

H2 Chemistry

Organic Chemistry

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Abstract

This set of notes is written with the intention to provide readers with a brief summary of each topic in the Singapore GCE A-Level Chemistry at the H2 Level. The full syllabus can be found [here](#).

As the notes are rather terse, you are recommended to use the lecture notes provided by your school for the understanding of more fundamental concepts.

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Question Types

1. Mechanism question

Remember to indicate: arrows, dipole moments, lone pairs

2. Synthesis question

- Change in functional group

Method 1: Change the functional group by substitution. If the functional group cannot be substituted to give the desired compound in a single step, substitute the functional group into another functional group that can undergo substitution readily (e.g. halogenoalkane)

Method 2: Convert the functional group by oxidation/reduction if the starting compound cannot undergo substitution.

- Change in position of functional group (may or may not be the same as starting reagent)

Step 1: Convert the starting reagent into an alkene by elimination of the functional group.

Step 2: Add the new functional group (same or different) back to the alkene.

- Increase in carbon chain length

Method 1: Electrophilic substitution of nitrile group onto compound with halogen group. Nitrile group can be further converted into amine or carboxylic acid group. [This method does not increase the number of functional groups in the compound.]

Method 2: Electrophilic Add the nitrile group into the compound using HCN. (i.e. The compound needs to have a carbonyl group already) The product formed will contain a hydroxyl group adjacent to the nitrile group. The nitrile group can be further converted into amine or carboxylic acid functional group. [This method increases the number of functional groups in the compound by 1.]

Method 3: Employ other reactions that will increase in number of carbon atoms by more than one. (e.g. Reaction of alcohol with carboxylic acid, phenol with acyl chloride, amine with acyl chloride)

- Decrease in carbon chain length

Method 1: Oxidise the alkene to rupture the C=C double bond.

Method 2: Oxidise the compound that contain $\text{CH}_3\text{CH}(\text{OH})$ - group or the CH_3CO - group using alkaline $\text{I}_2(\text{aq})$. This reduces the number of carbon atoms by one.

Method 3: Hydrolysis of esters and amides.

3. Structural elucidation question

4. Distinguishing test

5. Explanation question

§1 Introduction

§1.1 Formulae

Formula	Description
Empirical formula	simplest ratio of number of atoms of the elements
Molecular formula	actual number of atoms of the elements present
Structural formula	atoms sequentially arranged, using conventional groups for an unambiguous structure
Displayed formula (full structural formula)	detailed structure of all atoms and bonds, with relative placing of atoms
Skeletal formula	only show bonds and functional groups
Stereochemical formula	3D spatial arrangement

§1.2 Functional Groups

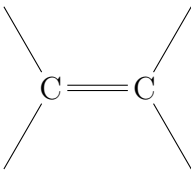
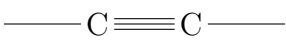
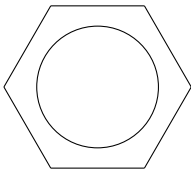

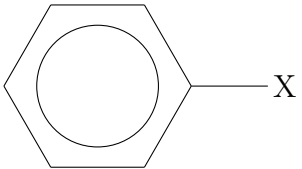
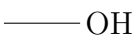
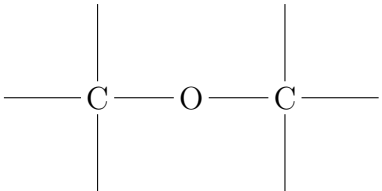
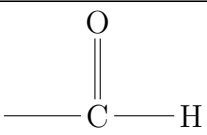
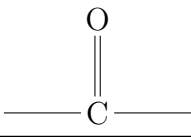
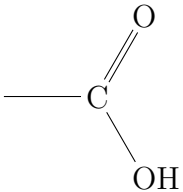
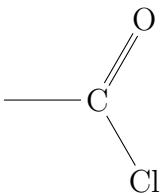
Classes of compounds

1. hydrocarbons (alkanes, alkenes, arenes)
2. halogen derivatives (halogenoalkanes, halogenoarenes)
3. hydroxyl compounds (alcohols, phenols)
4. carbonyl compounds (aldehydes, ketones)
5. carboxylic acids and derivatives (acyl chlorides, esters)
6. nitrogen compounds (amines, amides, amino acids, nitriles)

Definition 1.1: Functional group

An atom or a group of atoms common to a series, governs the principal chemical reaction of the series

Class of compound	General formula	Functional group
Alkane	C_nH_{2n+2}	

Class of compound	General formula	Functional group
Alkene	C_nH_{2n}	
Alkyne	C_nH_{2n-2}	
Benzene	C_6H_6	
Halogenoalkane	$C_nH_{2n+1}X$	
Halogenoarene	C_6H_5X	
Alcohol	ROH	
Ether	ROR'	
Aldehyde	$RCHO$	
Ketone	$RCOR'$	
Carboxylic acid	$RCOOH$	
Acyl chloride	$RCOCl$	

Class of compound	General formula	Functional group
Ester	RCOOR'	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---O---} \end{array}$
Amine	RNH_2	---NH_2
Amide	RCONH_2	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---N---H} \\ \\ \text{H} \end{array}$
Amino acid	$\text{H}_2\text{NC}_n\text{H}_{2n}\text{COOH}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N---C}_n\text{H}_{2n}\text{---C} \\ \\ \text{OH} \end{array}$
Nitrile	RCN	$\text{---C}\equiv\text{N}$

Definition 1.2: Homologous series

A family of organic compounds with similar general formula.

Successive members are represented by a general formula, differ by constant CH_2 units in the carbon skeleton

- Physical properties: graduation in physical properties (increase in molecular size and mass)
- Chemical properties: similar chemical properties (same functional group)

§1.3 Nomenclature

§1.4 Terminology for reactions

Types of organic species

Species	Notation	Definition	Description
free radical	$\text{Cl} \bullet$	Highly reactive, electrically neutral, has unpaired electron	Attack atom in a molecule to form new bond and generate another radical
nucleophile (Lewis base)	$:\text{Nu}^\ominus$	Electron pair donor	Electron-rich (negatively charged ion, lone pair, δ^- in polar bonds) Attracted to electron-deficient sites
electrophile (Lewis acid)	E^\oplus	Electron pair acceptor	Electron-deficient (positively charged ion, δ^+ in polar bonds) Attracted to electron-rich sites

Types of bond fission

homolytic fission	heterolytic fission
Breaking of covalent bond such that shared pair of electrons are split equally between the two atoms, which forms free radicals	Breaking of covalent bond such that shared pair of electrons are split unequally between the two atoms after bond broken, which forms ions
Movement of single electron (half arrow):	Movement of electron pair (full arrow):

Types of reactions¹

¹Do not use these terms when asked for the type of reaction! Give answers such as free radical substitution, electrophilic addition etc.

Reaction	Description	Bonds
addition	Two reactants added together to form one single product	One π bond broken, two σ bonds formed
substitution	An atom / a group of atoms replaces another atom / group of atoms	One σ bond broken, one σ bond formed
elimination	Two atoms / groups of atoms from adjacent atoms removed from one molecule	Two σ bonds broken, one π bond formed
condensation	Two molecules react to form a larger molecule + elimination of simple molecule	
hydrolysis	Reaction with water / H^+ / OH^-	
oxidation	Increase in oxidation state, oxidised by [O]	
reduction	Decrease in oxidation state, reduced by [H]	

§1.5 Hybridisation

One of 2s electron is promoted to empty 2p orbital (from ground state to excited state)
→ 4 singly occupied orbitals for forming 4 covalent bonds

Exercise 1.1: A-Level 2021/III/2(e)

Describe and explain, in terms of orbital overlap, the shape and bonding in an ethyne molecule C_2H_2 . [3]

Answer. Ethyne molecule is linear whereby all four atoms lie in a straight line.

Both carbons are sp -hybridised. In an sp -hybridised carbon, 2s orbital combines with $2p_x$ orbital to form two hybrid orbitals that are oriented at an angle of 180° with respect to each other, along x -axis. $2p_y$ and $2p_z$ orbitals remain unhybridised, orientated perpendicularly along y - and z -axes respectively.

$\text{C}-\text{C}$ σ bond is formed by the overlap of one sp orbital from each carbon atom. Two $\text{C}-\text{H}$ σ bonds are formed by overlap of the second sp orbital on each carbon with $1s$ orbital on hydrogen atom. $\text{C}\equiv\text{C}$ bond is formed by overlap of $2p_y$ and $2p_z$ orbitals of each carbon atom overlap sideways to form two π bonds between the carbons. \square

Exercise 1.2: A-Level 2017/II/7(a)(iii)

Describe the hybridisation of the orbitals in, and the bonds between, the carbon atoms within a naphthalene molecule. [3]

Answer. One of the 2s electrons in each carbon atom is promoted to the vacant 2p orbital, and the 2s orbital and two 2p orbitals hybridise to give three sp^2 hybrid orbitals.

Adjacent carbon atoms are bonded by a σ bond through head-on overlapping of sp^2 hybrid orbitals, and a π bond through sideways overlapping of unused p_z orbital of each carbon atom, that is $\text{C}=\text{C}$ bond. Due to delocalisation of electrons, all carbon atoms are covalently bonded by sp^2 - sp^2 overlap. \square

§2 Isomerism

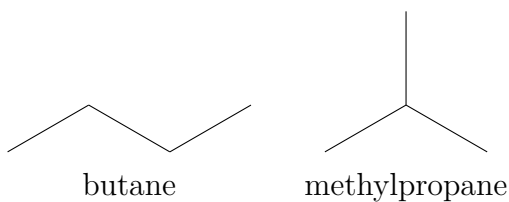
Definition 2.1: Isomers

Compounds having same molecular formula but different arrangement of atoms.

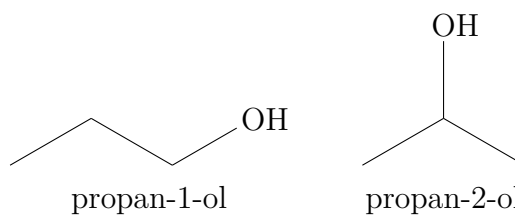
1. Structural isomerism

Same molecular formula but different arrangements of atoms

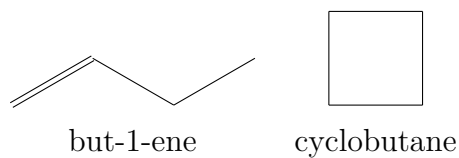
- **Chain isomerism:** different arrangement of carbon chain (straight or branched)



- **Positional isomerism:** different position of functional group

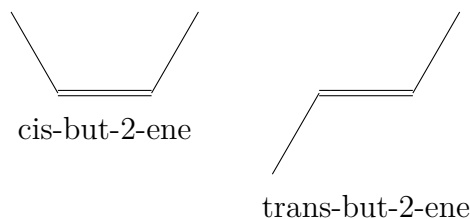


- **Functional group isomerism:** different functional group

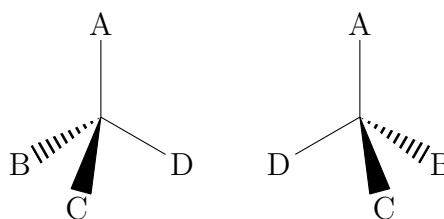


2. Stereoisomerism

- **Cis-trans isomerism**

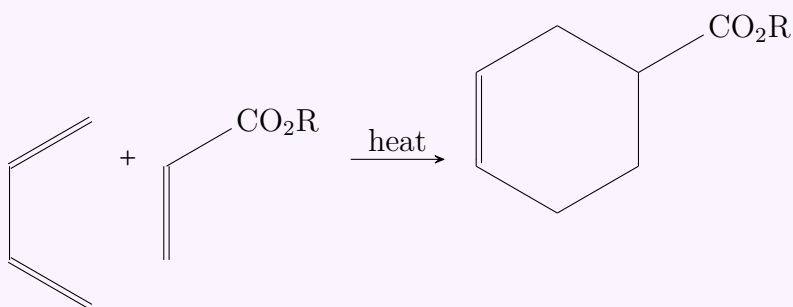


- **Enantiomerism**



Exercise 2.1: A-Level 2021/III/4(e)(ii)

The Diels-Alder reaction is a one-step reaction between a diene and a substituted alkene to form a substituted cyclohexene X.



Compound X has no effect on the plane of polarised light. Explain your reasoning. [1]

Answer. Diene can attack sp^2 carbon on $\text{C}=\text{C}$ bond of the substituted alkene from both top and bottom of the plane with equal probability, since it is trigonal planar.

As such, a racemic mixture is obtained which is optically inactive since optical activity of one enantiomer exactly cancels the other. \square

Part I

Hydrocarbons

§3 Alkanes

Chemical properties

Generally unreactive

- Fully saturated: all carbon atoms are sp^3 hybridised and C–C, C–H bonds are strong and difficult to break, so alkanes *do not undergo addition*.
- C–H bonds are non-polar: lack electron-rich (δ^-) and electron-deficient (δ^+) sites, so alkanes are *unreactive towards polar reagents*.

Small cycloalkanes (e.g. cyclopropane, cyclobutane) are unstable due to **ring strain**, as molecules are forced into smaller bond angles.

§3.1 Mechanism: Free radical substitution

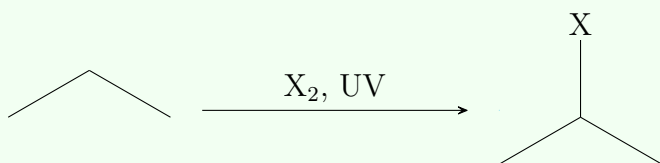
Mechanism 3.1: Free radical substitution

Step 1: Initiation

Step 2: Propagation

Step 3: Termination

Overall equation:



§3.2 Reactions

- Free radical substitution

§3.3 Preparation

- Reduction of alkene

§4 Alkenes

Chemical properties

Generally reactive

- Electron rich C=C bond is easily accessible to approaching reactants (π electrons are located above and below the plane of bond) \rightarrow act as nucleophiles, attract electrophiles OR induce dipoles in approaching molecules to form electrophiles
- Carbon atoms in C=C bond are unsaturated: sp^2 hybridised, can bond with one more atom \rightarrow undergo electrophilic addition

§4.1 Mechanism: Electrophilic addition

Mechanism 4.1: Electrophilic addition

Step 1: Addition of electrophile

formation of carbocation (Markovnikov's rule)

Step 2: Ions combine

§4.2 Reactions

1. Electrophilic addition

- Addition of halogen
- Addition of halogen in water²
- Addition of hydrogen halide
- Addition of water

2. Reduction

3. Oxidation

- Mild oxidation
- Strong oxidation (to form carbon dioxide, carboxylic acid, or ketone)

Remark. Remember how to write oxidation / reduction equations.

²If water is used as solvent, H_2O can act as nucleophile to attack product formed.

§4.3 Preparation

1. Elimination of alcohol
2. Elimination of halogenoalkane

§5 Benzene

Chemical properties

Resonance stability

- Due to overlapping p-orbitals, delocalised π electron cloud above and below plane of ring. Benzene is resonance stabilised, resonance structure of benzene is very stable i.e. aromaticity.
- Do not undergo reactions that destroy resonance stability (even through electron-rich due to presence of π electrons), e.g. electrophilic addition. Hence benzene only undergoes electrophilic substitution, remain resonance stabilised.

§5.1 Mechanism: Electrophilic substitution

Mechanism 5.1: Electrophilic substitution

Step 1: Generation of strong electrophile

Step 2: Addition into benzene ring

position dependent on group which is already present

Step 3: Deprotonation

§5.2 Reactions

1. Electrophilic substitution

- Electrophilic substitution of halogen (halogenation)
- Electrophilic substitution of nitro group (nitration)
- Electrophilic substitution of alkyl group (Friedel-Crafts alkylation)

2. Reduction

§6 Methylbenzene

Chemical properties

§6.1 Mechanism: Electrophilic substitution

Same as above.

§6.2 Reactions

1. Electrophilic substitution

- Electrophilic substitution of halogen (halogenation)
- Electrophilic substitution of nitro group (nitration)

2. Free radical substitution (side chain)

3. Oxidation (side chain)

§6.3 Preparation

1. Electrophilic substitution of benzene

Part II

Halogen Derivatives

§7 Halogenoalkane

§7.1 Mechanism: Nucleophilic substitution

Mechanism 7.1: Unimolecular nucleophilic substitution (S_N1)

Step 1: Formation of carbocation intermediate

Step 2: Attack of carbocation by nucleophile

Mechanism 7.2: Bimolecular nucleophilic substitution (S_N2)

Step 1: Nucleophile attacks from opposite side of halogen atom

Pentavalent transition state formed, where both nucleophile and halogen are partially bonded to carbon atom, both bond breaking and bond forming process take place simultaneously.

S_N1	S_N2
one molecule in first step	two molecules in first step
two steps	one step
Electronic: tertiary halogenoalkane gives stable tertiary carbocation intermediate	Electronic: methyl and primary halogenoalkane give less stable methyl carbocation and primary carbanion intermediate
Steric: tertiary halogenoalkane has three bulky groups which hinder approach of nucleophile to electron-deficient carbon atom, more steric hindrance	Steric: methyl and primary halogenoalkane have no or only one alkyl group which allows easy approach of nucleophile to electron-deficient carbon atom, less steric hindrance
Stereochemistry: inversion of stereochemical configuration (for chiral reactants)	Stereochemistry: racemic mixture (for chiral reactants)

Exceptions (due to other electronic and steric considerations)

•

§7.2 Reactions

1. Nucleophilic substitution

- Nucleophilic substitution of OH^-
- Nucleophilic substitution of CN^-
- Nucleophilic substitution of NH_3 (step-up reaction)
Acidic hydrolysis, basic hydrolysis, reduction
- Nucleophilic substitution of RO^- , formed from alcohol [FYI]

2. Elimination

§7.3 Preparation

1. Free radical substitution of alkane
2. Electrophilic addition of alkene
3. Nucleophilic substitution of alcohol

§7.4 Reactivities of Halogenoalkanes

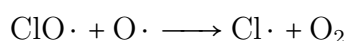
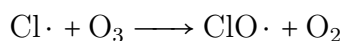
Down the group, atomic orbital of halogen atom becomes more diffused, effectiveness of orbital overlap decreases, strength of C-X bond decreases down the group, relative ease of breaking C-X bond increases, reactivity of R-X towards nucleophilic substitution increases

Remark. Do not use bond polarity to explain.

§7.5 Uses

Fluoroalkanes and fluorohalogenoalkanes are generally stable and unreactive (chemically inert) due to strong C-F bond (high bond energy), used as **inert materials** in fire extinguisher, refrigerant, aerosol propellant etc.

Chlorofluorocarbons (CFCs) lead to ozone depletion, by free radical substitution mechanism:



§8 Halogenoarene

Chemical properties

Unreactive towards nucleophilic substitution

- **Electronic:**

p orbital of halogen atom overlaps with p-orbitals of carbon atoms on benzene ring. Lone pair of electrons in p-orbital of halogen atom delocalises into benzene ring to form delocalised π electron cloud.

Partial double bond character in C–X bond, more energy required to break stronger C–X bond to displace halogen atom.

- **Steric:**

Rear side of C–X bond is blocked by bulky benzene ring. π electron cloud of benzene ring repulses lone pair of electrons of nucleophile, difficult for nucleophile to attack.

§8.1 Reactions

§8.2 Preparation

Part III

Hydroxy Compounds

§9 Alcohol

§9.1 Acidity

§9.2 Reactions

1. **Redox reaction** (acid-metal displacement)
2. **Condensation reaction**
 - Condensation using carboxylic acid
 - Condensation using acyl chloride
3. **Nucleophilic substitution**
4. **Elimination**
5. **Oxidation**
 - Oxidation of 1° and 2° alcohols
 - Oxidation of $\text{CH}_3\text{CH}(\text{OH})-\text{R}$ alcohols (tri-iodoform test)

§9.3 Preparation

1. Electrophilic addition of alkene
2. Nucleophilic substitution of halogenoalkane
3. Reduction of carbonyl compound

§10 Phenol

§10.1 Acidity

(i) its acidity; reaction with bases and sodium (ii) nitration of, and bromination of, the aromatic ring

§10.2 Reactions

1. Electrophilic substitution
 - Electrophilic substitution of halogen
 - Electrophilic substitution of nitro group (nitration)
2. Redox reaction (acid-metal displacement)
3. Neutralisation
4. Condensation
5. Complex formation

explain the relative acidities of water, phenol and ethanol in aqueous medium (interpret as Brønsted-Lowry acids)

Part IV

Carbonyl Compounds

§11 Aldehydes

(i) oxidation to carboxylic acid (ii) nucleophilic addition with hydrogen cyanide (iii) characteristic tests for aldehydes

§12 Ketones

- (i) nucleophilic addition with hydrogen cyanide (ii) characteristic tests for ketones
- (a) describe the formation of aldehydes and ketones from, and their reduction to, primary and secondary alcohols respectively (b) describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones (c) explain the differences in reactivity between carbonyl compounds and alkenes towards nucleophilic reagents, such as lithium aluminium hydride and hydrogen cyanide (d) describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) to detect the presence of carbonyl compounds (e) deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (i.e. Fehling's and Tollens' reagents; ease of oxidation) (f) deduce the presence of a $\text{CH}_3\text{CO}-$ group in a carbonyl compound from its reaction with alkaline aqueous iodine to form tri-iodomethane

Part V

Carboxylic Acid and Derivative

§13 Carboxylic acids

(i) formation from primary alcohols and nitriles (ii) salt, ester and acyl chloride formation

§14 Acyl chlorides

(i) ease of hydrolysis compared with alkyl and aryl chlorides (ii) reaction with alcohols, phenols and primary amines

§15 Esters

(i) formation from carboxylic acids and from acyl chlorides (ii) hydrolysis (under acidic and under basic conditions)

(a) describe the formation of carboxylic acids from alcohols, aldehydes and nitriles (b) describe the reactions of carboxylic acids in the formation of: (i) salts (ii) esters on condensation with alcohols, using ethyl ethanoate as an example (iii) acyl chlorides, using ethanoyl chloride as an example (iv) primary alcohols, via reduction with lithium aluminium hydride, using ethanol as an example (c) explain the acidity of carboxylic acids and of chlorine-substituted ethanoic acids in terms of their structures (d) describe the hydrolysis of acyl chlorides (e) describe the condensation reactions of acyl chlorides with alcohols, phenols and primary amines (f) explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides (g) describe the formation of esters from the condensation reaction of acyl chlorides, using phenyl benzoate as an example (h) describe the acid and base hydrolysis of esters

Part VI

Nitrogen Compounds

§16 Amines

(i) their formation (ii) salt formation (iii) other reactions of phenylamine

§17 Amides

(i) formation from acyl chlorides (ii) neutrality of amides (iii) hydrolysis (under acidic and under basic conditions)

§18 Amino acids

(i) their acid and base properties (ii) zwitterion formation

§19 Proteins

(i) formation of proteins (ii) hydrolysis of proteins

(a) describe the formation of amines as exemplified by ethylamine (through amide and nitrile reduction; see also Section 11.4) and by phenylamine (through the reduction of nitrobenzene) (b) describe the reaction of amines in the formation of salts (c) describe and explain the basicity of primary, secondary and tertiary amines in the gaseous phase (interpret as Lewis bases) (d) explain the relative basicities of ammonia, ethylamine and phenylamine in aqueous medium, in terms of their structures (e) describe the reaction of phenylamine with aqueous bromine (f) describe the formation of amides from the condensation reaction between RNH_2 and $\text{R}'\text{COCl}$ (g) explain why an amide is neutral in terms of delocalisation of the lone pair of electrons on nitrogen (h) describe the chemistry of amides, exemplified by the following reactions: (i) hydrolysis on treatment with aqueous alkali or acid (ii) reduction to amines with lithium aluminium hydride (i) describe the acid/base properties of amino acids and the formation of zwitterions [knowledge of isoelectric points is not required] (j) describe the formation of peptide (amide) bonds between α -amino acids, and hence explain protein formation (k) describe the hydrolysis of proteins