G. C. E. (Advanced Level)

CHEMISTRY

Grade 12

Resource Book

Unit 07. Basic concepts of organic chemistry
Unit 08. Hydrocarbons and halohydrocarbons
Unit 09. Oxygen containing organic compounds
Unit 10. Nitrogen containing organic compounds

Chemistry
Resource Book
Grade 12

Department of Science
Faculty of Science and Technology
National Institute of Education
Sri Lanka

Message from the Director General

The National Institute of Education takes opportune steps from time to time for the development of quality in education. Preparation of supplementary resource books for respective subjects is one such initiative.

Supplementary resource books have been composed by a team of curriculum developers of the National Institute of Education, subject experts from the national universities and experienced teachers from the school system. Because these resource books have been written so that they are in line with the G. C. E. (A/L) new syllabus implemented in 2017, students can broaden their understanding of the subject matter by referring these books while teachers can refer them in order to plan more effective learning teaching activities.

I wish to express my sincere gratitude to the staff members of the National Institute of Education and external subject experts who made their academic contribution to make this material available to you.

Dr. (Mrs.) T. A. R. J. Gunasekara
Director General
National Institute of Education
Maharagama.

Message from the Director

Since 2017, a rationalized curriculum, which is an updated version of the previous curriculum is in effect for the G.C.E (A/L) in the general education system of Sri Lanka. In this new curriculum cycle, revisions were made in the subject content, mode of delivery and curricular materials of the G.C.E. (A/L) Physics, Chemistry and Biology. Several alterations in the learning teaching sequence were also made. A new Teachers' Guide was introduced in place of the previous Teacher's Instruction Manual. In concurrence to that, certain changes in the learning teaching methodology, evaluation and assessment are expected. The newly introduced Teachers' Guide provides learning outcomes, a guideline for teachers to mould the learning events, assessment and evaluation.

When implementing the previous curricula, the use of internationally recognized standard textbooks published in English was imperative for the Advanced Level science subjects. Due to the contradictions of facts related to the subject matter between different textbooks and inclusion of the content beyond the limits of the local curriculum, the usage of those books was not convenient for both teachers and students. This book comes to you as an attempt to overcome that issue.

As this book is available in Sinhala, Tamil, and English, the book offers students an opportunity to refer the relevant subject content in their mother tongue as well as in English within the limits of the local curriculum. It also provides both students and teachers a source of reliable information expected by the curriculum instead of various information gathered from the other sources.

This book authored by subject experts from the universities and experienced subject teachers is presented to you followed by the approval of the Academic Affairs Board and the Council of the National Institute of Education. Thus, it can be recommended as a material of high standard.

Dr. A. D. A. De Silva
Director
Department of Science

A Note to Students from the Authors

This book has been written to specifically cover the contents of the Organic Chemistry units of the G.C.E. (A/L) Chemistry syllabus. The core content of the syllabus is concerned with the characteristic reactions of selected classes of compounds. Modern Organic Chemistry is founded on the basic idea that the chemical behavior of a compound can be accounted for by its structure. The book emphasizes the application of a limited number of fundamental concepts to rationalize and understand all the reactions covered. Simple descriptions of mechanisms are given and explained where relevant. Only the reactions specified in the syllabus are covered, and for any given reaction only the main product/products are considered. Experimental conditions are given only if they are critical.

The authors hope that the book will be useful to students to understand and appreciate organic chemistry, and to move away from rote memorization of isolated facts. This will build a solid foundation for more advanced study if the student wishes to do so.

Content

1. Basic Concepts of Organic Chemistry

Content

Introduction

Organic Chemistry is the chemistry of compounds of carbon. In these compounds, carbon atoms form the skeleton or backbone of the molecule. In addition to carbon, organic compounds usually contain hydrogen. Oxygen, nitrogen, sulphur, phosphorus and halogens are also found in certain organic compounds. These compounds can be natural or synthetic. Organic compounds form an essential component of all living organisms and play a central role in metabolic processes. Organic compounds also form an essential component in many of the materials that are essential for our daily life such as food, plastic items, textiles, cosmetics and medicines. The variety and number of compounds formed by carbon is very large compared to the compounds formed by other elements in the periodic table.

1.1 Organic chemistry in day to day life

Organic compounds are associated with nearly every aspect of our existence. For example:

> Food components: Carbohydrates, fats, proteins
> Plastic materials: PVC, polythene, polystyrene, polyesters, nylon
> Medicines: Paracetamol, aspirin, penicillin, amoxicillin
> Fuels: Petrol, diesel, kerosene, LP gas

1.1.1 Why carbon can form a large number of organic compounds with vast structural diversity? Uniqueness of carbon

Carbon-carbon and carbon-hydrogen bonds are the predominant bonds found in organic compounds. Between two C atoms strong single bonds, double bonds and triple bonds can be formed. The small electronegativity difference between C and H also leads to the formation of C–H covalent bonds. The presence of 4 electrons in its valence shell enables it to form 4 covalent bonds which include carbon-carbon double bonds and triple bonds. Due to these reasons, carbon is capable of forming linear and branched chains and rings leading to compounds with diverse carbon skeletons. As carbon can also form bonds with O, N, S, P and halogens, this leads to the formation of an enormous variety of organic compounds having a wide range of molecular weights. When compared to Si which is also in the fourth group of the periodic table to which C belongs, the C–C and C–H bonds possess higher bond energies than Si–Si and Si–H bonds. Some bond energies relevant to the discussion above are shown in **Table 1.1.**

Table 1.1 Bond energies of some bonds with C and Si

Bond	Bond energy/ kJ mol^{-1}
C–C	346
C=C	610
C≡C	835
C–H	413
Si–Si	226
Si–H	318

1.2 Diversity of organic compounds in terms of functional groups

Some organic compounds contain only C and H as the constituent elements. They are known as hydrocarbons. On the basis of the structure, hydrocarbons are divided into two main groups called aliphatic and aromatic. Hydrocarbons consisting of only open carbon chains are called as acyclic aliphatic hydrocarbons while those with cyclic carbon chains are called alicyclic hydrocarbons. The aliphatic hydrocarbons are classified as alkanes, alkenes, and alkynes. The cyclic organic compounds which are stabilized by forming a cyclic delocalized cloud of π electrons are called aromatic compounds. Benzene which is indicated by the molecular formula C_6H_6 is the simplest of aromatic hydrocarbon compounds. The classification of hydrocarbons is shown in the **Figure 1.1** with common examples of each type.
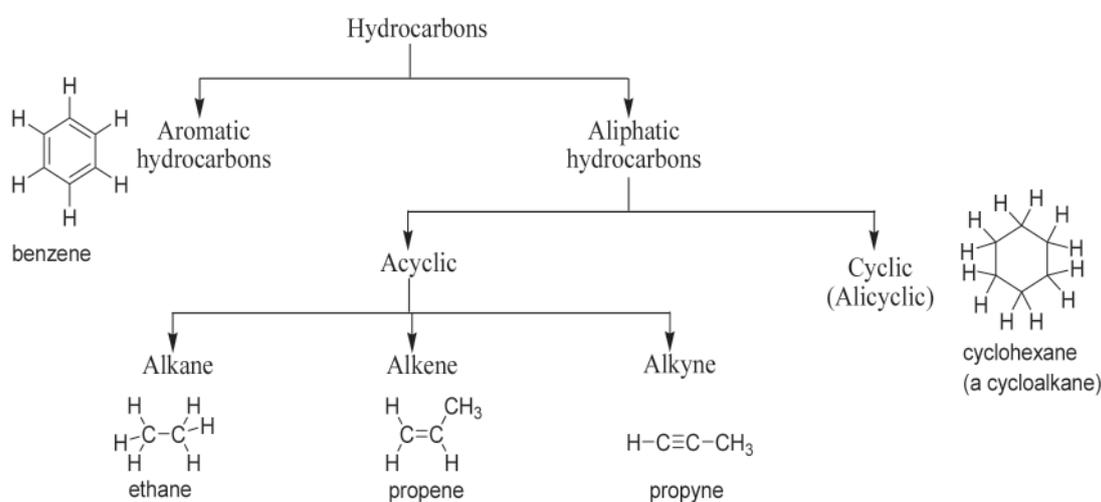
Figure 1.1 Classification of hydrocarbons

Note: Cycloalkanes, cycloalkenes and cycloalkynes are not included in the current G.C.E. (A/L) syllabus.

Compounds are classified according to the functional groups present in their molecules. A functional group is a group of atoms in a molecule where most of its reactions take place. Apart from the carbon-carbon double bond and carbon-carbon triple bond, a functional group contains one or more heteroatoms such as nitrogen and oxygen. Common functional groups and the names of the corresponding homologous series are given in **Table 1.2.**

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Table 1.2 Functional groups in organic compounds

Functional group	Name of the homologous series		Example with name	
$\diagdown C = C \diagup$	Alkene		$\begin{matrix} H \\ \diagdown \end{matrix} C = C \begin{matrix} H \\ \diagup \\ CH_3 \end{matrix}$	propene
$-C \equiv C-$	Alkyne		$H-C \equiv C-H$	ethyne
$-OH$	Alcohol		CH_3CH_2-OH	ethanol
$-\overset{\displaystyle O}{\underset{\displaystyle H}{C}}$	Aldehyde		$CH_3-\overset{\displaystyle O}{\underset{\displaystyle H}{C}}$	ethanal
$-\overset{\displaystyle O}{C}\diagdown$	Ketone		$CH_3-\overset{\displaystyle O}{\underset{\displaystyle CH_3}{C}}$	propanone
$-\overset{\displaystyle O}{\underset{\displaystyle O-H}{C}}$	Carboxylic acid		$CH_3-\overset{\displaystyle O}{\underset{\displaystyle O-H}{C}}$	ethanoic acid
$-\overset{\displaystyle O}{\underset{\displaystyle X}{C}}$	Acid halide	X = Cl; acid chloride X = Br; acid bromide	$CH_3-\overset{\displaystyle O}{\underset{\displaystyle Cl}{C}}$	ethanoyl chloride
$-\overset{\displaystyle O}{\underset{\displaystyle O-R}{C}}$	Ester		$CH_3-\overset{\displaystyle O}{\underset{\displaystyle O-CH_3}{C}}$	methyl ethanoate
$R_1-O\diagdown_{R_2}$	Ether		$CH_3-O\diagdown_{CH_2CH_3}$	ethylmethyl ether
$-\overset{\displaystyle O}{\underset{\displaystyle NH_2}{C}}$	Amide		$CH_3-\overset{\displaystyle O}{\underset{\displaystyle NH_2}{C}}$	ethanamide
$R_1-N\overset{R_2}{\underset{R_3}{\diagdown}}$	Amine		$CH_3CH_2-NH_2$ $CH_3CH_2-NH\diagdown_{CH_3}$	ethylamine ethylmethylamine
$-C \equiv N$	Nitrile		$CH_3CH_2-C \equiv N$	propanenitrile
$-X$	Alkyl halide	X = Cl; alkyl chloride X = Br; alkyl bromide X = I; alkyl iodide	CH_3CH_2-Cl CH_3CH_2-Br	chloroethane bromoethane
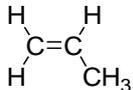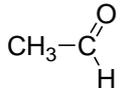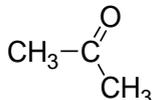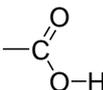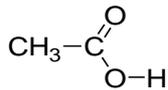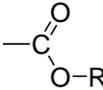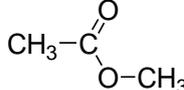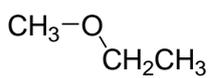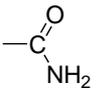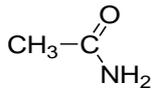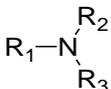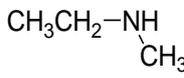
Note: Alkenes, alkynes, ethers and alkyl halides are not considered as functional groups in the IUPAC nomenclature system.

1.2.1   Classes of compounds with functional groups containing heteroatoms

1.2.1.1   Alcohol

Alcohols are compounds containing a hydroxyl group (–OH) attached to an alkyl group. Some examples are given in **Figure 1.2.**
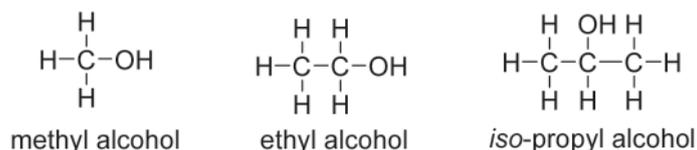
Figure 1.2 Some examples for alcohols

Note: An alkyl group is formally derived from an alkane by the removal of a hydrogen atom.

1.2.1.2   Ethers

Ethers are compounds containing an oxygen atom attached to two alkyl groups. Some examples are given in **Figure 1.3.**
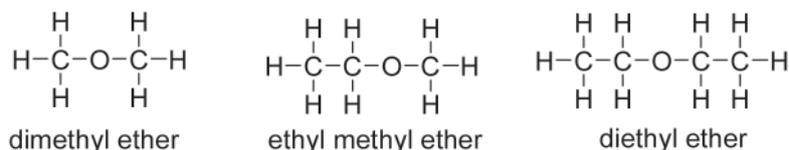
Figure 1.3 Some examples for ethers

1.2.1.3   Aldehyde

Aldehydes are compounds containing a carbonyl (C=O) group attached to an H atom. Some examples are given in **Figure 1.4.**
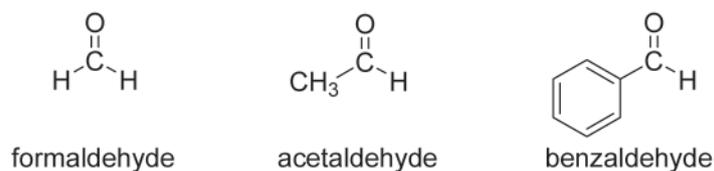
Figure 1.4 Some examples for aldehydes

1.2.1.4   Ketones

Ketones are compounds containing a carbonyl (C=O) group attached to two carbon atoms each of which may belong to an alkyl or aryl group. Some examples are given in **Figure 1.5.**
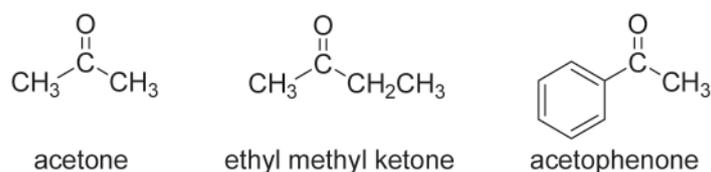
Figure 1.5 Some examples for ketones

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1.2.1.5 Alkyl halides

Alkyl halides are compounds containing a halogen atom bonded to an alkyl group. Some examples are given in **Figure 1.6.**

$$CH_3I \qquad CH_3CH_2Br \qquad \overset{\overset{\displaystyle Cl}{|}}{CH_3CHCH_3}$$

methyl iodide ethyl bromide *iso*-propyl chloride
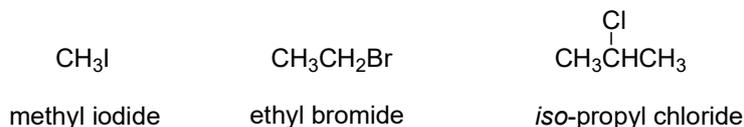
Figure 1.6 Some examples for alkyl halides

Note: Compounds containing a halogen atom joined to an aromatic ring are called aryl halides.

1.2.1.6 Carboxylic acids

Carboxylic acids are compounds containing the carboxylic acid (COOH) group. Some examples are given in **Figure 1.7.**

formic acid acetic acid benzoic acid
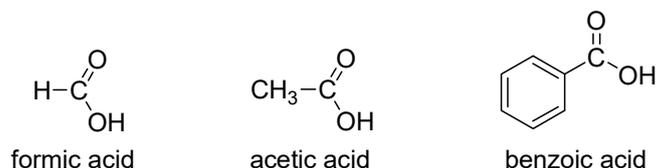
Figure 1.7 Some examples for carboxylic acids

1.2.1.7 Acid halides, esters and amides (derivatives of carboxylic acids)

Acid halides are compounds containing the COX group where X is a halogen atom. Esters are compounds containing the COOR group and amides are compounds containing the $CONH_2$ group. Some examples are given in **Figure 1.8.**

acetyl chloride ethyl acetate acetamide
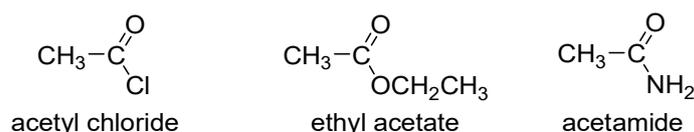
Figure 1.8 Some examples for derivatives of carboxylic acids

Note: Acid halides, esters and amides are derived by replacing the OH group in the COOH group by halogen, OR and NH_2 groups respectively.

1.2.1.8 Amines

Amines are compounds derived formally from ammonia by replacing its H atoms either by alkyl groups or aryl groups. Some examples are given in **Figure 1.9.**

$$CH_3CH_2NH_2 \qquad CH_3NHCH_2CH_3 \qquad \overset{\overset{\displaystyle CH_3}{|}}{CH_3NCH_3}$$

ethylamine ethylmethylamine trimethylamine aniline
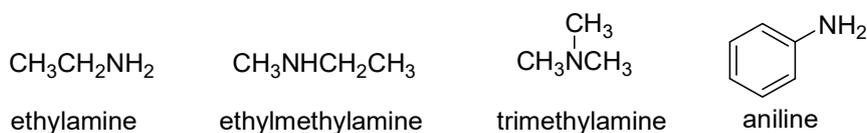
Figure 1.9 Some examples for amines

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1.3   IUPAC nomenclature of organic compounds

The set of rules for systematic nomenclature of organic compounds which is now in practice evolved through several international conferences and are known as International Union of Pure and Applied Chemistry rules (IUPAC rules). Therefore, this system of nomenclature is called the IUPAC nomenclature system. In addition to the IUPAC nomenclature many common organic compounds are known by trivial (non-systematic) names. Some examples are given at the end of this section.

1.3.1 IUPAC nomenclature

The IUPAC nomenclature system is governed by a large number of rules. In our discussion we will limit ourselves to understand the most important ones which can be used to name more common types of organic compounds. The most important feature of the IUPAC system would be that it will allow us to give one name to a given organic compound and to write only one structure for a given IUPAC name.

In this system, all the compounds with heteroatoms such as O, N, halogen, are considered to be derived from the corresponding hydrocarbon. Therefore, as a start, let us look at how hydrocarbons are named according to the IUPAC system of nomenclature.

1.3.2 Alkane hydrocarbons

All the names of saturated hydrocarbons end with the suffix **-ane.** The stem of the hydrocarbon name denotes the number of carbon atoms present in the longest carbon chain. Learning the stems is like learning to count in Organic Chemistry. Stem names up to 6 carbon atoms are given in **Table 1.3.**

Table 1.3 Stem names of hydrocarbons having up to six carbon atoms

Carbon Number	Stem name	Name of hydrocarbon	Structure
1	meth-	methane	CH_4
2	eth-	ethane	CH_3CH_3
3	prop-	propane	$CH_3CH_2CH_3$
4	but-	butane	$CH_3CH_2CH_2CH_3$
5	pent-	pentane	$CH_3CH_2CH_2CH_2CH_3$
6	hex-	hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$

Before we consider little more complex hydrocarbons, let us look at how we can name alkyl groups.

When we formally remove a H atom from an alkane an alkyl group is obtained. The name of an alkyl group ends with the suffix **-yl**. When the terminal H atom of an unbranched hydrocarbon is removed the unbranched alkyl group is formed. Some examples are given in **Table 1.4.**

Table 1.4 Some examples of alkyl groups

Hydrocarbon		Alkyl group	
H–CH$_3$	methane	–CH$_3$	methyl
H–CH$_2$CH$_3$	ethane	–CH$_2$CH$_3$	ethyl
H–CH$_2$CH$_2$CH$_3$	propane	–CH$_2$CH$_2$CH$_3$	propyl

1.3.3 Nomenclature of branched chain alkanes

Branched chain alkanes can be considered the hydrocarbons which have alkyl groups attached to its longest carbon chain. Let us go through the steps involved in naming of branched chain alkanes taking the following examples.
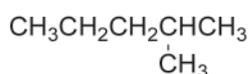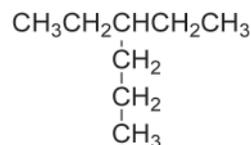
(1)   (2)

Step 1. Identify the longest continuous chain of carbon atoms and derive the hydrocarbon name.

(1)   (2)
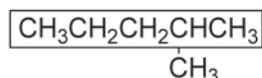
5 Carbon atoms – pentane   6 C atoms - hexane
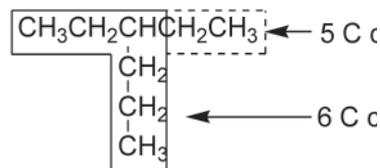
Note: A methyl group is attached to one of the C atoms of compound 1 and an ethyl group is attached to one of the C atoms of compound 2. A group that replaces an H atom of the hydrocarbon chain is called a substituent group. Therefore methyl group in compound 1 and ethyl group in compound 2 are substituents.

Step 2. Number the carbon atoms of the longest continuous carbon chain such that the C atom bearing the substituent group gets the lowest possible number.

(1)   (2)

8
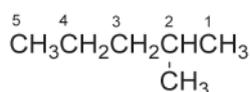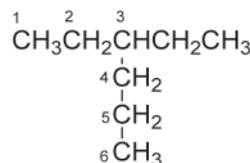
Note: The carbon chain of compound 1 is numbered from right to left. If the carbon chain of this compound is numbered from left to right, the carbon atom to which the methyl group is attached will be assigned number 4 which is a higher number than 2.

Step 3. Use the number obtained by applying the above step (2) to designate the location of the substituent. Write the name of the compound by placing the hydrocarbon name (name of the parent hydrocarbon) at last preceded by the substituent group with the number designating its location. Numbers are separated from words by a hyphen while numbers are separated by commas.

$$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H\overset{1}{C}H_3$$
$$\underset{CH_3}{|}$$

(1)
2-methylpentane

$$\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}HCH_2CH_3$$
$$\overset{4}{|}CH_2$$
$$\overset{5}{|}CH_2$$
$$\overset{6}{|}CH_3$$

(2)
3-ethylhexane

When two or more substituents are present they should get the lowest possible numbers designating their location on the longest carbon chain. The substituent groups should be placed alphabetically in the IUPAC name. Let us take two more examples.

	$\overset{1}{C}H_3\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H\overset{5}{C}H_2\overset{6}{C}H_3$ $\quad\underset{CH_3}{\|}\quad\quad\underset{CH_2CH_3}{\|}$	$\overset{CH_2CH_3}{\|}$ $\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}\overset{4}{C}H_2\overset{5}{C}H_3$ $\quad\quad\underset{CH_3}{\|}$
Longest hydrocarbon chain	Six - hexane	Five - pentane
Substituents and their location	2-methyl, 4-ethyl	3-methyl, 3-ethyl
IUPAC name	4-ethyl-2-methylhexane	3-ethyl-3-methylpentane

When two or more substituents are identical, they are indicated by the prefixes, di- (2), tri- (3), tetra- (4) etc. Every substituent should be given the number that shows its location on the longest carbon chain.

	$\overset{1}{C}H_3\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H\overset{5}{C}H_3$ $\quad\underset{CH_3}{\|}\quad\quad\underset{CH_3}{\|}$	$\overset{CH_3}{\|}$ $\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$ $\quad\quad\underset{CH_3}{\|}$
Longest hydrocarbon chain	Five - pentane	Six - hexane
Substituents and their location	2-methyl, 4-methyl	3-methyl, 3-methyl
IUPAC name	2,4-dimethylpentane	3,3-dimethylhexane

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1.3.4 Nomenclature of alkene and alkyne hydrocarbons

Alkenes contain carbon-carbon double bonds. According to IUPAC nomenclature, the suffix -ane is replaced by suffix -ene in alkenes with the number designating the location of the double bond in the parent hydrocarbon. Let us go through the steps involved in naming alkenes taking some examples.

$CH_3CH_2CH=CH_2$
(3)

$CH_3CH_2CH=CHCH_3$
(4)
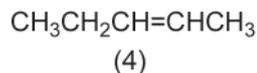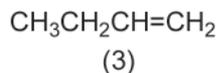
Step 1. Identify the longest continuous carbon chain including the carbon-carbon double bond. Number the carbon chain such that the double bond carbons get the lowest possible numbers.

$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H=\overset{1}{C}H_2$
(3)

$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H=\overset{2}{C}H\overset{1}{C}H_3$
(4)
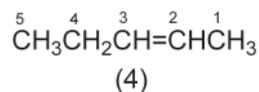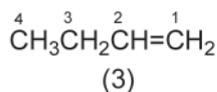
Step 2. Build the IUPAC name by placing the name representing the carbon number and suffix -ene with the lowest number designated to the location of the double bond.

	$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H=\overset{1}{C}H_2$ (3)	$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H=\overset{2}{C}H\overset{1}{C}H_3$ (4)
Longest carbon chain	Four - but	Five – pent
Double bond location	1,2	2,3
IUPAC name	but-1-ene (1-butene)	pent-2-ene (2-pentene)

Step 3. When substituents are present, they are placed in as prefixes along with the number designated to indicate their location in the longest carbon chain containing the double bond.

	$\overset{5}{C}H_3\overset{4}{C}H\overset{3}{C}H=\overset{2}{C}H\overset{1}{C}H_3$ $\underset{CH_3}{\shortmid}$	$\overset{6}{C}H_3\overset{5}{C}H\overset{4}{C}H_2\overset{3}{C}=\overset{2}{C}H\overset{1}{C}H_3$ $\underset{CH_3 \quad CH_3}{\shortmid \quad \shortmid}$
Longest carbon chain	Five - pent	Six - hex
Double bond location	2,3	2,3
Parent hydrocarbon name	pent-2-ene (2-pentene)	hex-2-ene (2-hexene)
Substituents with location	4-methyl	3-methyl, 5-methyl
IUPAC name	4-methylpent-2-ene (4-methyl-2-pentene)	3,5-dimethylhex-2-ene (3,5-dimethyl-2-hexene)

If the double bond gets the same set of numbers when the chain is numbered from either sides of the carbon chain, then the numbering should be done such that substituents get the lowest possible numbers.

	$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H=\overset{3}{C}H\overset{2}{C}H\overset{1}{C}H_3$ (numbered $\underset{1}{}\,\underset{2}{}\,\underset{3}{}\,\underset{4}{}\,\underset{5}{}\,\underset{6}{}$) $\underset{6}{C}H_3$	$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}=\overset{3}{C}H\overset{2}{C}H\overset{1}{C}H_3$ $\underset{6}{C}H_3 \quad \underset{6}{C}H_3$
Longest carbon chain	Six - hex	Six - hex
Double bond location	3, 4	3, 4
Parent hydrocarbon name	hex-3-ene (3-hexene)	hex-3-ene (3-hexene)
Substituents with location	2-methyl	2-methyl, 4-methyl
IUPAC name	2-methylhex-3-ene (2-methyl-3-hexene)	2,4-dimethylhex-3-ene (2,4-dimethyl-3-hexene)

Alkynes contain carbon-carbon triple bonds. They are named by replacing suffix **-ane** of alkane by suffix **-yne.** The rest follows similar to nomenclature of alkenes.

	$\overset{1}{C}H_3\overset{2}{C}\equiv\overset{3}{C}\overset{4}{C}H\overset{5}{C}H_3$ $\underset{}{C}H_3$	$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}\equiv\overset{3}{C}\overset{2}{C}H\overset{1}{C}H_3$ $\underset{}{C}H_3$
Longest carbon chain	Five - pent	Six - hex
Triple bond location	2, 3	3, 4
Parent hydrocarbon name	pent-2-yne (2-pentyne)	hex-3-yne (3-hexyne)
Substituents with location	4-methyl	2-methyl
IUPAC name	4-methylpent-2-yne (4-methyl-2-pentyne)	2-methylhex-3-yne (2-methyl-3-hexyne)

Let us now summarize the basic principles of naming hydrocarbons according to the IUPAC system. **This will be the foundation for the naming of compounds containing functional groups.**

(i) All the compounds are considered to be derived from the hydrocarbon containing the longest carbon chain.

(ii) When a double bond or a triple bond is present, the longest carbon chain should be chosen to include the double bond or the triple bond.

(iii) A suitable suffix (-ane, -ene or -yne) is added to the stem name which denotes the number of carbon atoms (parent hydrocarbon).

(iv) When double bonds or triple bonds are absent, the carbon atoms carrying substituents are given the lowest possible numbers.

(v) When a double bond or a triple bond is present it is given the lowest possible number.

(vi) Substituent names are placed as prefixes to the parent hydrocarbon name in the alphabetical order.

1.3.5 IUPAC nomenclature of compounds other than hydrocarbons

In this section nomenclature of compounds containing other functional groups **(Table 1.2)** will be discussed. This also follows the principles we have already discussed. In addition we now need a class name (suffix) to designate the functional group present in the molecule.

Let us take class names (suffixes) **(Table 1.5)** of some functional groups and study how these principles should be applied in naming compounds with one functional group.

Table 1.5 Class names of some functional groups

Functional group	Name of the homologous series	Class name (Suffix)
—OH	Alcohol	-ol
—C(=O)H (aldehyde group)	Aldehyde	-al
—C(=O) (ketone group)	Ketone	-one
—C(=O)O—H (carboxylic acid group)	Carboxylic acid	-oic acid

Let us now go through the steps involved in naming the following compounds.
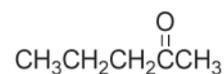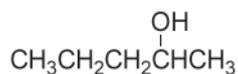
$CH_3CH_2CH_2CH_2OH$ $CH_3CH_2CH_2\overset{\overset{OH}{|}}{C}HCH_3$ $CH_3CH_2CH_2\overset{\overset{O}{\parallel}}{C}CH_3$

1. Identify the longest continuous carbon chain containing the functional group and number the carbon atoms of the carbon chain such that the C atom bearing the functional group gets the lowest possible number.

$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2OH$ $\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{\overset{\overset{OH}{|}}{C}}H\overset{1}{C}H_3$ $\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{\overset{\overset{O}{\parallel}}{C}}\overset{1}{C}H_3$

2. Derive the parent hydrocarbon name which shows the number of C atoms and whether it is saturated or contains a double bond or a triple bond.

$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2OH$	$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{\overset{\overset{OH}{|}}{C}}H\overset{1}{C}H_3$	$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{\overset{\overset{O}{\parallel}}{C}}\overset{1}{C}H_3$
4 C atoms: but	5 C atoms: pent	5 C atoms: pent
Saturated hydrocarbon chain: ane	Saturated hydrocarbon chain: ane	Saturated hydrocarbon chain: ane
but + ane; butane	pent + ane; pentane	pent + ane; pentane

3. Write the name of the compound by placing the hydrocarbon name deleting the last letter 'e' (name of the parent hydrocarbon) followed by the suffix identifying the functional group with the number designating its location.

$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2OH$$
butane + 1-ol
butan-1-ol (1-butanol)

$$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{\underset{\overset{|}{OH}}{C}}H\overset{1}{C}H_3$$
pentane + 2-ol
pentan-2-ol (2-pentanol)

$$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{\underset{\overset{||}{O}}{C}}\overset{1}{C}H_3$$
pentane + 2-one
pentan-2-one (2-pentanone)

The IUPAC names derived above give the following information:

(i) The number of C atoms in the longest continuous carbon chain (pent, but etc.).

(ii) The saturated nature of the carbon chain (-an-)

(iii) The functional group present in the molecule and its position (1-ol, 2-ol or 2-one).

Note: The hydroxyl group (OH) of alcohols can be positioned on any carbon atom including the terminal carbon atom of the carbon chain while the carbonyl group (C=O) of ketones cannot be positioned at the terminal carbon atom of the carbon chain. Thus in naming alcohols and ketones the number designating the location of the functional group has to be stated.

The carbonyl group (C=O) of the aldehydes and the carboxylic acids are always positioned at the terminal carbon atom of the carbon chain. Therefore it is not necessary to state the number designating their location.

Let us take the following two examples.

$$CH_3CH_2CH_2COOH \qquad\qquad CH_3CH_2CH_2CH_2CHO$$

1. Identify the longest continuous carbon chain containing the functional group and number the carbon atoms of the carbon chain such that the C atom of the functional group gets number 1.

$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}OOH \qquad\qquad \overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}HO$$

2. Derive the parent hydrocarbon name which shows the number of C atoms and whether it is saturated or contains a double bond or a triple bond.

$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}OOH \qquad\qquad \overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}HO$$
4 C atoms and saturated   5 C atoms and saturated
hydrocarbon (but + ane)   hydrocarbon (pent + ane)

3. Write the name of the compound by placing the hydrocarbon name deleting the last letter 'e' (name of the parent hydrocarbon) followed by the suffix identifying the functional group. Because aldehyde functional group and carboxylic acid functional group always get number 1, the number is not stated in the name.

$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}OOH$$
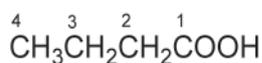
butane + oic acid
butanoic acid

$$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}HO$$
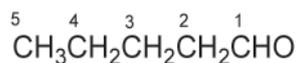
pentane + al
pentanal

Let us now take few examples containing alkyl substituents attached to the longest continuous carbon chain. Recall that aldehyde and carboxylic acid functional groups are always positioned at the terminal of the carbon chain. Hence the C of these two functional groups is given number 1 when numbering.

$$CH_3CHCH_2CHO$$
$$\quad | $$
$$\quad CH_3$$

$$CH_3CHCH_2CH_2COOH$$
$$\quad | $$
$$\quad CH_2CH_3$$
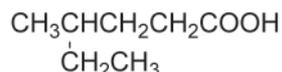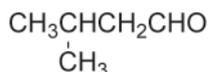
Let us go through the steps involved in naming the above examples.

1. Identify the longest continuous carbon chain containing the functional group and number the carbon atoms of the carbon chain such that the C atom of the functional group gets number 1.

$$\overset{4}{C}H_3\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}HO$$
$$\quad | $$
$$\quad CH_3$$

$$\overset{4}{C}H_3\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}H_2\overset{1}{C}OOH$$
$$\quad \overset{5}{C}H_2\overset{6}{C}H_3$$

2. Derive the parent hydrocarbon name which shows the number of C atoms and whether it is saturated or contains a double bond or a triple bond.

$$\overset{4}{C}H_3\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}HO$$
$$\quad | $$
$$\quad CH_3$$

$$\overset{4}{C}H_3\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}H_2\overset{1}{C}OOH$$
$$\quad \overset{5}{C}H_2\overset{6}{C}H_3$$
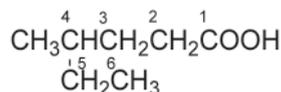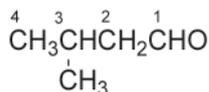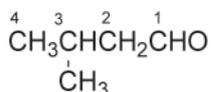
4 C atoms and saturated
hydrocarbon (but + ane)
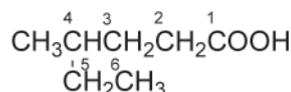
6 C atoms and saturated
hydrocarbon (hex+ ane)

3. Identify the substituent groups with the location.

$$\overset{4}{C}H_3\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}HO$$
$$\quad | $$
$$\quad CH_3$$
3-methyl
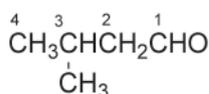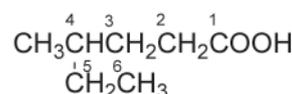
$$\overset{4}{C}H_3\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}H_2\overset{1}{C}OOH$$
$$\quad \overset{5}{C}H_2\overset{6}{C}H_3$$
4-methyl

4. Build the IUPAC name of the compound by placing the hydrocarbon name deleting the last letter 'e' (name of the parent hydrocarbon) followed by the suffix identifying the functional group. Place the substituent names with their locations as prefixes. When there are several substituents they should be placed in the alphabetical order.

$$\overset{4}{C}H_3\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}HO$$
$$\quad | $$
$$\quad CH_3$$
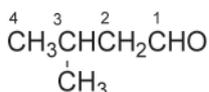
3-methyl+butane+al
3-methylbutanal

$$\overset{4}{C}H_3\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}H_2\overset{1}{C}OOH$$
$$\quad \overset{5}{C}H_2\overset{6}{C}H_3$$
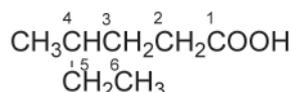
4-methyl+hexane+oic acid
4-methylhexanoic acid

Let us take two more examples.

	$\overset{5}{C}H_3\overset{4}{C}H\overset{3}{C}H_2\overset{2}{C}H\overset{1}{C}HO$ $\overset{|}{C}H_3 \quad \overset{|}{C}H_3$	$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H\overset{3}{C}H_2\overset{2}{C}H\overset{\overset{CH_3}{|}}{\overset{|}{C}}\overset{1}{C}OOH$ $\overset{|}{C}H_2CH_3$
Longest carbon chain	5C – pent	6C - hex
Parent hydrocarbon name	pentane	hexane
Functional group (with location)	1-al	1-oic acid
Substituents with locations	2-methyl, 4-methyl	2-methyl, 4-ethyl
IUPAC name	2,4-dimethylpentanal	4-ethyl-2-methylhexanoic acid

Carbon chains of compounds containing functional groups that can be placed on any carbon atom (such as alcohols and ketones) should be numbered such that the functional group gets the lowest possible number. Rest of the steps discussed will then be followed to build the IUPAC name.

Let us take few examples.

	$\overset{5}{C}H_3\overset{4}{C}H\overset{3}{C}H_2\overset{2}{C}H\overset{1}{C}H_2OH$ $\overset{|}{C}H_3 \quad \overset{|}{C}H_3$	$\overset{5}{C}H_3\overset{4}{C}H\overset{3}{C}H_2\overset{\overset{OH}{|}}{\overset{2}{C}}\overset{1}{C}H_3$ $\overset{|}{C}H_3 \quad \overset{|}{C}H_3$
Longest carbon chain	5C atoms - pent	5C atoms - pent
Parent hydrocarbon name	pentane	pentane
Functional group (with location)	OH at C-1 (1-ol)	OH at C-2 (2-ol)
Substituents with locations	2-methyl, 4-methyl	2-methyl, 4-methyl
IUPAC name	2,4-dimethylpentan-1-ol 2,4-dimethy- lpentanol	2,4-dimethylpentan-2-o1 2,4-dimethyl-2-pentanol

	$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H\overset{\overset{O}{\overset{||}{3}}}{C}-\overset{\overset{CH_3}{|}}{\overset{2}{C}}H\overset{1}{C}H_3$ $\overset{|}{C}H_2CH_3$	$\overset{1}{C}H_3\overset{\overset{O}{\overset{||}{2}}}{C}\overset{3}{C}HCH_3$ $\overset{4}{C}H_3\overset{5}{C}HCH_3$
Longest carbon chain	6C atoms - hex	5C atoms - pent
Parent hydrocarbon name	hexane	pentane
Functional group (with location)	C=O at C-3 (3-one)	C=O at C-2 (2-one)
Substituents with locations	2-methyl, 4-ethyl	3-methyl, 4-methyl
IUPAC name	4-ethyl-2-methylhexan-3-one 4-ethyl-2-methyl-3-hexanone	3,4-dimethylpentan-2-one 3,4-dimethyl-2-pentanone

When the compound contains a double bond or a triple bond (a multiple bond), the longest chain must contain both the functional group and the multiple bond. Accordingly the parent hydrocarbon will be either an alkene or an alkyne. Rest of the steps discussed will then be followed to build the IUPAC name. Let us take a look at few examples.

	$\overset{CH_3}{\underset{5}{CH_3}\overset{}{C}}\overset{4}{=}\overset{3}{CH}\overset{2}{CH}\overset{1}{CHCO_2H}$ $\underset{CH_3}{}$	$\overset{CH_2CH_3}{\underset{4}{CH_2}}\overset{3}{=}\overset{2}{CCHCH_3}\overset{1}{}$ $\underset{OH}{}$
Longest carbon chain	5C atoms - pent	4C atoms - but
Functional group with location	oic acid	2-ol
Double/triple bond with location	3-ene	3-ene
Parent hydrocarbon name	pent-3-ene	but-3-ene
Substituents with locations	2-methyl, 4-methyl	3-ethyl
IUPAC name	2,4-dimethylpent-3-enoic acid 2,4-dimethyl-3-pentenoic acid	3-ethylbut-3-en-2-ol 3-ethyl-3-buten-2-ol

	$\overset{CH_3}{\underset{6}{CH_3}}\overset{5}{C}\overset{4}{=}\overset{3}{CH}\overset{2}{CHCCH_3}\overset{1}{}$ $\underset{CH_3}{} \underset{O}{}$	$\overset{CH_3}{\underset{6}{CH_3}}\overset{5}{C}\overset{4}{\equiv}\overset{3}{C}\overset{2}{CHCH_2}\overset{1}{CHO}$
Longest carbon chain	6C atoms - hex	6C atoms - hex
Functional group with location	2-one	al
Double/triple bond with location	4-ene	4-yne
Parent hydrocarbon name	hex-4-ene	hex-4-yne
Substituents with locations	3-methyl, 5-methyl	3-methyl
IUPAC name	3,5-dimethylhex-4-en-2-one	3-methylhex-4-ynal
	3,5-dimethyl-4-hexen-2-one	3-methyl-4-hexynal

1.3.6 IUPAC nomenclature of compounds containing more than one functional group

There are many organic compounds containing several functional groups. Recall that in the foregoing discussion you learnt that compounds are named according to their functional group. In the IUPAC nomenclature system, functional groups are arranged in a priority order. When there are two functional groups in a molecule, the compound is named according to the functional group that gets the highest priority. The functional group with the highest priority is called the principal functional group. The remaining functional group is considered as a

substituent. When a functional group is considered as substituent, it is given a different name to be used as a prefix. The carbon chain is numbered so that the principal functional group gets the lowest possible number. Class names and substituent names of some functional groups are given in **Table 1.6** in the order of their priority.

Table 1.6 Class names and substituent names of some functional groups in their priority order

Functional group	Name of the homologous series	Substituent name (prefix)	Class name (suffix)
-COOH	Carboxylic acid	-	oic acid
-COOR	Ester	-	oate
-COCl	Acid chloride	-	oyl chloride
-CONH$_2$	Amide	-	amide
-CN	Nitrile	cyano	nitrile
-CHO	Aldehyde	formyl	al
-CO-	Ketone	oxo	one
-OH	Alcohol	hydroxy-	ol
-NH$_2$	Amine	amino	amine
-F		fluoro-	-
-Cl		chloro-	-
-Br		bromo-	-
-I		iodo-	-
- NO$_2$		nitro	-

Note: alkene (C=C) as "ene" and alkyne (C≡C) as "yne" are used as suffixes.

$$\overset{5}{C}H_3\overset{4}{C}=\overset{3}{C}H\overset{2}{C}\overset{1}{C}O_2H$$

(structure with CH$_3$ groups and OH)

Longest carbon chain	5C atoms - pent
Functional group with highest priority and its location	oic acid
Double/triple bond with location	3-ene
Parent hydrocarbon name	pent-3-ene
Substituents with locations	2-hydroxy, 2-methyl, 4-methyl
IUPAC name	2-hydroxy-2,4-dimethylpent-3-enoic acid 2-hydroxy-2,4-dimethyl-3-pentenoic acid

$$\overset{\overset{\displaystyle CH_3}{|}}{\underset{6}{CH_3}}\overset{5}{C}\overset{4}{CH_2}\overset{\overset{\displaystyle O}{\|}}{\underset{3}{C}}\overset{2}{C}H\overset{1}{O}H$$ (with CH_3 on C5 and CH_3 / OH on lower positions)

Longest carbon chain	6C atoms - hex
Functional group with highest priority and its location	3-one
Double/triple bond with location	none
Parent hydrocarbon name	hexane
Substituents with locations	2-hydroxy, 5,5-dimethyl
IUPAC name	2-hydroxy-5,5-dimethylhexan-3-one 2-hydroxy-5,5-dimethyl-3-hexanone

$$\underset{6}{CH_3}\overset{5}{C}=\overset{4}{CH}\overset{\overset{\displaystyle CH_3}{|}}{\underset{3}{C}}\overset{\overset{\displaystyle CH_3}{|}}{\underset{2}{C}H}\overset{1}{C}O_2H \quad (C3 = O)$$

Longest carbon chain	6C atoms - hex
Functional group with highest priority and its location	oic acid
Double/triple bond with location	4-ene
Parent hydrocarbon name	hex-4-ene (4-hexene)
Substituents with locations	3-oxo, 2-methyl, 5-methyl
IUPAC name	2,5-dimethyl-3-oxohex-4-enoic acid 2,5-dimethyl-3-oxo-4-hexenoic acid
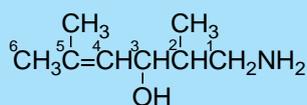
$$\underset{6}{CH_3}\overset{5}{C}=\overset{4}{CH}\overset{\overset{\displaystyle CH_3}{|}}{\underset{3}{C}H}\overset{\overset{\displaystyle CH_3}{|}}{\underset{2}{C}H}\overset{1}{C}H_2NH_2 \quad (C3: OH)$$

Longest carbon chain	6C atoms - hex
Functional group with highest priority and its location	3-ol
Double/triple bond with location	4-ene
Parent hydrocarbon name	hex-4-ene (4-hexene)
Substituents with locations	1-amino, 2,5-dimethyl
IUPAC name	1-amino-2,5-dimethylhex-4-en-3-ol 1-amino-2,5-dimethyl-4-hexen-3-ol

$$\overset{5}{C}H_3\overset{4}{C}H\overset{3}{C}\overset{2}{C}H_2\overset{1}{C}H_2OH$$

with CH_3 on C4 and O (double bond) on C3

Longest carbon chain	5C atoms - pent
Functional group with highest priority and its location	3-one (when numbered from either side) In such a case, the direction of numbering is chosen so as to give the lowest possible numbers to the substituent groups.
Parent hydrocarbon name	pentane
Substituents with locations	1-hydroxy, 4-methyl
IUPAC name	1-hydroxy-4-methylpentan-3-one 1-hydroxy-4-methyl-3-pentanone
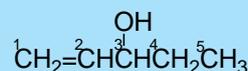
$$\overset{1}{C}H_2=\overset{2}{C}H\overset{3}{C}H\overset{4}{C}H_2\overset{5}{C}H_3$$

with OH on C3

Longest carbon chain	5C atoms - pent
Functional group with highest priority and its location	3-ol (when numbered from either side) In this case, we should give the lowest possible number to the double bond.
Double/triple bond with location	1-ene
Parent hydrocarbon name	pent-1-ene (1-pentene)
Substituents with locations	none
IUPAC name	pent-1-en-3-ol 1-penten-3-ol

$$\overset{1}{C}H_2=\overset{2}{C}-\overset{3}{C}-\overset{4}{C}H\overset{5}{C}H_2OH$$

with O (double bond) on C3, CH_3 on C4, and CH_3 on C2

Longest carbon chain	5C atoms - pent
Functional group with highest priority and its location	3-one (when numbered from either side). The lowest possible number should be given to the double bond. Recall how the substituted alkene and alkynes were named.
Double/triple bond with location	1-ene
Parent hydrocarbon name	pent-1-ene (1-pentene)
Substituents with locations	5-hydroxy, 2,4-dimethyl
IUPAC name	5-hydroxy-2,4-dimethylpent-1-en-3-one 5-hydroxy-2,4-dimethyl-1-penten-3-one
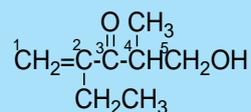
	$\overset{O}{\underset{1}{CH_2}}=\overset{2}{C}-\overset{3}{C}-\overset{4}{CH}\overset{CH_3}{\underset{5}{CH_2OH}}$ $\underset{CH_2CH_3}{}$
Longest carbon chain	5C atoms - pent (not hex; the carbon chain should include the C=C).
Functional group with highest priority and its location	3-one
Double/triple bond with location	1-ene
Parent hydrocarbon name	pent-1-ene (1-pentene)
Substituents with locations	5-hydroxy, 2-ethyl, 4-methyl
IUPAC name	2-ethyl-5-hydroxy-4-methylpent-1-en-3-one 2-ethyl-5-hydroxy-4-methyl-1-penten-3-one

Let us now summarize the stepwise approach to build the IUPAC name of a compound (other than hydrocarbons).

1.   Identify the longest hydrocarbon chain which includes the functional group having the highest priority (principal functional group) (Table 1.6) and any double or triple bonds.

2.   Number the hydrocarbon chain:

   a.   Such that the principal functional group gets the lowest possible number.

   b.   If the principal functional group gets the same number when the hydrocarbon chain is numbered from different directions, then the direction giving the lowest possible number to the multiple bond is chosen.

   c.   If the principal functional group gets the same number when the hydrocarbon chain is numbered from different directions and multiple bonds are absent, then the direction giving the lowest possible numbers to the substituents is chosen.

3.   Derive the hydrocarbon name using the name designated for the number of C atoms and suffix for the saturation or unsaturation with its position number (ane, ene or yne).

4.   Add the suffix designating the principal functional group.

5.   Add prefixes designating the substituent groups along with their position numbers.

6.   Then build the IUPAC name as follows:

Prefix	+	**Hydrocarbon name**	+	**Suffix**
Substituent groups with position numbers		Number of C atoms and suffix for the saturation or unsaturation with its position number		Class name of the principal functional group

Trivial Names

Prior to the development of systematic nomenclature organic compound were known by trivial (common) names. As the trivial names of common compounds are still used by chemists it is advisable to be familiar with these names. Trivial names of some common compounds and their corresponding IUPAC names are given in **Table 1.7.**

Table 1.7 Trivial names of some common compounds and their IUPAC names.

Compound	Trivial name	IUPAC name
CH_3COOH	acetic acid	ethanoic acid
CH_3CHO	acetaldehyde	ethanal
CH_3COCH_3	acetone	propanone
CH_3CN	acetonitrile	ethanenitrile
$HC{\equiv}CH$	acetylene	ethyne
$CHCl_3$	chloroform	trichloromethane
$HOCH_2CH_2OH$	ethylene glycol	ethane-1,2-diol
$HCHO$	formaldehyde	methanal
$HCOOH$	formic acid	methanoic acid

1.4 Isomerism

Isomerism is the existence of different compounds that have the **same molecular formula.** Different compounds having the same molecular formula are called isomers. Isomers can be subdivided into constitutional isomers and stereoisomers.

1.4.1 Constitutional (structural) isomerism

Isomers that differ from the order in which the constituent atoms are connected to each other are called **constitutional isomers.** Hence they have different structural formulae. A few examples of constitutional isomers are shown in **Table 1.8**.

Table 1.8 Some examples of constitutional isomers

Molecular formula	Constitutional isomers		
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	$CH_3\overset{CH_3}{\underset{}{C}HCH_2CH_3}$	$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_3$
C_3H_8O	$CH_3CH_2CH_2OH$	$CH_3\overset{CH_3}{\underset{}{C}HOH}$	$CH_3CH_2OCH_3$
C_4H_8O	$CH_3CH_2CH_2\overset{H}{\underset{}{C}}{=}O$	$CH_3\overset{CH_3}{\underset{H}{C}H}C{=}O$	$CH_3CH_2\overset{CH_3}{\underset{}{C}}{=}O$

Constitutional isomers are generally subdivided into *chain isomers, position isomers and functional group isomer*s. These subdivisions are not exclusive and can overlap.

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Chain isomers: Chain isomers are those which have different hydrocarbon chains for same molecular formula **(Figure 1.10)**.

$$CH_3CH_2CH_2CH_2CH_2OH \quad CH_3\overset{CH_3}{\underset{|}{CH}}CH_2CH_2OH \quad CH_3\overset{CH_3}{\underset{\underset{CH_3}{|}}{\overset{|}{C}}}CH_2OH$$
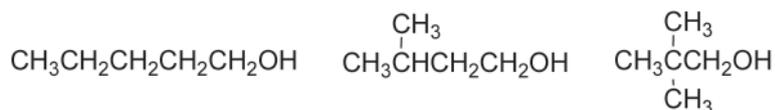
Figure 1.10 Chain isomers for the molecular formula $C_5H_{12}O$

Position isomers: Position isomers are those which have the same functional group and/or substituents in different positions in the same carbon chain **(Figure 1.11)**.

$$CH_3CH_2CH_2OH \qquad CH_3\overset{OH}{\underset{|}{CH}}CH_3 \qquad CH_3CH_2C\equiv CH \qquad CH_3C\equiv CCH_3$$

1-propanol   2-propanol   1-butyne   2-butyne

Position isomers for the molecular   Position isomers for the molecular
formula C_3H_8O formula C_4H_6
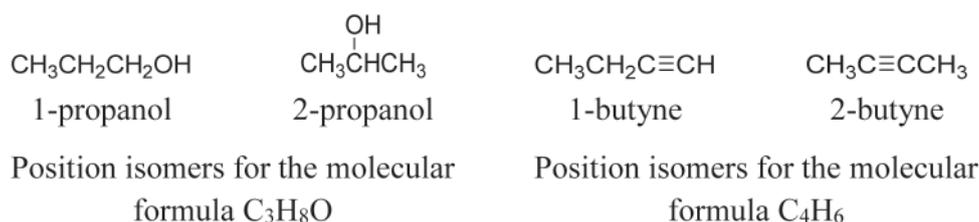
Figure 1.11 Examples of position isomers

Functional group isomers: Functional group isomers are those which have different functional groups in compounds having the same molecular formula **(Figure 1.12)**.

$$CH_3CH_2CH_2OH \qquad CH_3CH_2OCH_3 \qquad CH_3CH_2\overset{O}{\overset{\|}{C}}H \qquad CH_3\overset{O}{\overset{\|}{C}}CH_3$$

1-propanol   ethylmethylether   propanal   propanone

Functional group isomers for the   Functional group isomers for the
molecular formula C_3H_8O molecular formula C_3H_6O
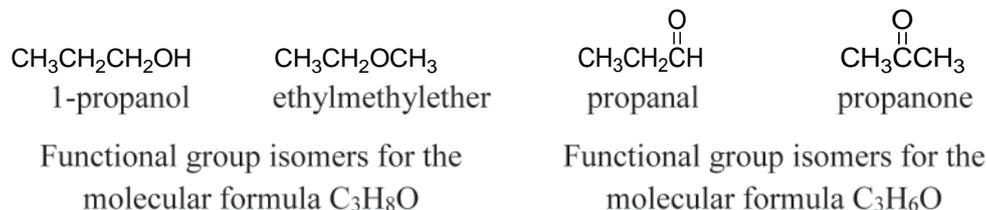
Figure 1.12 Examples of functional group isomers

Chain isomerism, position isomerism and functional group isomerism can overlap. Take a look at the isomers which have been drawn for the molecular formula C_4H_8O **(Figure 1.13)**.

$$CH_3CH_2CH_2CHO \qquad CH_3\overset{CH_3}{\underset{|}{CH}}CHO \qquad CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$$

$$CH_2=CHCH_2CH_2OH \qquad CH_3CH=CHCH_2OH$$

$$CH_2=CHCH_2OCH_3 \qquad CH_3CH=CHOCH_3 \qquad CH_2=CHOCH_2CH_3$$

$$CH_2=\overset{CH_3}{\underset{|}{C}}CH_2OH \qquad CH_2=\overset{CH_3}{\underset{|}{C}}OCH_3 \qquad CH_3\overset{OH}{\underset{|}{CH}}CH=CH_2$$
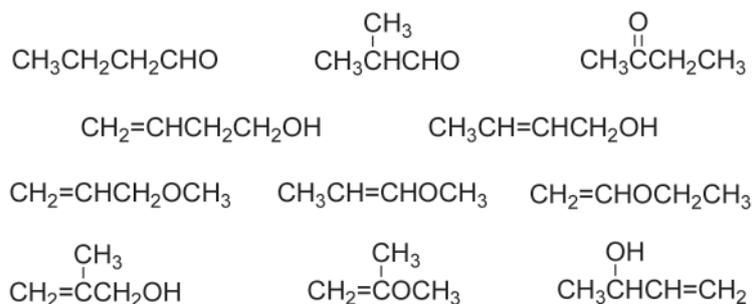
Figure 1.13 Constitutional isomers for the molecular formula C_4H_8O

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1.4.2 Stereoisomerism

Stereoisomerism is the existence of compounds whose structures differ from each other only in the orientation of bonds in three-dimensional space. **Stereoisomers** have the same structural formulae. They have the same connectivity: their constituent atoms are connected in the same order but differ in the manner in which atoms or groups are arranged in three-dimensional space. Therefore their structures cannot be **superimposed** on each other even though they have the same molecular and structural formulae. Pair of stereoisomers whose three-dimensional structures are mirror images of each other are **enantiomers** of each other. Pairs of stereoisomers whose three-dimensional structures are not mirror images of each other are **diastereomers** of each other.

The different types of isomers described above and their classification is shown in **Figure 1.14.**
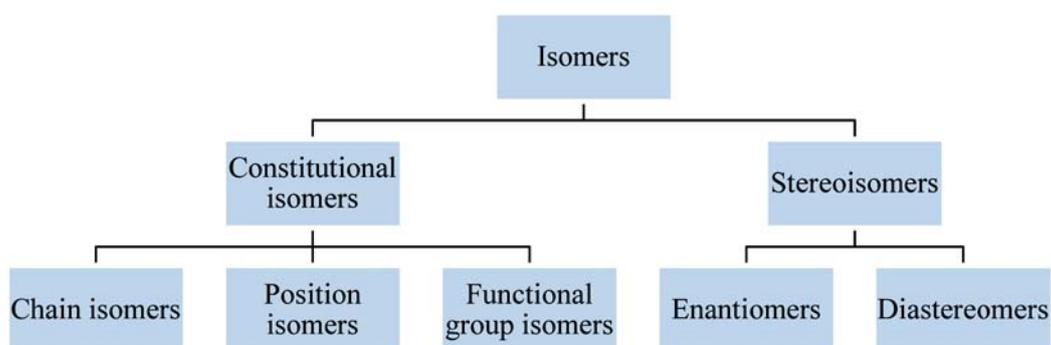
Figure 1.14 Classification of isomers

Diastereomerism

Geometric isomerism is one occasion where diastereomerism is seen. A C=C double bond consists of a σ-bond and a π-bond. Due to the π bond, the two carbon atoms cannot freely rotate about the σ-bond. Both alkene carbon atoms and the four atoms attached to them are all in one plane. For geometrical isomers to exist, the two groups attached to each carbon atom of the double bond should not be identical. In such an instance it is possible to have two compounds which differ from each other in the spatial arrangements of the groups joined to the two carbon atoms. These two compounds cannot be superimposed on each other and cannot interconvert by rotation around the carbon-carbon bond axis (due to the π-bond). Such compounds are known as geometrical isomers.

For example,

are diastereoisomers because the structures cannot be superimposed on each other.

However,

are the same because the structures can be superimposed on each other.

Cis and *trans nomenclature*

In alkenes the words *cis* and *trans* are used to indicate the geometrical relationship of two groups attached to different carbon atoms in the same double bond. Consider a plane passing through the C=C which is perpendicular to the plane of the molecule (See Figure 1.15). If the two groups are on the same side of this plane, then the relationship is *cis*. Observe that in **Figure 1.15** the two H-atoms are *cis* to each other and the two methyls are also *cis* to each other.
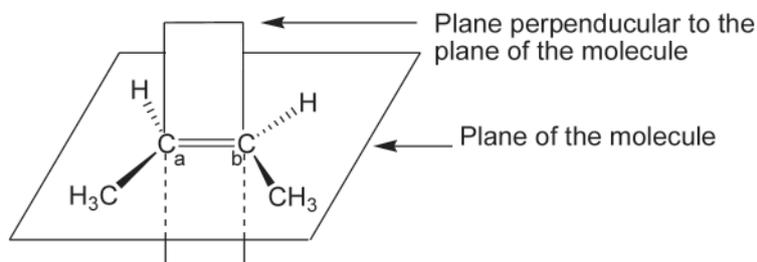
Figure 1.15 *cis*-2-butene showing the plane perpendicular to the plane of the molecule

If the two groups are on opposite sides of the plane then the relationship is *trans*. Observe that H atom on C_a is *trans* to the methyl group on C_b (see **Figure 1.16**).

Note that the geometrical isomer of *cis*-2-butene is *trans*-2-butene in which the two methyl groups are *trans* to each other (the two H atoms are also *trans* to each other).
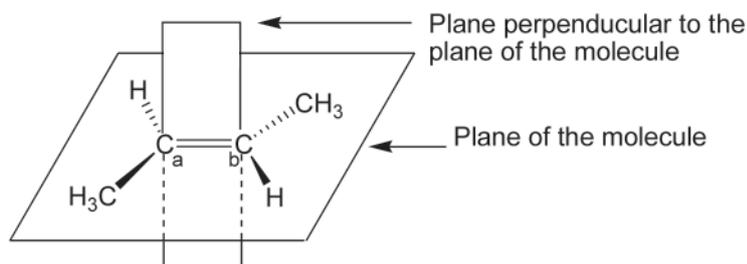
Figure 1.16 *trans*-2-butene

Enantiomerism

Isomers which are mirror images of each other are known as enantiomers (see **Figure 1.17**). A compound having a carbon atom which is joined to four different groups shows enantiomerism. Such a carbon atom is known as an asymmetric or chiral carbon atom. When plane polarized light is passed through a solution containing only one enantiomer, the plane of polarization rotates.

One enantiomer rotates the plane of polarization in one direction and the other enantiomer in the opposite direction. As the enantiomers rotate the plane of polarization, they are also known as optical isomers. Compounds which rotate the plane of plane polarized light are known as optically active compounds.
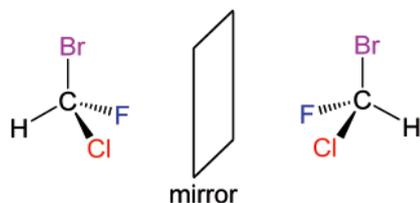
Figure 1.17 Enantiomers of bromochlorofluoromethane

Observe that the above mirror images of each other are not superimposable.

Note: Stereoisomers which are not mirror images of each other are known as diastereomers. Therefore geometrical isomers are diastereomers.
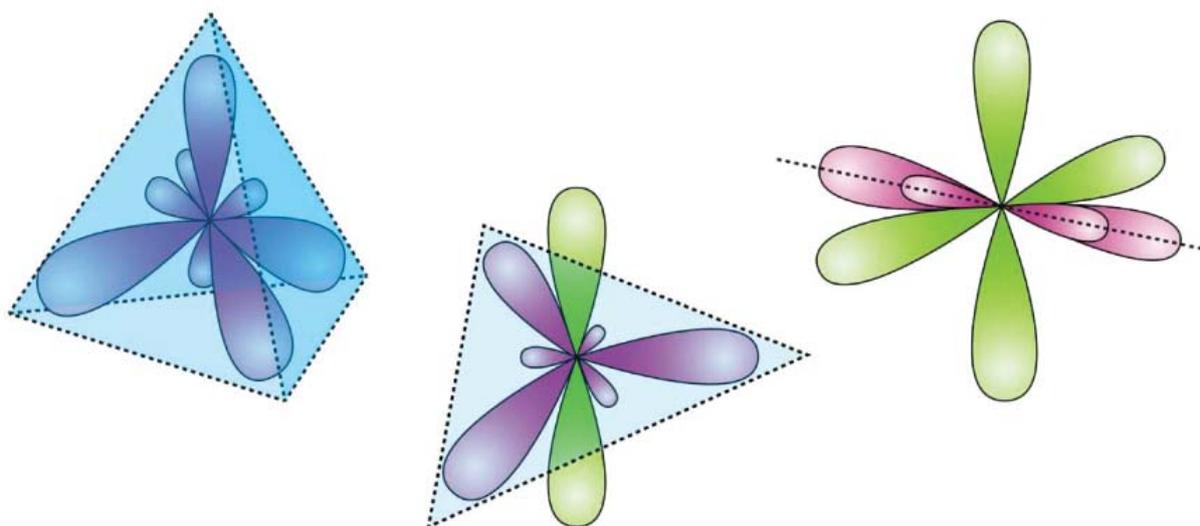
2. Hydrocarbons & Halohydrocarbons

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Introduction

Hydrocarbons are compounds containing only carbon and hydrogen. We have already discussed that aliphatic hydrocarbons are classified as alkanes, alkenes and alkynes. Halohydrocarbons are compounds containing one or more halogen atoms in addition to carbon and hydrogen.

2.1 Structure, physical properties and nature of bonds of aliphatic hydrocarbons

Alkane hydrocarbons are saturated hydrocarbons. Only carbon-hydrogen and carbon-carbon single bonds are found in these compounds. Methane (CH_4) is the simplest alkane hydrocarbon and it contains only one carbon atom. There are four hydrogen atoms attached to this carbon atom by four single bonds. The alkane which contains two carbon atoms is ethane (C_2H_6). In ethane the two carbons are bonded to each other with a single bond and each of these carbon atoms is bonded to three hydrogen atoms. The alkane with three carbon atoms is propane (C_3H_8). It will be noticed that the formula of ethane differs from that of methane by CH_2, and that the formula of propane differs from that of ethane also by CH_2. If two consecutive members of a series of compounds differ only by a CH_2 unit, such a series of compounds is called a homologous series.

A homologous series is a series of compounds with similar chemical properties which share the same general formula in which consecutive members of a series of compounds differ only by a CH_2 unit. The general formula of an alkane is C_nH_{2n+2} (where n = 1, 2, 3, ...) and all alkanes except cyclic alkanes follow this general formula.

2.1.1 Properties of alkanes

An alkane molecule is non-polar or very weakly polar. The attractive forces between two non-polar molecules are the dispersion forces. While the first few members of the series are gases at room temperature, the higher members are liquids and solids. As a result of increase in surface area down the series, dispersion forces also increase. While this leads to the aforesaid variation in the physical states of hydrocarbons, it also results in increase of the boiling points and melting points of unbranched hydrocarbons with the increase in molecular weight **(Table 2.1).**

Table 2.1 Melting points, boiling points and densities of some straight chain alkanes, showing regular increase of the property with the carbon number

Name	Formula	Melting point/ °C	Boiling point/ °C	Density (at 20 °C)/ g cm^{-3}
methane	CH_4	-183	-162	
ethane	CH_3CH_3	-172	-88.5	
propane	$CH_3CH_2CH_3$	-187	-42	
butane	$CH_3(CH_2)_2CH_3$	-138	-0.5	
pentane	$CH_3(CH_2)_3CH_3$	-130	36	0.626

Name	Formula	Melting point/ °C	Boiling point/ °C	Density (at 20 °C)/ g cm^{-3}
hexane	$CH_3(CH_2)_4CH_3$	-95	69	0.659
heptane	$CH_3(CH_2)_5CH_3$	-90.5	98	0.659
octane	$CH_3(CH_2)_6CH_3$	- 57	126	0.659
nonane	$CH_3(CH_2)_7CH_3$	- 54	151	0.718
decane	$CH_3(CH_2)_8CH_3$	- 30	174	0.730

With branching of the carbon chain the surface area of a molecules decreases and consequently dispersion forces become weaker and the boiling point decreases. As can be seen from the data given in **Table 2.2** the boiling points of alkanes with five carbon atoms decrease with the increase in branching of the carbon chain.

Table 2.2 Reduction of boiling points of isomeric pentanes as the branching occurs

Compound	Boiling point/ °C
pentane	36
2-methylbutane	28
2,2-dimethylpropane	9

2.1.2   Structure of alkanes

Let us consider the bonding of the simplest alkane, methane (CH_4). The carbon atom forms four covalent bonds with four hydrogen atoms. A covalent bond is formed by the overlap of two orbitals of two different atoms, each of which contains one electron. As the carbon atom in its ground state has only two p orbitals (p_x and p_y) containing one electron each, it could form only two covalent bonds at right angles to each other (recall that electronic configuration of C in its ground state is $1s^2 2s^2 2p^2$). If the two electrons in the $2s$ orbital are unpaired and one electron is promoted to the p_z orbital, then the carbon atom would have four orbitals, each containing one electron to form four bonds to four hydrogen atoms. The energy required to unpair and promote an electron could be compensated by the energy released by the formation of two extra bonds.

However, this overlap would result in a CH_4 molecule where three of the C–H bonds will be at right angles to each other and one C-H bond will not have any directionality. This would lead to a methane molecule which would have two types of C–H bonds. In order to explain the fact that in methane all four C–H bonds are equivalent, the $2s$ orbital and the three $2p$ orbitals are considered to be mixed with each other, to generate four equivalent orbitals pointing to the apices of a tetrahedron **(Figure 2.1)**.
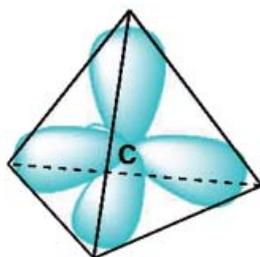
Figure 2.1 Shape and arrangement of sp^3 hybrid orbitals of carbon

The mixing of orbitals to generate new orbitals is termed 'hybridization'. The new orbitals are termed hybrid orbitals to differentiate them from pure atomic orbitals. In methane, the four hybrid orbitals of carbon are called sp^3 hybrid orbitals as one s orbital and three p orbitals are mixed to generate them. Such carbon atoms are referred to as **'sp^3 hybridized carbon'**. The energy of the sp^3 hybrid orbitals lies between the energy of the s orbital and the p orbitals **(Figure 2.2)**.
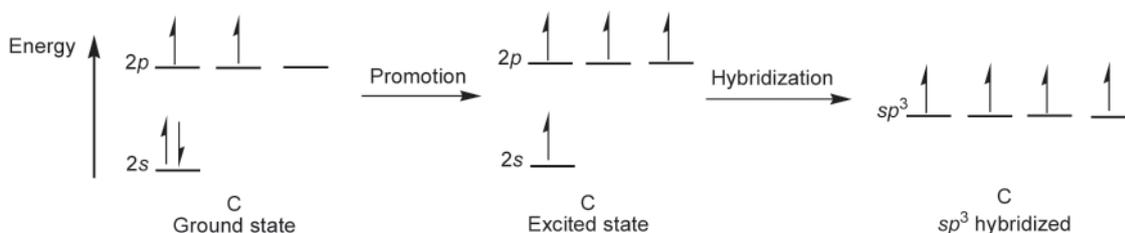
Figure 2.2 Graphical representation of hybridization of carbon in methane

In methane each of these four sp^3 hybridized orbitals overlap with s orbital of H atoms and forms four C–H bonds. The angle between any of these two C–H bonds is 109.5° and the four H atoms of methane are located at the apices of a tetrahedron **(Figure 2.3)**.
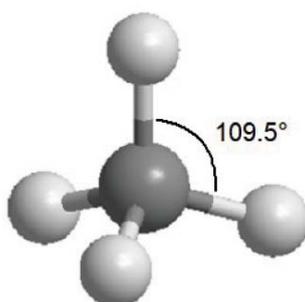
Figure 2.3 Tetrahedral shape of methane (CH_4) molecule

All carbon atoms joined to four other atoms in any organic compound are considered sp^3 hybridized. In alkanes, the carbon-hydrogen bonds are formed by the overlap of a sp^3 hybrid orbital of carbon with a $1s$ orbital of hydrogen while the carbon-carbon bonds are formed by the overlap of two sp^3 hybrid orbitals of two carbon atoms **(Figure 2.4)**.
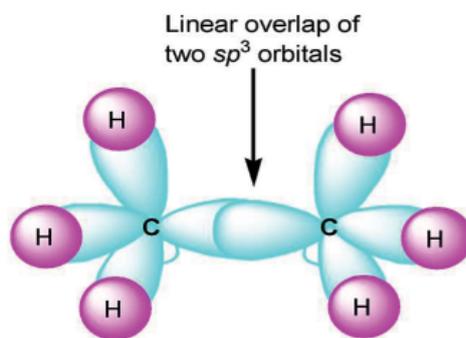
Figure 2.4 Structure of ethane showing overlap of orbitals to form C–C and C–H bonds

The overlap of the two sp^3 orbitals to form the carbon-carbon bond takes place along the direction of the orbitals. Such an overlap is called a **linear overlap** and results in the formation of a **σ bond.**

2.1.3 Properties of alkenes and alkynes

Both alkene and alkyne hydrocarbons are unsaturated compounds. Alkenes contain at least one carbon-carbon double bond while alkynes contain at least one carbon-carbon triple bond. Acyclic alkenes with one double bond but without any other functional group form the homologous series of alkenes with the general formula C_nH_{2n}. Alkynes with one triple bond and without any other functional group form the homologous series of alkynes with the general formula C_nH_{2n-2}.

Carbon-carbon double bond of an alkene and carbon-carbon triple bond in alkyne are stronger and shorter than a carbon-carbon single bond **(Table 2.3)**.

Table 2.3 Bond energies and bond lengths of carbon-carbon single, double and triple bonds

Bond	Bond energy/ kJ mol^{-1}	Bond length/ pm
C–C	347	154
C=C	611	133
C≡C	839	120

Alkenes show boiling points very similar to those of alkanes with the same number of C atoms. Ethene, propene and the isomeric butenes are gases at room temperature. All the rest are liquids. As with alkanes, boiling points of alkenes increase with the increase of molecular mass (chain length). Intermolecular forces of alkenes become stronger with increase in the size of the molecules. As the polarity of alkynes is also low, their physical properties are very similar to those of the corresponding alkanes and alkenes.

2.1.4 Structure of alkenes

Ethene (C_2H_4) is the simplest alkene. It contains a carbon-carbon double bond. Each carbon atom in ethene is sp^2 hybridized and forms three equivalent sp^2 hybrid orbitals which lie in the same plane and point to the three corners of an equilateral triangle **(Figure 2.5)**. The unhybridized p orbital lies perpendicular (90º) to this plane.
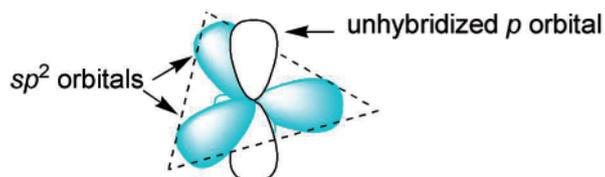
Figure 2.5 Shape and arrangement of sp^2 hybrid orbitals an unhybridized p orbital of carbon

These sp^2 orbitals are formed by mixing of the 2s orbital with two 2p orbitals leaving one unhybridized p orbital **(Figure 2.6)**.
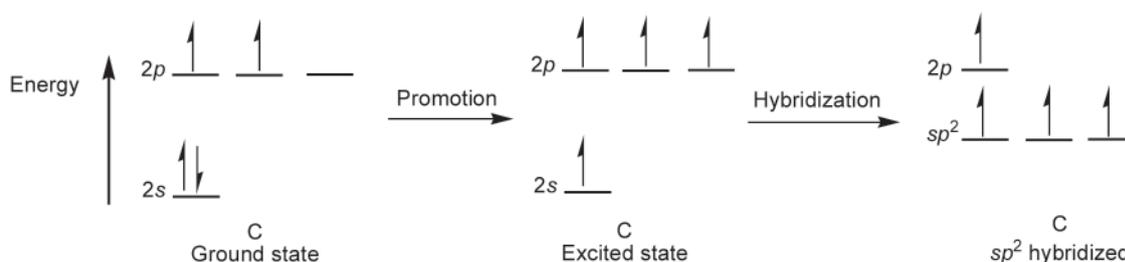
Figure 2.6 Graphical representation of sp^2 hybridization of carbon in ethane

In ethene each carbon uses two sp^2 orbitals to form two C–H bonds each. The remaining sp^2 orbital in each carbon is used to form a carbon-carbon σ bond by linear overlap. The unhybridized p orbitals of each carbon atom which are parallel to each other overlap laterally to form another carbon-carbon bond. This bond formed by the lateral overlap of p orbitals is called a π bond. All alkenes contain a carbon-carbon double bond which consists of a σ bond and a π bond. The π bond is weaker than the σ bond **(Figure 2.7)**.

Figure 2.7 Structure of ethene showing overlap of orbitals to form C–C and C–H bonds

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The 2 carbon atoms used to form the double bond and the four atoms attached directly to them lie in the same plane. The angle between any two atoms attached to the sp^2 hybridized carbon will be 120° **(Figure 2.8).**
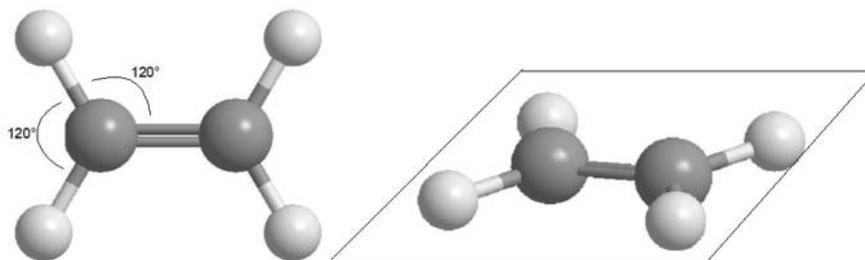
Figure 2.8 Planar shape of ethene (C_2H_4) molecule

2.1.5 Structure of alkynes

Ethyne (C_2H_2) is the simplest alkyne. It contains a carbon-carbon triple bond. Each carbon atom in ethyne is *sp* hybridized and forms two equivalent *sp* hybrid orbitals which lie in the same straight line and point in opposite directions **(Figure 2.9)**. The two unhybridized *p* orbitals lie perpendicular (90º) to each other and to these two *sp* orbitals.

unhybridized *p* orbitals
(perpendicular to each
other and perpendicular
to the both *sp* orbitals

sp orbital   *sp* orbital
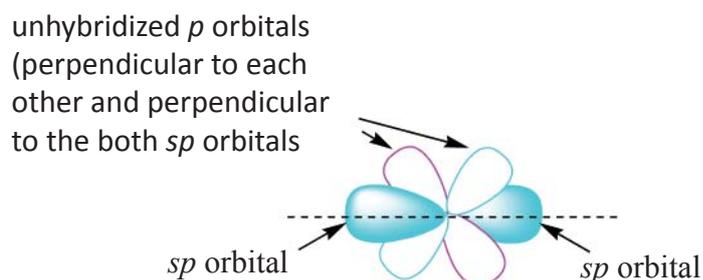
Figure 2.9 Shape and arrangement of *sp* hybrid orbital and unhybridized *p* orbitals of carbon

These *sp* orbitals are formed by mixing of the *2s* orbital with one *2p* orbital leaving two unhybridized *p* orbitals **(Figure 2.10)**.
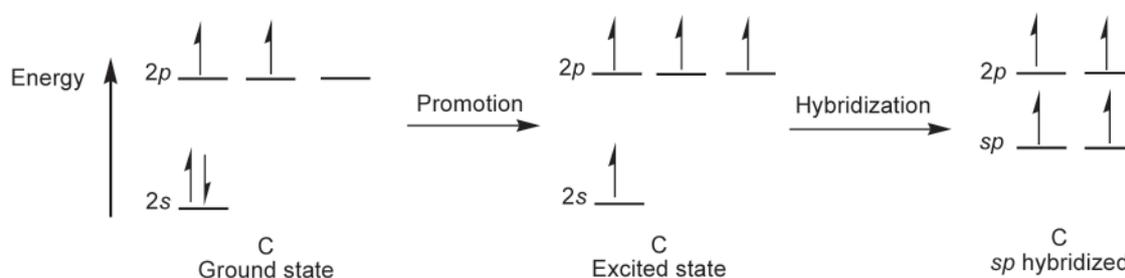
Figure 2.10 Graphical representation of *sp* hybridization of carbon in ethyne

In ethyne each carbon uses one *sp* orbital to form a C–H bond each. The remaining *sp* orbital in each carbon is used to form a carbon-carbon σ bond by linear overlap. The two unhybridized

p orbitals of each carbon atom overlap laterally to form another two carbon-carbon bonds (two π bonds). Thus all alkynes contain a carbon-carbon triple bond which consists of a σ bond and two π bonds **(Figure 2.11)**.

Lateral overlap of *p* orbital (π bonds)

Lateral overlap of *sp* orbital (σ bonds)
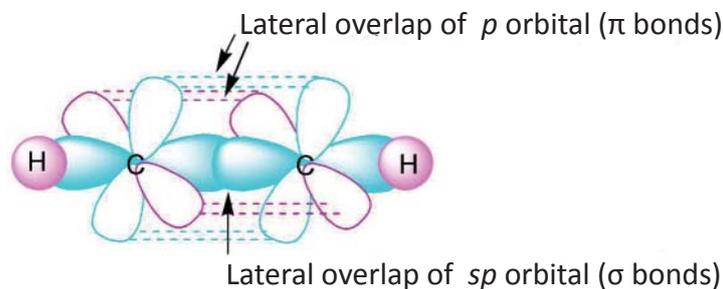
Figure 2.11 Structure of ethyne showing overlap of orbitals to form C–C and C–H bonds

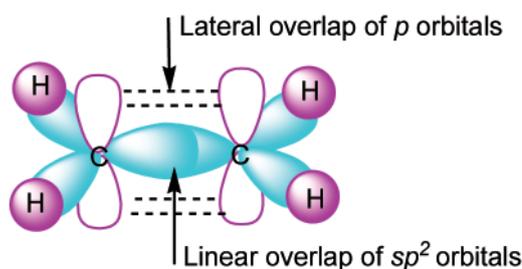The 2 carbon atoms used to form the triple bond and the two atoms attached directly to them lie in the same straight line. The angle between the two atoms attached to the *sp* hybridized carbon will be 180° **(Figure 2.12)**.
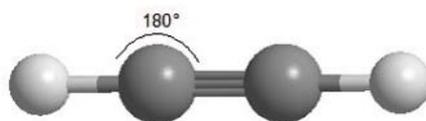
Figure 2.12 Linear shape of ethyne (C_2H_2) molecule

2.2   Chemical reactions of alkanes, alkenes and alkynes in terms of their structures

Covalent bond cleavage during organic reactions

Any organic reaction involves the cleavage (breaking) and formation of covalent bonds. Bond cleavage can take place in two different ways.

(i)   Heterolytic cleavage

In heterolytic cleavage the two electrons involved in the bond will remain with one of the atoms (the more electronegative atom). This will result in a positively charged species (cation) and a negatively charged species (anion).

When writing mechanisms, heterolytic cleavage is shown by a curved arrow which indicates the movement of a pair of electrons.
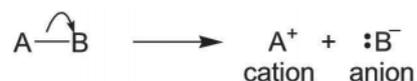
(ii)   Homolytic cleavage

In homolytic cleavage the two electrons involved in the bond will be equally divided such that one electron will remain with each atom. This will result in two neutral species each having one unpaired electron. Such species are called free radicals.

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When writing mechanisms, homolytic cleavage is shown by a pair of fishhooks. Each fishhook indicates the movement of a single electron.

2.2.1 Reactions of alkanes

In alkanes all the bonds are either C–C or C–H bonds. Because the polarity of those C–C and C–H bonds is low, alkanes do not have atoms which bear high positive (electron deficient) or negative charges (electron rich). Therefore, they do not react with common polar reagents such as OH^-, CN^-, H^+ under normal conditions.

2.2.1.1 Chlorination of alkanes

Although alkanes do not react with common polar reagents, they tend to react with free radicals by homolytic cleavage of C–H bonds. For example, alkanes react with reagents such as chlorine and bromine free radicals (Cl atoms and Br atoms) which can be generated by the homolytic cleavage Cl_2 and Br_2. This can be achieved by irradiation of Cl_2 or Br_2 with ultra-violet light. Thus, methane in the presence of ultra-violet light reacts with Cl_2 to give a mixture of chloromethanes, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4. These products are formed by a sequence of reactions where the product of one reaction, becomes the starting material for the subsequent reaction of the sequence. Such reactions are called **chain reactions**.

The mechanism of the reaction is given below. The first step of the reaction is the formation of chlorine free radicals by the homolysis of the covalent bond between two chlorine atoms. This is called the **chain initiation step**.

The chlorine free radical reacts with CH_4 to produce methyl free radical ($\bullet CH_3$). The methyl free radical reacts with another molecule of chlorine (Cl_2) producing CH_3Cl and $Cl^\bullet$. The chlorine radical produced in this step can react either with a molecule of CH_4 or a molecule of CH_3Cl to produce the corresponding carbon free radicals as shown in the reaction sequence given below.

$$H_3\overset{\cdot}{C}-H \quad \overset{\cdot}{C}l \longrightarrow H_3\overset{\cdot}{C} + HCl$$

$$H_3\overset{\cdot}{C} \quad Cl-Cl \longrightarrow CH_3Cl + \overset{\cdot}{C}l$$

Chain propagation steps

$$ClH_2\overset{\cdot}{C}-H \quad \overset{\cdot}{C}l \longrightarrow Cl\overset{\cdot}{C}H_2 + HCl$$

$$ClH_2\overset{\cdot}{C} \quad Cl-Cl \longrightarrow CH_2Cl_2 + \overset{\cdot}{C}l$$

$$Cl_2H\overset{\cdot}{C}-H \quad \overset{\cdot}{C}l \longrightarrow Cl_2H\overset{\cdot}{C} + HCl$$

$$Cl_2H\overset{\cdot}{C} \quad Cl-Cl \longrightarrow CHCl_3 + \overset{\cdot}{C}l$$

$$Cl_3\overset{\cdot}{C}-H \quad \overset{\cdot}{C}l \longrightarrow Cl_3\overset{\cdot}{C} + HCl$$

$$Cl_3\overset{\cdot}{C} \quad Cl-Cl \longrightarrow CCl_4 + \overset{\cdot}{C}l$$

Chain propagation steps
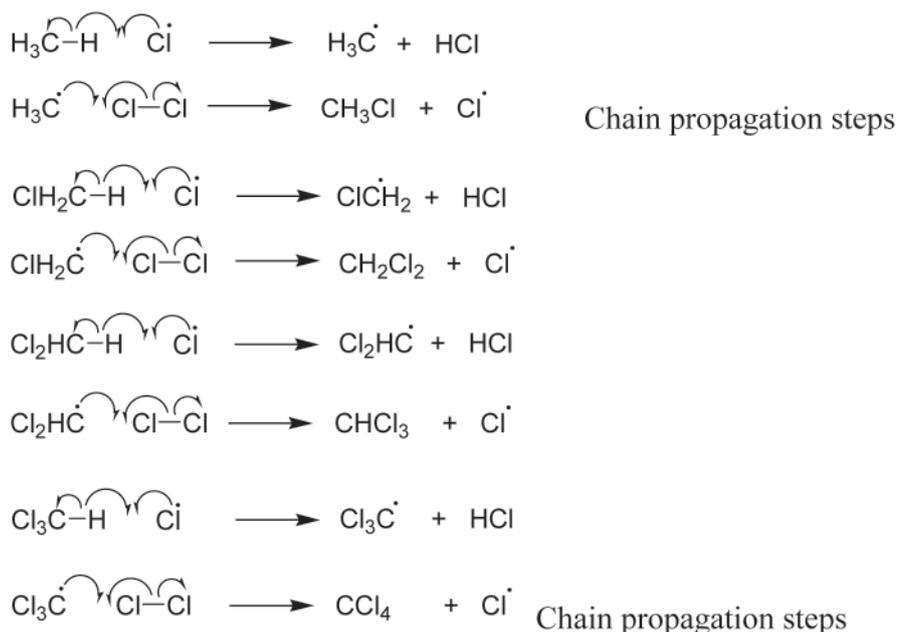
These steps are called **chain propagation steps.** In these chain propagation steps, free radicals are used and are also generated. Therefore the reaction sequence can proceed without stopping until all the H atoms in CH_4 are replaced by Cl. The carbon free radicals produced in this reaction sequence are called **reactive intermediates** in the free radical chlorination of methane.

A chain reaction can be stopped by **chain terminating reactions**. There are many chain terminating reactions (steps) that can occur during a chain reaction. In these chain terminating reactions the radicals are used but not generated. A few such chain terminating reactions are shown below.

$$\overset{\cdot}{C}l \quad \overset{\cdot}{C}l \longrightarrow Cl_2$$

$$H_3\overset{\cdot}{C} \quad \overset{\cdot}{C}l \longrightarrow CH_3Cl$$

$$H_3\overset{\cdot}{C} \quad \overset{\cdot}{C}H_3 \longrightarrow CH_3CH_3$$

Chain terminating steps
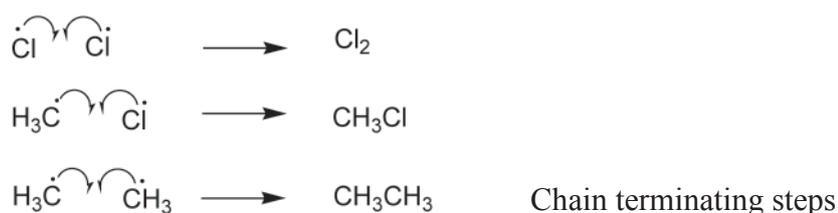
It should be noted that, as free radical chlorination (and bromination) of alkanes produces a mixture of products, it is of limited use in the synthesis of chloro or bromo hydrocarbons in the laboratory.

2.2.2   Reactions of alkenes

The reactions of alkenes take place at the carbon-carbon double bond. Carbon-carbon double bond is formed from a σ bond and a π bond. The double bond of an alkene is an electron rich area due to the presence of the pi-electron cloud above and below the plane of the alkene. Therefore it can attract a species which can accept a pair of electrons. Such species are electron deficient and are known as **electrophiles**.

As each of the doubly bonded C atoms is bonded only to three atoms, they are unsaturated and another atom can be attached (added) to each of these two carbon atoms during a reaction.

Therefore the typical reactions of alkenes are **electrophilic addition reactions**. Let us study the electrophilic addition reaction with its mechanism, using a few examples.

2.2.2.1   Addition of hydrogen halides (HCl, HBr or HI)

The electron deficient pole of a hydrogen halide molecule is H (eg. $H^{\delta+}- Br^{\delta-}$). This acts as an electrophile and reacts initially with the double bond. During the reaction the H-Br bond breaks releasing a Br- ion. Thus, the H reacts as if it was a H^+ ion and forms a bond with carbon using the two electrons from the π-bond.

During these electrophilic addition reactions, intermediate carbocations are formed *(Carbocations are electron deficient positively charged trivalent carbon species).*

Let us look at the mechanism of addition of HBr to ethene. The reaction proceeds in two steps.
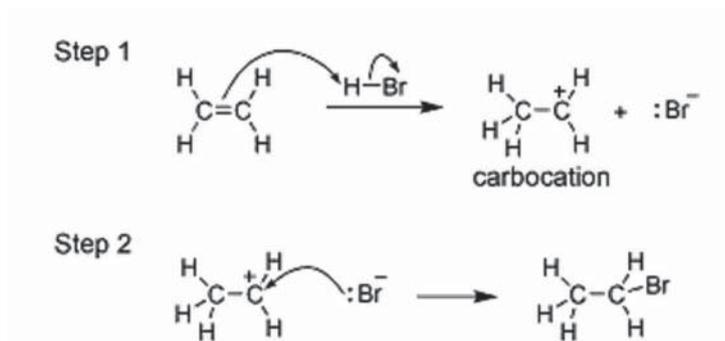
Carbocations are classified as primary, secondary and tertiary carbocations depending on the number of hydrogen atoms attached to the positively charged carbon atom.

Stability of these carbocations follows the order shown below.
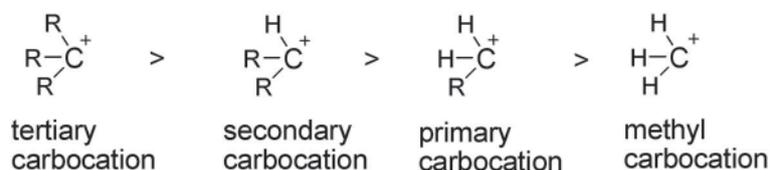
When alkyl groups are attached to the positively charged C atom of the carbocation, stability of the carbocation increases. The reason for this is the release of electrons by the alkyl groups through C–C bonds towards the positively charged carbon atom to which they are attached. This results in spreading the positive charge thereby stabilizing the ion. When asymmetrically substituted alkenes undergo electrophilic addition reactions with hydrogen halides, two different carbocations can be formed after the bonding of the electrophile (H^+). The more stable of these two carbocations forms more easily. Let us take addition of HBr to propene as an example.
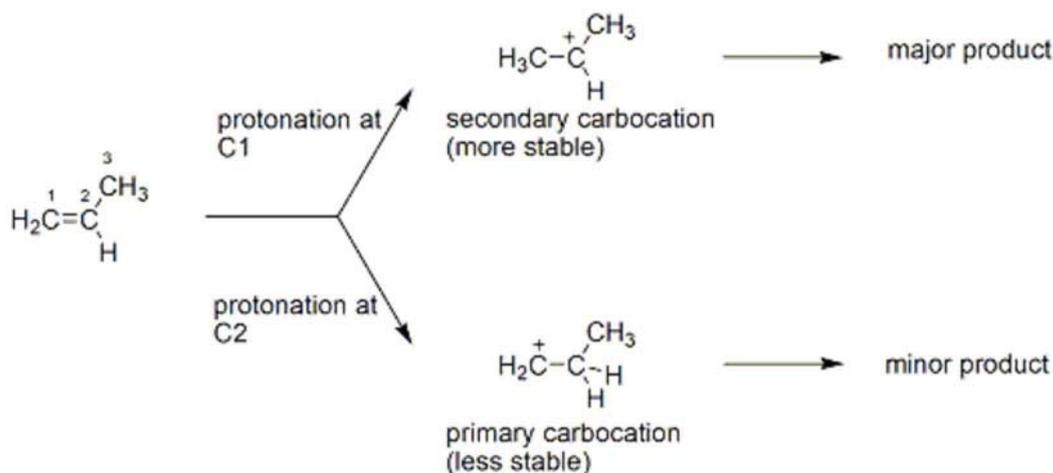
The more stable carbocation is obtained when the electrophile gets attached to the carbon atom to which the higher number of hydrogen atoms is attached. This is the explanation for 'Markovnikov's rule' which states that when a protic acid HX adds to an asymmetric alkene, the H adds to the carbon atom bonded to the higher number of H atoms.

The mechanism of addition of HBr to propene can be shown as follows.
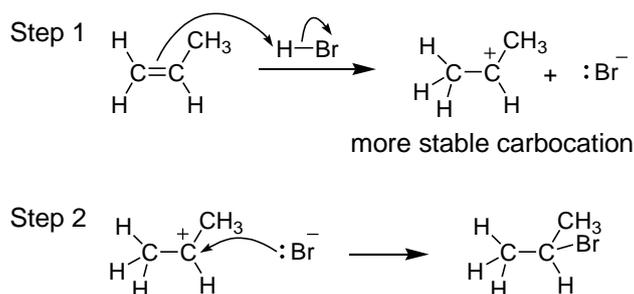
Hydrogen bromide adds in the opposite way to this rule (anti-Markovnikov addition) when there are peroxides in the reaction medium (i.e. the H adds to the carbon bonded to the lower number of H atoms). The reason for this is that in the presence of peroxides the reaction between hydrogen bromide (HBr) and the alkenes takes place via a free radical mechanism and not the ionic mechanism described above. *A description of the mechanism of this reaction is not expected.* It is to be noted that the direction of addition of HCl and HI is not changed in the presence of peroxides.

$$CH_3CH=CH_2 \ + \ HBr \ \xrightarrow[\text{(peroxide)}]{\text{RO—OR}} \ CH_3CH_2CH_2Br$$
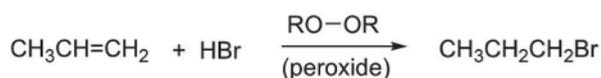
2.2.2.2 Addition of bromine to alkenes

Bromine is a not a polar molecule, but polarity is induced in it during the reaction with alkenes. When a bromine molecule approaches the electron rich double bond, a dipole is induced with the Br atom closer to the pi-bond having a partial positive charge. In the first step of the reaction, this Br atom reacts with the double bond and forms a bromonium ion, which is a three membered cyclic intermediate with a positive charge on the Br atom.

In the second step of the reaction, a bromide ion (Br^-) acting as a nucleophile, forms a bond to one of the carbon atoms bonded to Br^+. The bond formed by that carbon atom to Br^+ is broken during this step, giving an open chain structure again.

The mechanism is as follows.
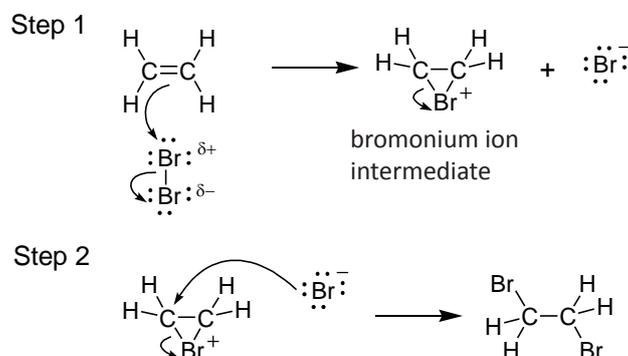
2.2.2.3 Addition of sulphuric acid and the hydrolysis of the addition product

Alkenes react with cold concentrated sulphuric acid to form alkyl hydrogen sulphates. The reaction is an electrophilic addition reaction and proceeds *via* a carbocation intermediate as in the case of the addition of HBr.
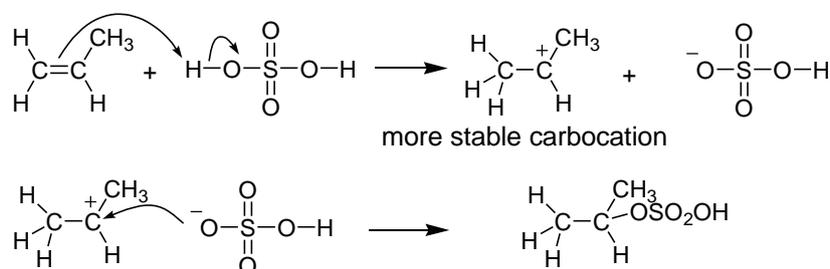
The reaction is carried out by passing the gaseous alkene through cold concentrated H_2SO_4 or stirring the liquid alkene with the cold concentrated H_2SO_4. When the solutions of alkyl hydrogen sulphates are diluted with water and heated, they undergo hydrolysis to give an alcohol bearing the same alkyl group as the original alkyl hydrogen sulphate. Let us look at few examples of this reaction.
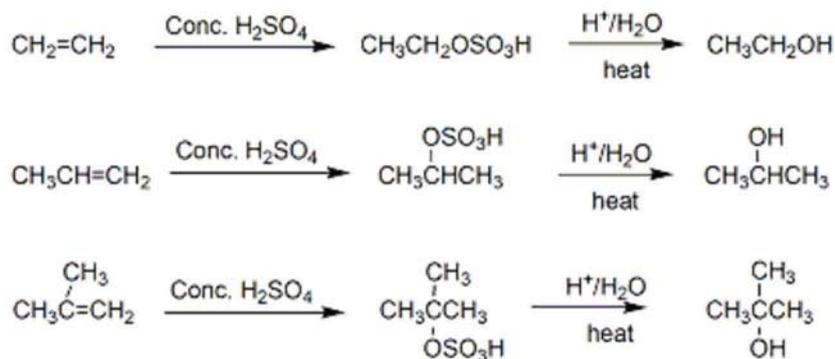
It is seen that the final product of this sequence of reactions is the alcohol that would be obtained by the Markovnikov addition of water (H-OH) to the alkene. The same products can be obtained directly by the direct addition of water to alkenes in the presence of dilute sulphuric acid. However the preparation of ethanol by direct addition of water to ethylene is difficult under laboratory conditions.

2.2.2.4 Catalytic addition of hydrogen (Hydrogenation)

In the presence of catalysts such as finely powdered Pt, Pd or Ni, alkenes react with hydrogen to produce alkanes.
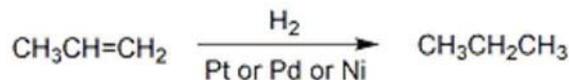
2.2.2.5 Reaction of alkenes with cold, alkaline, dilute potassium permanganate

Alkenes react with cold, alkaline, dilute $KMnO_4$ solution to produce diols (glycols). When this reaction takes place the purple colour of permanganate is disappeared and a brown precipitate of MnO_2 is formed. This reaction is used as a test for unsaturation (carbon-carbon double bonds and triple bonds). This is named as Baeyer test for unsaturation. However easily oxidisable substances such as aldehydes will also answer this test.

2.2.3 Reactions of alkynes

Alkynes have a triple bond which consists of one sigma bond and two π bonds. Alkynes also undergo electrophilic addition reactions with reagents that add to alkenes. The two pi-bonds react independently of each other.

2.2.3.1 Addition of bromine

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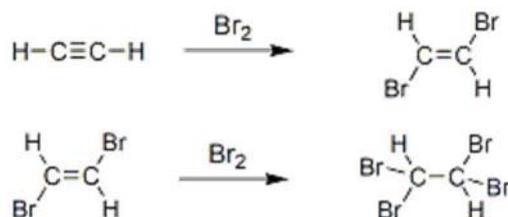
2.2.3.2   Addition of hydrogen halides
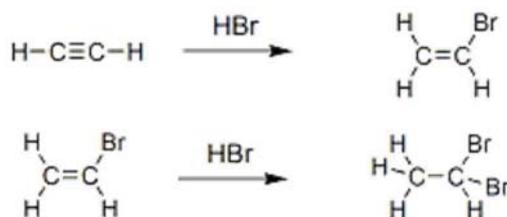
2.2.3.3   Addition of water

In the presence of Hg^{2+} and dilute H_2SO_4, one molecule of water adds to an alkyne producing an enol. A molecule containing a hydroxyl group attached to a carbon atom in a carbon-carbon double bond is known as an **enol.**
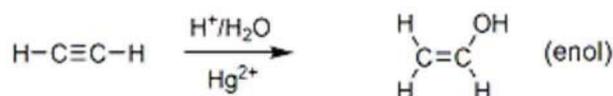
Enols are unstable and rapidly rearrange to a more stable keto form (aldehydes or ketones)
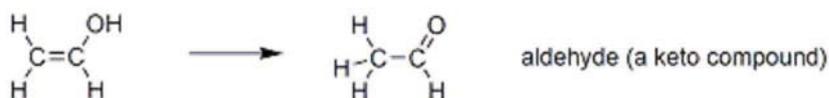
The addition of water to alkynes takes place according to the Markovnikov's rule as shown below by the reaction of propyne.
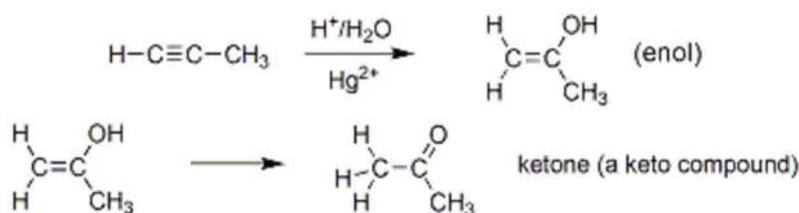
2.2.3.4   Catalytic addition of hydrogen (Hydrogenation)

Alkynes react with hydrogen in the presence of catalysts such as Pt, Pd or Ni to give alkanes.
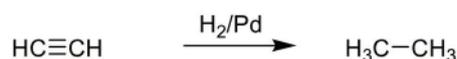
During this reaction the alkyne is first reduced to the alkene which is further reduced to the alkane under the reaction conditions. The reaction can be stopped at the alkene stage by using a less active catalyst. Very often, Pd catalyst deposited on $BaSO_4$ deactivated (poisoned) by quinoline is used.
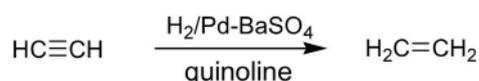
2.2.4 Acidic nature of alkynes with terminal hydrogen

The triple bond C atoms are *sp* hybridized. A C-H bond involving a triple bond carbon is formed by the linear overlap of a *sp* orbital of C and a *s* orbital of H.

Since a *sp* orbital has more *s* character (50% *s* character) than sp^2 or sp^3 orbitals, the bonding electrons in the C–H bond of alkynes are closer to the carbon nucleus than in the case of C–H bonds in alkenes and alkanes. Therefore the H attached to a triple bond carbon has a higher acidity than the H in alkene or alkane C–H bonds. However, the acidity of H attached to terminal alkynes is less than that of water and alcohol.

The H of a terminal alkyne can react as H^+ with strong bases such as $NaNH_2$ and active metals such as Na. The resulting acetylide anion is stable because the two non-bonded electrons (negatively charged) are close to the carbon nucleus (positively charged).

$$H_3C-C \equiv C-H \xrightarrow{\text{Na}} H_3C-C \equiv \overset{-}{C} \ Na^+ \ + \ H_2$$

$$H_3C-C \equiv C-H \xrightarrow{\text{NaNH}_2} H_3C-C \equiv \overset{-}{C} \ Na^+ \ + \ NH_3$$
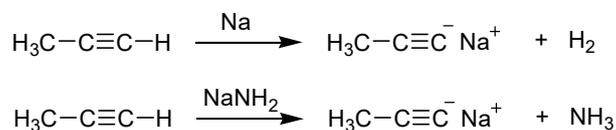
Terminal alkynes react with certain heavy metal ions such as Ag^+ and Cu^+ to form insoluble metal acetylides. These two reactions can be used to identify terminal alkynes.

$$H_3C-C \equiv C-H \xrightarrow{\text{NH}_3/\text{Cu}_2\text{Cl}_2} H_3C-C \equiv C-Cu \downarrow$$

$$H_3C-C \equiv C-H \xrightarrow{\text{NH}_3/\text{AgNO}_3} H_3C-C \equiv C-Ag \downarrow$$
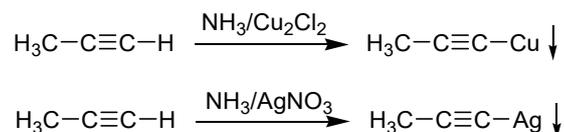
2.3 The nature of bonding in benzene

The molecular formula of benzene is C_6H_6 which indicates that it is an unsaturated compound. Under normal conditions benzene does not answer the tests for unsaturation. Therefore, benzene cannot have a structure similar to that of a simple alkene or an alkyne.

2.3.1 Structure of benzene

The structure proposed for benzene by Kekulé contained a six-membered ring of carbon atoms with alternating three double and three single bonds **(Figure 2.13)**.
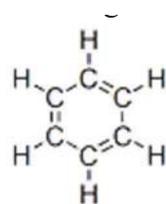
Figure 2.13 Structure of benzene proposed by Kekulé in 1865

This structure was based on the evidence available regarding the relationships of aromatic isomeric compounds. No isomer has been found for any mono-substituted benzene (C_6H_5X; X= -CH$_3$, -C$_2$H$_5$, -OH, -Cl, -Br, -CHO etc.), implying that all six atoms in benzene are equivalent. Therefore substitution at any one carbon atom will always give a single compound.

It was found that there are three isomeric disubstituted benzenes. Kekulé proposed structures with 1,2-disubstitution, 1,3-disubstitution and 1,4-disubstitution **(Figure 2.14)**, later named as -*ortho, -meta* and -*para* isomers.

1,2-bromochlorobenzene | 1,3-bromochlorobenzene | 1,4-bromochlorobenzene
(*ortho*-bromochlorobenzene) | (*meta*-bromochlorobenzene) | (*para*-bromochlorobenzene)
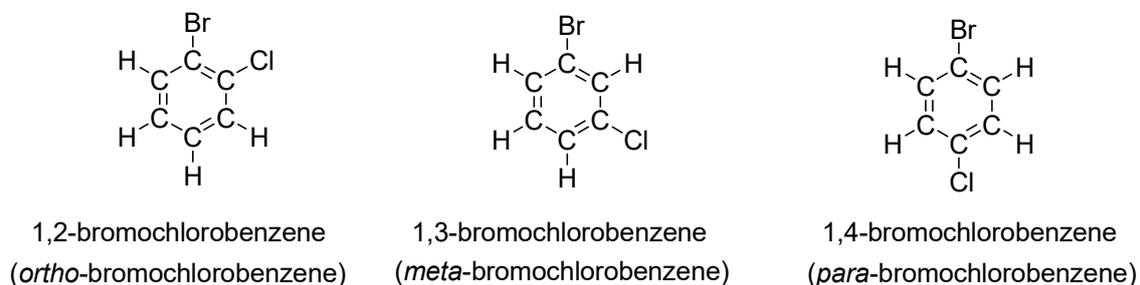
Figure 2.14 Three isomeric disubstituted benzenes

However these structures implied that two distinct *ortho*- disubstituted benzenes are possible, depending on whether the substituted carbons are separated by a double bond or a single bond. Since two different *ortho*- isomers have never been found, Kekulé proposed that benzene molecule could be represented by two equivalent structures which are in equilibrium **(Figure 2.15)** so that single and double bonds continually interchange positions.

Figure 2.15 Proposed rapid equilibrium of two equivalent structures of *ortho*-bromochlorobenzene

This proposal explains that benzene has two possible structures and that both of them exist at room temperature. However, no experimental evidence has been found for the existence of two such structures for benzene.

Further the bond length between any two adjacent carbon atoms in benzene is the same. The carbon-carbon bond length of benzene is 1.39×10^{-10} m which is in-between the length of a carbon-carbon double bond (1.34×10^{-10} m) and the length of a carbon-carbon single bond (1.54×10^{-10} m).

The structure of benzene is now considered to be a resonance hybrid of two structures as given in **Figure 2.16**.
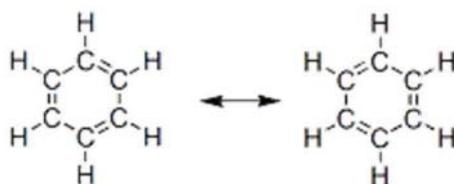
Figure 2.16 Resonance structures of benzene

For convenience, the resonance hybrid of benzene is written as shown below.

Take note of the difference between the resonance sign (the double headed arrow) and the equilibrium sign. In an equilibrium, the compounds shown by structures really exist while in the concept of a resonance hybrid, none of the compounds represented by the structures really exist. They are drawn because there is no other way of representing the real molecule. Each structure contributes to the real structure of the compound. The extent of contribution depends on the relative stability of each resonance structure with the more stable structure making a larger contribution to the real structure. In the case of benzene, both structures have the same stability and contribute equally.

All C atoms of benzene are sp^2 hybridized. Each carbon bears an unhybridized p orbital which can overlap with the unhybridized p orbitals on either sides of it **(Figure 2.17)**. From this, a cyclic delocalized electron cloud common to all six carbon atoms is formed. Hence, the real structure of benzene is considered to be a hybrid of two Kekulé structures. The real structure of benzene with delocalized electrons is more stable than the hypothetical Kekulé structure with three double bonds. The concept of resonance is used when there are delocalized electrons to be depicted using conventional structures which are drawn using localized bonds.
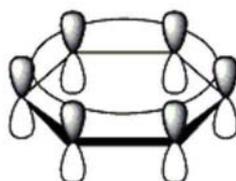
Figure 2.17 Benzene showing lateral overlap of p orbitals forming a cyclic delocalized electron cloud

2.3.2   Stability of benzene

The data for the standard enthalpy of hydrogenation helps to illustrate the stability of a benzene molecule.
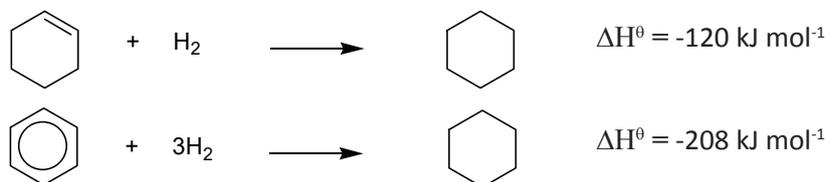
Since the standard enthalpy of hydrogenation of cyclohexene (six-membered cyclic hydrocarbon with one double bond) is -120 kJ mol^{-1}, the standard enthalpy of hydrogenation of benzene should be 3 x -120 kJ mol^{-1} = -360 kJ mol^{-1} if it possesses three double bonds similar to alkenes. The standard enthalpy of hydrogenation of benzene is found to be -208 kJ mol^{-1}, which is -152 kJ mol^{-1}

less than the expected value for the hydrogenation of three double bonds **(Figure 2.18)**. Hence, benzene is more stable than its Kekulé structure by an amount equal to (360-208) = 152 kJ mol^{-1}. This stability is due to the cyclic delocalization of six pi-electrons, and is termed the resonance stabilization (or aromatic stabilization) energy of benzene.
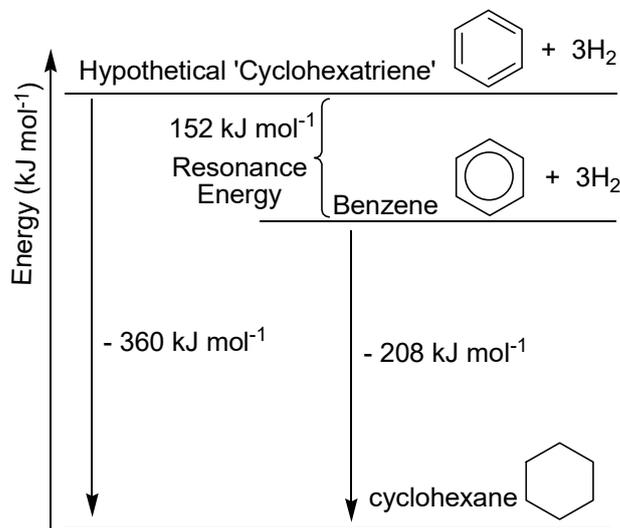
Figure 2.18 Standard enthalpies of hydrogenation of benzene and hypothetical cyclohexatriene.

2.4 Characteristic reactions of benzene exemplifying its stability

Benzene contains loosely bound delocalized electron cloud on both faces of the planar benzene molecule. This makes benzene ring electron rich and hence reactive toward electrophiles, similar to alkenes. As we have discussed, benzene shows extra stability due to this delocalization of electrons. Therefore benzene does not easily undergo reactions which destroy this cyclic delocalization. Hence the characteristic reactions of benzene are electrophilic substitution reactions and not electrophilic addition reactions as in the case of alkenes.

2.4.1 Electrophilic substitution reactions of benzene

In electrophilic substitution reactions, hydrogen atoms attached to the benzene ring are substituted by electrophiles (E$^+$).
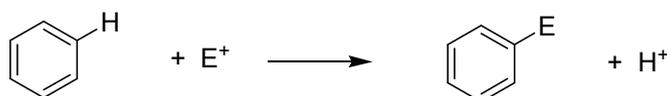
The first step in this reaction is the formation of a bond between the electrophile (E$^+$) and a carbon atom in the benzene ring giving rise to a carbocation (arenium ion). This step is very similar to the first step of the electrophilic addition of HBr to an alkene.

The intermediate carbocation thus formed is stabilized by the delocalization of the positive charge by conjugation with the two π bonds. This can be shown by resonance as follows.
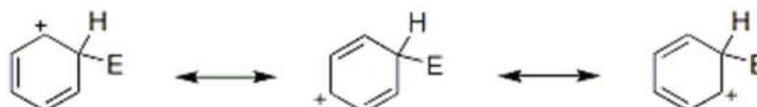
However, in going from benzene to the above carbocation the cyclic delocalization of π electrons is broken, and the aromatic stabilization energy is lost. It is energetically more favourable for the intermediate carbocation to lose a proton and re-establish the cyclically delocalized electron cloud, than to react with a nucleophile and give an addition product as in the case of alkenes.

The proton is usually taken up by one of the bases (B:$^-$) present in the reaction mixture. Thus, the result is the substitution of a H atom on the benzene ring with E.
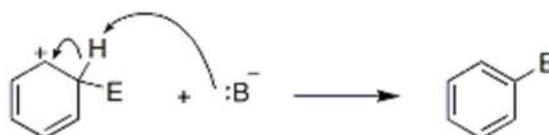
2.4.1.1 Nitration

Benzene reacts with a mixture of conc. HNO_3 and conc. H_2SO_4 to give nitrobenzene which is formed by the substitution of H by a nitro group.
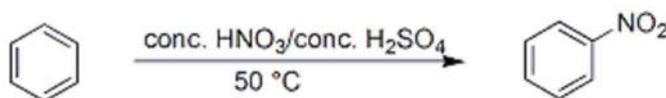
The electrophile in this reaction is $^+NO_2$ which is generated in the medium by the dehydration of nitric acid by sulphuric acid as follows.
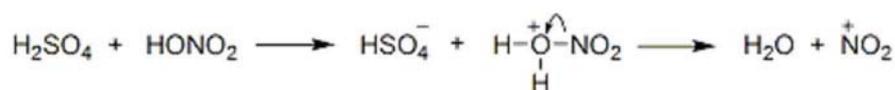
The $^+NO_2$ ion reacts with benzene and in the final step the proton is removed by the hydrogensulphate (bisulphate) ion which act as the base.
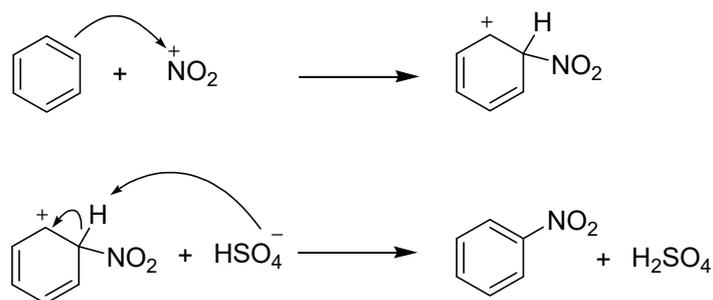
2.4.1.2 Friedel - Crafts alkylation

Benzene reacts with alkyl halides in the presence of a Lewis acid such as anhydrous $AlCl_3$ to give alkyl benzene, in which a H attached to the benzene is substituted by an alkyl group.
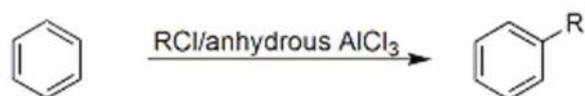
In the case of secondary and tertiary halides (see section 8.6) the electrophile of this reaction is R^+, and is generated in the first step by the reaction between alkyl halide and the Lewis acid.

$$RCl + AlCl_3 \longrightarrow R^+ + AlCl_4^-$$

In the final step a proton is removed by $AlCl_4^-$.

$$AlCl_4^- + H^+ \longrightarrow AlCl_3 + HCl$$

Let us see an example.
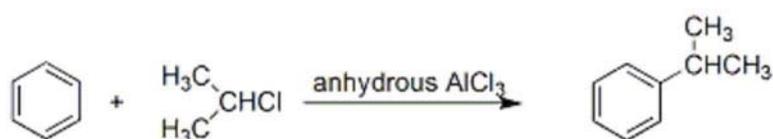
The mechanism of this reaction is as follows.
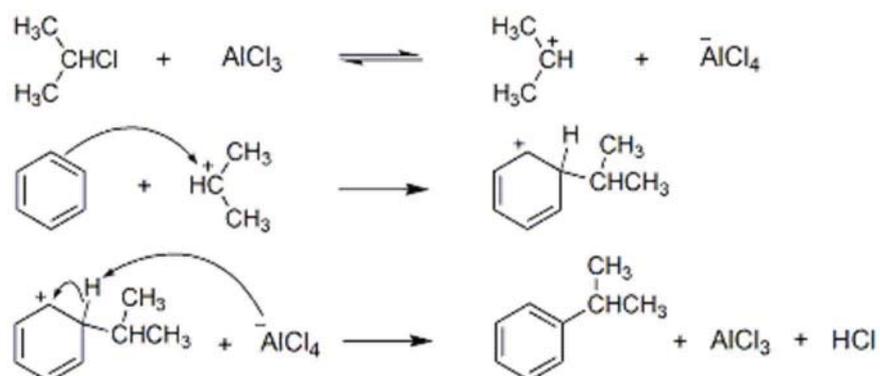
As you can see the first step of this reaction is formation of carbocation from the alkyl halide. In the second step benzene interacts with this carbocation to form an arenium ion. Removal of proton takes place in the final step restoring the aromatic stability in the product.

In cases where RX is a primary alkyl halide (eg. CH_3Cl) the species actually reacting with the benzene molecule may not be R^+, but be a R-Cl molecule polarized by coordination to $AlCl_3$, which will transfer R^+ to the benzene molecule during the reaction by cleavage of the R-Cl bond.

The possible mechanism is as follows.
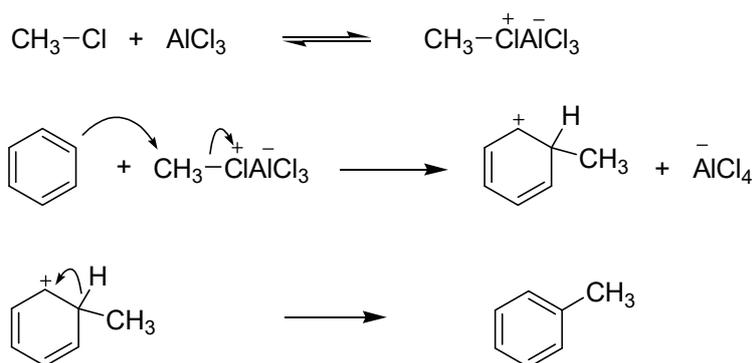
The Friedel - Crafts alkylation does not take place in mono substituted benzenes where the substituent group has a stronger electron attracting ability than halogen.   (eg. nitrobenzene).

2.4.1.3   Friedel - Crafts acylation

Benzene reacts with acid chlorides in the presence of a Lewis acid such as anhydrous $AlCl_3$, giving acyl benzene, in which a H is substituted by an acyl group.
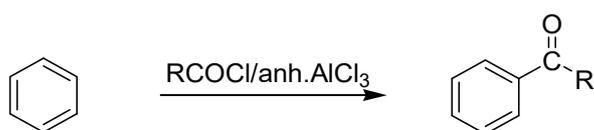
The electrophile in this reaction is acylium ion (RCO^+). This is formed in the first step by reacting $AlCl_3$ with acyl chloride as follows.
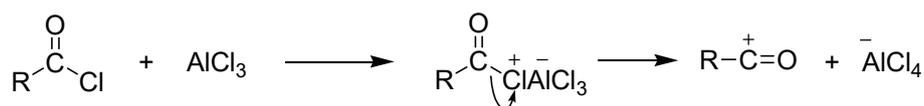
In the step 2, the acylium ion reacts with benzene to form an arenium ion and in the final step a proton is removed restoring the aromatic stability.
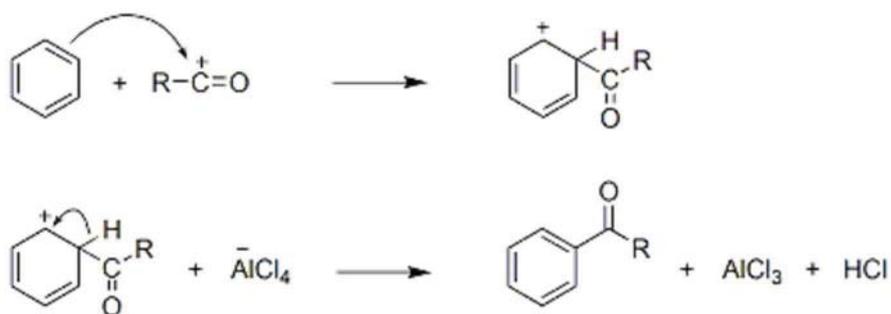
2.4.1.4 Halogenation

When benzene reacts with Cl_2 or Br_2 in the presence of a Lewis acid such as $FeCl_3$, $FeBr_3$, $AlCl_3$ or $AlBr_3$, under anhydrous conditions, substitution by a halogen atom takes place in the benzene ring.
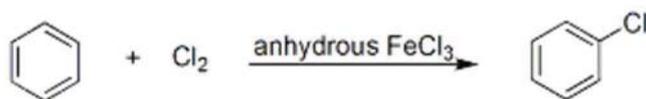
The effective electrophile in the above reaction is Cl^+. It is transferred to the benzene ring from the complex during the reaction. Proton is removed in the last step restoring the aromatic stability.
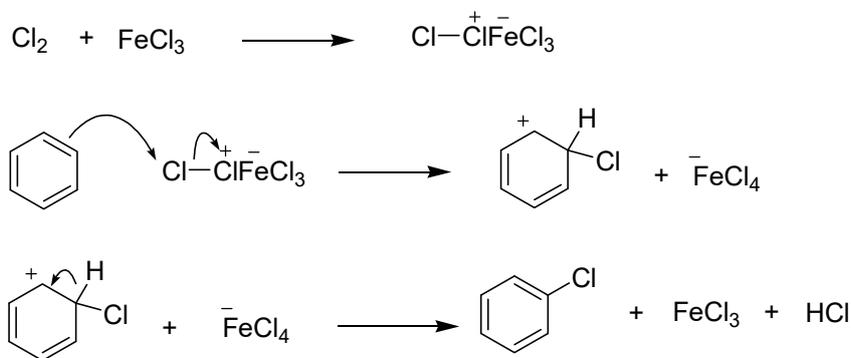
2.4.2 Resistance of benzene ring towards oxidation

Benzene does not get oxidized by normal oxidizing agents like $H^+/KMnO_4$ due to its stability. However, the alkyl group in alkyl substituted benzene can be oxidized by $H^+/KMnO_4$ to a carboxylic acid group. $H^+/K_2Cr_2O_7$ can also be used for this oxidation.
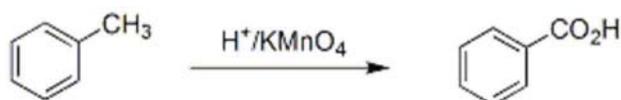
Tertiary alkyl groups do not get oxidized under the conditions in which primary and secondary alkyl groups get oxidized. More vigorous conditions under which tertiary alkyl groups can be oxidized also result in cleavage of the benzene ring.

2.4.3 Resistance of benzene ring towards hydrogenation

Although benzene does not undergo electrophilic addition reactions, like alkenes, it can undergo addition of hydrogen in the presence of suitable catalysts at higher temperatures in comparison to alkenes.
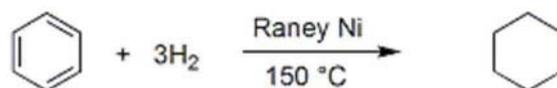
2.5 Directing ability of substituent groups of mono substituted benzene

When a monosubstituted benzene undergoes an electrophilic substitution reaction, the place where the second substituent group attaches will be determined by the nature of the first substituent group. Substituent groups can be categorized into two basic types.

2.5.1 Ortho para directing groups

eg. -OH, -R, $-NH_2$, -NHR, $-OCH_3$, halogens

Other than halogen, the *ortho para* directing groups activate the benzene ring towards electrophilic substitution by making it more electron rich than benzene.

ortho   para
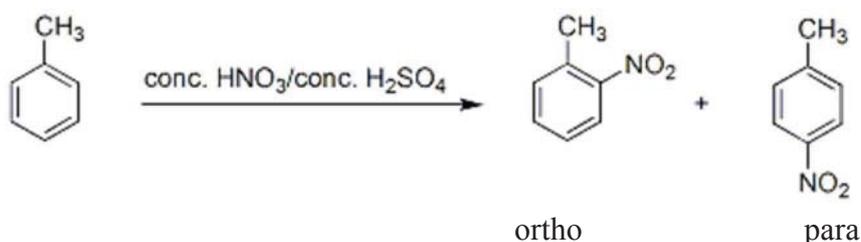
2.5.2 Meta directing groups

eg. - NO_2, -CHO, -COR, -COOH, -COOR

Meta directing groups deactivate the benzene ring towards electrophilic substitution by withdrawing electrons from it.

meta
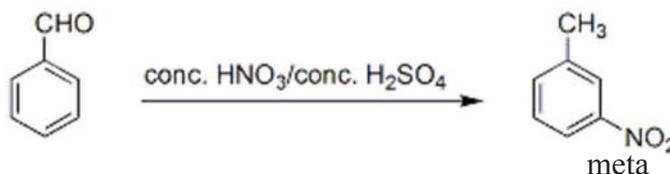
2.6 Structure and reactions of alkyl halides

Alkyl halides are classified as primary, secondary or tertiary depending on the number of H atoms attached to the carbon atom which carries the halogen atom.

Primary alkyl halide   Secondary alkyl halide   Tertiary alkyl halide
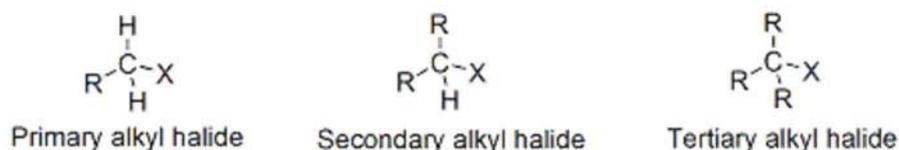
Alkyl halides are polar compounds. Although they are polar, the solubility of alkyl halides in water is very low. One reason for this is that they do not form hydrogen bonds with water.

Due to the higher electronegativity of the halogen atom relative to the carbon atom, the carbon-halogen bond is polarized. As a result, there is a deficiency of electrons in that carbon atom. Therefore, it is possible that nucleophiles attack this position. Nucleophiles are basic, electron rich reagents which can utilize a pair of electrons to form a bond with an electron deficient carbon atom.

A few common examples are:

$$^-OH \quad ^-OR \quad ^-NH_2 \quad ^-CN \quad RC\equiv C^- \quad H_2O \quad NH_3$$

Characteristic reactions of alkyl halides are nucleophilic substitution reactions. During nucleophilic substitution reaction, the carbon atom forms a new bond with the nucleophile and the halogen atom leaves as a halide ion.

$$Nu\!:^- + R\!-\!X \longrightarrow Nu\!-\!R + X^-$$

Let us look at some examples:
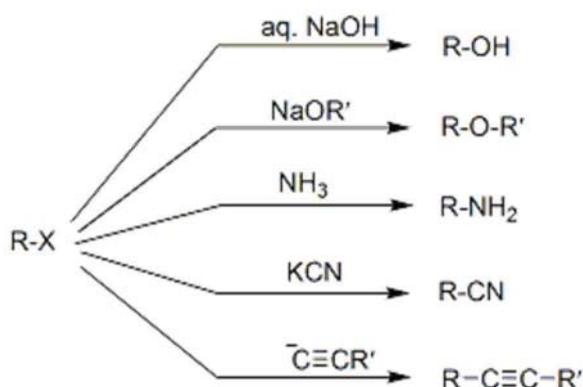
As a nucleophile possesses a pair of electrons, any nucleophile can also act as a base by forming a bond with H^+. Therefore, when an alkyl halide is reacted with a reagents such as: OH^-, OR^-, it can also undergo an elimination reaction by the mechanism shown below.
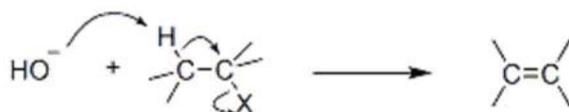
In this reaction, instead of reacting OH^- group as a nucleophile with carbon, it reacts as a base and removes a H^+ from the carbon atom adjacent to the carbon atom bearing halogen. The hydrogen atoms attached to the carbon atom adjacent to the carbon atom bearing the halogen atoms, have a low acidity due to the polarization of the C-X bond. Thus substitution and elimination are competing reactions in alkyl halides. The balance between substitution and elimination is influenced by the solvent used in the reaction. In the laboratory, aqueous KOH is used when substitution is desired, and ethanolic KOH is used when elimination is desired.

$$CH_3CH_2CH_2Br \xrightarrow{\text{alcoholic KOH}} CH_3CH=CH_2$$

Alkyl halides react with Mg in the medium of **dry ether** to form **Grignard reagents.** Grignard reagents are organometallic reagents.

$$R\text{-}X + Mg \xrightarrow{\text{dry ether}} R\text{-}MgX$$
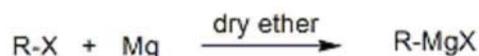
When an alkyl halide forms a Grignard reagent the polarity of the carbon atom originally joined to halogen, changes as shown below.

$$\overset{\delta+}{\underset{}{C}}\overset{\delta-}{-X} \longrightarrow \overset{\delta-}{\underset{}{C}}\overset{\delta+}{-MgX}$$

Thus, an electron deficient carbon atom is converted to an electron rich carbon atom. In fact, the alkyl group attached to Mg can utilize the pair of electrons in the C-Mg bond and behave as a strong base as well as a strong nucleophile.

Therefore Grignard reagents cannot be prepared or used in organic reactions in the presence of compounds which have even weakly acidic H atoms, including water.

$$R\text{-}MgX + H_2O \longrightarrow RH + Mg\overset{OH}{\underset{X}{<}}$$

The strong basic character of the Grignard reagent can be shown by the following reactions.

$$RMgX + CH_3CO_2H \longrightarrow RH + CH_3\overset{O}{\overset{\|}{C}}OMgX$$

$$RMgX + CH_3OH \longrightarrow RH + CH_3OMgX$$

$$RMgX + C_6H_5OH \longrightarrow RH + C_6H_5OMgX$$

$$RMgX + NH_3 \longrightarrow RH + H_2NMgX$$

$$RMgX + CH_3NH_2 \longrightarrow RH + CH_3NHMgX$$

$$RMgX + CH_3C\equiv C-H \longrightarrow RH + CH_3C\equiv CMgX$$
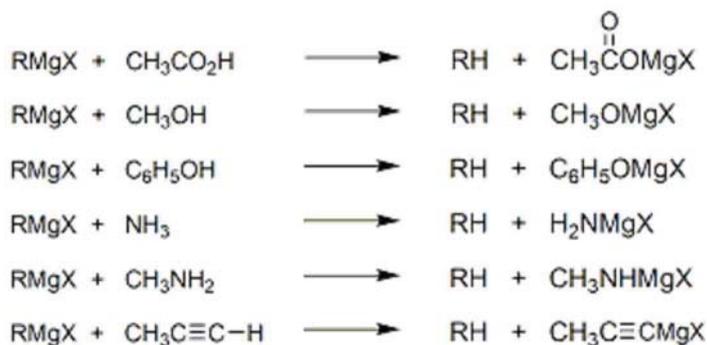
The last reaction of the above list is the reaction of a Grignard reagent with a terminal alkyne. Note that the product is also another Grignard reagent. This reaction can be used to prepare acetylenic Grignard reagents.

2.7 Nucleophilic substitution reactions of alkyl halides in terms of the timing of bond making and bond breaking steps

During reactions, bonds are broken and new bonds are formed. Nucleophilic substitution reactions of alkyl halides involve the breaking of a carbon-halogen bond and the formation of a carbon-nucleophile bond. To study the mechanism of nucleophilic substitution reactions of alkyl halides the time interval between bond breaking and bond making steps can be considered.

When the breaking of the C-X bond and the formation of the new bond to the nucleophile takes place simultaneously, the nucleophilic substitution reaction of the alkyl halide takes place as a one-step reaction.

Accordingly, for the reaction of an alkyl bromide with the hydroxyl ion, the one-step reaction can be presented as follows.
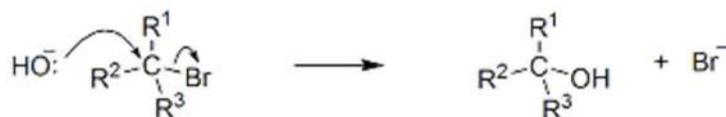
When the breaking of the C-X bond takes place at first and then the formation of the new bond to the nucleophile takes place, the nucleophilic substitution reaction of the alkyl halide takes place as a two-step reaction.

Accordingly, the reaction that takes place by two steps can be presented as follows
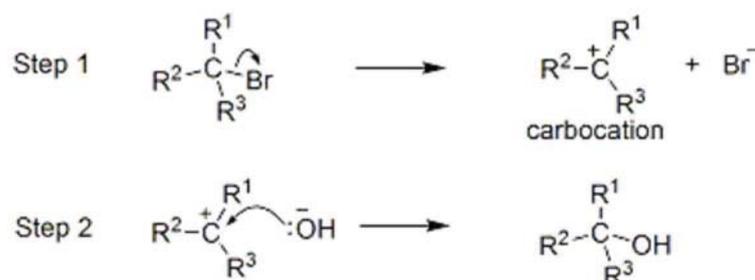
The reaction that takes place by two steps goes through a carbocation intermediate. On considering the stability of the carbocation formed, the tertiary alkyl halides (R^1, R^2, R^3 = alkyl) which are able to form a more stable tertiary carbocations tend to undergo nucleophilic substitution in two steps. The primary alkyl halides (R^1, R^2 = H, R^3 = H or alkyl) tend to undergo nucleophilic substitution reactions in one step as the primary carbocations they form are less stable.

Generally, both pathways are taken by the secondary alkyl halides (R^1 = H, R^2, R^3 = alkyl) to extents which depend on the reaction conditions.

Vinyl and phenyl carbocations are unstable and therefore, vinyl halides and aryl halides they do not react by the two step pathway. They also do not react by the one step pathway because the C-X bond is stronger than in alkyl halides due to its double bond character. This can be shown by resonance.

Resonance structures of vinyl halide:

Resonance structures of chlorobenzene:

3. Oxygen Containing Organic Compounds

Content

Introduction

The common oxygen containing organic compounds includes alcohols, phenols, ethers, carbonyl compounds (aldehydes and ketones) and carboxylic acids and carboxylic acid derivatives (esters, amides and acid halides). Alcohols are compounds containing OH group attached to aliphatic carbon atom while phenols are aromatic compounds in which an OH group is attached to a benzene ring. Aldehydes, ketones, carboxylic acids and carboxylic acid derivatives all contain a carbonyl (C=O) group. These classes of compounds differ from each other based on the nature of the two groups attached to the carbonyl carbon.

3.1   Structure, properties and reactions of alcohols

Alcohols are compounds containing an O–H group attached to a sp^3 hybridized carbon atom. Alcohols with one OH group are called monohydric alcohols while those with two, three, four etc. are called dihydric alcohols, trihydric alcohols, tetrahydric alcohols etc. Compounds with many OH groups are commonly called polyhydric alcohols. Our discussion will be mainly confined to monohydric alcohols.

3.1.1   Classification of monohydric alcohols

Similar to the alkyl halides monohydric alcohols are classified into three types depending on the number of H atoms attached to the carbon atom bearing the OH group (carbinol carbon atom) as primary (2 H atoms), secondary (1 H atom) and tertiary (no H atoms attached) as shown below.
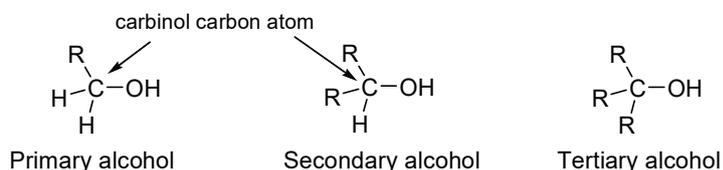
3.1.2   Physical properties

In alcohols the O–H bond is polarized as $R-O^{\delta-}-H^{\delta+}$. Hence, inter-molecular hydrogen bonds are formed between alcohol molecules **(Figure 3.1)**.
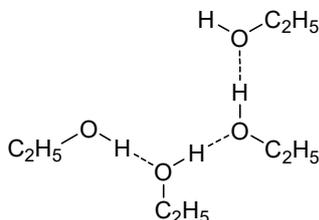
Figure 3.1 Intermolecular H-bonding in ethanol

Because of these relatively strong intermolecular bonds, the boiling points of alcohols have higher values compared to the alkanes and ethers with comparable relative molecular masses **(Table 3.1)**. The boiling point increases in going down the series of alcohols. Similar to alkanes, branching of the alkyl part of the molecule leads to a reduction of boiling point.

Table 3.1 Boiling points of alcohols, ethers and alkanes of comparable relative molecular masses

Compound	Structural formula	Relative molecular mass	Boiling point/ °C
ethanol	CH_3CH_2OH	46	78
dimethyl ether	CH_3OCH_3	46	–25
propane	$CH_3CH_2CH_3$	44	–42
1-propanol	$CH_3CH_2CH_2OH$	60	97
2-propanol	$(CH_3)_2CHOH$	60	83
ethylmethyl ether	$CH_3CH_2OCH_3$	60	11
butane	$CH_3CH_2CH_2CH_3$	58	0
1-butanol	$CH_3CH_2CH_2CH_2OH$	74	118
2-butanol	$CH_3CH(OH)CH_2CH_3$	74	99
2-methyl-2-propanol	$(CH_3)_3COH$	74	82
diethyl ether	$CH_3CH_2OCH_2CH_3$	74	35
pentane	$CH_3CH_2CH_2CH_2CH_3$	72	36
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	88	138
ethyl propyl ether	$CH_3CH_2CH_2OCH_2CH_3$	88	64
hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	86	68

Alcohols with low relative molecular masses are soluble in water. The solubility of alcohols in water is due to the OH group which can forms H - bonds with water molecules. The non-polar alkyl group in the alcohol molecule is a hindrance to the solubility in water. In going down the homologous series of alcohols the size of the non - polar alkyl group gradually increases relative to the OH group. Accordingly the solubility of alcohols in water gradually decreases **(Table 3.2).**

Table 3.2 Boiling points and solubility (in water) of some long chain alcohols

Alcohol	Structural formula	Boiling point/ °C	Solubility (g/ 100g H_2O)
methanol	CH_3OH	65	∞
ethanol	CH_3CH_2OH	78	∞
1-propanol	$CH_3CH_2CH_2OH$	82	∞
1-butanol	$CH_3(CH_2)_2CH_2OH$	118	7.9
1-penatanol	$CH_3(CH_2)_3CH_2OH$	138	2.3
1-hexanol	$CH_3(CH_2)_4CH_2OH$	158	0.6
1-heptanol	$CH_3(CH_2)_5CH_2OH$	176	0.2
1-octanol	$CH_3(CH_2)_6CH_2OH$	195	0.05

∞ - Miscible in any proportion.

3.1.3 Reactions of alcohols

Alcohols undergo reactions involving cleavage of O–H bond and cleavage of C–O bond.

3.1.3.1 Reactions involving cleavage of O-H bond

(a) *Reaction with sodium (and other alkali metals)*

Alcohols show acidic behaviour because of the polarization of the O–H bond and react with sodium liberating hydrogen and forming sodium alkoxides. The alkoxide ion is a strong nucleophile and also a strong base.

$$RO{-}H \ + \ Na \ \longrightarrow \ RO^- \ + \ H_2$$

However alcohols are not acidic enough to give a substantial reaction with sodium hydroxide to give sodium alkoxide. Thus the equilibrium shown below lies essentially on the side of the alcohol. Hence alcohols are weaker acids than water.

$$ROH \ + \ NaOH \ \rightleftharpoons \ RO^-Na^+ \ + \ H_2O$$

(b) *Reaction with carboxylic acid (Acylation of alcohols to give esters)*

Alcohols react with carboxylic acids to form esters (esterification reaction). Concentrated H_2SO_4 acid acts as a catalyst for this esterification reaction.

$$C_2H_5OH \ + \ CH_3COOH \ \underset{}{\overset{conc.\ H_2SO_4/heat}{\rightleftharpoons}} \ CH_3COOC_2H_5 \ + \ H_2O$$

3.1.3.2 Nucleophilic substitution reactions involving cleavage of C-O bond

(a) *Reaction with hydrogen halides* (HBr or HI)

Alcohols undergo nucleophilic substitution reaction with HBr or HI to give the corresponding alkyl bromides or alkyl iodides. Protonation of the O atom in the presence of acid (HBr or HI), converts the -OH group into a better leaving group (H_2O).

This is a nucleophilic substitution reaction. In this reaction Br^- ion acts as the nucleophile and the leaving group is H_2O.

Alcohols react with HCl only in the presence of Lewis acids or acids.

The Lucas test to distinguish primary, secondary and tertiary alcohols makes use of this fact. In this reaction, ROH is converted to RCl. $ZnCl_2$ which is a Lewis acid acts as the catalyst in this reaction. Because alkyl halides are insoluble in water, as the reaction proceeds the reaction mixture becomes cloudy and turbid. The time taken for the turbidity to appear, after the mixing of reagents, can be used to distinguish between primary, secondary and tertiary alcohols. Under the given reaction conditions the above nucleophilic substitution reaction takes place in two steps. Tertiary alcohols form stable

intermediate tertiary carbocations and therefore, tertiary alcohols in the presence of the Lucas reagent form turbidity in a very short time. Secondary alcohols take longer time to produce turbidity and primary alcohols react very slowly.

(b) *Reaction with phosphorus trihalides* (PCl_3 or PBr_3)

Alcohols react with PCl_3 and PBr_3 to give alkyl chlorides and alkyl bromides respectively.

$$3\ ROH\ +\ PCl_3 \longrightarrow 3\ RCl\ +\ H_3PO_3$$
$$3\ ROH\ +\ PBr_3 \longrightarrow 3\ RBr\ +\ H_3PO_3$$
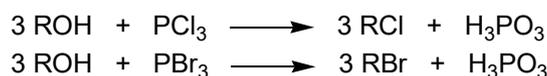
(c) *Reaction with phosphorus pentachloride* (PCl_5)

Alcohols react with PCl_5 to give alkyl chlorides.

$$ROH\ +\ PCl_5 \longrightarrow RCl\ +\ POCl_3\ +\ HCl$$

Reactions of alcohols with phosphorous halides described in (b) and (c) above are also nucleophilic substitution reactions where the halide ion acts as the nucleophile.

3.1.3.3 Elimination reaction

Alcohols undergo an elimination reaction when heated with conc. H_2SO_4 or when heated with alumina to a higher temperature. The reaction is the dehydration of alcohols, in which a molecule of water is eliminated from an alcohol. During this reaction an alkene is formed as the product.
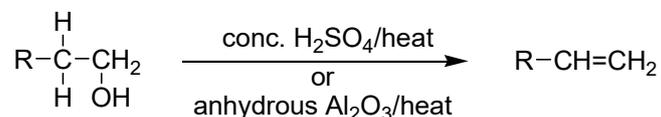
3.1.3.4 Oxidation of alcohols

Alcohols can be oxidized with several oxidizing agents. The product of oxidation depends on whether the alcohol is primary, secondary or tertiary. Oxidation of alcohols can be carried out with $H^+/KMnO_4$ or $H^+/K_2Cr_2O_7$ or H^+/CrO_3.

(a) *Oxidation of primary alcohols*

Primary alcohols are oxidized to carboxylic acids through the corresponding aldehyde with the above oxidizing reagents.
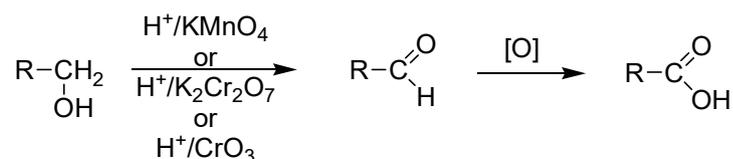
The oxidation reaction will be stopped at the stage where aldehyde is formed when pyridinium chlorochromate $[C_5H_5NH]^+[CrO_3Cl]^-$ (PCC) is used.

$$R-CH_2-OH \xrightarrow{PCC} R-C\underset{H}{\overset{O}{\diagup}}$$
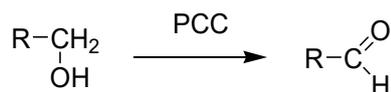
(b)   *Oxidation of secondary alcohols*

Secondary alcohols are oxidized to give ketones with any of the above reagents.

$$\underset{R}{\overset{R}{\diagdown}}CH-OH \xrightarrow[\substack{or \\ H^+/K_2Cr_2O_7 \\ or \\ H^+/CrO_3 \\ or \\ PCC}]{H^+/KMnO_4 \\ or} \underset{R}{\overset{R}{\diagdown}}C=O$$
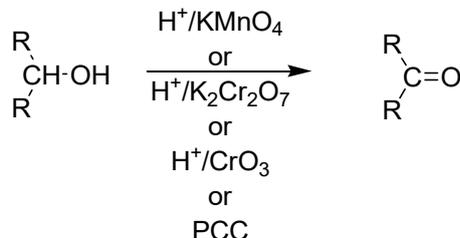
(c)   *Oxidation of tertiary alcohols*

Generally the tertiary alcohols do not undergo oxidation under conditions that primary and secondary alcohols are oxidized.

3.2   Structure, properties and reactions of phenols

3.2.1   Acidity of phenols

Aromatic compounds, in which an OH group is joined directly to a carbon atom of a benzene ring, are called phenols. Alcohols and phenols dissociate in aqueous solutions as shown below.

$$ROH + H_2O \rightleftharpoons RO^- + H_3O^+$$

$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$$
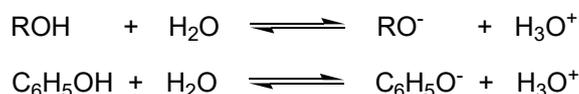
Phenols are more acidic than alcohols. This means that in the above equilibria, the equilibrium point for phenols is more towards the right than alcohols. The reason for this is that the stability of phenoxide ion relative to phenol is greater than the stability of the alkoxide ion relative to the alcohol. This can be understood by considering the resonance structures for phenol and its anion.

Resonance structures of phenol

Resonance structures of phenoxide ion
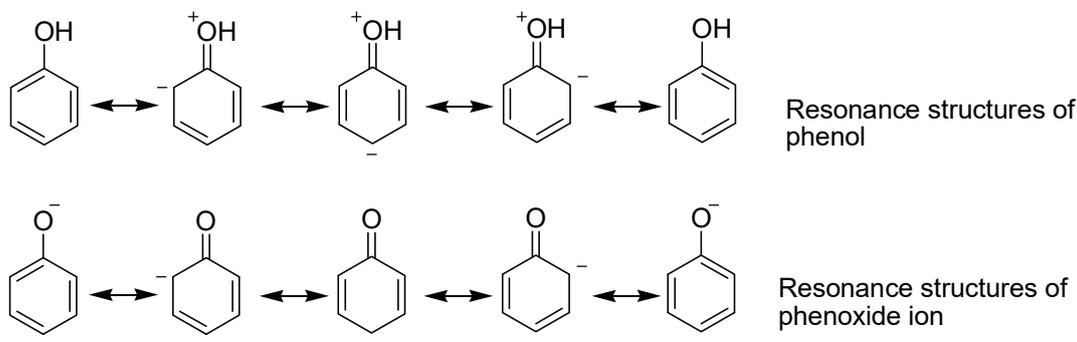
Figure 3.2 Resonance structures of phenol and phenoxide ion

The stabilization of the anion by resonance is greater than the stabilization of the phenol because unlike in the phenol there is no charge separation in the resonance structures of the anion **(Figure 3.2).** There is no corresponding resonance stabilization of alcohol or its anion.

3.2.2 Reactions involving cleavage of the O-H bond

The higher acidity of phenols is confirmed by the following examples. Unlike alcohols, phenols react with NaOH to give sodium phenoxide. However, neither phenols nor alcohols are acidic enough to react with $NaHCO_3$ and evolve CO_2.

$$2\ C_6H_5OH\ +\ 2Na\ \longrightarrow\ 2\ C_6H_5O^-\ Na^+\ +\ H_2$$

$$C_6H_5OH\ +\ NaOH\ \longrightarrow\ C_6H_5O^-\ Na^+\ +\ H_2O$$
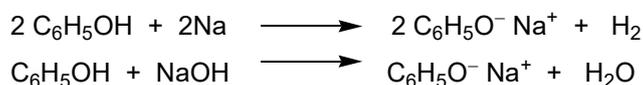
3.2.3 Non-occurrence of nucleophilic substitution reactions by breaking C-O bond

Unlike alcohols phenols do not undergo nucleophilic substitution reactions. Neither the one step nor the two step mechanism takes place because,

(a)   The C–O bond is shorter (sp^2 hybridized C atom) and stronger (double bond nature) due to delocalization of lone pair of electrons on the oxygen atom into the benzene ring. This can be shown by resonance.
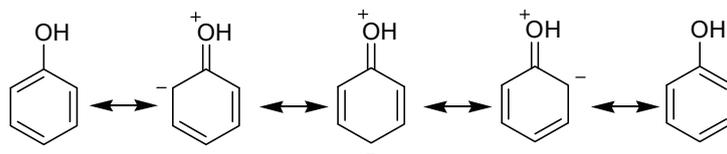
(b)   Phenyl cation is unstable.

3.3   Reactivity of the benzene ring in phenols

The benzene ring in phenol is electron rich compared to benzene due to the delocalization of a lone pair of electrons on the oxygen atom over the benzene ring in phenol. Therefore the benzene ring in phenol is more reactive towards electrophilic reagents than benzene itself. The O–H group of phenol directs the electrophilic substitution to the *ortho* and *para* positions with respect to the phenolic OH group.

When the electrophilic substitution reactions of phenol are compared with the corresponding reactions of benzene along with the relevant conditions, it is clear that the benzene ring of phenol is more reactive towards electrophiles. Consider the following examples.

3.3.1   Reaction of phenol with Br_2

Phenol reacts readily with bromine to form 2,4,6-tribromophenol while benzene does not react with bromine.
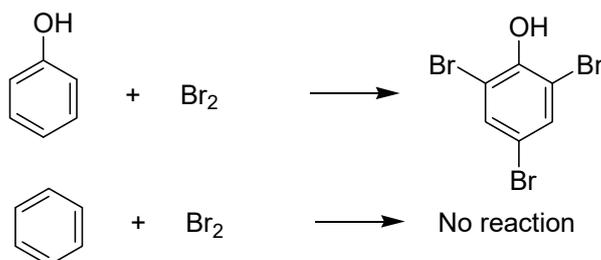
When this reaction is carried out with bromine water 2,4,6-tribromophenol is observed as a white precipitate.

3.3.2 Nitration of phenol

Nitration occurs even with dilute HNO_3 at 20 °C while benzene requires conc. HNO_3/conc. H_2SO_4 and higher temperatures for nitration.
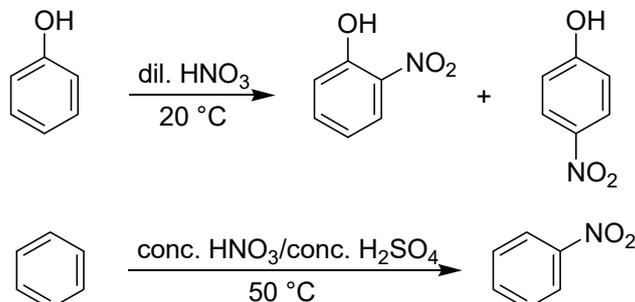
It should be noted that Friedel-Crafts alkylation reactions cannot be carried out with phenols because of the complex formation between Friedel-Crafts catalyst and phenols.

3.4   Structure, properties and reactions of aldehydes and ketones

Both aldehydes and ketones contain the carbonyl (C=O) functional group. In aldehydes the carbonyl carbon is attached to an H atom and an alkyl or aryl (aromatic) group. However, the simplest aldehyde, formaldehyde (methanal) has two H atoms attached to the carbonyl carbon. In ketones each of the groups attached to the carbonyl carbon is either an alkyl group or an aryl group. The carbonyl C atom is sp^2 hybridized and the three atoms attached to it lie in one plane (trigonal planar). The carbon oxygen double bond consists of a σ bond and a π bond.

3.4.1 Physical properties

Boiling points of aldehydes and ketones are higher than those of alkanes of comparable relative molecular masses due to the presence of intermolecular dipole-dipole interactions. However their boiling points are lower than alcohols of comparable relative molecular masses as they do not form intermolecular H-bonds **(Table 3.3)**.

Table 3.3 Boiling points and water solubility of aldehydes, ketones, alcohols and alkanes of comparable relative molecular masses

| Compound	Structural formula	Relative molecular mass	Boiling point/ °C	Water Solubility (g/100 mL)*
ethanal	CH_3CHO	44	21	∞
ethanol	CH_3CH_2OH	46	78	∞
propane	$CH_3CH_2CH_3$	44	–42	none
propanal	CH_3CH_2CHO	58	49	16
propanone	CH_3COCH_3	58	56	∞
1-propanol	$CH_3CH_2CH_2OH$	60	97	∞
2-propanol	$(CH_3)_2CHOH$	60	83	∞
butane	$CH_3CH_2CH_2CH_3$	58	0	none
butanal	$CH_3CH_2CH_2CHO$	72	76	7
2-butanone	$CH_3COCH_2CH_3$	72	80	26
1-butanol	$CH_3CH_2CH_2CH_2OH$	74	118	7.9
2-butanol	$CH_3CH(OH)CH_2CH_3$	74	99	29
pentane	$CH_3CH_2CH_2CH_2CH_3$	72	36	none
penatanal	$CH_3CH_2CH_2CH_2CHO$	86	103	1
2-pentanone	$CH_3COCH_2CH_2CH_3$	86	102	6
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	88	138	2.3
hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	86	68	none

∞ - Miscible in any proportion.

However aldehydes and ketones can participate in intermolecular H-bonding with water **(Figure 3.3).** Therefore aldehydes and ketones with relatively lower molecular masses are soluble in water **(Table 3.3)**.
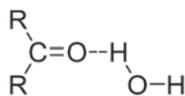
Figure 3.3   Intermolecular H-bonding of aldehydes and ketones with water

3.4.2   Reactions of aldehydes and ketones

The carbonyl group is a polar group because of the electron negative O atom ($^{\delta+}C=O^{\delta-}$). Hence the C atom is electron deficient and can react with a nucleophile. The C atom is unsaturated because it is attached only to three atoms. It can therefore form a new bond with a nucleophile. During this process the two π electrons are transferred to the oxygen atom which thereby acquiring a negative charge. This negative charge is neutralized by the attachment of a positively charged species (very often a proton). Therefore the characteristic reactions of aldehydes and ketones are nucleophilic addition reactions.

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3.4.3   Nucleophilic addition reactions

3.4.3.1   Addition of HCN to aldehydes and ketones

Addition of HCN to aldehydes and ketones is a nucleophilic addition reaction. This is carried out by adding a dilute mineral acid into a mixture of the carbonyl compound and an aqueous solution of sodium cyanide. Here the CN^- ion acts as the nucleophile.
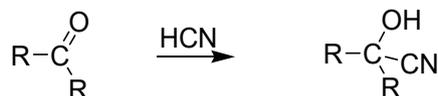
Mechanism of the reaction is as follows.
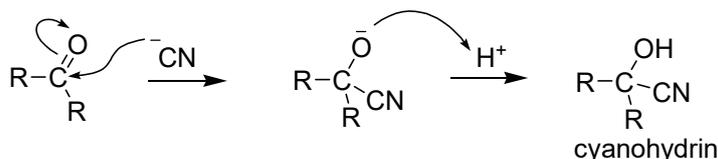
3.4.3.2   Reaction with Grignard reagents

In Grignard reagents the C–Mg bond is polarized as follows.

$$\overset{\delta-\ \ \ \delta+}{R-MgX}$$

Therefore the R group of the Grignard reagent together with the electron pair of R–Mg bond reacts as a nucleophile with the carbonyl carbon. This leads to the formation of an alkoxy magnesium halide.
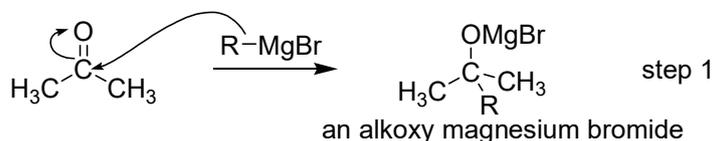
Hydrolysis of the alkoxy magnesium halide gives the corresponding alcohol. This is carried out by an aqueous acid.
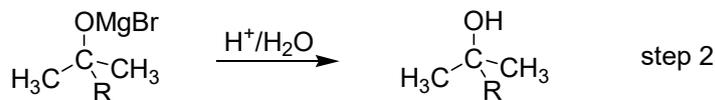
The overall reaction is as follows:
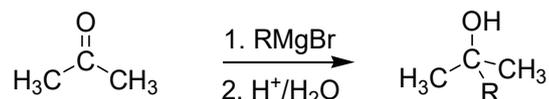
All aldehydes except formaldehyde give secondary alcohols whereas ketones give tertiary alcohols with Grignard reagents. Formaldehyde gives primary alcohols.

Grignard reagents are prepared and reacted with aldehydes and ketones under anhydrous conditions. Hence the formation of the alkoxy magnesium halide and its hydrolysis are two distinct steps.

3.4.3.3 Reaction with 2,4-dinitrophenylhydrazine (2,4-DNP or Brady reagent)

In this reaction, nucleophilic addition of 2,4-dinitrophenylhydrazine to the aldehyde or ketone takes place first. Then a water molecule is eliminated from the intermediate product to form the final product, which is a 2,4-dinitrophenylhydrazone.

2,4-dinitrophenylhydrazone
(a dark yellow or orange precipitate)
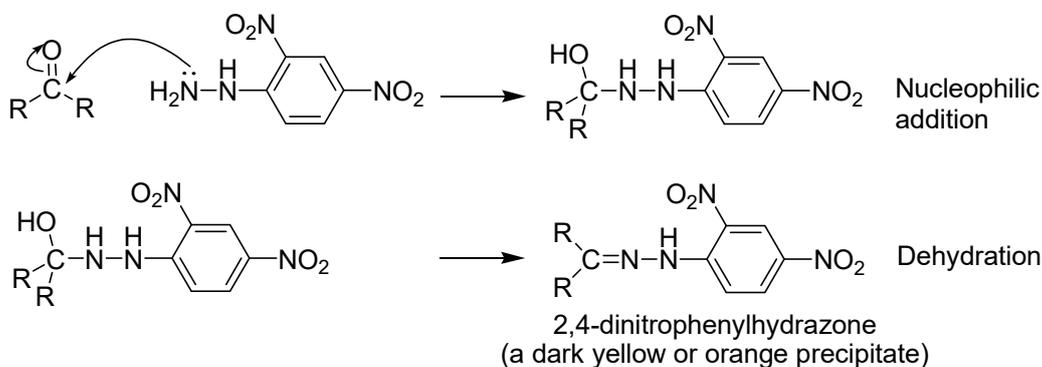
Although this reaction takes place in two steps as shown above, the hydroxy product first obtained by the nucleophilic addition cannot be isolated under the reaction conditions and dehydrates to give the final product. This reaction is used to identify aldehydes and ketones.

3.4.4 Self-condensation reactions of aldehydes and ketones

Due to the strong electron withdrawing nature of the carbonyl group, H atoms attached to the carbon atoms directly bound to the carbonyl carbon (the α-H) become acidic. This α-H can be abstracted as a proton by a base (e.g.: OH⁻). The carbanion so formed is stabilized by resonance as shown below.
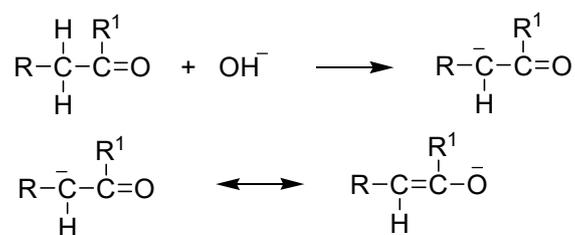
This carbanion reacts as a nucleophile and attacks the carbon atom of the carbonyl group of an un-ionized aldehyde molecule. Hence aldehydes and ketones with α-hydrogens undergo base catalyzed self-condensation reactions.

Let us see some examples.

Reaction of acetaldehyde in the presence of aqueous NaOH

$$H_3C-\overset{\overset{\displaystyle H}{|}}{C}=O \quad + \quad OH^- \longrightarrow H_2\overset{-}{C}-\overset{\overset{\displaystyle H}{|}}{C}=O \quad + \quad H_2O$$

$$H_3C-\overset{\overset{\displaystyle H}{|}}{C}=O \qquad H_2\overset{-}{C}-\overset{\overset{\displaystyle H}{|}}{C}=O \longrightarrow H_3C-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2CHO$$

$$H_3C-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2CHO \quad + \quad H_2O \longrightarrow H_3C-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2CHO \quad + \quad OH^-$$

The overall reaction is:

$$2CH_3CHO \xrightarrow{\text{aq. NaOH}} H_3C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2CHO$$
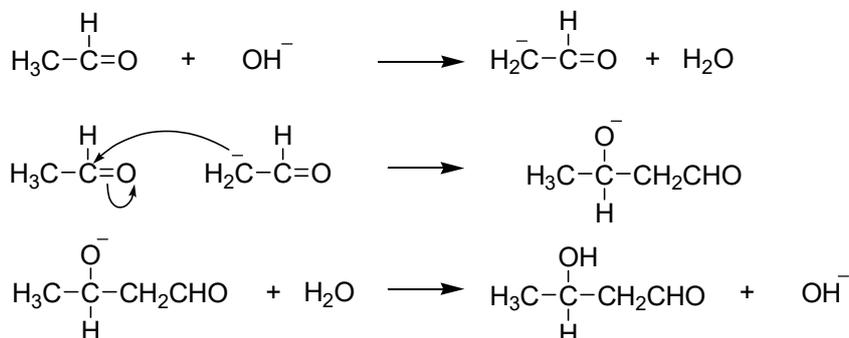
Condensation of acetone in the presence of aqueous NaOH

$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}=O \xrightarrow{OH^-} H_2\overset{-}{C}-\overset{\overset{\displaystyle CH_3}{|}}{C}=O$$

$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}=O \qquad H_2\overset{-}{C}-\overset{\overset{\displaystyle CH_3}{|}}{C}=O \longrightarrow H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2\overset{\overset{\displaystyle O}{||}}{C}CH_3$$

The overall reaction is:

$$2\ CH_3\overset{\overset{\displaystyle O}{||}}{C}CH_3 \xrightarrow{\text{aq. NaOH}} H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2\overset{\overset{\displaystyle O}{||}}{C}CH_3$$
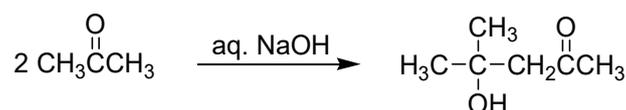
The addition products obtained above undergo dehydration easily when heated with acids.

$$H_3C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2CHO \xrightarrow{H^+/\Delta} H_3C-\overset{\overset{\displaystyle H}{|}}{C}=CHCHO$$
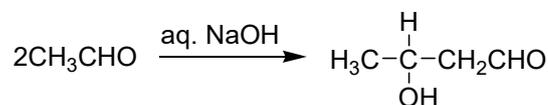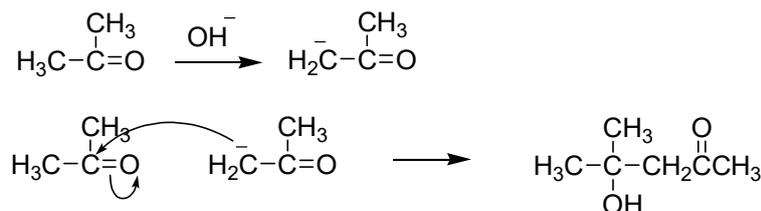
$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2\overset{\overset{\displaystyle O}{||}}{C}CH_3 \xrightarrow{H^+/\Delta} H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH\overset{\overset{\displaystyle O}{||}}{C}CH_3$$
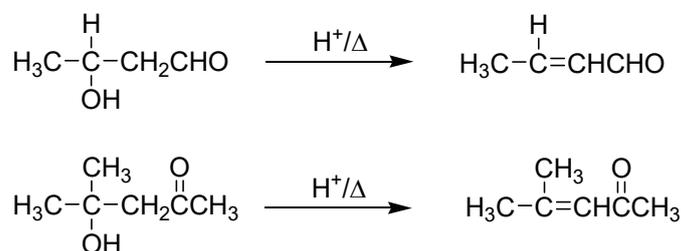
3.4.5 Reduction of aldehydes and ketones by lithium aluminium hydride (LiAlH$_4$) or sodium borohydride(NaBH$_4$)

Aldehydes are reduced to primary alcohols with LiAlH$_4$ or NaBH$_4$ while ketones are reduced to give secondary alcohols. In these reductions both LiAlH$_4$ and NaBH$_4$ provide hydride ions (H$^-$). The hydride ion reacts with the carbonyl C as a nucleophile. Thus these reductions can be considered as nucleophilic addition reactions.

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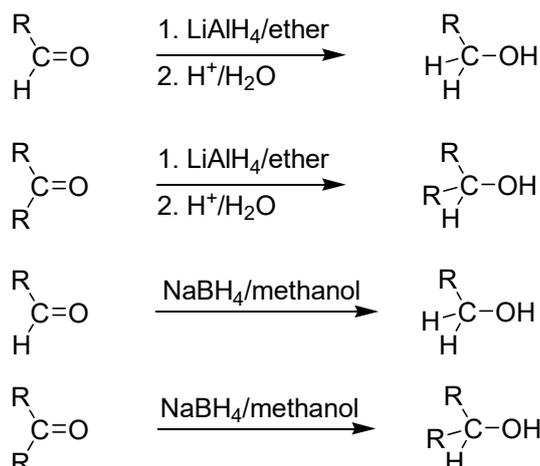
Note that $LiAlH_4$ is too reactive to be used in the presence of water or methanol.

3.4.6 Reduction of aldehydes and ketones by Zn(Hg)/ conc.HCl (Clemmenson reduction)

In this reduction reaction, C=O group is reduced to a methylene (CH_2) group. Thus, both aldehydes and ketones can be converted to hydrocarbons.

3.4.7 Oxidation of aldehydes

Aldehydes are oxidized to carboxylic acids by oxidizing agents such as acidified potassium dichromate, acidified chromic oxide or acidified potassium permanganate and even by m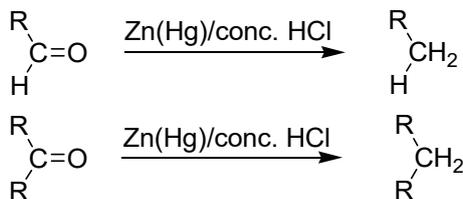ild oxidizing agents such as Tollen reagent and Fehling solution. In acidic medium aldehydes are oxidized to carboxylic acids while with Tollen and Fehling solution, which are alkaline, the product is a salt of the carboxylic acid. Ketones do not undergo oxidation with these reagents.

3.4.7.1 Oxidation by Tollens reagent

Tollens reagent, is a solution containing Ag^+ in the form $[Ag(NH_3)_2]^+$. During the oxidation of aldehydes to carboxylic acids, Ag^+ ions are reduced to metallic silver giving a silver mirror in the test tube.
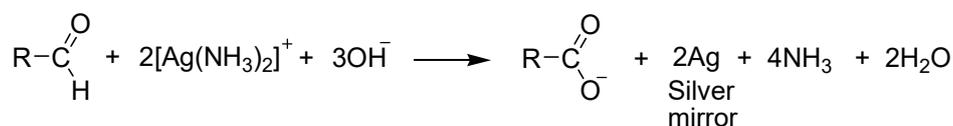
Oxidation of aldehydes by Tollens reagent or the silver mirror test is used to distinguish between aldehydes and ketones.

3.4.7.2 Oxidation by Fehling solution

A solution of Copper (II) tartrate in aqueous NaOH is known as Fehling solution. This is a dark blue solution. When a few drops of an aldehyde are added to this reagent and heated, the blue colour of the solution gradually disappears and a brick red precipitate of cuprous oxide is formed.

$$R-\underset{\underset{H}{|}}{\overset{\overset{O}{\parallel}}{C}} + 2Cu^{2+} \text{ (Tartrate)} + 5OH^- \longrightarrow R-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\parallel}}{C}} + \underset{\substack{\text{Brick-red} \\ \text{precipitate}}}{Cu_2O} + 3H_2O$$

Aldehydes and ketones can be distinguished from each other by reacting with Fehling solution.

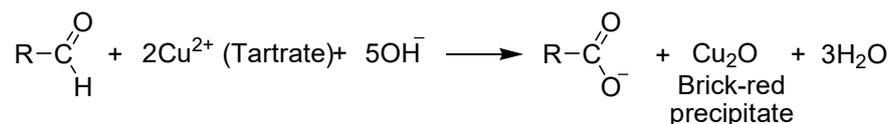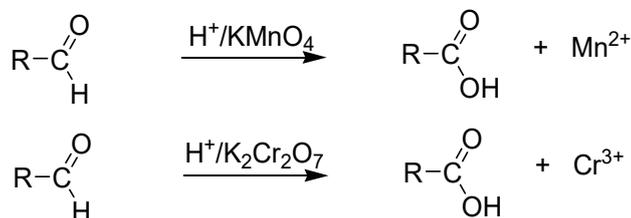### 3.4.7.3 Oxidation by acidified potassium dichromate or acidified chromic oxide or acidified potassium permanganate

Aldehydes get oxidized to carboxylic acids by reacting with oxidizing agents such as acidified potassium dichromate or acidified chromic oxide or acidified potassium permanganate.

$$R-\underset{\underset{H}{|}}{\overset{\overset{O}{\parallel}}{C}} \xrightarrow{H^+/KMnO_4} R-\underset{\underset{OH}{|}}{\overset{\overset{O}{\parallel}}{C}} + Mn^{2+}$$

$$R-\underset{\underset{H}{|}}{\overset{\overset{O}{\parallel}}{C}} \xrightarrow{H^+/K_2Cr_2O_7} R-\underset{\underset{OH}{|}}{\overset{\overset{O}{\parallel}}{C}} + Cr^{3+}$$

The pink colour of $H^+/KMnO_4$ solution becomes colourless in the presence of an aldehyde while the orange colour of $H^+/Cr_2O_7^{2-}$ solution turns green. By using these reagents aldehydes and ketones can be distinguished from each other.

Since ketones do not contain an H atom attached to the C=O group, they do not undergo oxidation with these oxidizing reagents.

However strong oxidizing agents like potassium permanganate can oxidize ketones when heated. During this oxidation carbon-carbon bonds are broken resulting in the decomposition of the ketone.

3.5 Structure, properties and reactions of carboxylic acids

Carboxylic acids are compounds containing carboxyl (COOH) group which consists of a C=O and OH groups **(Figure 3.4)**. Carboxylic acids are generally more acidic than other organic compounds containing OH groups but weaker than the common mineral acids.
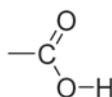
Figure 3.4 Structure of the carboxyl group

3.5.1 Physical properties

Carboxyl group is a polar functional group. Due to the polarity of C–O and O–H groups it forms intermolecular hydrogen bonds. Carboxylic acids are capable of forming dimeric structures in which carboxylic acid molecules are attached by hydrogen bonds as pairs **(Figure 3.5)**.
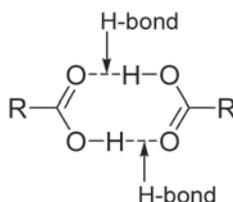

Figure 3.5 Dimeric structure of carboxylic acids due to H-bonding

Due to these reasons carboxylic acids show higher boiling points than the alcohols, aldehydes and ketones with comparable relative molecular masses **(Table 3.4)**.

Table 3.4 Boiling points of some carboxylic acids, alcohols, aldehydes and ketones of comparable relative molecular masses

Compound	Structural formula	Relative molecular mass	Boiling point/ °C
methanoic acid	HCO_2H	46	100
ethanol	CH_3CH_2OH	46	78
ethanal	CH_3CHO	44	20
ethanoic acid	CH_3CO_2H	60	118
1-propanol	$CH_3CH_2CH_2OH$	60	97
2-propanol	$(CH_3)_2CHOH$	60	83
propanal	CH_3CH_2CHO	58	49
propanone	$(CH_3)_2C=O$	58	56
propanoic acid	$CH_3CH_2CO_2H$	74	141
1-butanol	$CH_3CH_2CH_2CH_2OH$	74	118
2-butanol	$CH_3CH(OH)CH_2CH_3$	74	99
butanal	$CH_3CH_2CH_2CHO$	72	75
butanone	$CH_3COCH_2CH_3$	72	80

Carboxyl group can form H-bonds with water. Therefore carboxylic acids of C_1 to C_4 dissolve well in water. When the number of carbon atoms increases solubility decreases. Aromatic

carboxylic acids are water insoluble and exist as solid crystalline substances. Almost all the carboxylic acids are soluble in organic solvents.

3.5.2 Comparison of the reactivity pattern of -COOH group with >C=O group in aldehydes and ketones and -OH group in alcohols and phenols

Similar to alcohols, the O–H group of carboxylic acids also undergoes reactions involving cleavage of both C–O bond and O–H bond.
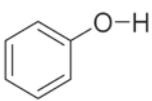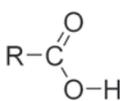
3.5.2.1 Reactions involving cleavage of the O–H bond

Carboxylic acids are acidic. They react with alkali metals such as sodium and potassium, alkali such as NaOH and KOH and bases such as Na_2CO_3 and $NaHCO_3$.

$$2\ RCOOH\ +\ 2\ Na\ \longrightarrow\ 2\ RCOO^-Na^+\ +\ H_2$$

$$RCOOH\ +\ NaOH\ \longrightarrow\ RCOO^-Na^+\ +\ H_2O$$

$$2\ RCOOH\ +\ Na_2CO_3\ \longrightarrow\ 2\ RCOO^-Na^+\ +\ CO_2\ +\ H_2O$$

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

A comparison of the reactions of alcohols, phenols and carboxylic acids with sodium, sodium hydroxide and sodium bicarbonate is given in the **Table 3.5.**

Table 3.5 Reactions of alcohols, phenols and carboxylic acids with sodium, sodium hydroxide, sodium carbonate and sodium bicarbonate

Compound	Reaction with		
	Metallic Na	**aq. NaOH**	**aq. Na_2CO_3 or $NaHCO_3$**
R–O–H	Liberates H_2 gas forming RO^-Na^+	No reaction	No reaction
(phenol) O–H	Liberates H_2 gas forming $C_6H_5O^-Na^+$	Dissolves in aq. NaOH forming a solution of $C_6H_5O^-Na^+$	No reaction
R–C(=O)O–H	Liberates H_2 gas forming $RCOO^-Na^+$	Dissolves in aq. NaOH forming a solution of $RCOO^-Na^+$	Dissolves in aq. Na_2CO_3 or aq. $NaHCO_3$ forming a solution of $RCOO^-Na^+$ and liberating CO_2 gas

Thus the acidic strengths of alcohols, phenols and carboxylic acids vary as follows.

Alcohols < Phenols < Carboxylic acids

In aqueous medium carboxylic acids exist in the following equilibrium.

$$R-\overset{\displaystyle O}{\underset{\displaystyle O-H}{C}} \quad + \quad H_2O \quad \rightleftharpoons \quad R-\overset{\displaystyle O}{\underset{\displaystyle O^-}{C}} \quad + \quad H_3O^+$$

The equilibrium point of the above equilibrium is more shifted towards the right side relative to the corresponding equilibrium attained by the phenols. The reason for this is that the stabilization of the carboxylate ion relative to the carboxylic acid is greater than the stabilization of the phenoxide ion relative to phenol. Both the carboxylate ion and carboxylic acid are stabilized by resonance **(Figure 3.6)** as in the case of phenoxide ion and phenols **(Figure 3.2)**.

Resonance structures of a carboxylic acid

Resonance structures of a carboxylate anion

**Figure 3.6** Resonance structures of a carboxylic acid and a carboxylate anion

The stabilization of the carboxylate anion by resonance is greater than the stabilization of the acid because unlike in the acid there is no charge separation in the resonance structures of the anion **(Figure 3.6)**.

The higher acidity of the carboxylic acids can be explained by the fact that the carboxylate ion is stabilized by the delocalization of the negative charge between two equivalent electronegative oxygen atoms in contrast to the delocalization of the negative charge on oxygen and carbon atoms in phenoxide anion.

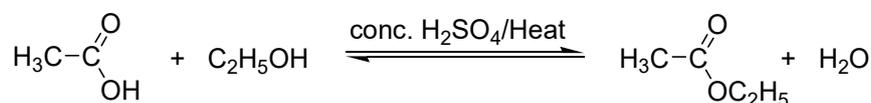### 3.5.2.2 Reactions involving cleavage of the C–O bond

(a) *Reaction with PCl$_3$ or PCl$_5$*

Carboxylic acids react with PCl$_3$ or PCl$_5$ giving carboxylic acid chlorides.
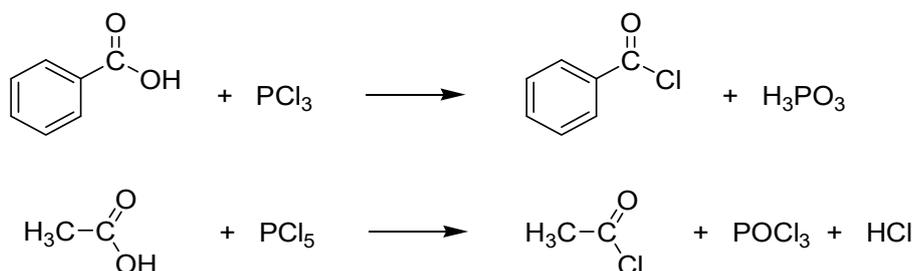

(b) *Reaction with alcohols*

Carboxylic acids react with alcohols in the presence of acid catalyst to give esters.

Although the above reaction appears to be a simple nucleophilic substitution reaction (OH being replaced by OC_2H_5) it actually involves first the nucleophilic addition of the C_2H_5OH molecule across the C=O to give a tetrahedral intermediate. Under acidic condition of the reaction this intermediate loses a molecule of water to give the ester.
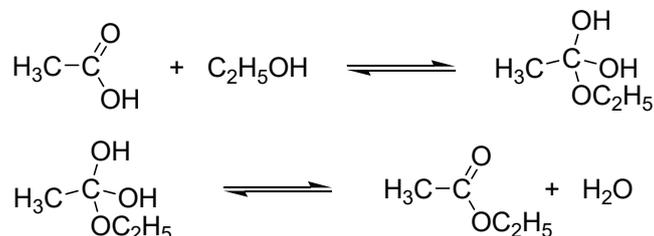
Note: Please also see the discussion in the Section 3.6.

3.5.2.3 Reduction of carboxylic acids with LiAlH$_4$

Carboxylic acids react with LiAlH$_4$ which is a powerful reducing agent to give alcohols. Note that carboxylic acids and their derivatives are not reduced by NaBH$_4$ which is a less powerful reducing agent than LiAlH$_4$.
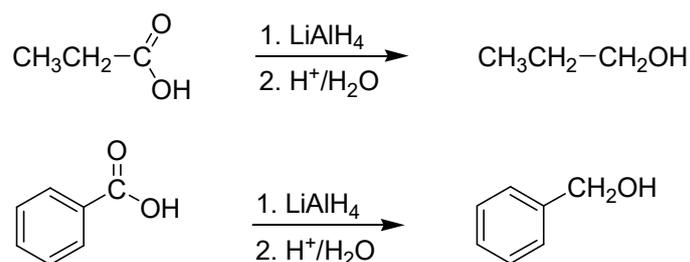
3.6 Reactions of carboxylic acid derivatives

It is instructive to compare the reactions of carboxylic acid derivatives and carboxylic acids with those of aldehydes and ketones **(Figure 3.7)**.
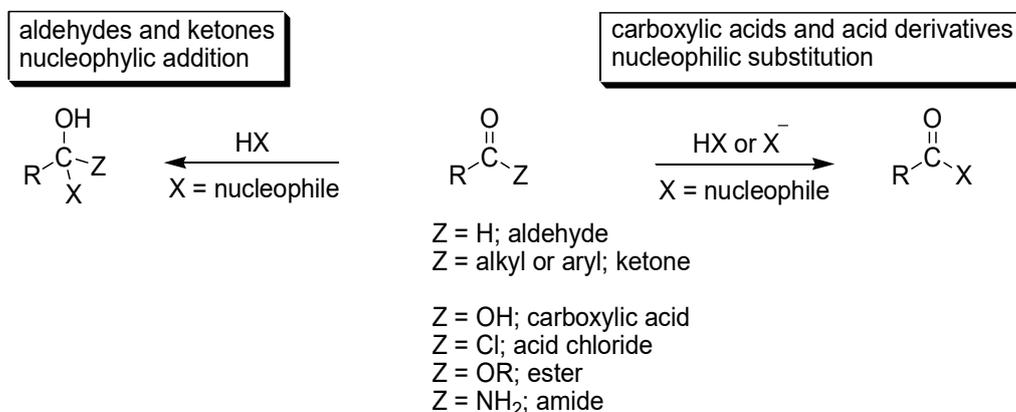

Z = H; aldehyde
Z = alkyl or aryl; ketone

Z = OH; carboxylic acid
Z = Cl; acid chloride
Z = OR; ester
Z = NH$_2$; amide

Figure 3.7 Comparison of characteristic reactions of aldehydes/ ketones with those of carboxylic acids and their derivatives

The essential difference is that in contrast to aldehydes and ketones, the Z group in carboxylic acid derivatives and carboxylic acids is capable of behaving as a leaving group. That is in reactions involving heterolytic cleavage of C–Z bond, Z leaves with the electron pair of the bond.

As in the case of aldehydes and ketones the first step of the reaction is the attack of a nucleophile on the carbonyl carbon of acids and acid derivatives with the opening of the carbon oxygen double bond to give a tetrahedral intermediate. This is followed by re-formation of the carbon oxygen double bond with the loss of Z as Z^- under basic or neutral conditions or as ZH under acidic conditions.

Thus the carbon atom regains its trigonal geometry and the overall reaction is the substitution of Z with a nucleophile. This reaction pathway is not available in aldehydes and ketones as H, alkyl and aryl do not behave as leaving group.
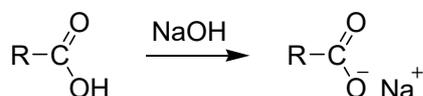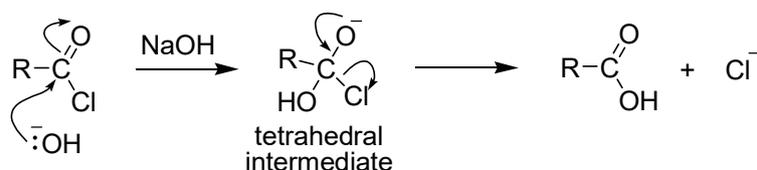
3.6.1 Reactions of acid chlorides

3.6.1.1 Reaction with aqueous sodium hydroxide

Acid chlorides react with aqueous NaOH to form the corresponding carboxylic acid which reacts with excess NaOH to form its sodium salt.
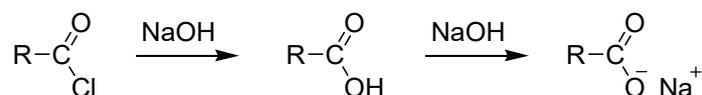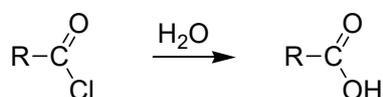

The mechanism of the reaction is as follows.

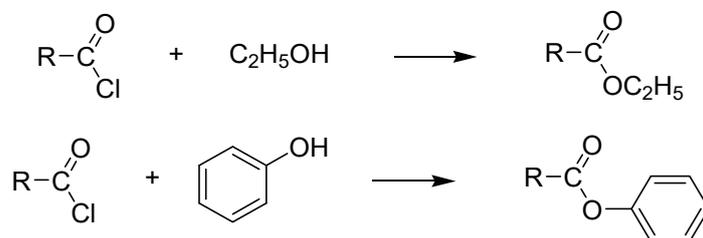In the above reaction the OH^- is the nucleophile and Cl^- is the leaving group.

3.6.1.2 Reaction with water

Acid chlorides react with water by a similar mechanism to form the corresponding carboxylic acid.
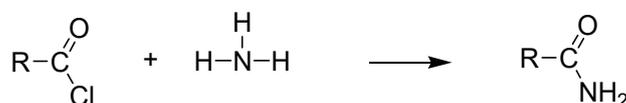

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3.6.1.3 Reaction with alcohols and phenols

Acid chlorides react with alcohols and phenols to form alkyl esters and phenyl esters respectively.
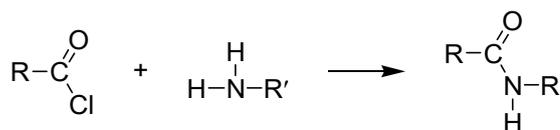

3.6.1.4 Reaction with ammonia and primary amines

Acid chlorides react with ammonia to form primary amides.

Acid chlorides react with primary amines to form secondary amides.

Note: Amides are classified as primary amides when two H atoms are attached to the N atom. If one H atom is replaced by an alkyl group, it is classified as a secondary amide and if both H atoms are replaced by two alkyl groups the amide is classified as tertiary amide.

3.6.2 Reactions of esters

3.6.2.1 Reaction with dilute mineral acids

Esters react with dilute acids and give corresponding carboxylic acid and the alcohol as the products. In this reaction water acts as the nucleophile and the ester undergoes hydrolysis. This reaction also goes through the same tetrahedral intermediate involved in the formation of esters as given in **Section 3.5.2.2** (b).
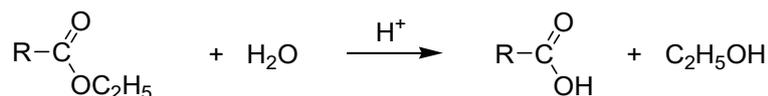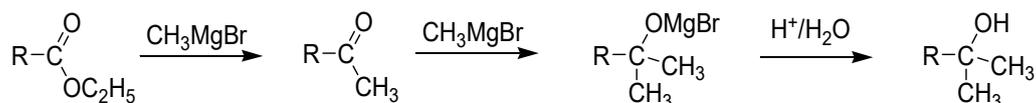

3.6.2.2 Reaction with aqueous sodium hydroxide

Esters when reacted with aqueous NaOH form the sodium salt of corresponding carboxylic acid and the alcohol. The mechanism of this reaction is similar to the mechanism of the reaction of acid chlorides with NaOH **(Section 3.6.1.1)**.

$$R-C(=O)OC_2H_5 \xrightarrow{\text{NaOH}} R-C(=O)O^- Na^+ \quad + \quad C_2H_5OH$$
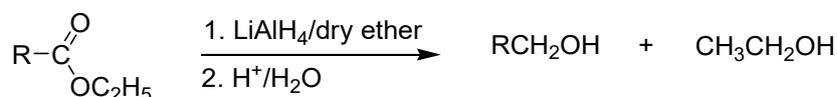
3.6.2.3 Reaction with Grignard reagent

Esters react with Grignard reagents to give tertiary alcohols. In this reaction, the ester is first converted to a ketone which reacts rapidly with the Grignard reagent again to give the tertiary alcohol as the product.

$$R-C(=O)OC_2H_5 \xrightarrow{\text{CH}_3\text{MgBr}} R-C(=O)CH_3 \xrightarrow{\text{CH}_3\text{MgBr}} R-\underset{CH_3}{\underset{|}{C}}(OMgBr)CH_3 \xrightarrow{\text{H}^+/\text{H}_2\text{O}} R-\underset{CH_3}{\underset{|}{C}}(OH)CH_3$$

Note that as ketones react faster than esters with Grignard reagents it is not possible to stop the reaction at the ketone stage.

3.6.2.4 Reduction by LiAlH$_4$

Esters react with LiAlH$_4$ and reduce to give alcohols.

$$R-C(=O)OC_2H_5 \xrightarrow[\text{2. H}^+/\text{H}_2\text{O}]{\text{1. LiAlH}_4/\text{dry ether}} RCH_2OH \quad + \quad CH_3CH_2OH$$

3.6.3 Reactions of amides

3.6.3.1 Reaction with aqueous sodium hydroxide

When amides are warmed with an aqueous solution of NaOH, the sodium salt of the corresponding carboxylic acid is formed with liberation of gaseous NH$_3$.

$$R-C(=O)NH_2 \xrightarrow[\Delta]{\text{aq. NaOH}} R-C(=O)O^- Na^+ \quad + \quad NH_3$$
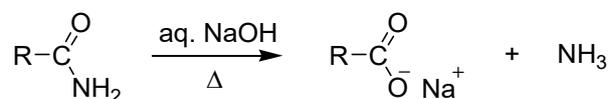
3.6.3.2 Reduction with LiAlH$_4$

Amides are reduced to the corresponding primary amine with LiAlH$_4$.

$$R-C(=O)NH_2 \xrightarrow[\text{2. H}^+/\text{H}_2\text{O}]{\text{1. LiAlH}_4/\text{dry ether}} RCH_2NH_2$$

4. Nitrogen Containing Organic Compounds

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4.3.2 Reactions in which the diazonium ion acts as an electrophile

Introduction

Common organic compounds containing N includes amines and amides. Reactions of amides have been discussed under derivatives of carboxylic acids because of the presence of acyl group which are common to all derivatives of carboxylic acids. In this unit properties and reactions of amines in relation to their structures will be discussed. Amines can be defined as compounds where alkyl or aryl groups are attached to nitrogen in place of hydrogen atoms in ammonia.

4.1 Structure, properties and reactions of primary amines and aniline

4.1.1 Classification of amines

Unlike in alkyl halides and alcohols, amines are classified as primary, secondary and tertiary according to the number of alkyl or aryl groups attached to the hetero atom (N in amines). The compounds in which an alkyl or an aryl group is attached in place of one of the three hydrogen atoms in ammonia are called primary amines. The compounds in which two groups, each of which could be an alkyl or aryl group are attached in place of two atoms of hydrogen in ammonia are called secondary amines and the compounds in which three such groups are attached in place of the three atoms of hydrogen are called tertiary amines.

methylamine
(primary amine)

dimethylamine
(secondary amine)

trimethylamine
(tertiary amine)
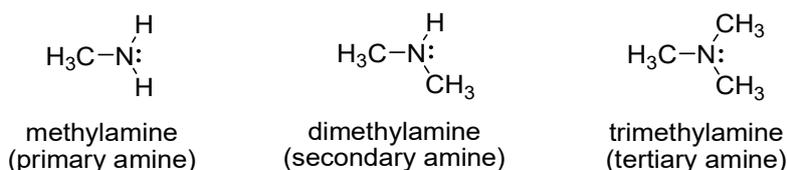
The compounds in which at least one aryl group (aromatic ring) is attached to the nitrogen atom are called aromatic amines.

aniline
(primary aromatic amine)

N-methylaniline
secondary aromatic amine
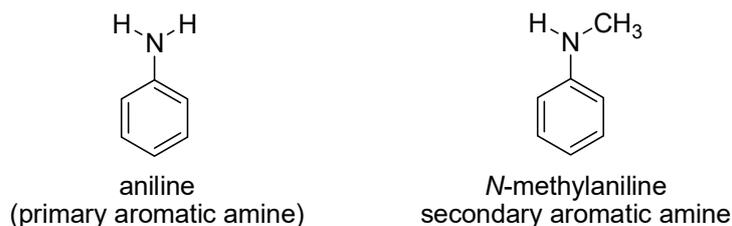
The simplest aromatic amine is the one with NH_2 attached to a benzene ring (aniline)

4.1.2 Reactivity of the benzene ring of aniline

Similar to phenol, aniline readily reacts with bromine to give 2,4,6-tribromoaniline because the -NH_2 group activates the benzene ring towards electrophilic substitution.
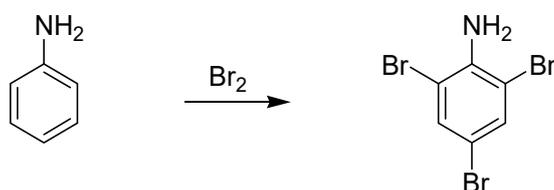
When this reaction is carried out with bromine water 2,4,6-tribromoaniline is observed as a white precipitate.
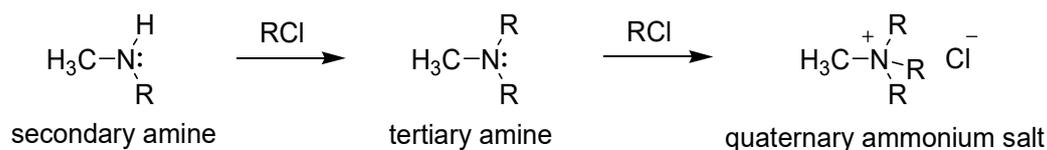
4.1.3 Reactions of primary amines

Amines can act as nucleophiles as the N atom contains a lone pair of electrons. The following are some of the reactions of primary amines with various reagents where the amine acts as a nucleophile.

4.1.3.1 Reaction of amines with alkyl halides

Primary amines react with alkyl halides to give secondary amines.

$$CH_3NH_2 \xrightarrow{\;RCl\;} H_3C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{N}}:$$
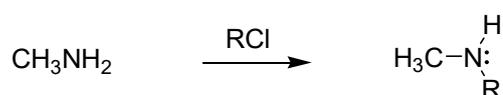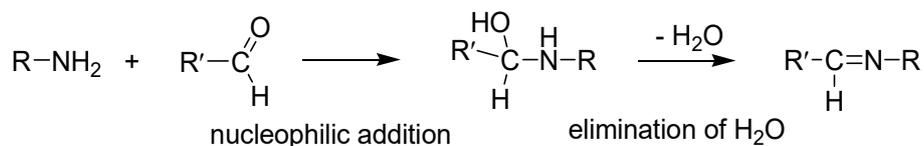
These secondary amines too have a lone pair of electrons on N atom and hence can further react with alkyl halide to form tertiary amines. Thus formed tertiary amine can react with alkyl halide further, because it also has a lone pair of electrons, to give a quaternary ammonium salt.

$$\underset{\text{secondary amine}}{H_3C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{N}}:} \xrightarrow{\;RCl\;} \underset{\text{tertiary amine}}{H_3C-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{N}}:} \xrightarrow{\;RCl\;} \underset{\text{quaternary ammonium salt}}{H_3C-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{\overset{+}{N}}}-R \quad Cl^-}$$

Therefore the reaction between primary amine and alkyl halides give a mixture of products.

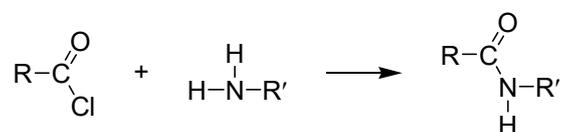#### 4.1.3.2 Reaction of amines with aldehydes and ketones

Amines show nucleophilic addition followed by elimination with aldehydes and ketones. The products are called imines.

$$R-NH_2 \; + \; R'-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{}}{C}} \xrightarrow{\underset{\text{nucleophilic addition}}{}} R'-\overset{\overset{\displaystyle HO}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{N}-R \xrightarrow[\text{elimination of } H_2O]{-\,H_2O} R'-C=\overset{\overset{\displaystyle }{}}{\underset{\underset{\displaystyle H}{|}}{N}}-R$$

This reaction corresponds to the reaction of aldehydes and ketones with the 2,4-dinitrophenylhydrazine (Brady reagent).

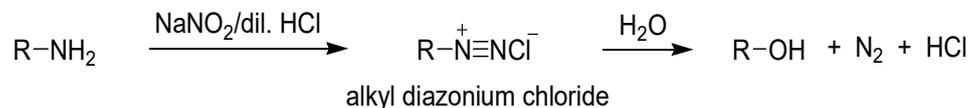#### 4.1.3.3 Reaction of amines with acid chlorides

Primary amines react with acid chlorides to give secondary amides.

$$R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle Cl}{}}{C}} \; + \; H-\overset{\overset{\displaystyle H}{|}}{N}-R' \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle }{}}{C}}\underset{\underset{\displaystyle H}{|}}{\overset{}{N}}-R'$$

## 4.1.3.4 Reaction of amines with nitrous acid (NaNO$_2$/HCl)

Primary amines react with nitrous acid to form diazonium salts. As alkyl diazonium salts are unstable they rapidly convert to alcohols with the evolution of nitrogen gas.

$$R-NH_2 \xrightarrow{\text{NaNO}_2/\text{dil. HCl}} R-\overset{+}{N}\equiv N\overset{-}{Cl} \xrightarrow{\text{H}_2\text{O}} R-OH + N_2 + HCl$$

alkyl diazonium chloride

Aromatic diazonium salts formed from aromatic amines are more stable than alkyl diazonium salts. Therefore solutions of aromatic diazonium salts may be obtained at low temperatures.

4.2 Basicity of amines

Aliphatic amines are basic and the basicity is comparable to that of ammonia. Aqueous mineral acids or carboxylic acids convert amines into their salts. These salts react readily with hydroxide ions to regenerate the amine.

$$R-NH_2 + H_3O^+ \longrightarrow R-\overset{+}{N}H_3 + H_2O$$

$$R-\overset{+}{N}H_3 + {}^-OH \longrightarrow R-NH_2 + H_2O$$
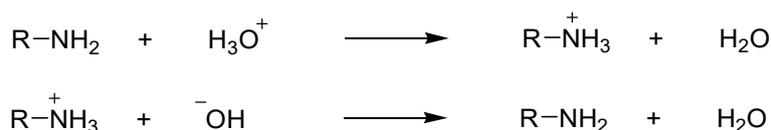
4.2.1 Basicity of amines versus alcohols

Nitrogen is less electronegative than oxygen. Therefore it has a higher tendency to donate lone pair of electrons than oxygen. On the other hand, nitrogen atom can bear a positive charge more easily than oxygen due to its lower electronegativity when compared to oxygen. Therefore the stability of the alkyl ammonium ion relative to the amine is more than the stability of the alkyl oxonium ion relative to the alcohol. Hence, amines are more basic than alcohols.

4.2.2 Basicity of primary aliphatic amines and aniline

Aliphatic primary amines are more basic than aniline. In aniline the lone pair of electrons on the nitrogen is delocalized on to the aromatic ring by resonance **(Figure 4.1)**. Therefore it is not easily available to a proton. Due to this reason aniline show lower basicity than primary aliphatic amines.
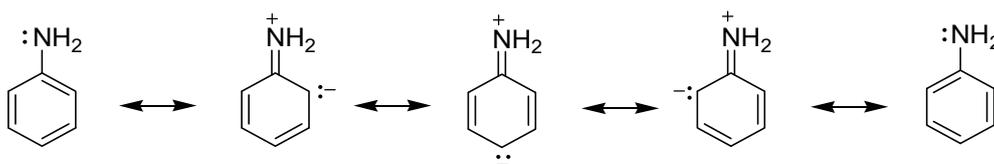

Figure 4.1 Resonance structures of aniline

4.2.3 Basicity of amines compared to amides

Amides are less basic than amines. It is because the pair of electrons on the nitrogen of the amide group is delocalized on to the carbonyl group by resonance **(Figure 4.2)** making them less available to a proton than is the lone pair of electrons on the N atom of amines.
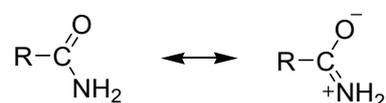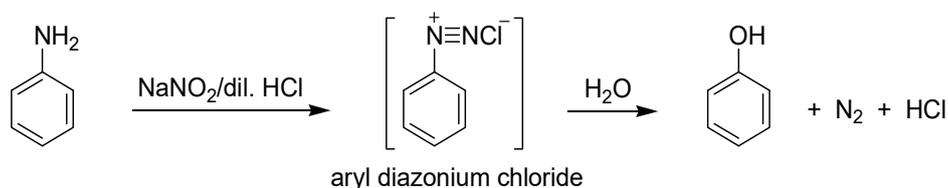

Figure 4.2 Resonance structures of amides

4.3 Reactions of aromatic diazonium salts

Aromatic amines such as aniline when reacted with nitrous acid ($NaNO_2/HCl$) give aromatic diazonium salts which undergo decomposition at room temperature to give phenols.

aryl diazonium chloride

Aromatic diazonium salts are more stable than aliphatic diazonium salts. Therefore, when this reaction is carried out at low temperatures, the conversion of the aromatic diazonium salt to the phenol can be slowed down, and the diazonium salt can be isolated.

Therefore aromatic diazonium salts are prepared by the treatment of aromatic primary amines with an aqueous solution of $NaNO_2$ in the presence of dilute mineral acid such as dil. HCl or dil. H_2SO_4 at low temperature ($0 - 5\,°C$). Since diazonium salts slowly decompose even at these temperatures, the solutions of diazonium salts are used immediately after preparation for any desired reaction.
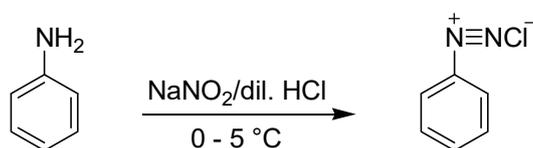

Diazonium salts undergo a large number of reactions. They can be divided into two classes: **replacement** of the diazonium group by another atom or a group; and **coupling** in which diazonium ion act as an electrophile and the nitrogen atoms are retained in the product.

4.3.1   Reactions in which the diazonium group is replaced by another atom or a group

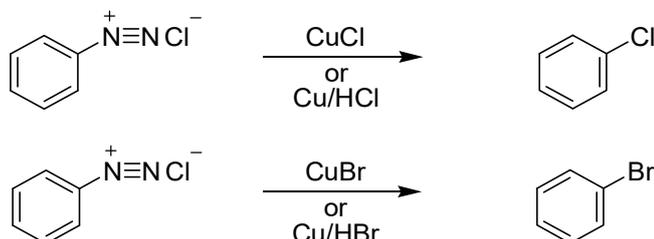**4.3.1.1   Reaction of diazonium salts with water**

When aqueous solutions of diazonium salts are heated, phenols are formed.
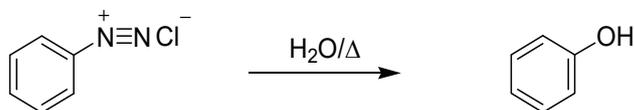
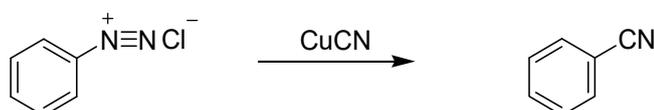**4.3.1.2   Reaction of diazonium salts with hypophosphorous acid (H_3PO_2)**

When diazonium salts are treated with hypophosphorous acid (H_3PO_2), the diazonium group is replaced by an H atom.
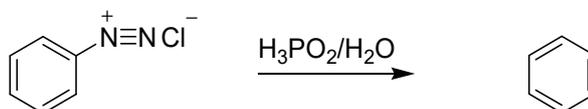
**4.3.1.3   Reaction of diazonium salts with CuCl and CuBr**

When diazonium salts are reacted with CuCl or CuBr, the corresponding aromatic halide is formed. This reaction can also be carried out with copper powder and hydrogen halide (Cu/HCl or HBr) instead of copper(I) halide.

4.3.1.4   Reaction of diazonium salts with CuCN

When diazonium salts are reacted with CuCN, the diazonium group is replaced by CN group.

**4.3.1.5   Reaction of diazonium salts with KI**

When diazonium salts are reacted with KI, the diazonium group is replaced by I.
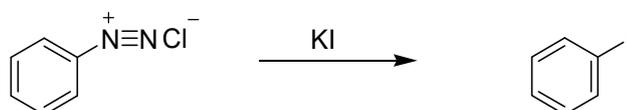
4.3.2 Reactions in which the diazonium ion acts as an electrophile

Aryl diazonium ions can participate as electrophiles as it contains a positive charge on N. They react with phenols under alkaline conditions.

Benzene diazonium chloride reacts with phenol in the presence of aqueous NaOH to give an orange coloured compound, and with β-naphthol (2-naphthol) in the presence of aqueous NaOH to give a red coloured compound.
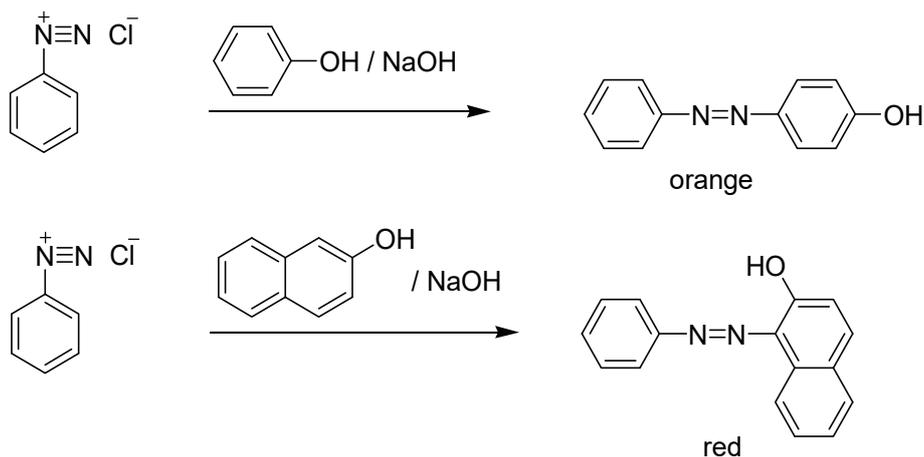
Reference:

Morrison, R. T. and Boyd, R. N. (2010) *Organic Chemistry*: Pearson.

Solomons, T. W. G. and Fryhle C. B. (2011) *Organic Chemistry*: John Wiley and Sons Inc.