

A. Reactions with bases:

Alkanoic acids show appreciable acidity. Although much weaker than the strong mineral acids (such as sulfuric, HCl, nitric acid etc), they are much stronger acids than water. Sodium hydroxide readily converts them to their salts.
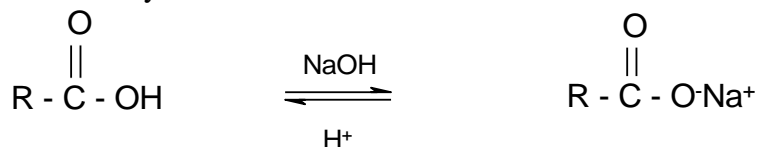
Aqueous acids readily convert the salts back to the acid.

We can test for the presence of an alkanoic acid by the addition of sodium bicarbonate. If the acid is present it will react with the base to produce carbon dioxide gas.

$$RCOOH \quad + \quad NaHCO_3 \quad \longrightarrow \quad CO_2 \ + \ H_2O \ + \ RCOO^-Na^+$$

B. Reactions with Alkanols.

Alkanoic acids react with alkanols (in the presence of a small amount of mineral acid catalyst) to give compounds known as esters.

$$CH_3\overset{\|}{\underset{O}{C}}\text{-OH} \quad + \quad CH_3OH \quad \xrightarrow[\substack{\text{vigorous} \\ \text{heat}}]{H+} \quad CH_3\overset{\|}{\underset{O}{C}}\text{-O-CH}_3 \quad + \quad H_2O$$

ester
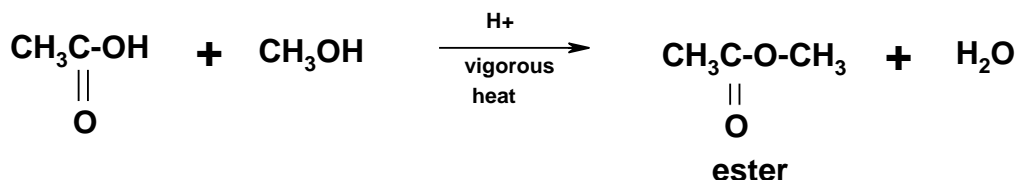
Dicarboxylic Acids

It is possible to have more than one carboxyl group in a molecule. In this course we will also look at the dicarboxylic acids (those with two carboxyl groups). Many of these compounds have an important place in nature.

For example ethanedioic acid (also known as oxalic acid) is commonly found in plants such as spinach and rhubarb. It is quite toxic, as it is a successful calcium ion scavenger in the body. 2,3-dihydroxybutanedioic acid (tartaric acid) is an important component in flavouring wines.

Nomenclature

Dicarboxylic acids are named by adding the suffix -dioic acid to the name of the parent compound that contains both of the carboxyl groups.

e.g.

HOOC - COOH   **ethanedioic acid**

Esters

This name is given to those generally pleasant smelling substances that contain the ester functional group

$$\text{R-C-O-R}$$
$$\underset{\text{O}}{\overset{\|}{}}$$
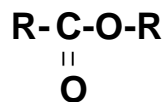
The sweet and pleasant odours and tastes of many foods are due to complex mixtures of organic compounds, of which esters are generally the most prevalent component. Table 11 lists some of the esters that are used as flavouring agents.
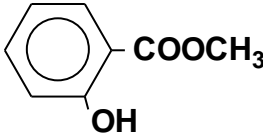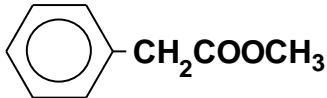
Name	Structure	Odour or Flavour
methyl butanoate		apple
ethyl butanoate		strawberry
butyl butanoate		pineapple
pentyl ethanoate		banana
3-methyl-2-butenyl ethanoate		juicy fruit
methyl 2-hydroxybenzoate (common name methyl salicylate)	$COOCH_3$ OH	wintergreen
methyl 2-phenylethanoate	CH_2COOCH_3	jasmine

Table 11: **Esters that are important as food flavour or odour components**

Phthalate esters are found in great quantities in the environment. The annual world production of phthalates exceeds 1 million tonnes. The phthalates are used mainly as plasticisers, in particular to make polyvinyl chloride (PVC) flexible. They are ubiquitous n the environment and are amongst the most notorious laboratory contaminants encountered when analysing environmental samples.
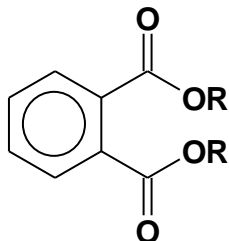
Phthalate Ester

Where R = C1-C10

Nomenclature

It is useful to think of esters as being derived from alkanoic acids and alkanols.

Acid Part   R-C O-R   **Alkanol part**
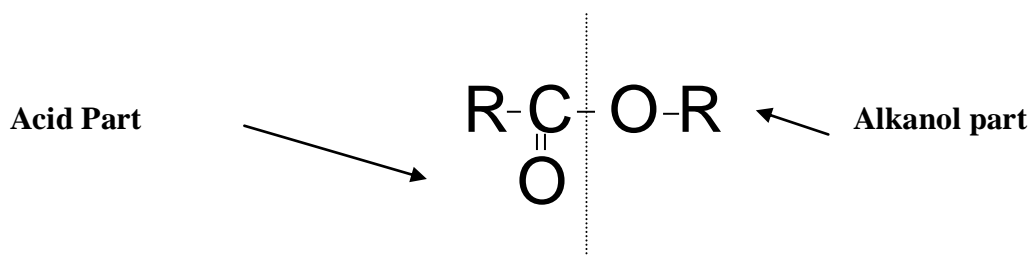
Esters are named as derivatives of the corresponding alkanoic acid. The alkanol part is named first but the -ol is dropped. Next the name of the acid is added, but the **-oic acid** suffix is replaced by **-oate.**

e.g.

acid part (propanoic acid) ⟶ CH_3CH_2C ⎯ OCH_3 ⟵ alkanol part
(methanol)
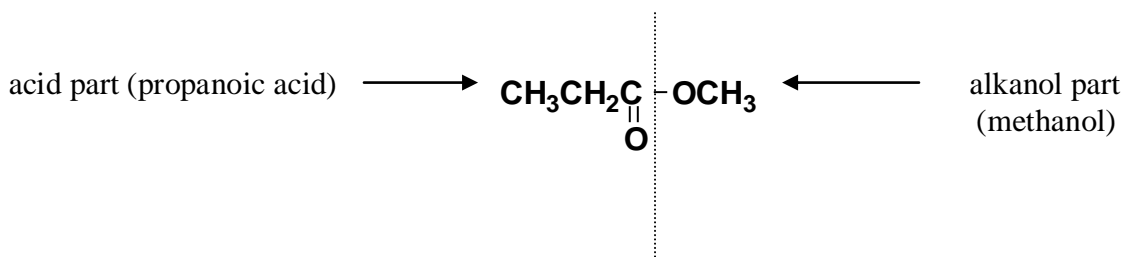
This compound is named as **methyl propanoate.** Note that a **space** is left between the alkanol and acid portions of the name.

Class Exercise.

1. **Draw the esters whose structures are not shown in table 11.**

2. **Name the following esters.**

A. $CH_3CH_2\text{-}O\text{-}\underset{\underset{O}{||}}{C}\text{-}H$

B. $CH_3\underset{\underset{O}{||}}{C}\text{-}O\text{-}CH_3$

C. $\underset{\underset{\underset{O}{||}}{C}}{CH_3\overset{\overset{CH_3}{|}}{C}HCH_2}\text{-}O\text{-}CH_2CH_3$

D. $CH_3CH_2CH_2CH_2\underset{\underset{O}{||}}{C}\text{-}O\text{-}CH_2\overset{\overset{}{|}}{C}HCH_2CH_2CH_3$
$\phantom{CH_3CH_2CH_2CH_2C\text{-}O\text{-}CH_2CH}CH_2CH_2CH_3$

E. $CH_3\overset{\overset{Br}{|}}{C}HCH_2\underset{\underset{O}{||}}{C}\text{-}O\text{-}CH_2CH_3$
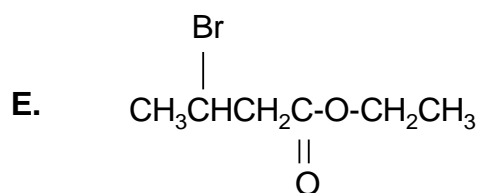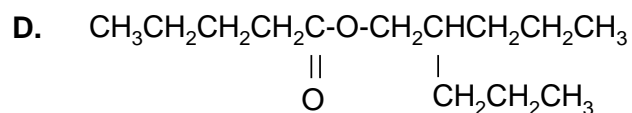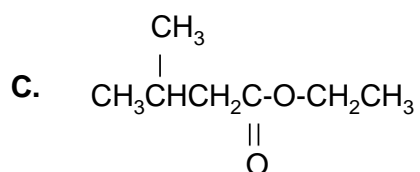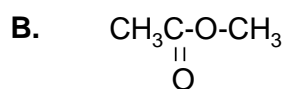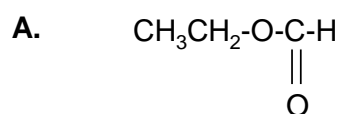
PREPARATION

A. Preparation from acid and Alkanol.

It has already been stated that an ester can be considered as a combination of an alkanol and an alkanoic acid. This is in fact one of the ways in which these compounds can be produced. The two are simply added together with a small amount of an acid catalyst (usually sulfuric). **e.g.**

$$R\text{-}C\text{-}OH \quad + \quad H\text{-}O\text{-}R' \quad \xrightarrow[\text{heat}]{H^+} \quad R\text{-}C\text{-}O\text{-}R' \quad + \quad H_2O$$
$$\underset{O}{\overset{||}{\phantom{R\text{-}C\text{-}O\text{-}R'}}}$$
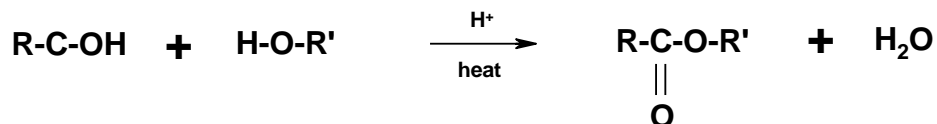
A molecule of water is eliminated to form the ester (condensation). This reaction is called **esterification.**

Class Exercise.

For the esterification reaction of the following two compounds, butanoic acid and propanol, write the reaction and name the product.

HYDROLYSIS

This is the name given to the reverse reaction of esterification. Here an ester is converted back to the alkanol and acid from which it was derived. Essentially the ester just reacts with H_2O in the presence of a small amount of acid or base catalyst.

Acid catalysed hydrolysis

Strong acids such as sulfuric are generally used to hydrolyse esters. **e.g.**

$$R\text{-}C\text{-}O\text{-}R' \quad + \quad H_2O \quad \xrightarrow[\text{heat}]{H^+} \quad R\text{-}C\text{-}OH \quad + \quad R'OH$$

ester	water		alkanoic acid	alkanol
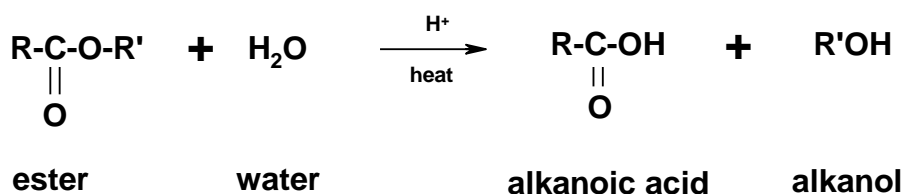
Base catalysed hydrolysis

Esters can also be hydrolysed with basic catalysts (typically NaOH) **e.g.**

$$R-\underset{\underset{O}{\|}}{C}-O-R' \quad + \quad H_2O \quad \xrightarrow[\text{heat}]{OH^-} \quad R-\underset{\underset{O}{\|}}{C}-O^- \quad + \quad R'OH$$

ester   **water**   **salt of acid**   **alkanol**
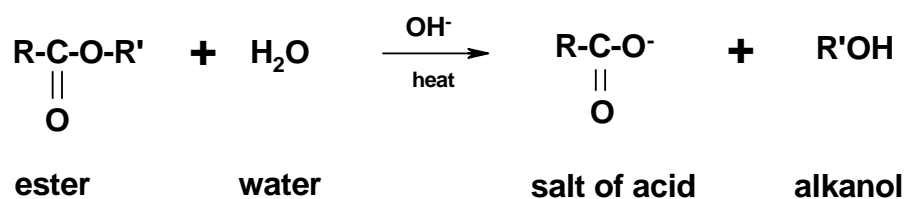
The base catalysed hydrolysis of esters is often referred to by a specific name, **SAPONIFICATION**. This word is derived from the fact that this process has been used for centuries for making soap (see notes on fats and oils for more details).

Amines

Amines are organic compounds that contain nitrogen that is bonded to only a carbon or a hydrogen atom.

$$R_1 - N - R_2$$
$$| $$
$$R_3$$
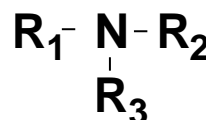
Amines are very important biological compounds and are responsible for most of the fishy odours that we detect in nature. They are also found in decomposing tissues (such as off meat). Amines are building blocks of many natural and synthetic materials – proteins, textiles, plastics, adhesives, and pharmaceuticals.

Amines are derivatives of ammonia that has three hydrogen. We classify amines according to the number of hydrogen that are replaced by alkyl or phenyl groups. **e.g**

NH_3 **Ammonia**

$R-NH_2$ **Primary Amine** (has one hydrogen replaced by R group)

$R-NH-R$ **Secondary Amine** (has two hydrogen replaced by R groups)

R-N-R
  |
  R   **Tertiary Amine** (has all hydrogen replaced by R groups)

NOTE:

The terms primary, secondary and tertiary are used in a different sense here to alkanols where the term applies to how many groups are attached to the C next to the –OH group.

$$
\begin{array}{c}
CH_3 \\
| \\
CH_3\text{-}C\text{-}NH_2 \\
| \\
CH_3
\end{array}
\quad \textbf{is a primary amine}
$$
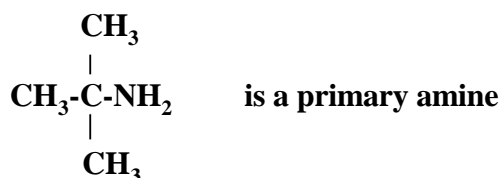
Class Exercise.

Classify each of the following compounds are being primary, secondary or tertiary amines.

a. $CH_3CH_2NHCH_3$

b. $CH_3CH_2NH_2$

c. $CH_3\text{-}N\text{-}CH_3$

d.
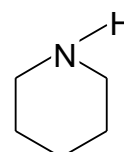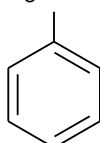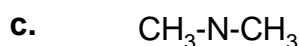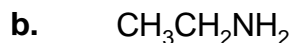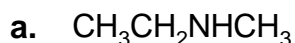
Nomenclature

Amines are named in much the same fashion as alkanols – except that the suffix **-amine** replaces the **-ol**. Thus the structure below would be called 2-butanamine.
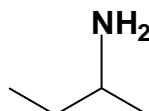
When more than one C atom is attached to the N we find the longest C chain attached to it and name the other C groups as N substituents. For example in the molecule below the longest C chain attached to the N is 3. Therefore it is a propanamine, but a 2C (ethyl) group and a 1C (methyl) group are also attached. These are named as N-ethyl and N-methyl.
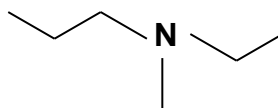
N-ethyl-N-methylpropanamine
If an amine group is an attached group (i.e. it is not the most important functional group in the molecule) it is called an amino group.

Class Exercise.

Draw structures for the following amines:

a. N-methylethanamine

b. N,N-diethylbutanamine

c. N-cyclohexylhexanamine

d. ethanamine

Name the following amines:

a

$$CH_3-N-CH \overset{CH_3}{\underset{CH_3}{\big<}}$$
with H below N

b

c

NH-CH₃ on benzene ring

d

$$CH_3-N-CH_3$$
$$|$$
$$CH_3$$

e.

$$CH_3-N-CH_3$$
$$|$$
$$CH_2CH_3$$

f.

$$CH_3CHCH_2NH_2$$
$$|$$
$$CH_3$$

g.

$$\overset{CH_2CH_3}{\underset{}{N}}-CH_2CHCH_3$$
Br on cyclohexane ring, with CH₃ below
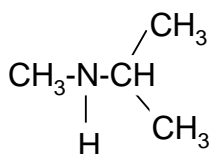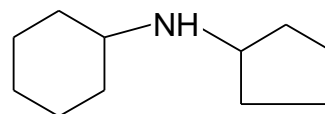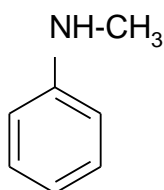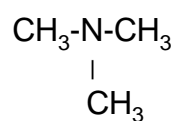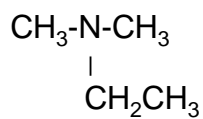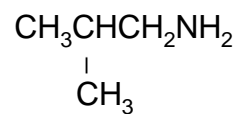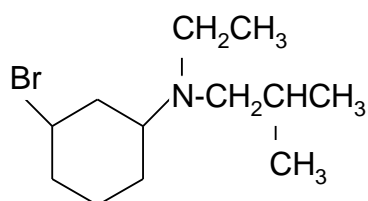
When it is necessary to name –NH$_2$ as a group it is called the AMINO group.

 is called 3-amino-2-bromocyclopentanol
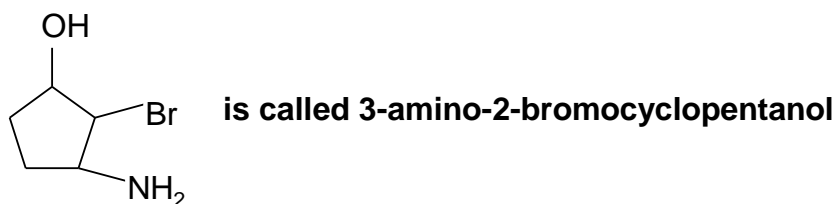
Note: **The alkanol group takes precedence over the amine group when numbering the ring.**

Physical Properties of Amines

The boiling points of amines are less than those of alkanols. This is because they form H-bonds with each other, but these are not as strong as those formed by alkanols. Amines are more soluble in water than alkanols of comparative molecular weigh due to their basicity.

Basicity of Amines

Amines are bases. This is their most important chemical **property.** They are the only important organic bases hence we can be fairly sure that any organic compound that is basic will be an amine. They will react with acids to form salts. This is how cooks reduce the fishy odour of foods – by adding enough acid (such as lemon juice) to convert the volatile amines to less volatile amine salts – reducing the smell.

When an amine reacts with an acid it accepts a proton and forms a positive ion. e.g.

$$CH_3NH_2 \quad + \quad HCl \longrightarrow CH_3NH_3^+ \quad + \quad Cl^-$$

methanaminium ion

Amides

These are organic compounds containing the functional group $-\overset{\underset{\parallel}{O}}{C}-\overset{\underset{|}{R_2}}{N}R_1$ where R_1 and R_2 are H or carbon chains.
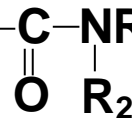
Amides are important biological compounds that make up proteins and peptides.

Nomenclature

Amides are named after their corresponding alkanoic acids by changing the **–oic** ending to –**amide**. Thus the structure below which is derived from ethanoic acid would be called ethanamide.

$$CH_3\overset{\underset{\parallel}{O}}{C}-NH_2$$
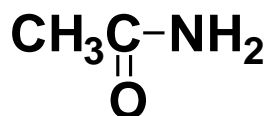
Class Exercise.

Name the following amides:

a.
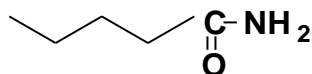
b.
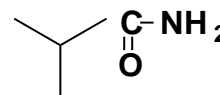
c.
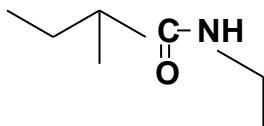
d.
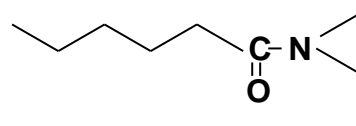
Ethers

These are substances that contain two organic groups attached to the same **OXYGEN** atom. i.e. They contain the functional group -

$$R - O - R'$$

The R groups may be aromatic or aliphatic or they may be part of a ring structure.

Some important ethers include diethyl ether (the one which is traditionally called ether) that was used as a general anesthetic, and methyl phenyl ether (commonly called anisole) which is used extensively in the perfume industry.

CH$_3$CH$_2$-O-CH$_2$CH$_3$

diethyl ether

O-CH$_3$
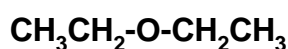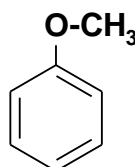
methyl phenyl ether

Nomenclature of Ethers

The nomenclature of ethers is complicated by the fact that two different systems are allowed under systematic rules. Simple ethers are generally named by identifying the two organic parts and adding the work ether

e.g. **CH$_3$ – O – CH$_2$CH$_3$**
is called ethyl methyl ether
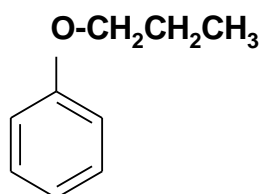
O-CH$_2$CH$_2$CH$_3$

is called propyl phenyl ether

In symmetrical ethers the prefix di- is used. e.g.

CH$_3$CH$_2$ – O – CH$_2$CH$_3$ **is called diethyl ether.**

If more than one ether group is present in the molecule or if there are other functional groups present, the ether is best named as an alkoxy substituted parent compound, e.g.

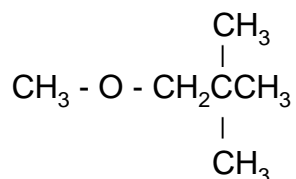**CH$_3$ – O –CH$_2$CH$_3$**   **is called methoxy ethane**

Class Exercise.

Name the following organic structure formulae:

1.

$$CH_3 - O - CH_2CH_2 - O - CH_3$$

2.

$$CH_3 - O - CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_3$$
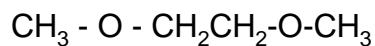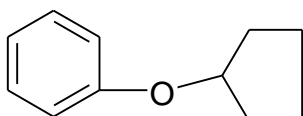
3.

Preparation of Ethers

There are two main methods of preparing ethers, as shown below.

1. Preparation by dehydration of alkanols.

Diethyl ether and other simple ethers are prepared industrially by the acid catalysed (usually H_2SO_4 or H_3PO_4) dehydration of alkanols as in the equation below.

$$2CH_3CH_2OH \quad \xrightarrow{\quad H_2SO_4 \quad} \quad CH_3CH_2OCH_2CH_3 \quad + \quad H_2O$$

This method of ether preparation is limited to the synthesis of symmetrical ether from primary alkanols, since secondary and tertiary alkanols dehydrate to give alkenes.

Aromatics

These are compounds that contain the benzene ring as part of their structure.
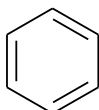
The Aromatic Character of Benzene

Aromatic compounds show completely different behavior to aliphatic compounds, and hence it is not difficult to deduce that they have a special chemical structure.

We will use benzene as an example, to describe what is meant chemically by the term aromatic.

Benzene has unusual chemical stability when compared to similar aliphatic compounds. For example benzene does not undergo addition reactions and is not oxidized by $KMnO_4$ as does cyclohexene.

Spectroscopic studies show further evidence of benzene's unusual chemical nature. All of the carbon-carbon bonds in benzene have the same length, intermediate between a normal single and a normal double bond. It is a flat molecule (unlike cyclohexene) with all of the C-C bond angles being 120^0.

Representations of Benzene

There are two accepted ways of representing the structure of benzene. The first is the Kekule structure that is written as shown below. Two so-called resonance structures are required, as one structure cannot fully represent the molecule. The molecule is said to alternate very rapidly between the two structures.
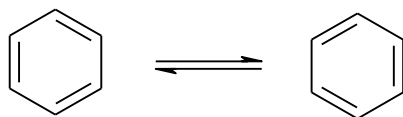
The best method for drawing the structure of benzene is that which involves the representation of the pi electrons as a circle in the centre of the hexagon (as shown below). This structure correctly shows the C-C bonds as being equivalent.
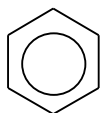
Both of these methods are commonly used in books and you should be aware of them.

Nomenclature of Aromatic Compounds

For molecules having alkyl groups or other simple substituents attached to the benzene ring **benzene is used as the parent name and the attached groups are named in alphabetical order before it.**
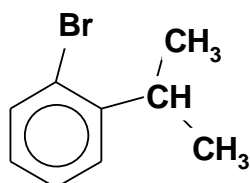**e.g.**

$CH_2CH_2CH_3$
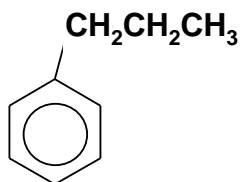
is called 1-propylbenzene

If more than one substituent is attached to the benzene ring, their locations are specified by numbers. The lowest possible numbers are used and the substituents are named in alphabetical order.
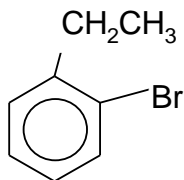
e.g.

CH_3

CH_3

CH_3
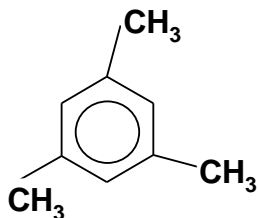
is called 1,3,5-trimethylbenzene

Br CH_3

CH

CH_3

is called 2-bromo-1-(methylethyl)benzene

When only two substituents are present the prefixes ortho-, meta- and para are used in place of 1,2-, 1,3- and 1,4- respectively.
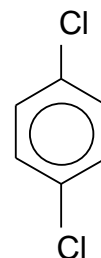
e.g.

CH_2CH_3

Br

o-bromoethylbenzene

Br

NO_2
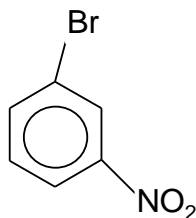
m-bromonitrobenzene

Cl

Cl

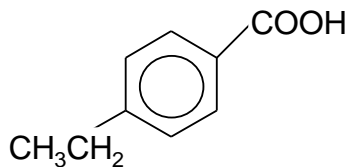*p*-dichlorobenzene

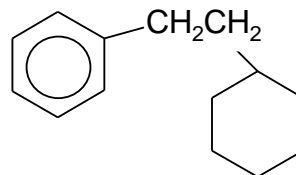Ortho-, meta- and para- are generally abbreviated to o-, m- and p- in most cases.
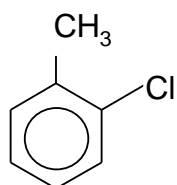
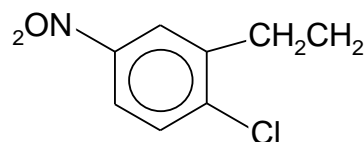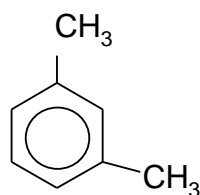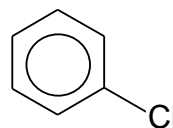# Class Exercise.
Name the following aromatic compounds.

a.

b

c.

d.

e.

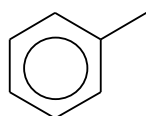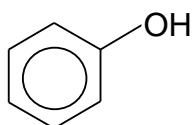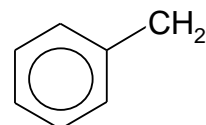**f.**

Naming Problems
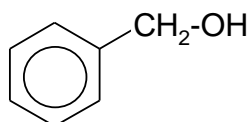When to use 'phenyl or 'phenol' or 'benzene' or 'benzyl'.
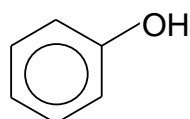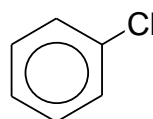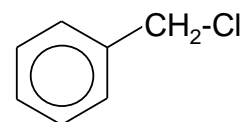

phenyl group

phenol

benzyl group

phenylmethanol

phenol

chlorobenzene

chloromethylbenzene

Substitution Reactions of Benzene

Because of its greater stability than alkenes benzene tends to undergo substitution reactions rather than addition reactions (as do the alkenes).

Nitration.

Benzene reacts with a mixture of concentrated nitric and sulfuric acids to produce nitrobenzene as shown in the reaction below. The process is termed nitration. Sulfuric acid is the catalyst and the mixture must be warmed to about 50^0C to initiate the reaction.

Halogenation.

Both bromine and chlorine react with benzene if iron is present. The actual catalyst is $FeCl_3$ or $FeBr_3$ (metallic iron also works as a catalyst because it reacts with halogens to produce the above salts). The substitution by bromine, called bromination is given as an example below. Notice that only one atom of bromine reacts with the benzene, the other combines with the displace hydrogen to form HBr which escapes as a gas.

benzene

bromobenzene

Alkylation (Friedel-Crafts reaction)

Substitution of an alkyl group onto a benzene ring is called alkylation. The reaction is very similar to halogenation except that aluminium chloride is used to catalyse the reaction, as shown in the reaction below. In general an alkyl halide RX is used in the substitution to produce an alkyl-benzene.

benzene

chloroethane

ethylbenzene