08 Extension Topic – Organic Chemistry Introduction

GUIDING QUESTIONS

- What are the main classes of organic compounds?
- What are some terms commonly used in the description of organic reactions and reactivities?
- What are the main types of organic reactions?
- How do electrons flow in polar organic reactions?

LEARNING OUTCOMES

Students should be able to:

11.1 (a) interpret, and use the nomenclature, general formulae and displayed formulae of the following classes of compound:
  (i) hydrocarbons (alkanes, alkenes and arenes)
  (ii) halogen derivatives (halogenoalkanes and halogenoarenes)
  (iii) hydroxyl compounds (alcohols and phenols)
  (iv) carbonyl compounds (aldehydes and ketones)
  (v) carboxylic acids and derivatives (acyl chlorides and esters)
  (vi) nitrogen compounds (amines, amides, amino acids and nitriles)

*students are expected to be able to interpret and use the following types of representations in the description of organic molecules: empirical formula, molecular formula, structural formula, full structural or displayed formula, skeletal formula and stereochemical formula.

11.1 (b) interpret, and use the following terminology associated with organic reactions:
  (i) functional group
  (ii) degree of substitution: primary, secondary, tertiary, quaternary
  (iii) homolytic and heterolytic fission
  (iv) carbocation
  (v) free radical, (initiation, propagation, termination – refer to Alkanes notes)
  (vi) electrophile, nucleophile (Lewis acid, Lewis base)
  (vii) addition, substitution, elimination, condensation, hydrolysis
  (viii) oxidation and reduction
  [in equations for organic redox reactions, the symbols [O] and [H] are acceptable]

11.1 (c) interpret, and use the following terminology associated with organic reactivities:
  (i) delocalisation
  (ii) electronic effect (electron-donating and electron-withdrawing effect)
  (iii) steric effect (steric hindrance)

11.1 (d) describe sp^3 hybridization, as in ethane molecule, sp^2 hybridization, as in ethene and benzene molecules, and sp hybridization, as in ethyne molecule (Refer to Topic 2 Chemical Bonding and Topic 12 Arenes)

11.1 (e) explain the shapes of, and bond angles in, the ethane, ethene, benzene and ethyne molecules in relation to σ and π carbon-carbon bonds (Refer to Topic 2 Chemical Bonding and Topic 12 Arenes)

11.1 (f) predict the shapes of, and bond angles in, molecules analogous to those specified in **11.1 (e)**

11.1 (g) apply **11.1 (b)** and **11.1 (c)** to the understanding of mechanisms in terms of organic structure and bonding

11.1 (h) recognise that the mechanisms of polar reactions involve the flow of electrons from electron-rich to electron-poor sites

*students are expected to be able to interpret and use the curly arrow notation to represent the movement of electrons in organic reaction mechanisms.

REFERENCES

1. Peter Cann and Peter Hughes, *Chemistry for Advanced Level*, 5th Ed., Hodder Education, Chapter 12
2. John McMurry, *Organic Chemistry*, 8th Ed., Brooks/Cole, Chapter 2

1 INTRODUCTION

LOOKING BACK

In this extension topic, we will see how the fundamental concepts learnt in previous topics can be applied onto the area of organic chemistry. The study of organic chemistry in the A-Level syllabus is based on the chemistry of different functional groups. Besides the first two general topics on Introduction and Isomerism, each topic in organic chemistry will cover one functional group: its nature, physical properties, chemical reactivity, reactions and mechanisms. There are a total of ten topics in organic chemistry, six of which is covered in year 1 and another four to be covered in year 2.

To make sense of the properties of the many organic compounds and reactions, it is useful to understand that the nature and reactivity of all functional groups can be explained in terms of **structure and bonding concepts**, in particular, atomic orbitals, hybridization, covalent bonding, intermolecular forces and electronegativity. The reactions and mechanisms can be understood on the basis of both **thermodynamic and kinetic considerations**, for example, bond energies, transition states, intermediates, rate equations and orders of reaction as well as fundamental concepts of stoichiometry, redox and acid-base reactions. Each functional group (and hence each topic) should also not be studied in isolation. It is important, during our study of organic chemistry, to understand how each functional group is related to each other via functional group inter-conversions.

In the mid-1700s, when chemistry was evolving into a modern science, unexplainable differences were noted between substances obtained from living sources and those obtained from minerals. The Swedish chemist Torbern Bergman in 1770 was the first to express this difference between “organic” and “inorganic” substances and the term organic chemistry soon came to mean the chemistry of compounds found in living organisms.

To many chemists at that time, they believed that organic compounds must contain a “vital force” as a result of their origin in living forces, and could not be prepared or manipulated in the laboratory, making them different from inorganic compounds. However, this theory of Vitalism suffered two major blows when in 1816, Michael Chevreul discovered that an organic compound (fat) could be converted to another (fatty acids and glycerin) without the intervention of an outside “vital force”; and in 1828, Friedrich Wöhler discovered that the “organic” substance found in human urine, urea, could be synthesized by heating ammonium cyanate, an “inorganic” salt. This observation demonstrated for the very first time, that an organic compound could be synthesized from an inorganic source, which led eventually to the rejection of Vitalism as a scientific theory.

Today, chemistry is unified and the same principles that explain inorganic compounds explain the organic ones as well. The only distinguishing characteristic of organic compounds is that all contain the element carbon.

Organic chemistry is the study of the structure, properties, composition, reactions, and preparation of carbon-containing compounds, which include not only hydrocarbons but also compounds with any number of other elements, such as hydrogen, nitrogen, halogens, phosphorus, silicon and sulfur. Carbon is also present in all large and complex molecules in all living species. Compounds such as fuels, plastics, painkillers, antibiotics and vitamins have become vital to our present way of life.

Carbon has important properties that enable it to form so many stable compounds:

- A carbon atom can form covalent bonds to as many as 4 other atoms
- It can form stable and strong covalent bonds with other carbon atoms and/or atoms of many different elements
- It can form different types of bonds, e.g. single, double and triple bonds
- It can form long chains or rings of carbon atoms

2 FORMULAE, FUNCTIONAL GROUPS AND NAMING OF ORGANIC COMPOUNDS

2.1 Types of Formulae

Empirical formula

- simplest formula that shows the ratio of number of atoms of the elements present in one molecule

Molecular formula

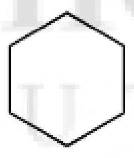
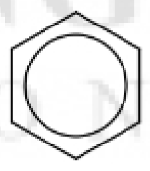
- shows the actual number of atoms of the elements present in one molecule

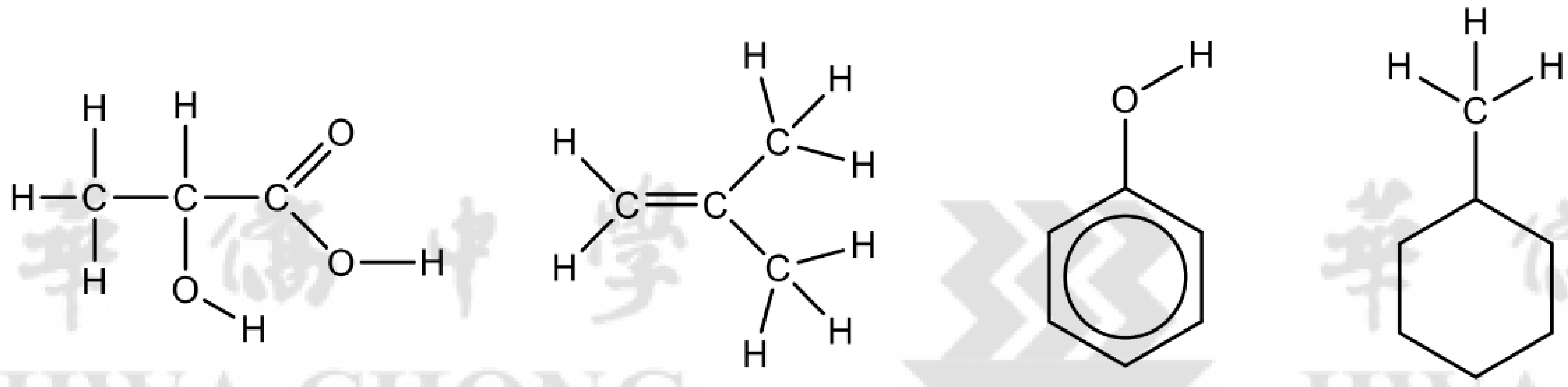
For example, the empirical formula and molecular formula for lactic acid are CH_2O and $C_3H_6O_3$ respectively; ethanol has its empirical formula same as its molecular formula, C_2H_6O.

Structural formula

- shows how the constituent atoms of a molecule are joined together with minimal detail, using conventional groups, for an unambiguous structure.
- There are different ways to show the structure of an organic molecule.

(i) *Displayed formula / Full structural formula*

- detailed structure of molecule showing the relative placing of atoms and the number of bonds between them, showing **all** the bonds
- common omission: students often forget to display the **O–H bonds**
- for ring structures (including benzene rings), all C and H atoms (and their associated bonds) can be omitted
- the symbols  and  are used for representing the cyclohexane ring and benzene ring respectively



lactic acid 2-methylpropene phenol methylcyclohexane

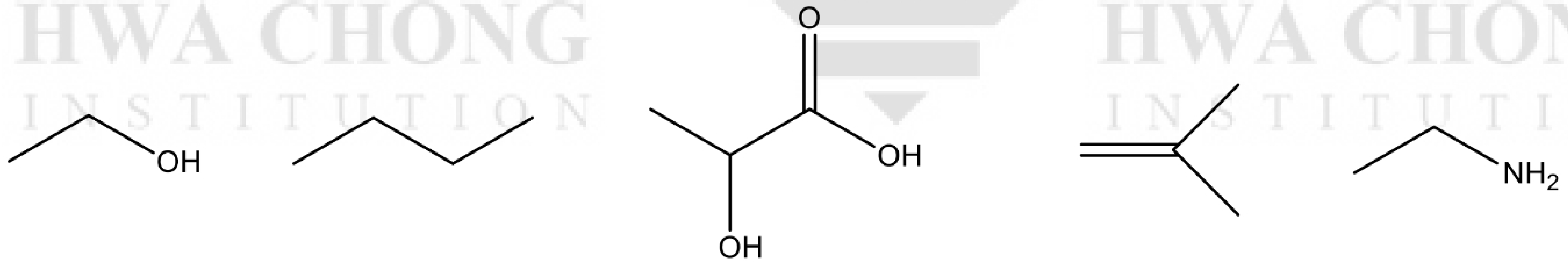
Figure 1. Examples of displayed formulae

(ii) *Condensed structural formula*

- shows the arrangement of atoms in an **unambiguous manner**, without showing the bonds, e.g. the condensed structural formula for lactic acid is $CH_3CH(OH)CO_2H$, and that for 2-methylpropene is $CH_2C(CH_3)_2$

(iii) *Skeletal formula*

- simplified representation of an organic formula, often used for larger and more complicated molecules
- derived from structural formula by omitting the hydrogen atoms and their associated bonds and carbon atoms from alkyl chains, leaving just carbon–carbon bonds in the carbon skeleton and the associated functional groups
- each C–C bond in the carbon skeleton is a line (each end is a carbon atom)
- double and triple lines indicate double and triple bonds respectively



ethanol butane lactic acid 2-methylpropene ethylamine

Figure 2. Examples of skeletal formulae

- Partial-skeletal representations are acceptable where they are unambiguous:

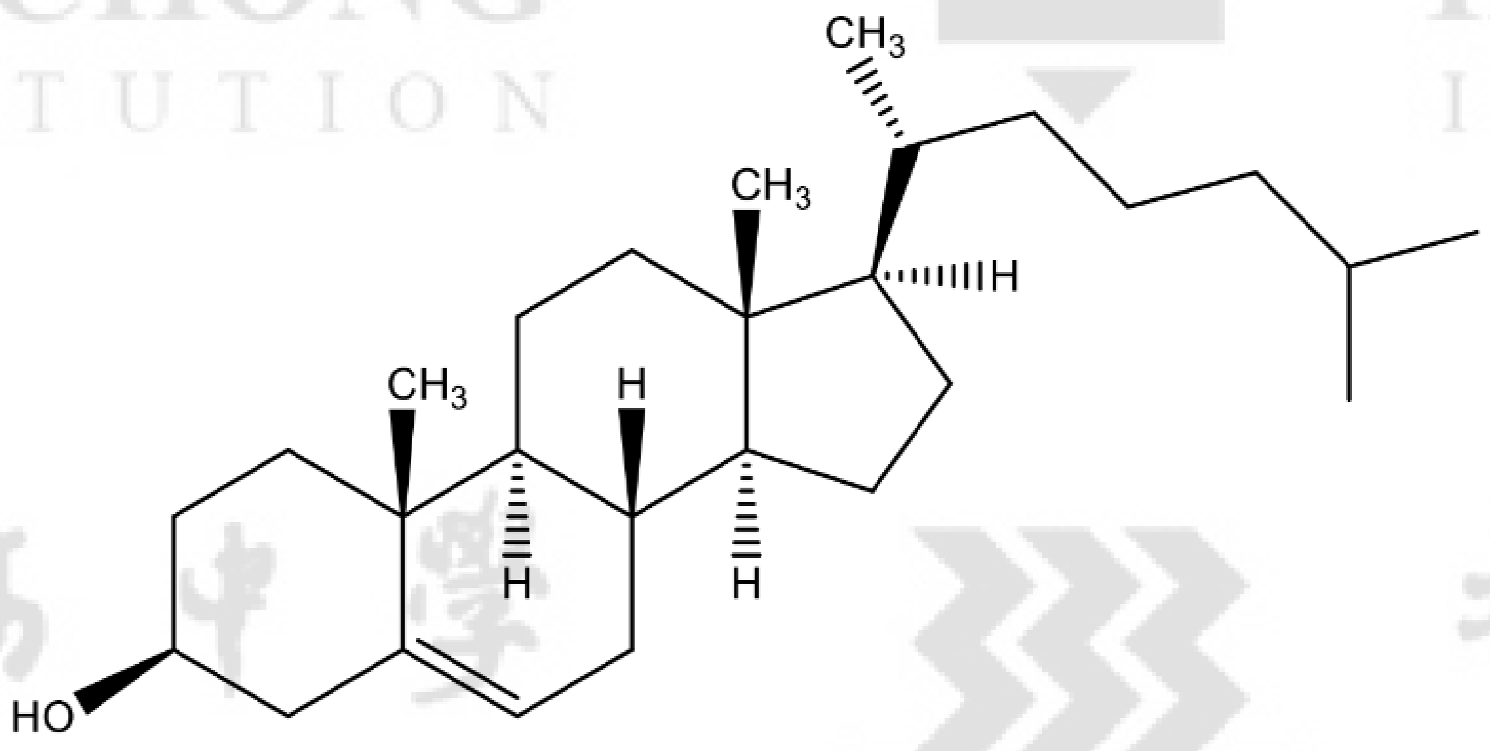


Figure 3. Cholesterol

(iv) *Stereochemical formula*

- shows the three-dimensional spatial arrangement of bonds, atoms and groups around a key part of a molecule (usually a stereochemical centre)
- solid wedges (▬) indicate bonds to an atom **pointing out** of the plane of the paper
- dashed wedges or hashed lines (''''''''''') indicate bonds to an atom **pointing into** the plane of the paper
- normal lines (——) indicate bonds on the plane of the paper, e.g.

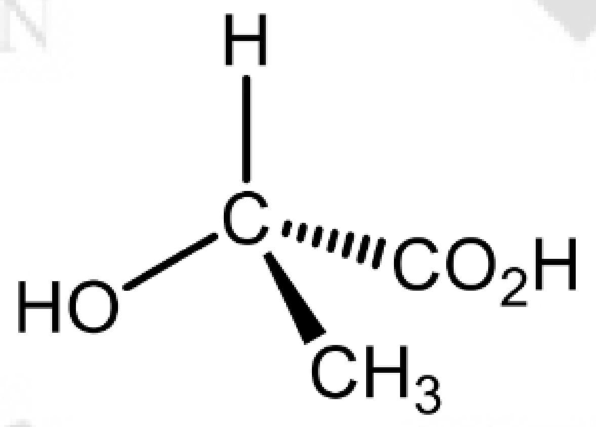
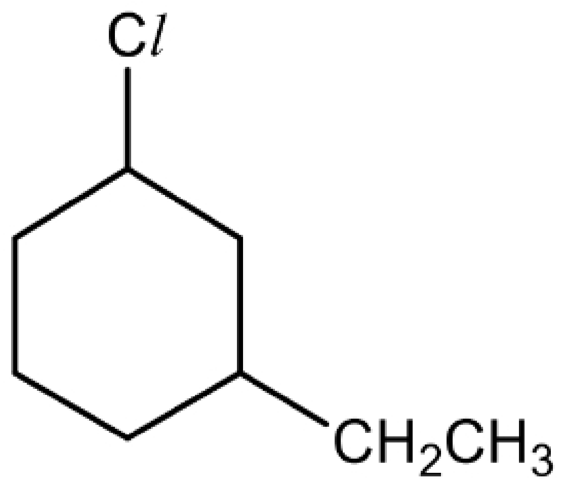
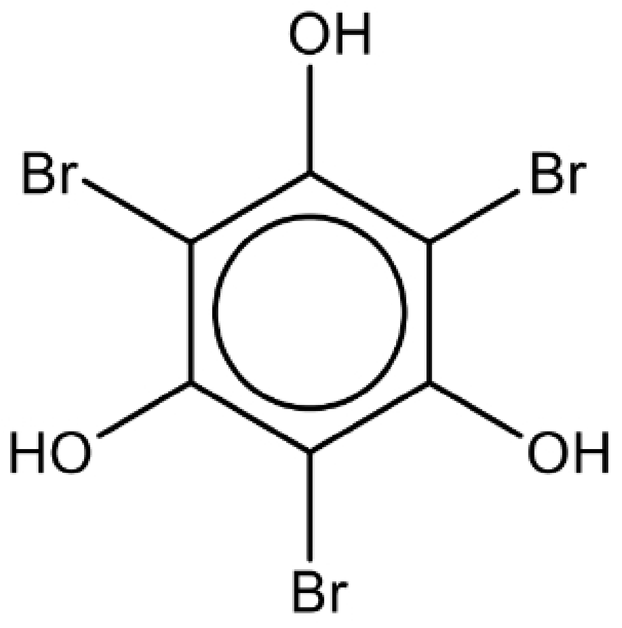


Figure 4. 3-dimensional arrangement around the C atom of lactic acid

Lecture Exercise 2.1

Complete the following table using the various types of formulae.

Empirical formula		
Molecular formula		
Condensed structural formula		
Displayed formula		
Skeletal formula		

2.2 Overview of Functional Groups

Functional groups are part of a larger molecule and are composed of an atom or a group of atoms that have special chemical properties and which define the chemistry of that organic compound.

All molecules containing the same functional group can be considered as members of the same family and have similar properties. More about the various functional groups will be covered in the relevant topics. (Note: R typically represents alkyl and aryl groups in organic chemistry. The terms are explained below.)

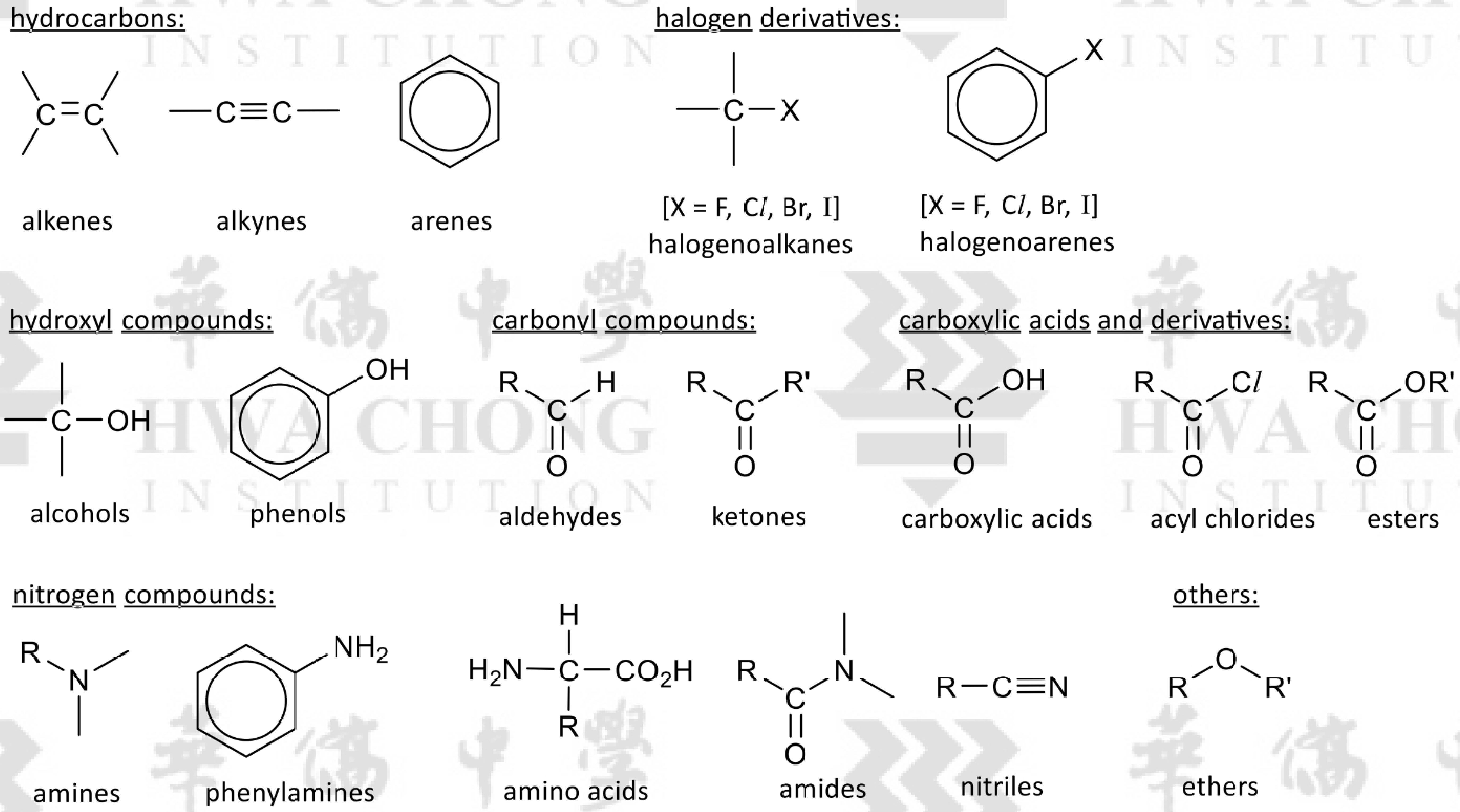


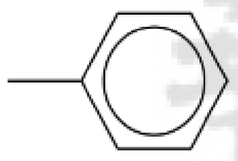
Figure 5. Common functional groups

Some terms to be familiar with:

- An **alkyl group** is a substituent group derived from an alkane by removal of a hydrogen atom:

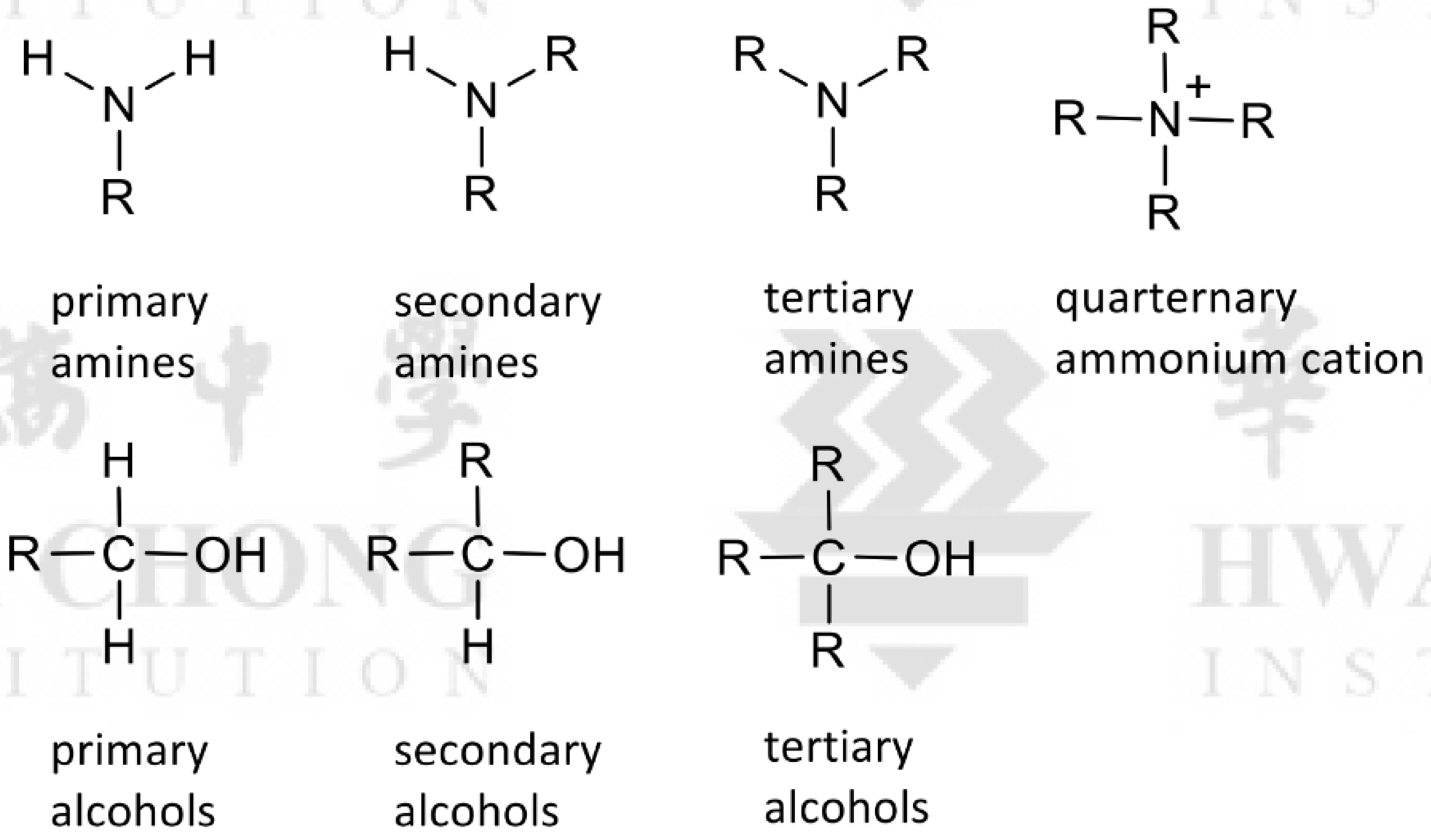
No. of carbons atoms in the alkyl group	Prefix	Meaning
1	Methyl	$-CH_3$
2	Ethyl	$-CH_2CH_3$
3	Propyl	$-CH_2CH_2CH_3$
4	Butyl	$-CH_2CH_2CH_2CH_3$

Table 1. Examples of alkyl groups

- An **aryl group** is a functional group that is derived from an aromatic ring (such as a benzene ring) by removal of a hydrogen atom. (An example of an aryl group is the phenyl group, represented by  .)

- A **substituent group** is normally an atom or group of atoms substituted in place of a hydrogen atom on the hydrocarbon chain.

- Many organic compounds are classified as **primary (1^0)**, **secondary (2^0)**, **tertiary (3^0)** or **quarternary (4^0)** depending on how many substituent groups (usually alkyl) are joined to the carbon atom which the functional group is attached to, or the nitrogen atom in the case of amines. Using the example of amines, we can see that primary, secondary, tertiary and quarternary amines have one, two, three and four alkyl groups attached to the nitrogen atom. Similarly, primary, secondary, tertiary alcohols have one, two and three alkyl groups attached to the hydroxyl carbon respectively.



primary amines

secondary amines

tertiary amines

quarternary ammonium cation

primary alcohols

secondary alcohols

tertiary alcohols

Figure 6. Different classes of amines and alcohols

2.3 Homologous series

A homologous series of organic compounds is a family of compounds containing the same functional group, and in which each successive member increases by one $-CH_2-$ unit.

Compounds of the same homologous series:

1. can be represented by the same general molecular formula
2. can usually be prepared by similar methods
3. show a gradual change in physical properties as molar mass increases
4. have similar chemical properties

Formula	Name	M_r	Boiling point / °C
CH_4	methane	16	–162
CH_3CH_3	ethane	30	–89
$CH_3CH_2CH_3$	propane	44	–42
$CH_3CH_2CH_2CH_3$	butane	58	0
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	36
$CH_3CH_2CH_2CH_2CH_2CH_3$	hexane	86	69

Table 2. Homologous series of alkanes

2.4 Classes of organic compounds

Aliphatic compounds

- compounds with open chains of carbon atoms, e.g. propane
- may be unbranched or branched
- may contain single, double or triple bonds or combinations of these

Alicyclic compounds

- compounds with closed rings of carbon atoms, e.g. cyclohexane

An organic compound (aliphatic or alicyclic) which contains only single bonds (i.e. only C–C and C–H bonds in the case of hydrocarbons) is **saturated**.

Aromatic compounds

- compounds containing at least one aromatic system such as a benzene ring.

2.5 Nomenclature

Naming organic molecules

- <u>Common (or trivial) names</u>:

  Many organic molecules have 'common names' that relate to the living organisms or sources from which they were originally identified/extracted; e.g. formic acid (Latin: *formica*, "ant"), acetic acid (Latin: *acetum*, "vinegar"), menthol (peppermint, binomial name *Mentha piperita*), etc. However, this naming of compounds is not systematic (there are no logical naming conventions). Trivial names may also be ambiguous or mean different substances in different industries.

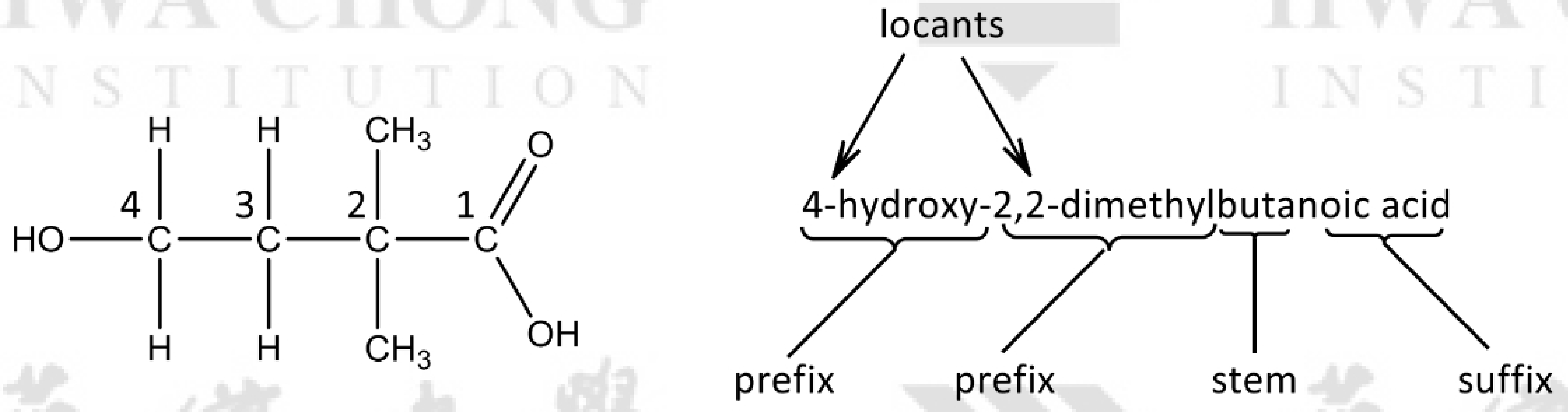
- <u>Systematic names</u>:

  Chemists have devised an internationally recognized system of naming (IUPAC), which is the convention that will be required for this A-level course. The IUPAC Rules are a system of naming organic molecules developed by the International Union of Pure and Applied Chemistry.

IUPAC (systematic) names consist of five parts:

1. Stem/Parent hydrocarbon
2. Suffix (family)
3. Prefix (substituent)
4. Locants (appropriate numbers that indicate where the functional group or substituent is positioned)
5. Stereochemical identifier *if applicable* (only *cis* and *trans* will be used in our course)

Example:



Stem

The stem is normally the name of an aliphatic or alicyclic hydrocarbon. All other compounds are regarded as being derived from these parent hydrocarbons by the replacement of hydrogen atoms by alkyl or other groups. The stem takes its name according to:

(a) The number of carbon atoms in the longest chain in the carbon skeleton.

No. of carbons	1	2	3	4	5	6	7	8	9	10
Stem	Meth-	Eth-	Prop-	But-	Pent-	Hex-	Hept-	Oct-	Non-	Dec-

(b) Type of bonding in the carbon skeleton.

For a saturated carbon chain, name of stem ends with -an(e)
For a chain containing a C=C, name of stem ends with -en(e)
For a chain containing a C≡C, name of stem ends with -yn(e) [not in syllabus]

The carbon atoms in the parent hydrocarbon (the stem) are usually numbered from one end to the other. When the parent chain is unsaturated, the appropriate number (called the locant) is added to show the position of the multiple bond. The number can be omitted if the structure can be deduced from the name without the number.

Suffix

The suffix gives the principal functional group in the compound. If more than one functional group is present, the highest priority functional group is named as the suffix according to the following hierarchy:

- Carboxylic acid (highest priority)
- Ester
- Acid halide
- Amide
- Nitrile
- Aldehyde
- Ketone
- Alcohol
- Amine
- Alkene (lowest priority)

Prefix

The prefix is used to denote any substituent in an organic compound. The main prefixes are shown in the summary table on pages 13 and 14.

- all groups substitute one H atom except the 'oxo' groups which substitute two.
- the carbon number in the stem to which the substituent is attached is written in front of the prefix.
- if there is more than one prefix, the prefixes are placed in **alphabetical order**.
- Recall on page 8, the prefixes methyl, ethyl, propyl and butyl etc. are used to indicate alkyl groups as substituents.

Condensed IUPAC Rules of Nomenclature

Step 1: Determine the principal functional group in the compound (if present). If more than one functional group is present, the principal functional group is the one with highest priority. Other functional groups will be named as substituents.

Step 2: Find and name the longest continuous carbon chain in which the principal functional group occurs (if present) as the parent chain. Any side-chains will be named as substituents.

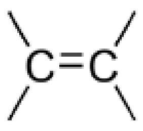
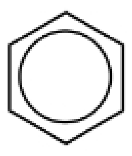
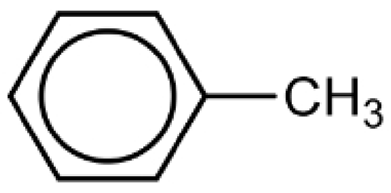
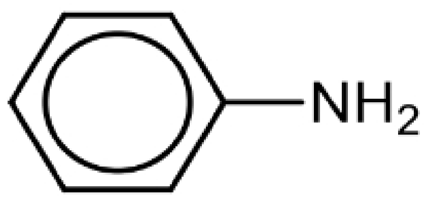
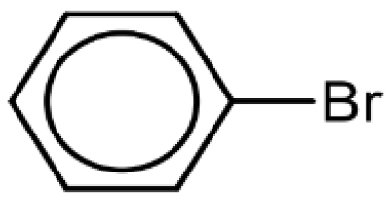
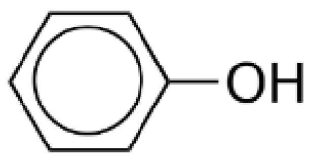
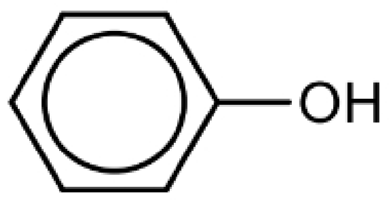
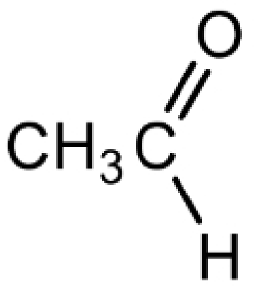
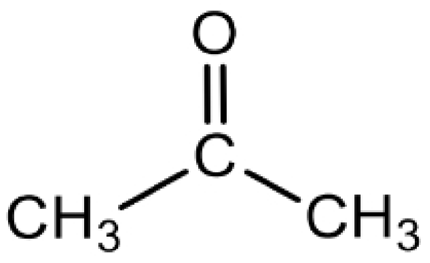
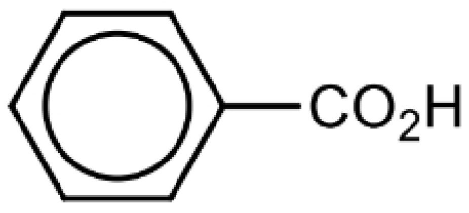
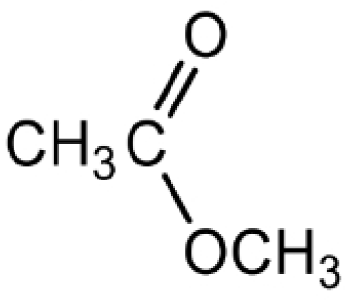
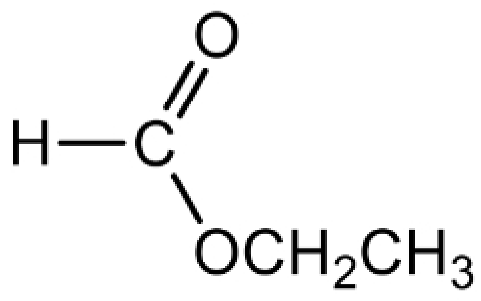
Step 3: Number the chain consecutively, starting at the end nearer the principal functional group. If there is no functional group, start at the end nearer the first substituent.

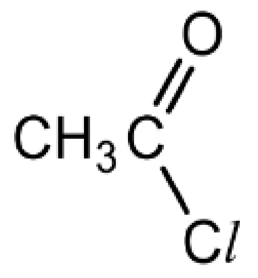
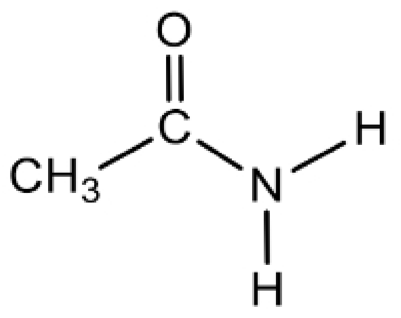
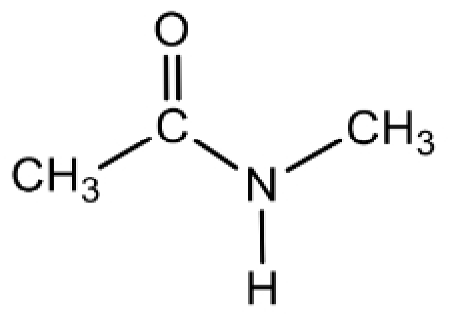
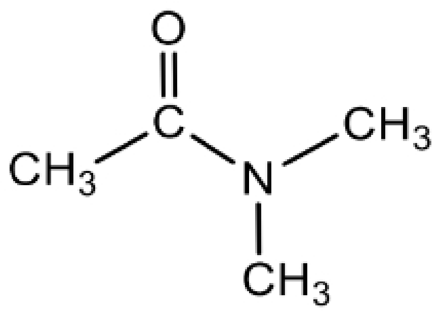
Step 4: Identify and name groups attached to this chain. If the same functional group or substituent occurs more than once, indicate using proper multipliers (eg. di-, tri-, tetra-, penta-, etc). Designate the location of each functional group / substituent using the appropriate locants if necessary.

Step 5: Assemble the name consisting of prefix(es), stem and suffix, using commas to separate the numbers and hyphens to join letters and numbers. Substituent groups are listed in alphabetical order. Multipliers are not used for alphabetization purposes (i.e. ethyl before dimethyl). Add any stereochemical identifier(s) at the front of the name if applicable.

In the later topics of Organic Chemistry, we will look at how to name compounds containing specific functional groups, using the above IUPAC rules.

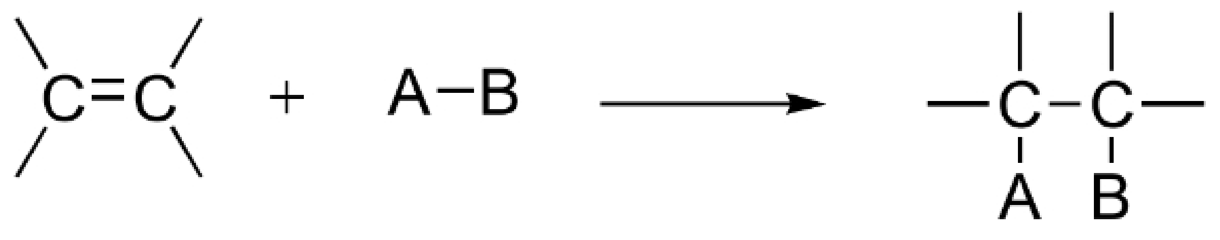
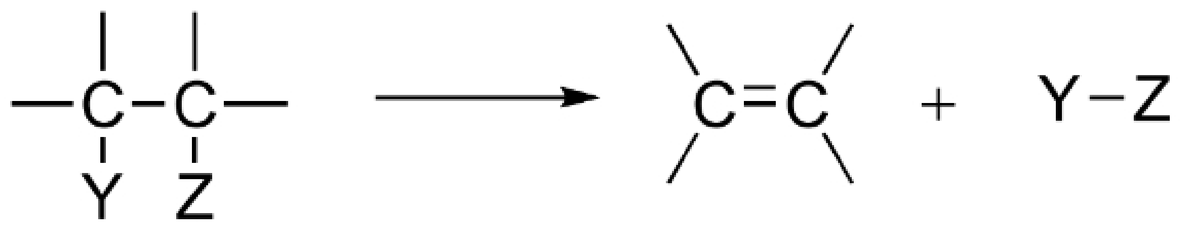
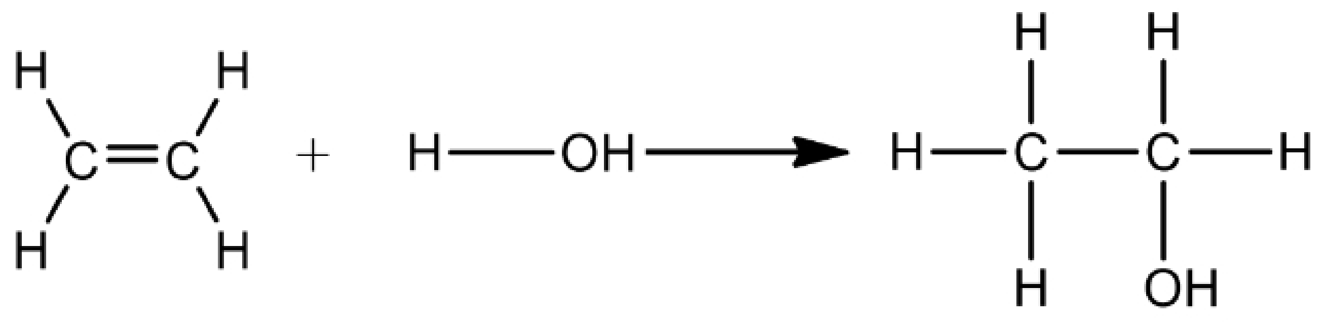
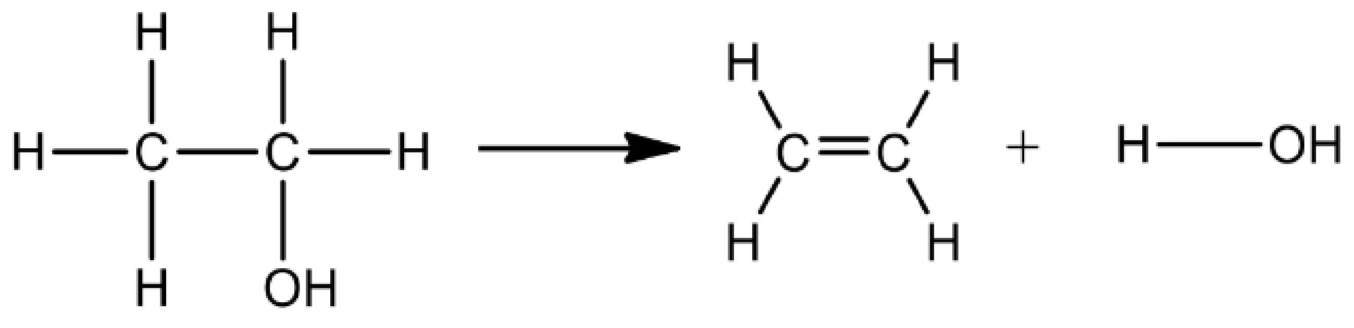
Summary Table of Functional groups, prefixes and suffixes

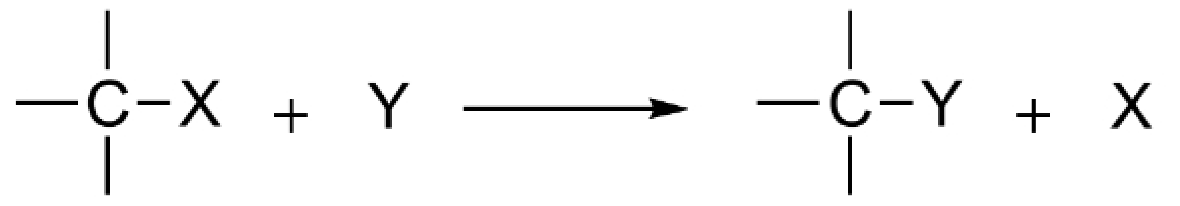
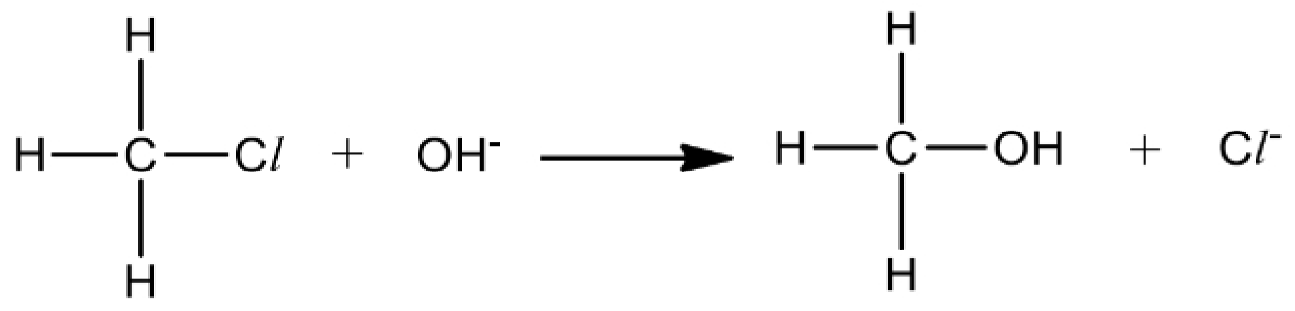
Functional Group	Prefix name	Suffix name	Examples
Alkenes 	–	-ene	ethene $CH_2=CH_2$
Arenes 	phenyl	benzene	methylbenzene  phenylamine 
Halogenoalkanes / Halogenoarenes —F —Cl —Br —I	fluoro chloro bromo iodo	–	chloroethane CH_3CH_2Cl bromobenzene 
Alcohols / Phenols R–OH 	hydroxy	–ol	ethanol CH_3CH_2OH phenol  hydroxyethanoic acid $HOCH_2CO_2H$
Aldehydes —CHO	formyl	–al	ethanal 
Ketones –CO–	oxo	–one	Propanone 
Carboxylic acids —CO_2H	–	–oic acid	ethanoic acid CH_3CO_2H benzoic acid 
Esters —CO_2R	–	–oate	methyl ethanoate  ethyl methanoate 

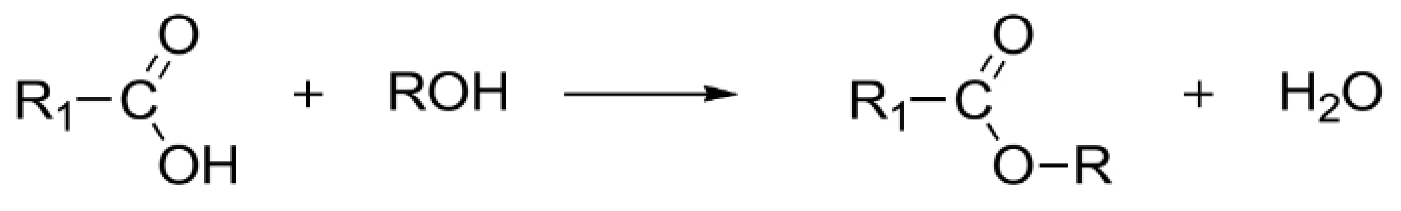
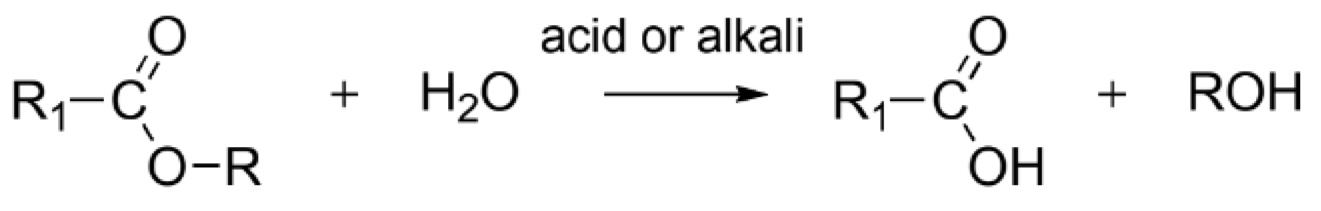
Functional Group	Prefix name	Suffix name	Examples
Acyl halides —COX [X = C*l*, Br]	–	–oyl halide	ethanoyl chloride 
Amines —NH_2	amino	–amine	ethylamine $CH_3CH_2NH_2$
Amides —$CONH_2$	–	–amide	ethanamide  N-methylethanamide  N,N-dimethylethanamide 
Nitriles —CN	cyano	–nitrile	ethanenitrile CH_3CH_2CN
Nitro –NO_2	nitro	–	nitromethane CH_3NO_2

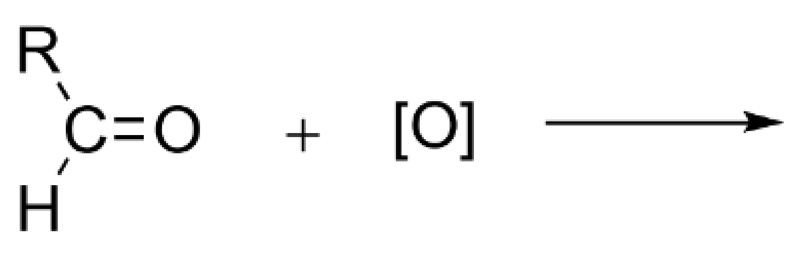
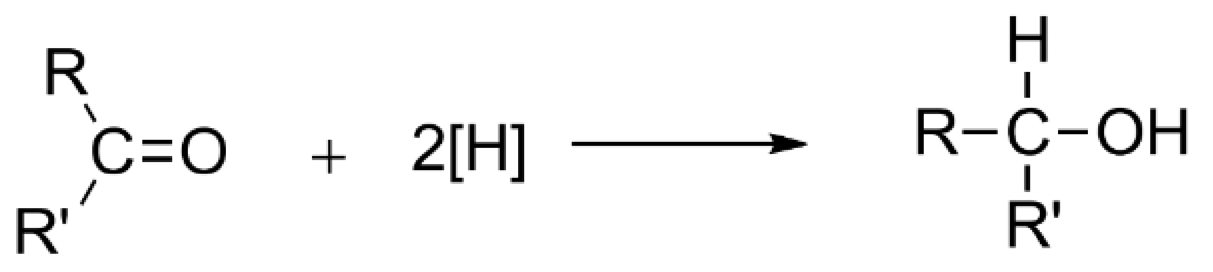
3 KEY IDEAS IN ORGANIC CHEMISTRY

3.1 Types of organic reactions

Addition	Elimination
	
when two substances react together to form a single product. An unsaturated functional group is usually present in one of the reactants, in which a π bond breaks to form two σ bonds.	when an alkene is formed by the removal of a molecule of H_2O from a molecule of an alcohol, or a molecule of HX from a molecule of a halogenoalkane. This is the opposite of addition.
e.g 	e.g 

Substitution

when one atom or group of atoms is substituted by another. There are always at least two products.
e.g 

Condensation	Hydrolysis
when two molecules come together to form a bigger molecule, with the elimination of a small molecule such as water or HC*l* etc. Note that condensation is **not** the same as elimination.	a reaction in which a molecule is split into two by the action of water, often catalysed by dilute acids or dilute alkalis.
	

Oxidation	Reduction
a reaction in which oxygen is added to the molecule or hydrogen removed from the molecule. In equations, the symbol [O] is used to denote oxidation. (+ O_2 if oxidised by air)	a reaction in which oxygen is removed from the molecule or hydrogen added to the molecule. The symbol [H] is used to denote reduction. (+ H_2 if reduced by H_2)
	

How do we balance equations using [O] or [H]?

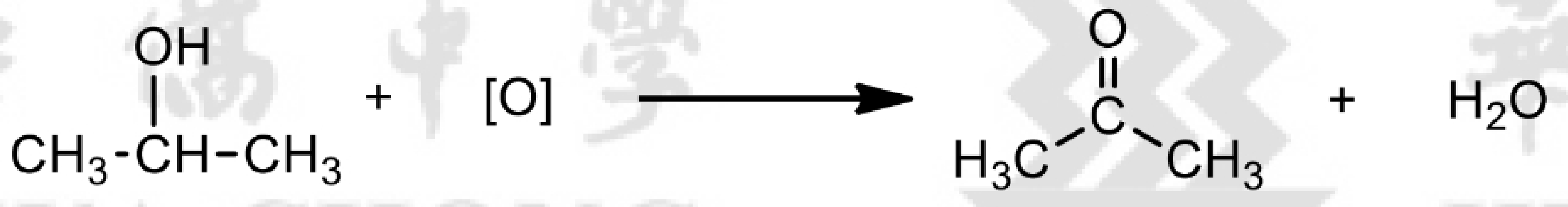
For oxidation reactions, when required to balance the equation, add H_2O to balance the H and then [O] to balance the remaining O. Conversely, for reduction reactions, add H_2O to balance the O and the [H] to balance the remaining H.

Lecture Exercise 3.1

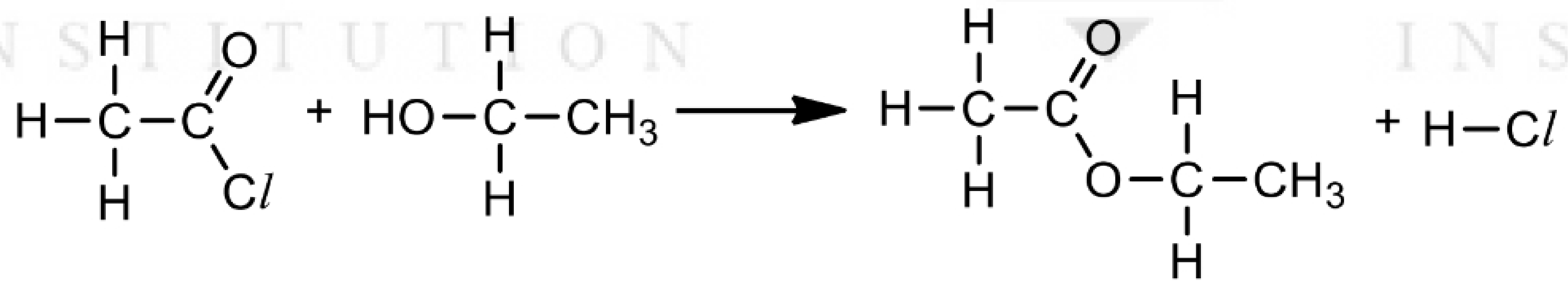
(a) The following are examples of organic reactions. Indicate what type of reaction is taking place.

(i) $CH_3Br + NH_3 \longrightarrow CH_3NH_2 + HBr$

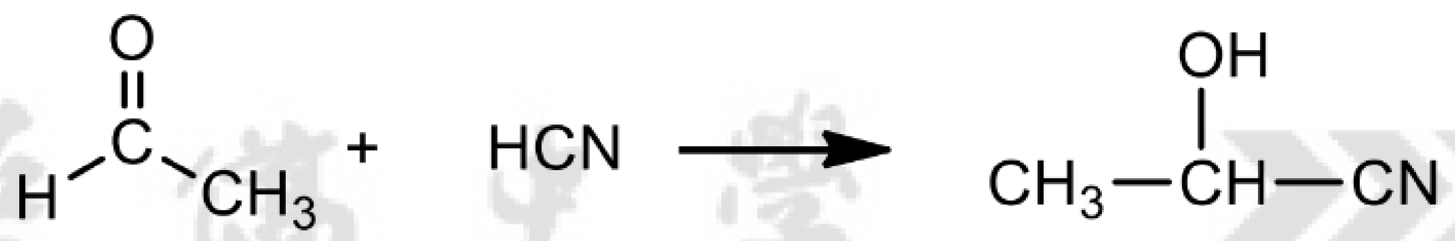
(ii)



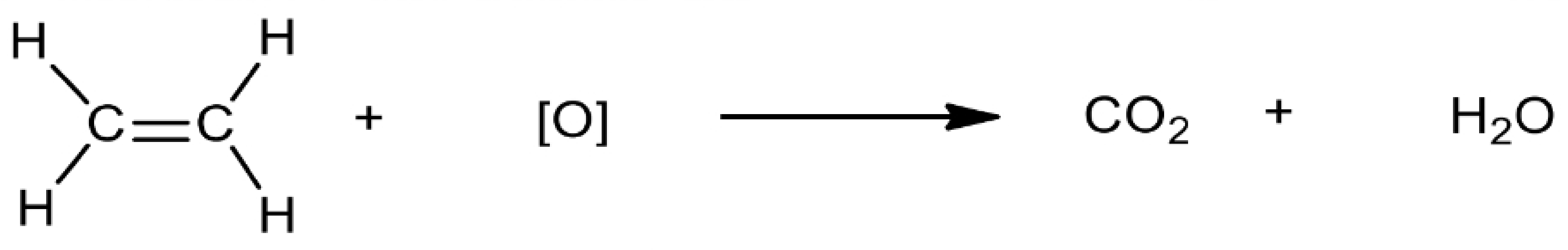
(iii)



(iv)



(b) Balance the equation for the following organic reaction.



3.2 Mechanisms of organic reactions

The mechanism of a reaction is a detailed description of which bonds break, which bonds form, and in what order these processes occur. Since bonds are shared electrons, the mechanism of a reaction essentially describes the electron rearrangements that happen as reactants are converted to products.

Recall in Topic 6 Reaction Kinetics, we learnt that a reaction mechanism should be consistent with the reaction stoichiometry, the rate law and with all other available experimental data, such as the stereochemical course of the reaction and the isolation or detection of any reactive intermediates. However, a proposed mechanism is only a postulate and can be extended, altered or completely reconstructed as a result of new evidence.

Most mechanisms in organic chemistry can be represented by a series of labelled diagrams in which plausible electron rearrangements in the particles are shown using the curly arrow notation through a sequence of steps.

3.2.1 Polar mechanisms

Other than free radical substitution (to be taught in Topic 10 Alkanes), most organic reaction mechanisms in the A-level syllabus are polar mechanisms. In polar mechanisms, the bond breaking and forming processes are heterolytic, involving movement of electron pairs.

<u>Heterolytic bond breaking (heterolytic fission)</u>

- The splitting of a bond resulting in unequal sharing of the bonding electrons to each resulting fragment
- Heterolytic fission usually results in the **formation of ions**:

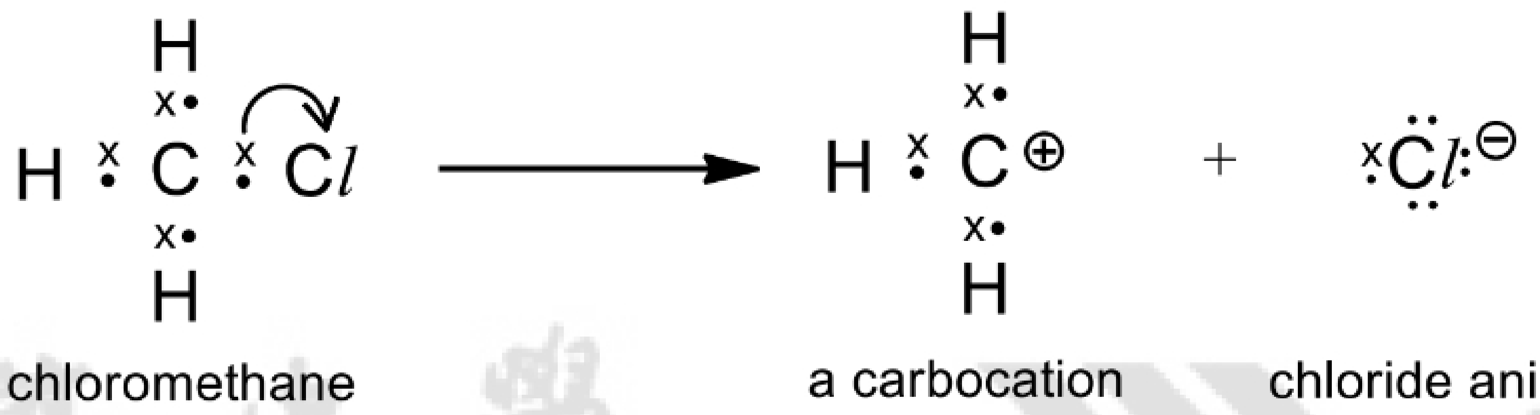
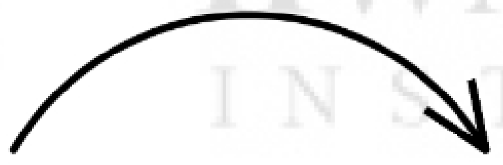


Figure 7. Heterolytic bond breaking of C–Cl bond in chloromethane

A full head on the arrow indicates the movement or shift of **<u>a pair of electrons</u>**:



The curly arrow notation: rather than using dot-and-cross diagrams, it is more common to represent the movement of electrons using curly arrows. We also usually draw displayed formulae to show bonds that are broken and formed in the reaction and condensed formulae for the rest of the species:

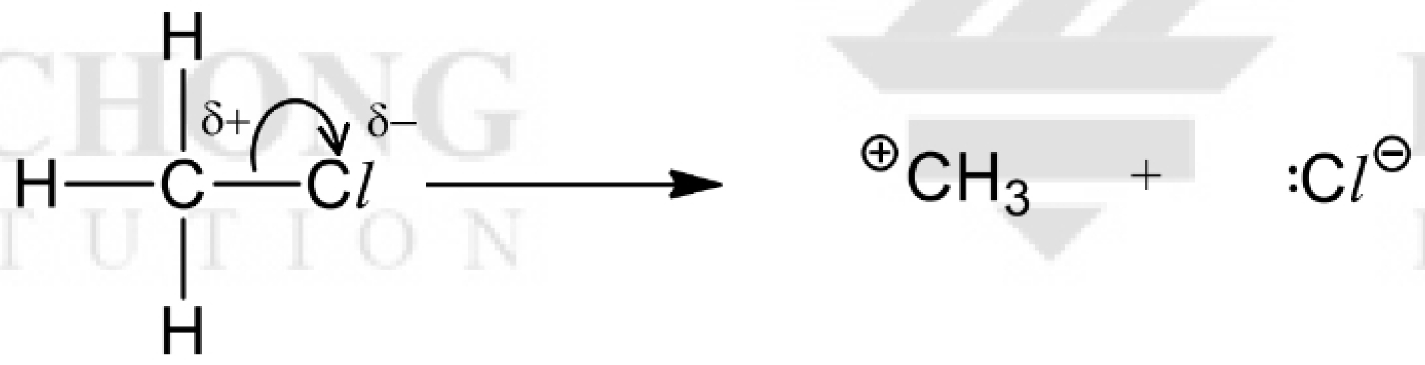


Figure 8. Representing heterolytic bond breaking of C–Cl bond in chloromethane using curly arrows

Heterolytic bond forming

Bond forming is essentially the reverse process of bond breaking. The electrons move in such a way as to create new bonds. Figure 9 shows the movement of the electrons from Cl^- to $^+CH_3$ using the curly arrow notation. Note that a full arrow is again used to show the movement of an electron pair.

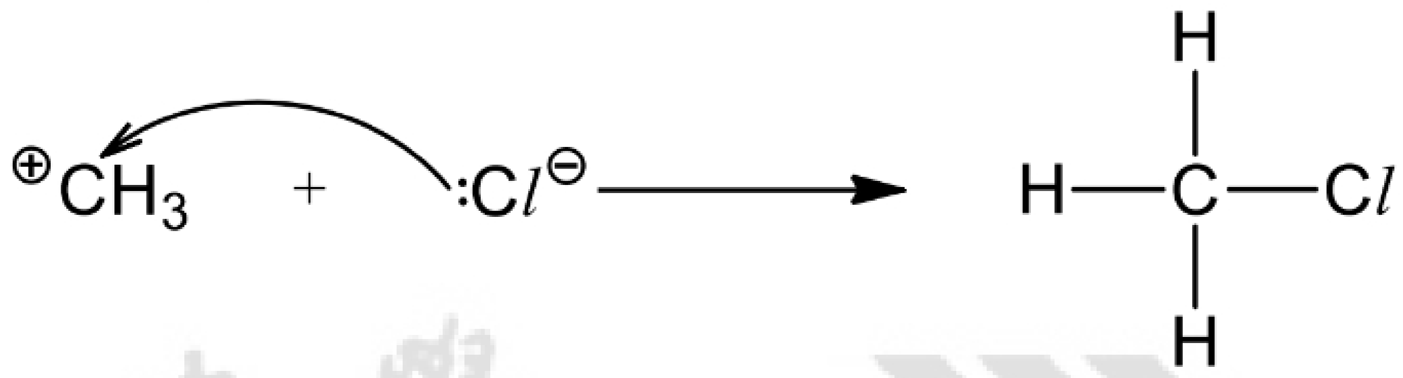


Figure 9. Representing heterolytic bond forming of C–Cl bond using curly arrows

In polar mechanisms, electrons always flow from electron-rich to electron-poor (or electron-deficient) species during bond formation. It is important to understand the terms below, used to describe these species.

Electrophiles

An electrophile is an electron-deficient species that accepts an electron pair from an electron-rich species in a reaction to form a new covalent bond. Electrophiles possess either a positively-charged centre (e.g. CH_3^+, Br^+, NO_2^+, H^+) or an atom which can carry an induced or permanent partial positive charge "δ+" (e.g. polarised Br_2, HBr).

Nucleophiles

A nucleophile is a species that donates an electron pair to an electron-deficient species in a reaction to form a new covalent bond. All nucleophiles possess electrons that can be shared e.g. lone pairs of electrons with or without a negative charge (H_2O, NH_3, OH^-, CN^-), a π bond (e.g. ethene, benzene) or a partial negative charge "δ–" (CH_3Li).

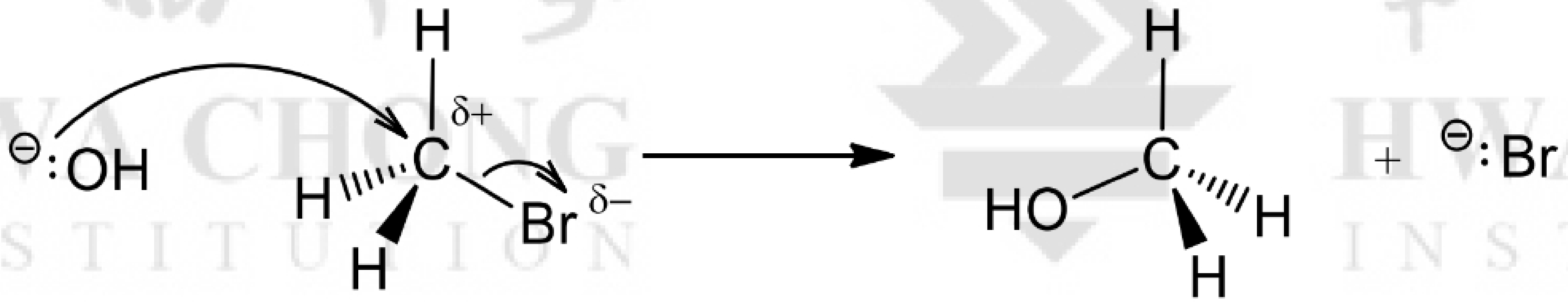


Figure 10. Mechanism involving a nucleophile and an electrophile

In the above example, OH^- is the nucleophile and CH_3Br is the electrophile as OH^- donates a lone pair of electrons to the electron-deficient carbon atom in CH_3Br. Recall that according to the Lewis Theory of acids and bases (Topic 4 Reactions and Stoichiometry), Lewis acids are species that accept an electron pair and Lewis bases are species that donate an electron pair. This theory can be applied to the reaction above, where OH^- is the Lewis base and CH_3Br is the Lewis acid.

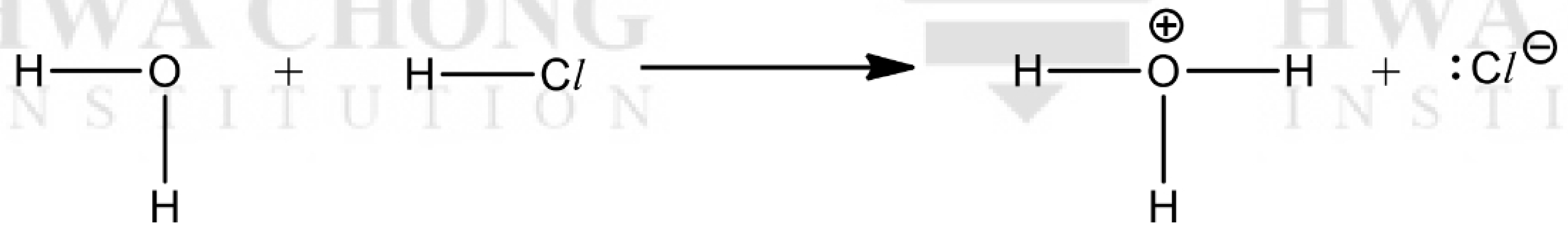
In general, electron pairs always flow

from:	**to:**
negative or δ– site	positive or δ+ site
electron-rich site	electron-deficient site
nucleophile (nucleophilic site)	electrophile (electrophilic site)
Lewis base (Lewis basic site)	Lewis acid (Lewis acidic site)

> *Did you know?*
>
> “Phile”: a word element meaning “loving”, “friendly” or “lover” - *Websters’ encyclopaedic unabridged dictionary of the English Language*
>
> So “electrophile” means “electron-loving” and nucleophile means “nucleus-loving”!

Writing a full organic chemistry mechanism

How do we draw the mechanism for a given reaction, such as the one below?



By observing the reactants and products, we can tell which bonds are broken and formed in the reaction. In this case, a new O–H bond forms between the H of the HC*l* and the O of the H_2O, while the H–C*l* bond breaks.

Hence, we can deduce that the lone pair on O is used to form a bond with H of HC*l* (recall that **every single bond** drawn on the structure represents **two electrons**). The H–C*l* bond then breaks heterolytically such that both electrons in the bond go to C*l* to form Cl^-.

A possible mechanism would be:

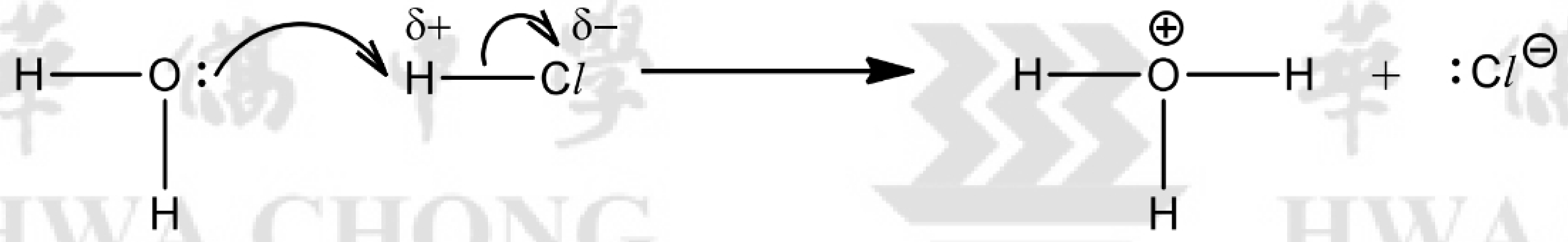


Figure 11. A possible full mechanism for the reaction between H_2O and HCl

Tip: Treat arrows as if they are electrons. A full arrow represents the movement of two electrons. Indicate partial charges and full charges on the relevant species.

3.2.2 Non-polar mechanisms

We will encounter non-polar mechanisms when we study free radical substitution in Topic 10 Alkanes. In non-polar mechanisms, the bond breaking and forming processes are homolytic, involving movement of single electrons rather than electron pairs.

Homolytic bond breaking (homolytic fission)

- The splitting of a single bond giving an equal share of bonding electrons to each resulting particle.
- Homolytic fission results in the formation of **radicals** (radicals possess unpaired electron(s)).

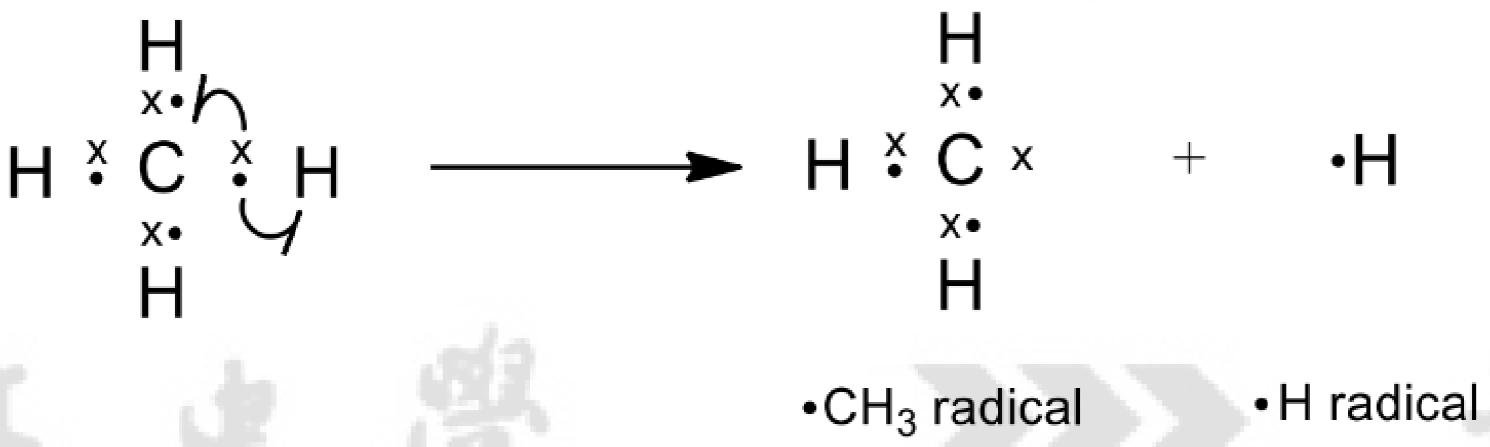


Figure 12. Homolytic bond breaking of C–H bond in methane

- Movement of electrons in the reaction is represented by fish-hook curly arrows.

A partial head (fish hook) on the arrow indicates the movement or shift of **a single electron**:

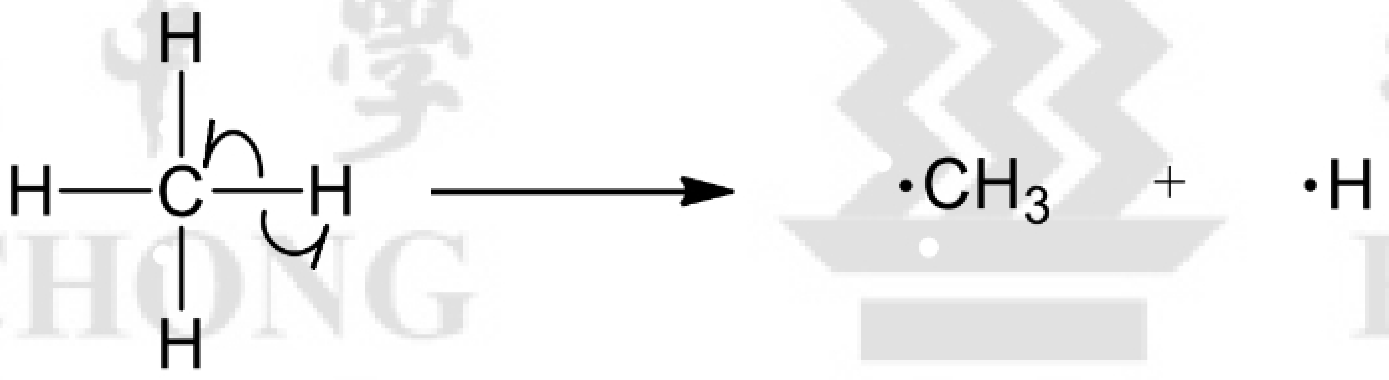


Figure 13. Representing homolytic bond breaking of C–H bond in methane using curly arrows

Homolytic bond forming

- Use fish-hook arrows for movement of single electrons to form a new bond:

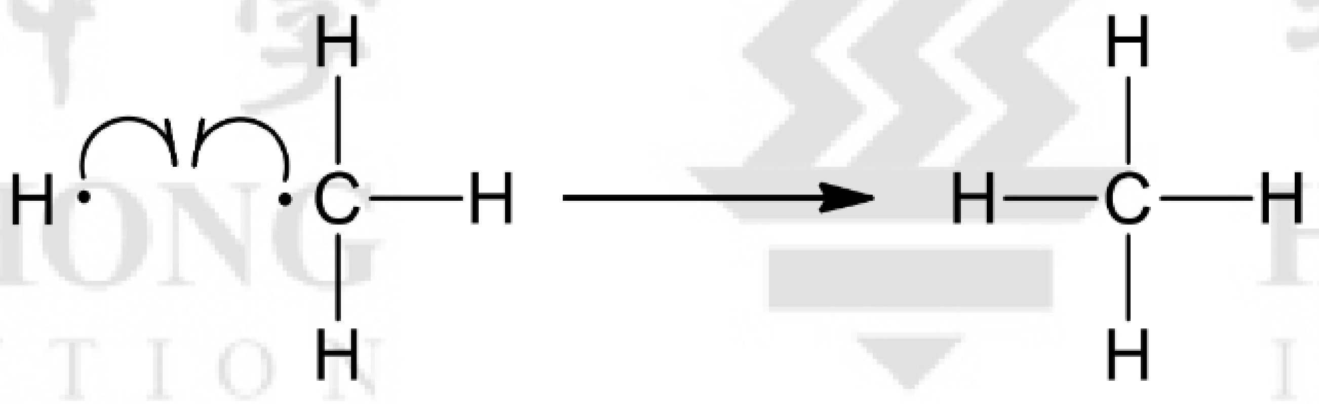
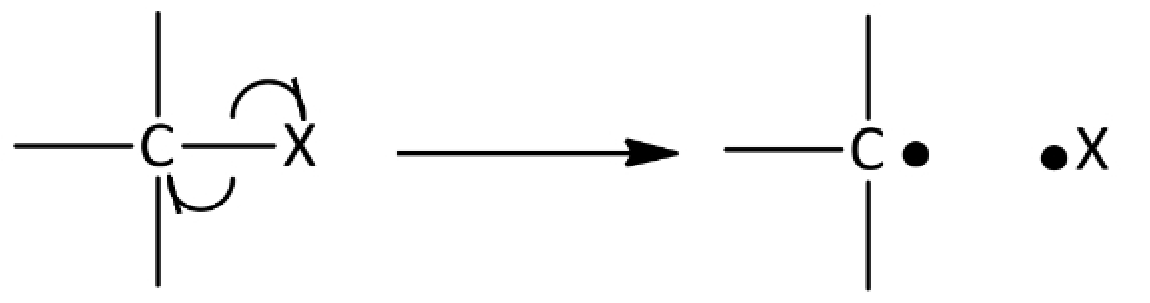
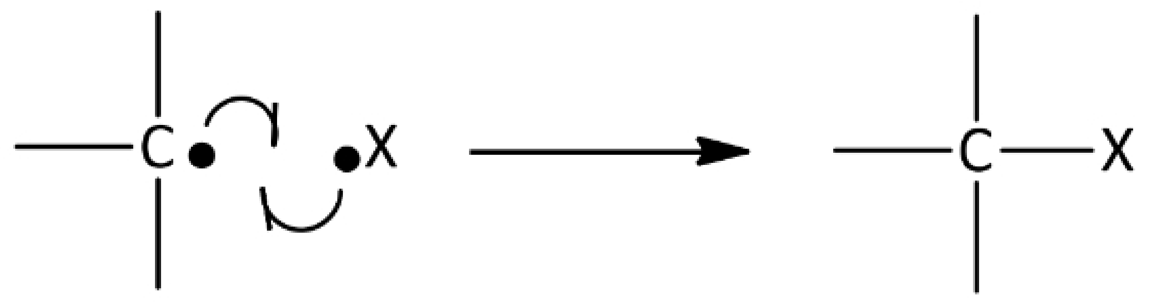
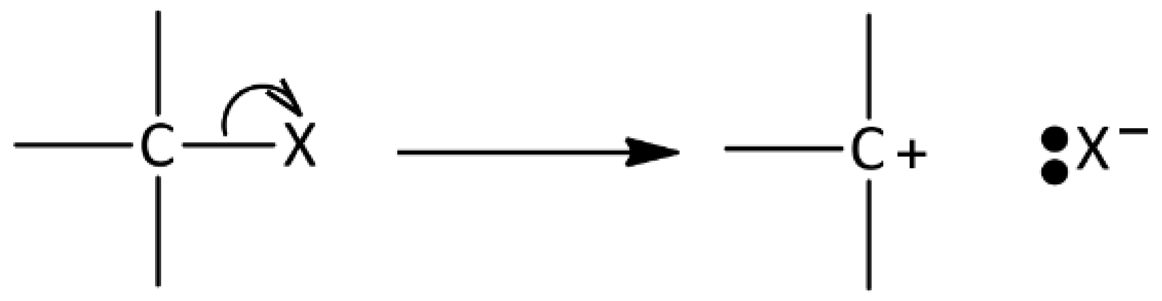
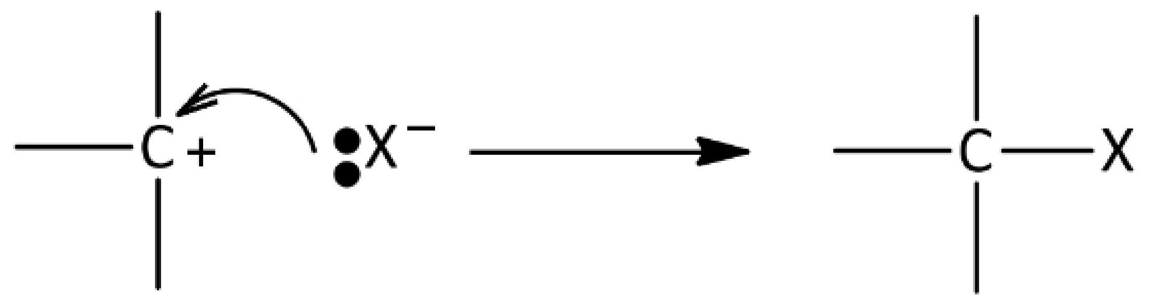
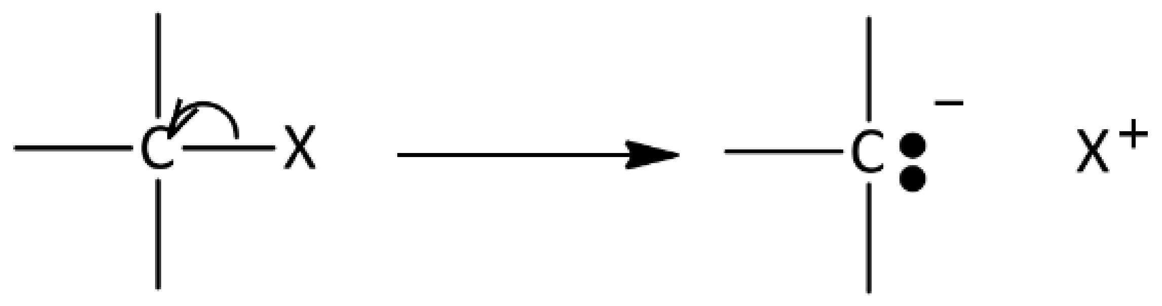
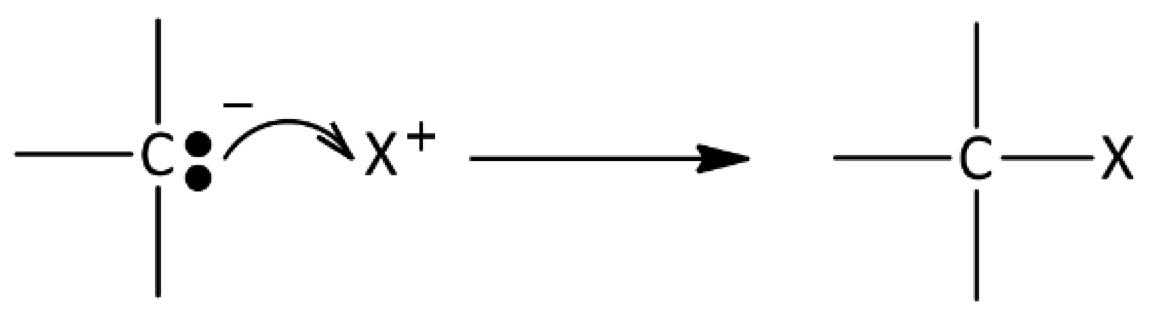


Figure 14. Representing homolytic bond forming of C–H bond using curly arrows

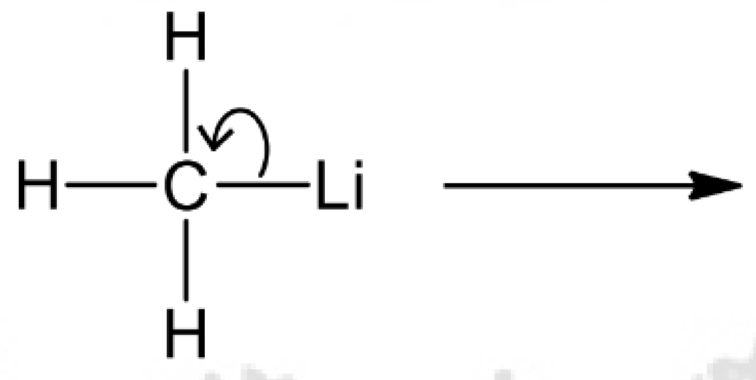
Summary - Curly arrow notation

	Bond-breaking	Bond-forming
homolytic		
heterolytic		
		

Lecture Exercise 3.2

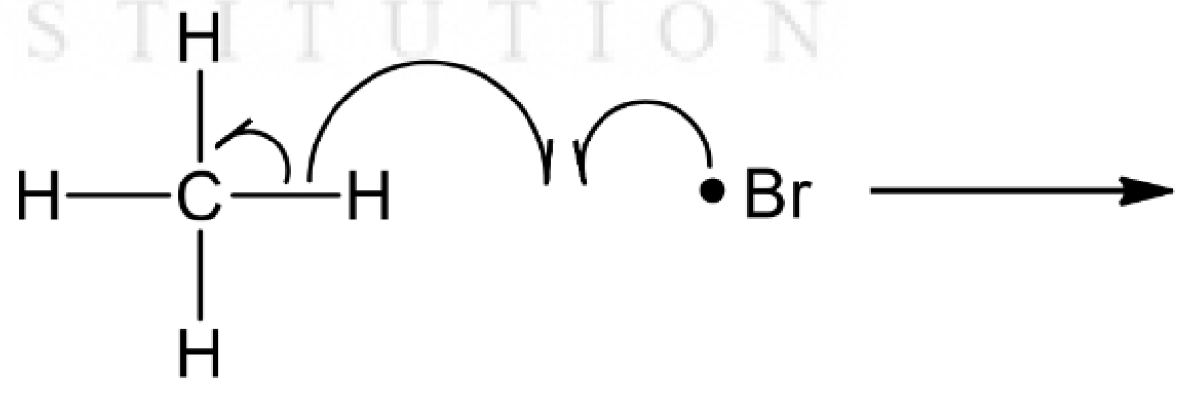
(a) Draw the products that result from the following:

(i) heterolytic fission

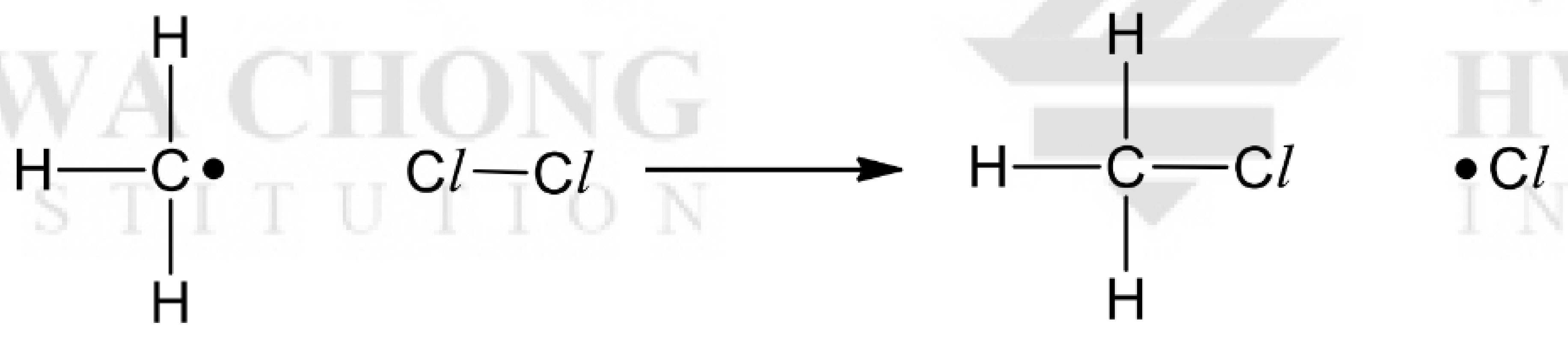


methyl lithium

(ii) homolytic fission



(b) Draw curly arrows for the mechanism below.



3.2.3 Reaction Intermediates

In Topic 6 Reaction Kinetics, we learnt that reaction intermediates are species that are formed in one of the steps of the reaction mechanism and are consumed in later steps. The energy minimum represents an intermediate in the reaction pathway. An **intermediate** is a definite species that exists for a finite length of time. It may be stable and thus isolated, or it may be reactive and short-lived (~10^{-5} s), but nonetheless detectable. In contrast, a **transition state** is a hypothetical species that exists only during the time that the reactants are in contact with each other (~10^{-15} s) and thus cannot be isolated. Transition states correspond to the highest energy (or energies) along the reaction pathway.

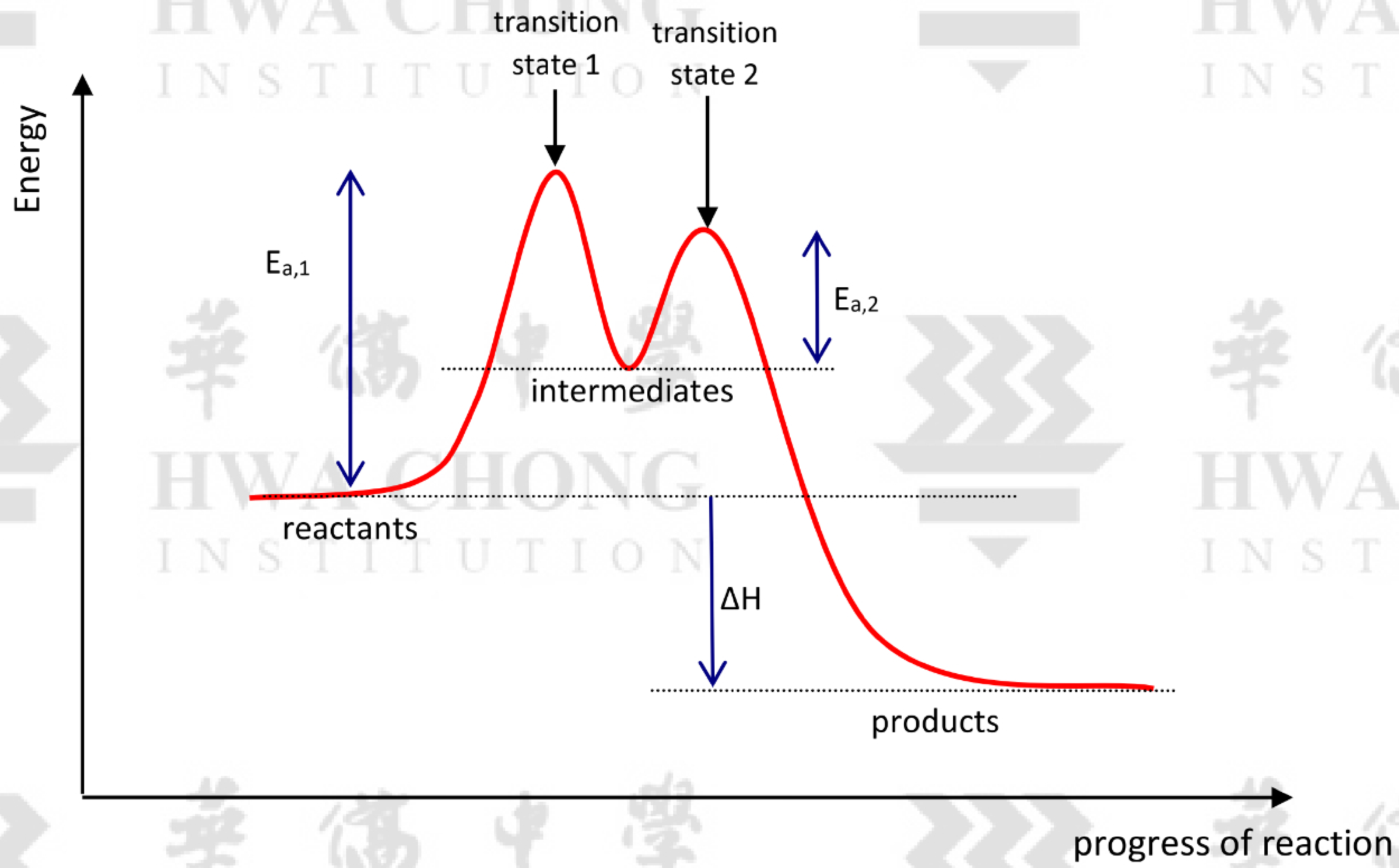
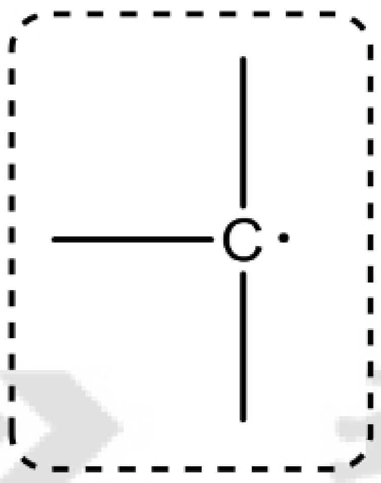
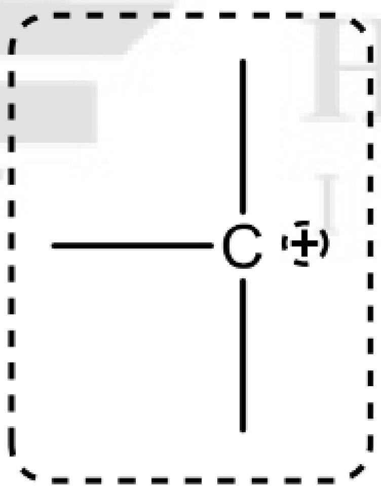
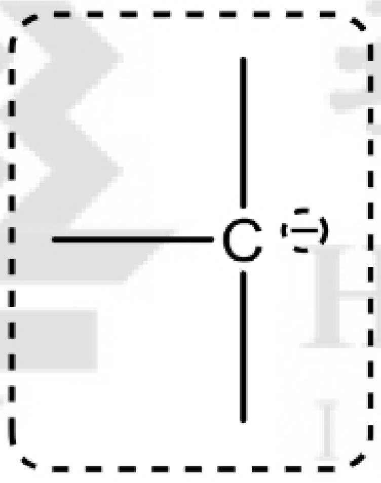


Figure 15. Energy profile diagram of a two-step reaction

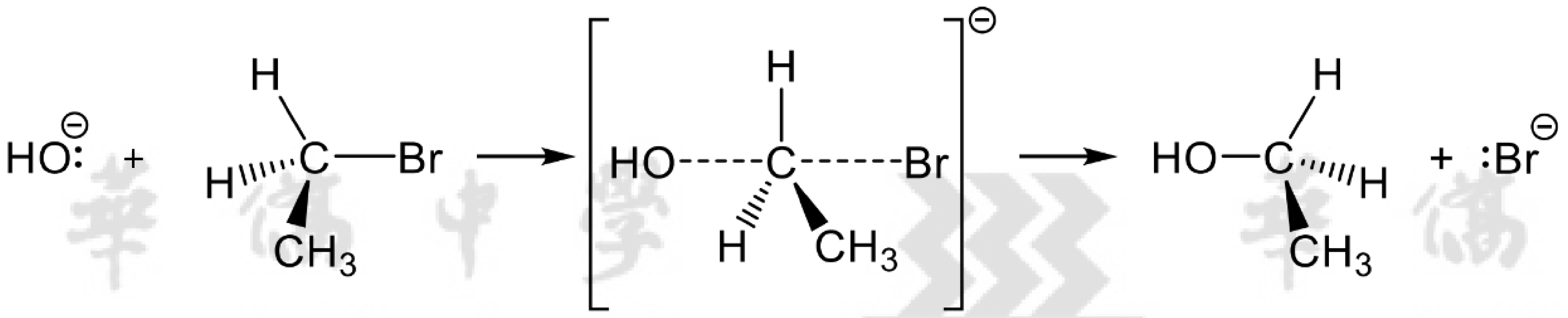
Reaction intermediates can be either of the following species:

	**Free radicals** A free radical is an atom or group of atoms that has an unpaired electron. Free radicals are extremely reactive because the unpaired electron readily combines with an electron in another atom to form a stable bond. Free radicals are electrically neutral and are represented by a structure with a single dot representing the unpaired electron.
	**Carbocations (Carbonium ion)** A carbocation is a species that contains a carbon atom bearing a positive charge. The positively charged carbon atom is bonded to three other atoms, has only six electrons in its valence shell and has no lone pairs. A carbocation is electron-deficient and a strong electrophile.
	**Carbanions** A carbanion is a species that contains a carbon atom bearing a negative charge. The negatively charged carbon atom is bonded to three other atoms and has eight electrons in its valence shell (three bonds and one lone pair). A carbanion is electron-rich and a strong nucleophile. Formally, the cyanide ion, CN^-, is a carbanion with the negative charge on the carbon.

Lecture Exercise 3.3

For the mechanism shown below,

(a) state the type of reaction,
(b) label the electrophile, nucleophile, and transition state, and
(c) draw curly arrows to show the transfer of electrons



4 INDUCTIVE, RESONANCE AND STERIC EFFECTS

Inductive and resonance effects are two types of electronic effects (i.e. effects that influence the distribution of electrons in a particular chemical species, and hence the reactivity of the species itself) that some atoms or functional groups can have within a chemical species.

4.1 Inductive Effect (Polarisation)

Defined

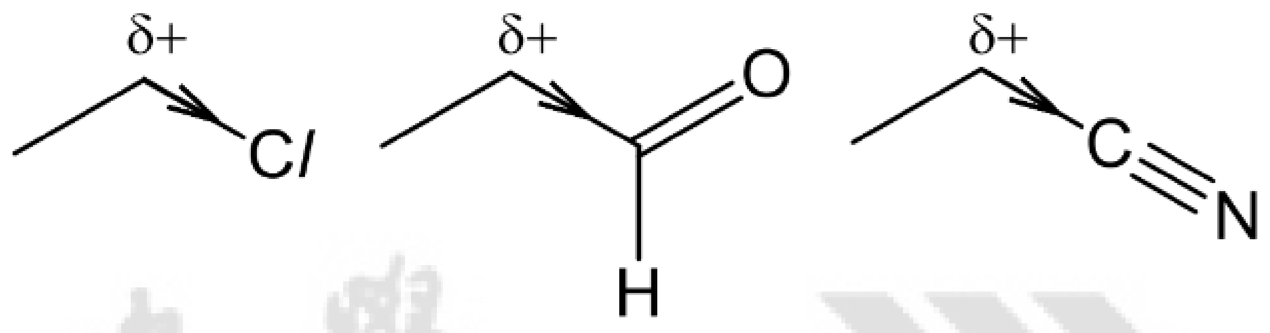
The inductive effect refers to the polarisation of the electron density in a bond due to the electronegativity of nearby atoms.

The inductive effect:

- Is a permanent but weak effect
- Can be electron-donating or electron-withdrawing
- Occurs through σ bonds
- Is distance dependent (becomes weaker the further you get from the influencing functional group)

Example 1

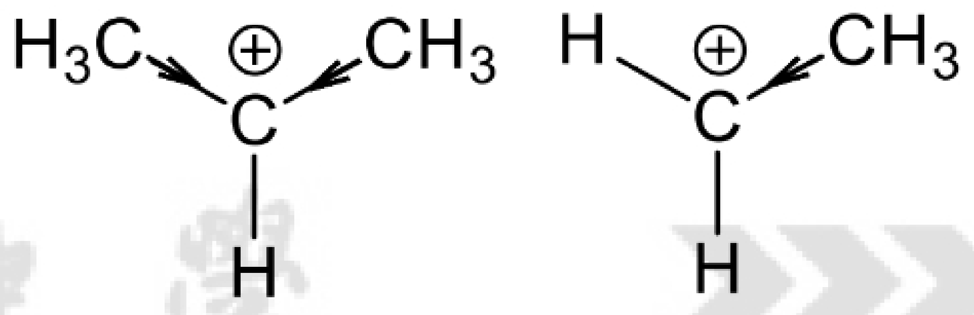
The electronegative atoms involved in the functional groups below all inductively withdraw electron density from the carbon, as shown by its resulting partial positive charge.



Here, the arrow represents the *electron-withdrawing* effect through the sigma bond. We say that -C*l*, -CHO, and -CN are inductively electron-withdrawing groups.

Example 2

Alkyl groups are considered inductively electron-donating groups, as they can increase the electron density in nearby atoms.

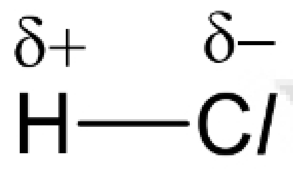


Here, the positive charge on the carbon atom is stabilised by the action of the electron-donating alkyl groups. (Which do you think is more stable?)

Note: the actual reason that deals with hyperconjugation will not be covered here

Where have we seen the inductive effect before?

Any time you encounter a polar covalent bond, you are essentially seeing the inductive effect at work. The charge separation that results from the difference in electronegativity of the atoms in the bond is a result of an inductive effect!



$$\overset{\delta+}{H}-\overset{\delta-}{Cl}$$

Where/when will this effect be relevant?

- Stability of carbocations, carbanions and radicals
- Activating/deactivating effects of substituent groups on reactions of benzene derivatives
- Strength of acids and bases via stability of their conjugates

4.2 Resonance (Delocalisation)

Defined

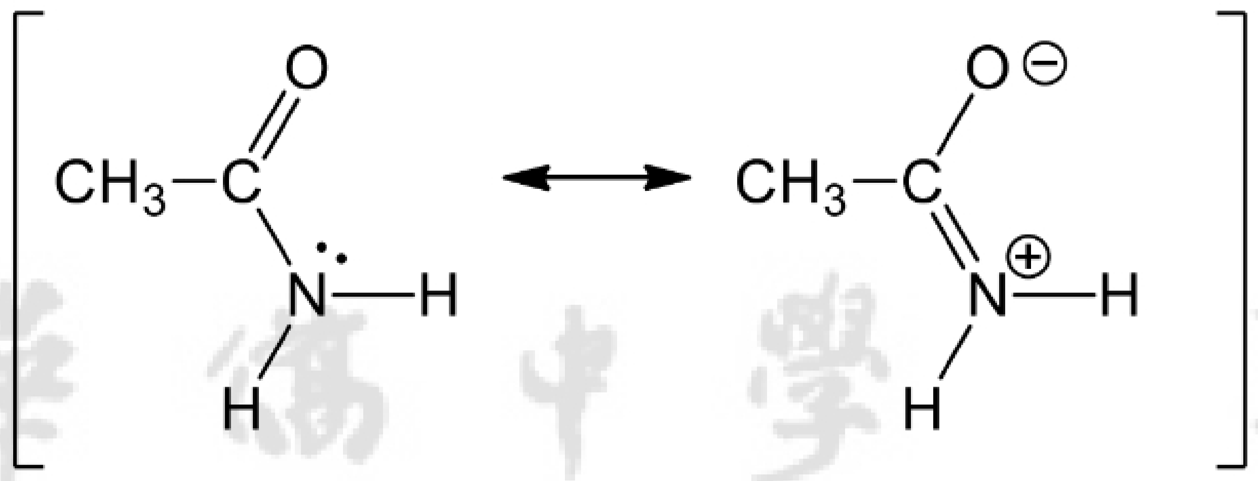
Resonance occurs when π electrons are allowed to flow through the overlap of neighbouring *p* orbitals. Such electrons are said to be delocalised.

Influence of resonance (sometimes called mesomeric effect):

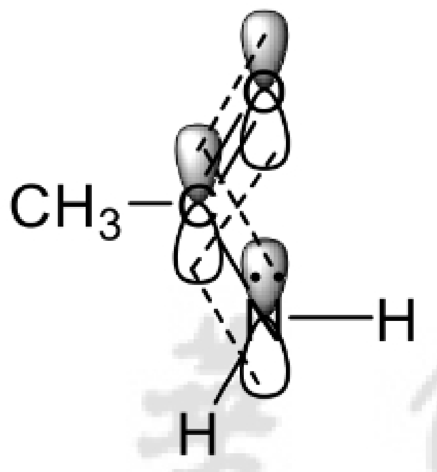
- Is a permanent effect
- Can be electron-donating or electron-withdrawing
- Occurs through π-system, which must be in a plane
- Independent of distance

Example 1

The amide functional group exhibits resonance. The nitrogen atom can donate its lone pair of electrons into the overlapping system of *p* orbitals, effectively increasing the electron density in the adjacent carbonyl group (C=O) by delocalisation of electrons (i.e. resonance).



resonance structures of ethylamide



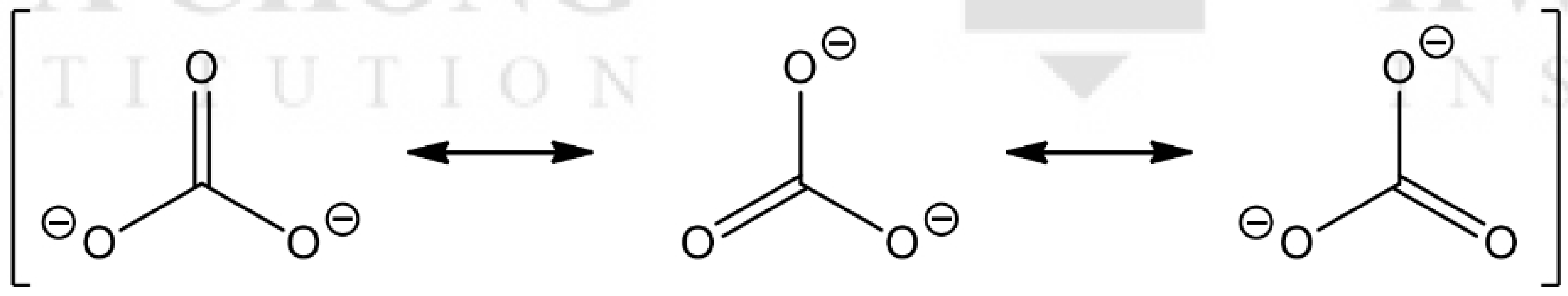
system of overlapping p orbitals, i.e. π system

The effect of this resonance is to remove electron density from the nitrogen atom and increase electron density on the oxygen atom.

Where have we seen resonance before?

In the chapter on Chemical Bonding, we saw that some species can have more than one equivalent Lewis structure. Each of these structures is called a 'resonance structure', and the actual species' characteristics are a mix of each individual resonance structure.

Example



Resonance structures of the carbonate anion, CO_3^{2-}

Where/when will this effect be relevant?

- Resonance stabilisation of certain molecules/species (e.g. benzene, ozone, etc)
  The classic example of resonance will be seen in the benzene ring, where the six π electrons are shared amongst all six carbon atoms in the ring, making them 'delocalised'.
- Activating/deactivating effects of substituent groups on reactions of benzene derivatives.
- Strength of acids and bases via stability of their conjugates

Note:

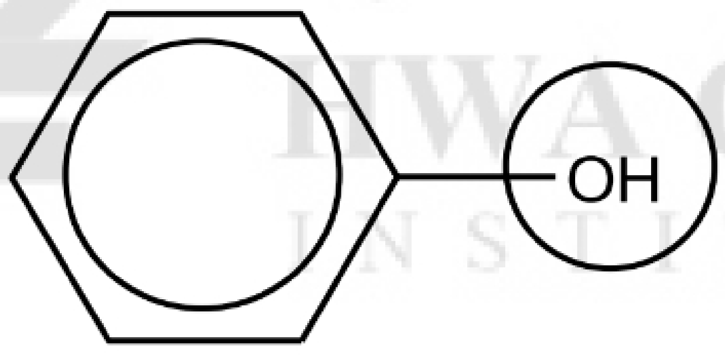
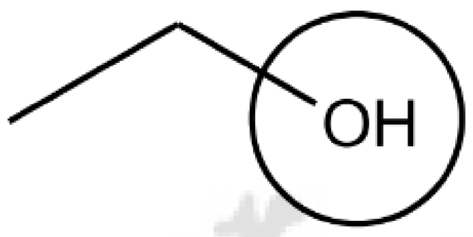
Inductive effects and resonance can sometimes act in **opposite directions**. This is particularly the case when the functional groups involved contain a very electronegative atom that is also able to donate a lone pair through resonance. See the table that follows.

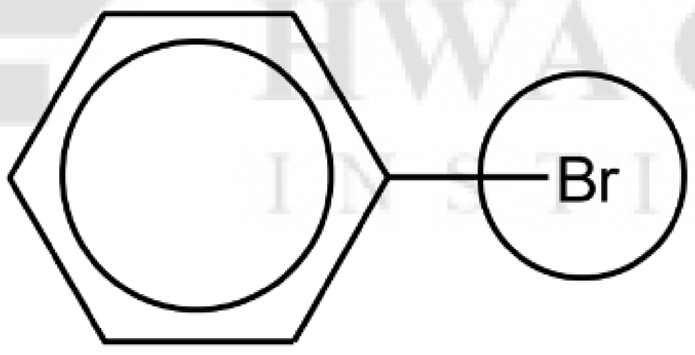
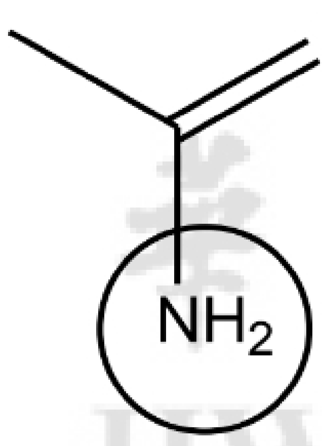
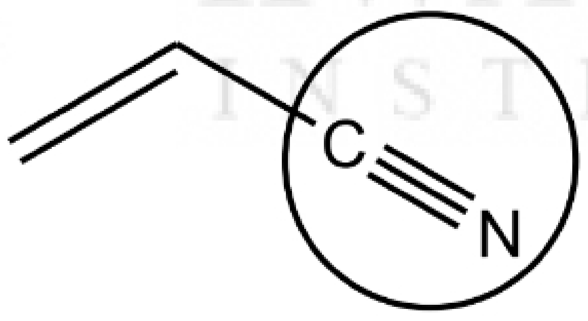
Table of inductive and resonance effects of different groups

Name	Functional Group	Inductive effect	Resonance effect	Overall effect
Ester	$-CO_2R$	Electron-withdrawing	Electron-withdrawing	Electron-withdrawing
Nitro	$-NO_2$			
aldehyde/ ketone	$-CHO$, $-COR$			
Cyano	$-CN$			
carboxylic acid	$-CO_2H$			
Halide	−X (X = F, *Cl*, Br, I)	Electron-withdrawing	Electron-donating	Electron-withdrawing
Hydroxyl	$-OH$	Electron-withdrawing	Electron-donating	Electron-donating
Amine	$-NH_2$			
Alkyl	$-R$	Electron-donating	None	Electron-donating

Lecture Exercise 4.1

Determine the types of inductive and resonance effects exhibited by the circled groups. State the overall effect if both are present. The first example has been completed for you.

Molecule	Inductive effect	Resonance effect	Overall effect
	Electron-withdrawing	Electron-donating	Electron-donating
			

			
	Electron-withdrawing	Electron-donating	Electron-donating
	Electron-withdrawing	Electron-withdrawing	Electron-withdrawing

4.3 Steric effect

Effects that result from the number and size of substituents and the repulsion between them are called **steric effects**. When this steric effect hinders the rate and extent of a reaction, we call it **steric hindrance**. A hindered, bulky reactant could prevent easy approach of the other reactant due to repulsion of the electron clouds of both species, making bond formation difficult. For example, if an electron-deficient carbon atom with bulky substituents is "shielded" from the approach of the incoming nucleophile, the reaction will proceed more slowly compared to one of a less hindered carbon.

This is exemplified in nucleophilic substitution of halogenoalkanes (Topic 13 Halogen Derivatives).

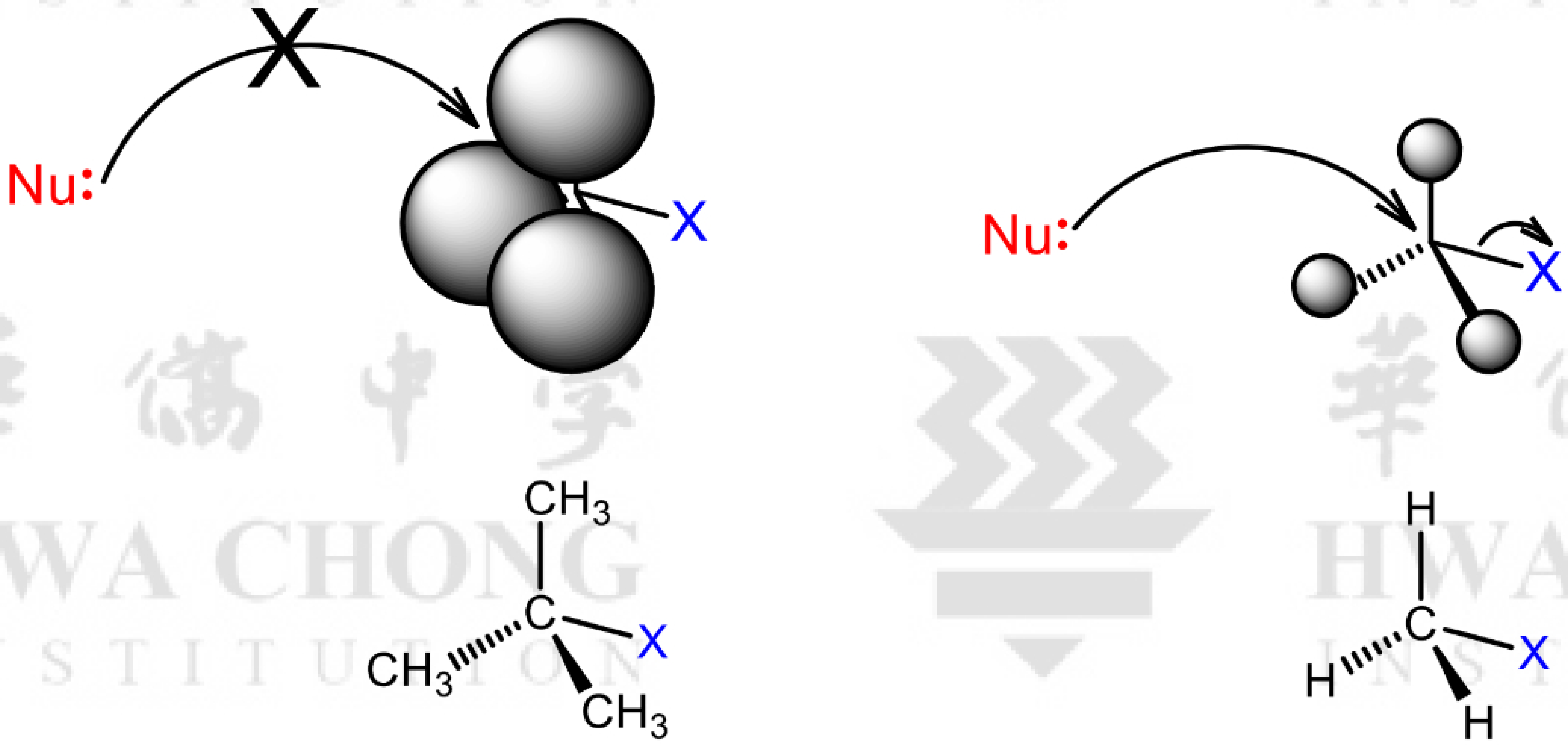


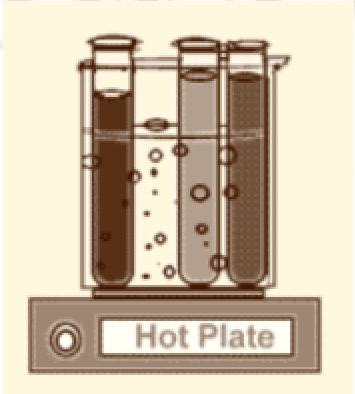
Figure 16. Steric hindrance due to bulky substituents in a nucleophilic substitution reaction

5 PRACTICAL ASPECTS OF ORGANIC CHEMISTRY

5.1 Distinguishing Tests

A **distinguishing test** is a simple chemical test that aims to confirm the presence of a particular compound, or differentiate between organic compounds, through the identification of certain key functional groups. Such tests require a **detectable chemical change** (e.g. colour change, appearance of precipitate, evolution of a gas, etc.) and are usually quick tests carried out in test tubes (unlike in synthesis) with **minimal use of complicated set-up or equipment** (unlike that for reflux).

<u>Planning an experiment involving distinguishing tests</u>



You may be asked to:

- Present the sequence of tests. (You may use a flowchart or table.)
- Write the procedure with essential details of quantities and conditions for each test.
  - In general, all tests are carried out in clean test-tubes using about 1 cm^3 (1 cm depth) of the unknown solution or 1 spatula of the unknown solid unless otherwise required.
  - Reagents are added dropwise until no further change occurs.
  - Heating, when required, is carried out using a water/oil/sand bath or a heating mantle.)
- State the expected observations for both positive and negative tests.
- Explain the chemistry underlying each test e.g. type of reaction, identity of species responsible for precipitate / gas / colour change, name / structure of functional group, structure of organic product.

5.2 Synthesis

An organic **synthesis** generally involves carrying out a reaction to form the desired product with reasonable yield and purity. Various strategies are therefore used in syntheses to obtain maximum yield and good purity. This usually involves careful sequencing of steps, controlled reaction conditions, complex set-up and/or equipment, and often, the investment of time. The product must also be isolated (i.e. separated from the reaction mixture) and purified.

The different stages in an organic synthesis are:

- Carrying out the reaction by heating the reaction mixture under reflux.
- Separation and purification by filtration, use of separating funnel, distillation and/or recrystallisation.
- Checking of purity by determining the melting or boiling point.

Carrying out the reaction

Compared to inorganic reactions between ionic compounds in solutions, organic reactions are generally slow (as such reactions involve breaking of covalent bonds) so the organic reaction mixture needs to be heated for some time. You will be learning many reactions that involve heating reagents under reflux in the A-level organic chemistry syllabus.

Heating under **reflux** means to heat a flask so that the solvent boils continually. A condenser is placed vertically in the neck of the flask to condense the solvent vapour. This method allows the temperature of the reaction mixture to be kept at the boiling point of the solvent, while minimizing the loss of reactants or products due to evaporation.

Generic procedure for heating under reflux

1. **Measure** (state quantity/quantities) of (reactant/reactants) using a (state apparatus e.g. measuring cylinder for liquids or electronic mass balance and weighing bottle for solids). **Transfer** to a 100 cm^3 /250 cm^3 **round–bottom flask**).
2. **Set up** the apparatus as shown in the diagram.
3. Gently **heat** the mixture under reflux for (state duration).

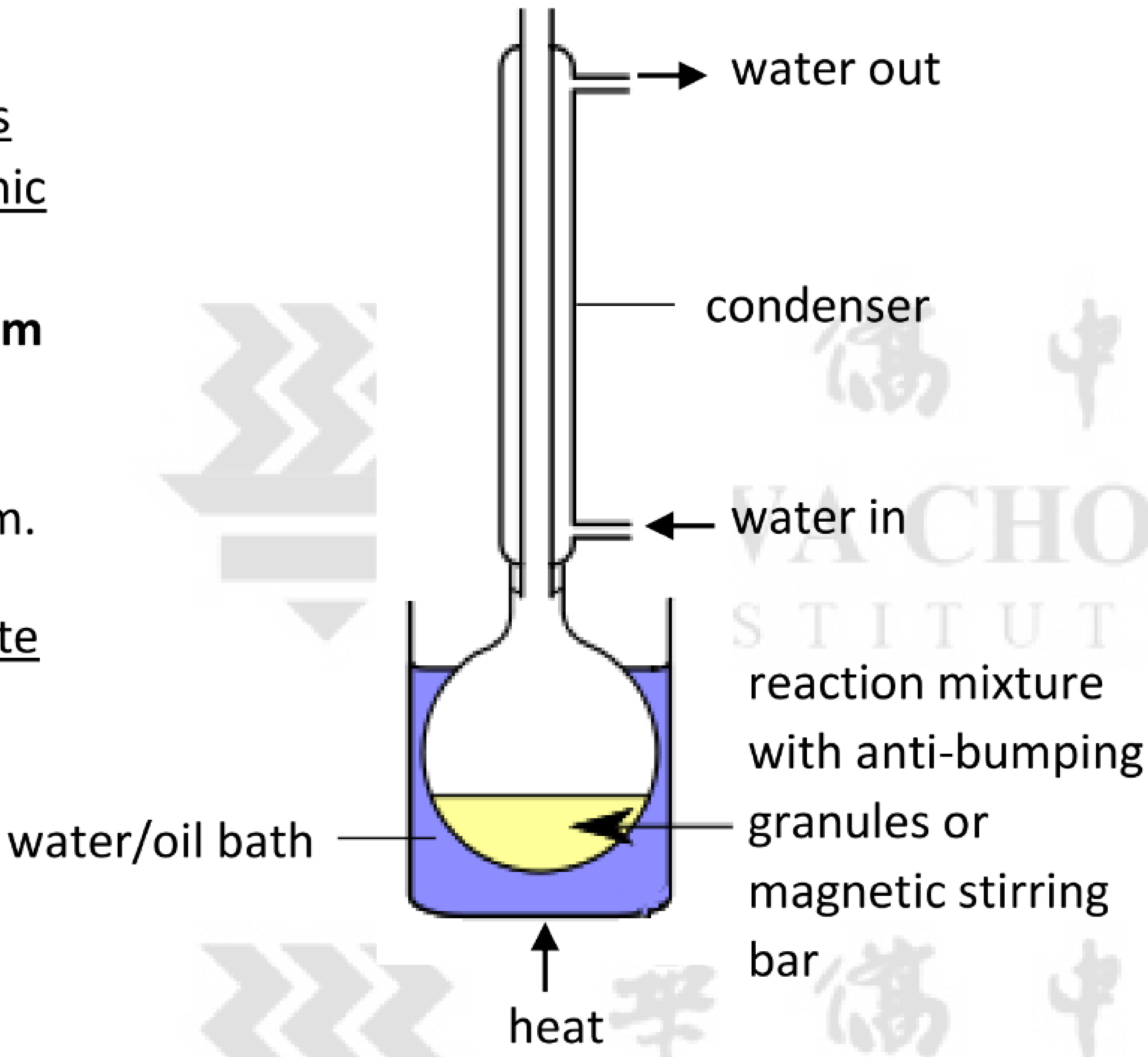


Figure 17: A reflux set-up

Notes:

✓ As most organic compounds are volatile and flammable, heating is done in a **reflux** set–up to prevent vapours from escaping during heating, using a **water/oil/sand bath** or **heating mantle**.

✓ For very exothermic reactions, cooling may be necessary when adding the reagents to each other. For example, when diluting a concentrated acid. In this case, cooling is done by immersing the reaction flask in an ice–water bath.

✓ A **dropping funnel** is used if the reactant needs to be added slowly (see diagram below).

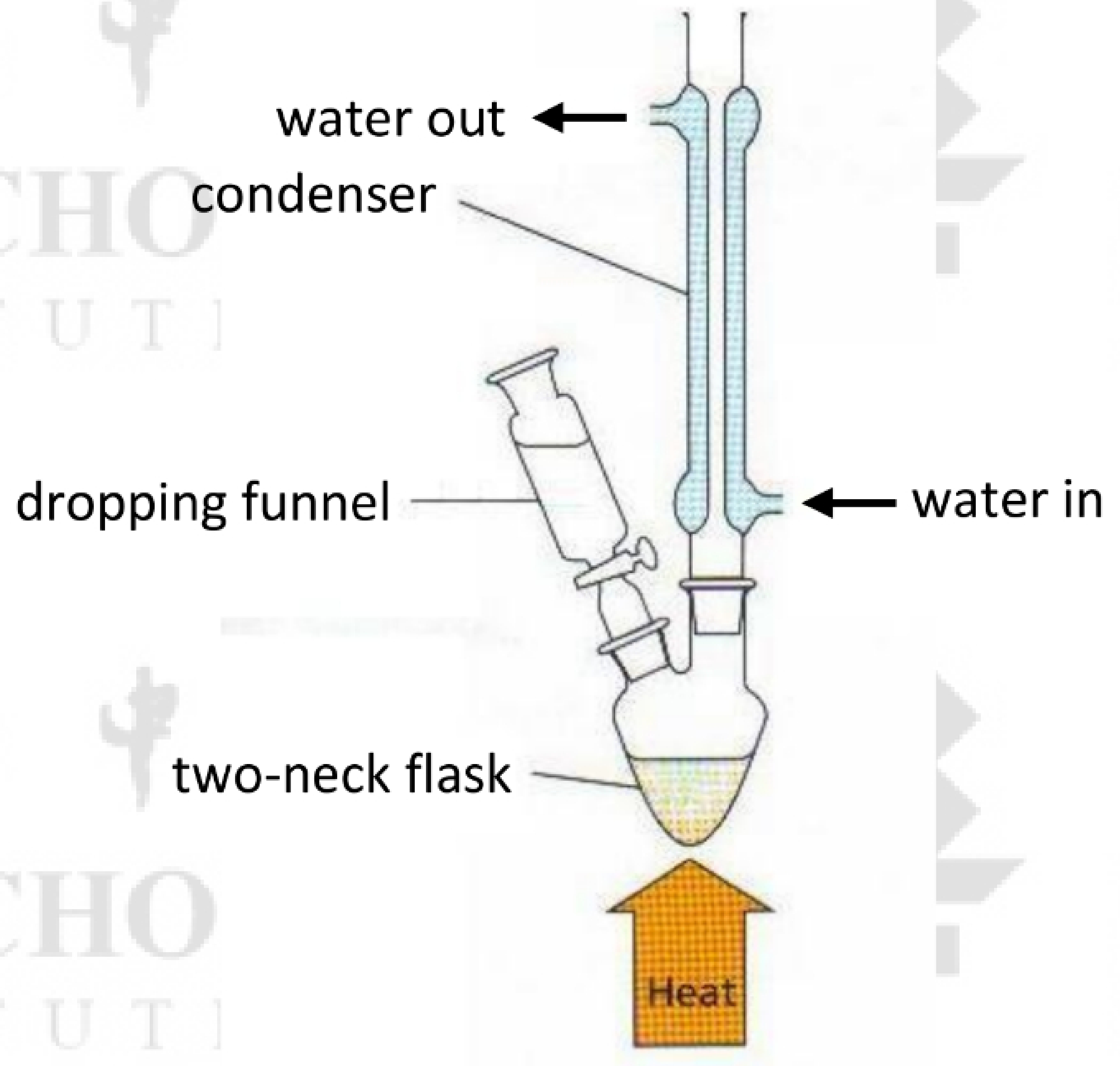


Figure 18: Two-neck flask with dropping funnel and condenser

Separation and Purification Techniques

One or more of the following techniques may be used to isolate and purify the crude product.

- Filtration

Used to separate a solid product from a solid-liquid mixture. The flask may be connected to a vacuum pump for rapid filtration

Figure 19: vacuum filtration set-up

- Extraction

Extraction involves two *immiscible* (do not mix) solvents. The first solvent contains the reaction mixture and crude product. A second solvent is chosen such that the solubility of the product in the second solvent is greater than that in the first. The two liquids are shaken together and left to stand. The product will be isolated in the second solvent and obtained by evaporating the solvent.

Generic procedure for extraction

1. **Place** (e.g. crude organic product / reaction mixture) into a **separating funnel**.
2. Using a measuring cylinder, **add** (state quantity) of (usually an acid or base/suitable solvent .
3. **Stopper and shake** well. **Leave to stand** to allow the two (immiscible) layers to separate.
4. **Collect** the (usually organic) layer which is at the top / bottom in a conical flask. **Discard** the (usually aqueous) layer.
5. **Add** (state drying agent) to the (usually organic) layer.
6. **Filter** and collect the (usually organic) layer (filtrate).
7. **Evaporate** the solvent to obtain the organic product.

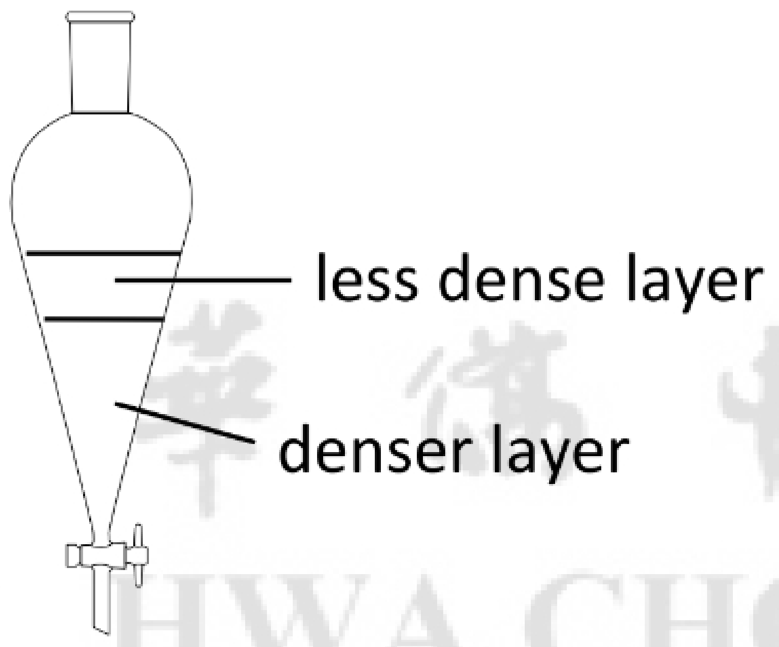


Figure 20: separating funnel (common capacities: 50 – 500 cm³)

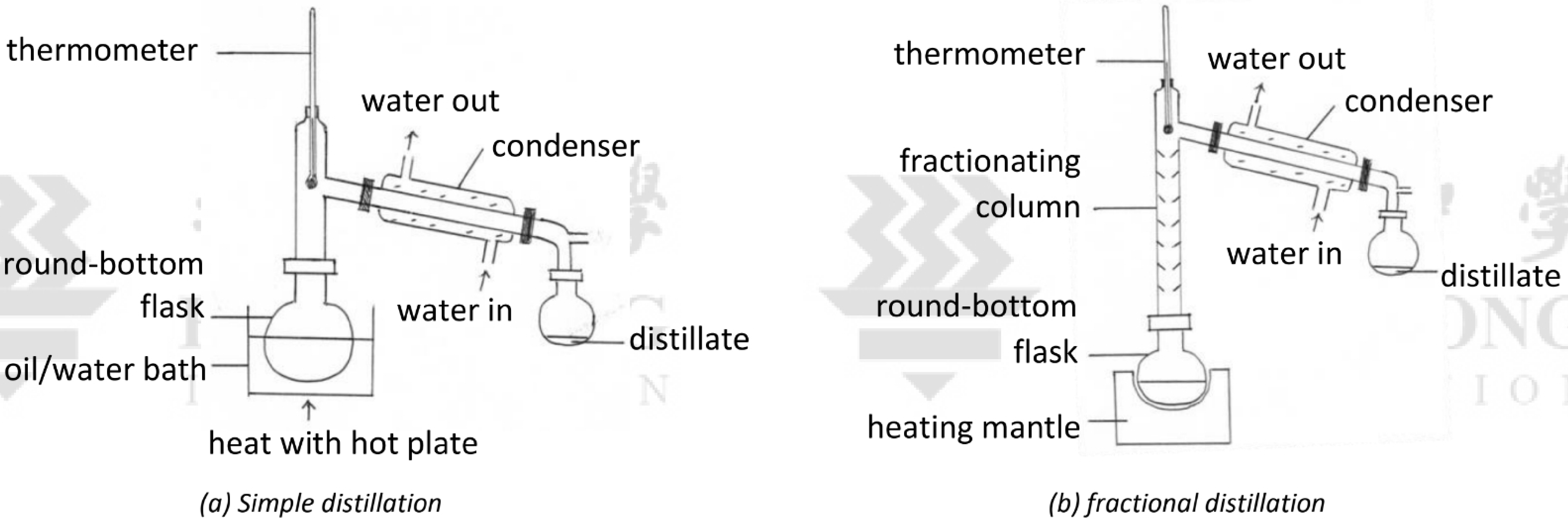
Notes:

- ✓ As a precaution, when shaking the separating funnel, pressure should be released regularly especially if a gas is produced e.g. when $NaHCO_3$ (aq) is used to remove acid impurities, CO_2 gas is formed.
- ✓ Do not assume the aqueous layer is always the denser layer. (If you do not know the densities of the compounds, check for the aqueous layer by adding water and noting which layer the water enters.)
- ✓ Common **drying agents**: anhydrous calcium chloride ($CaCl_2$), anhydrous sodium sulfate (Na_2SO_4) or anhydrous magnesium sulfate ($MgSO_4$).

- Distillation (for liquids)

Simple distillation is usually used to separate a volatile liquid from non-volatile impurities or to separate two liquids that differ in boiling point by at least 10 °C. See Figure 21(a) for the experimental setup. The **pure** desired compound is collected at its **boiling point**. Moisture in the purified liquid distillate will make it appear cloudy and is removed with a drying agent. An example of a reaction involving distillation is in the oxidation of primary alcohols to aldehydes, taught in the Topic 17 Carbonyl compounds.

To separate liquids with boiling points that are close to each other (< 10 °C apart), fractional distillation is used instead – see Figure 21(b).



(a) Simple distillation *(b) fractional distillation*

Figure 21. Experimental setup for distillation

- <u>Recrystallisation (for solids)</u>

Recrystallisation is used to purify a crude product using a suitable solvent.

<u>Generic procedure for recrystallisation</u>

1. **Dissolve** the crude solid product in a **minimal** volume of **hot** solvent in a conical flask to obtain a saturated solution.
2. **Filter** the hot solution to remove any solid impurities.
3. **Cool** the (saturated) solution in an ice-bath to obtain the crystallised solid.
4. **Filter** the solution to obtain the pure solid crystals as residue. **Wash** the crystals with a small volume of **cold** solvent.
5. Collect the crystals and allow the crystals to **dry**.

<u>Notes</u>:

✓ A suitable solvent dissolves the product when hot but not when cold.

✓ The solid may be dried in air or in a desiccator, shown below. If the solid is thermally stable, it can be dried in an oven or under an infra-red lamp.

Figure 22. A desiccator

Checking of purity

A simple way to check the purity of the product is by measuring its melting point (for solid) or boiling point (for liquid) and comparing the value with reference tables or databases.

Most pure organic solids melt at a **sharp temperature**.
Pure liquids are clear (not cloudy) and should distil over a **narrow temperature range** (±2 °C) at the boiling point.

Note:
- Melting and boiling points can be affected by impurities and moisture.
- Other techniques to check purity include thin-layer chromatography (TLC) and infra-red (IR) spectroscopy.

Self-practice 5.1
Refer to the reflux set up on page 29 and answer the following questions.

i. What is the purpose of adding anti-bumping granules?

ii. What is one advantage of using a magnetic stirrer instead of anti-bumping granules?

iii. Why should the condenser not be stoppered?

Refer to the generic procedure for recrystallisation on page 32 and answer the following questions.

i. What is the purpose of using "**hot**" solvent in step 1?

ii. Why use only a "**minimal**" volume of the solvent in step 1? What happens when we use too much solvent?

iii. Why is "**cold**" solvent used to wash the crystals in step 4?

09 Extension Topic - Organic Chemistry
Isomerism

GUIDING QUESTIONS

- What is isomerism? What are the different types of isomerism
- What are the structural criteria for exhibition of the different types of isomerism?
- How do the physical and chemical properties of different types of isomers differ?

LEARNING OUTCOMES

Students should be able to:

11.2(a) describe constitutional (structural) isomerism

11.2(b) describe *cis–trans* isomerism in alkenes, and explain its origins in terms of restricted rotation due to the presence of π bonds

11.2(c) explain what is meant by a chiral centre

11.2(d) deduce whether a given molecule is chiral based on the presence or absence of chiral centres and/or a plane of symmetry

11.2(e) recognize that an optically active sample rotates plane – polarised light and contains chiral molecules

11.2(f) recognise that enantiomers have identical physical properties except in the direction in which they rotate plane – polarised light

11.2(g) recognise that enantiomers have identical chemical properties except in their interaction with another chiral molecule

11.2(h) recognise that different stereoisomers exhibit different biological properties, for example in drug action

11.2(i) deduce the possible isomers for an organic molecule of known molecular formula

11.2(j) identify chiral centres and/or *cis–trans* isomerism in a molecule of given structural formula

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1. Albert Lehninger, *Principles of Biochemistry*, 5th Edition, W.H. Freeman
2. Peter Cann, *Chemistry for Advanced Level*, Hodder Education
3. IUPAC Compendium of Chemical Terminology, The Gold Book, http://goldbook.iupac.org/index.html