

As Per Revised Syllabus of
[Swami Ramanand Teerth Marathwada University, Nanded]

A Text Book of Organic Chemistry

(FORB.Sc. THIRD YEAR)
(Semester VI)

-: By :-

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(B.Sc. THIRD YEAR)

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**DEDICATED TO
STUDENTS OF B. SC. THIRD YEAR**

PREFACE

We have great pleasure to place this first edition of “**A Text book of Organic Chemistry**” in the hands of **B. Sc III [Semester-VI]** students. This book has been written according to the new revised B. Sc III year Course of **Swami Ramanand Teerth Marathwada University, Nanded.**

Our long experience, however, I have tried best to make this book very informative as well as simple and lucid.

Keeping in the view the need and demands from the students of **B.Sc. III year.** The effort is made to present the topics in simple and lucid language and explained the same with suitable examples, structures and figures.

We hope that, simple and lucid explanation of the curriculum will help to understand and will make the students perfect in organic chemistry.

We are tried our level best to present a complete **A Text book of Organic Chemistry.** We shall welcome suggestions from teachers and students for further improvement of the book.

Authors

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I grateful to Aruna publication and Aruna publication team for excellent work.

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1. SPECTROSCOPY

INTRODUCTION -

The word spectroscopy is derived from spectro (related to spectrum) + scopy (study or observation). Thus spectroscopy is the production, measurement, and analysis of electromagnetic spectra produced as a result of the emission or absorption of energy by various substances. The electromagnetic spectrum is the range of all possible frequencies of electromagnetic radiation. The “electromagnetic spectrum” of an object is the characteristic distribution of electromagnetic radiation emitted or absorbed by that particular object. **The molecular spectroscopy is the study of the interaction of electromagnetic waves and matter.** The scattering of sun’s rays by raindrops to produce a rainbow and appearance of a colorful spectrum when a narrow beam of sunlight is passed through a triangular glass prism are the simple examples where white light is separated into the visible spectrum of primary colors. This visible light is merely a part of the whole spectrum of electromagnetic radiation, extending from the radio waves to cosmic rays. All these apparently different forms of electromagnetic radiations travel at the same velocity but characteristically differ from each other in terms of frequencies and wavelength.

ELECTROMAGNETIC RADIATIONS

Electromagnetic radiation (sometimes abbreviated EMR) is a ubiquitous (everywhere) phenomenon that takes the form of self-propagating waves in a vacuum or in matter. It consists of electric and magnetic field, components that oscillate in phase perpendicular to each other and perpendicular to the direction of energy propagation. The propagation of these radiations involves both electric and magnetic forces which give rise to their common class name electromagnetic radiation. In spectroscopy, only the effects associated with electric component of electromagnetic wave are important. Therefore, the light wave traveling through space is represented by a sinusoidal trace (figure 1). In this diagram λ is the wavelength and distance A is known as the maximum amplitude of the wave. Although a wave is frequently characterized in terms of its wavelength λ , often the terms such as wavenumber (ν), frequency (ν), cycles per second (cps) or hertz (Hz) are also used.

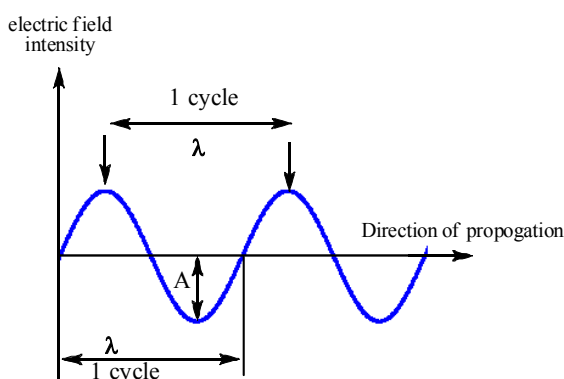


Figure 1 : Wave like propagation of light (λ = wavelength and A = amplitude)

Electromagnetic radiation is classified into several types according to the frequency of its wave. These types include (in order of increasing frequency and decreasing wavelength): radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays and gamma rays. EM radiation carries energy and momentum that may be imparted to matter with which it interacts.

The electromagnetic spectrum

Radiation type	Wave length λ , (Å)	Frequency $= c / \lambda$, (Hz)	Applications
Radio	10^{14}	3×10^4	
Nuclear magnetic resonance	10^{12}	3×10^6	
Television	10^{10}	3×10^8	Spin orientation
Radar	10^8	3×10^{10}	
Microwave	10^7	3×10^{11}	
Far infrared	10^6	3×10^{12}	Rotational
Near infrared Vibrational	10^4	3×10^{14}	
Visible	$8 \times 10^3 - 4 \times 10^3$	$3.7 \times 10 - 7.5 \times 10^{14}$	
Ultraviolet	3×10^3	1×10^{15}	Electronic
X-rays	1	3×10^{18}	
Gamma rays	10^{-2}	3×10^{20}	Nuclear transitions
Cosmic rays	10^{-4}	3×10^{22}	

UNITS USED IN SPECTROSCOPY (A) WAVELENGTH (B) WAVENUMBER (C) FREQUENCY:

1. Wave length :(λ)

It is the distance between the two adjacent crests(c-c) or trough (T-T) in a particular waves. It is denoted by the letter (λ).

The unit commonly used to describe the wavelength is centimeters (cm), the different units are used to express the wavelengths in different parts of the electromagnetic spectrum. For example, in the ultraviolet and visible region, the units use is angstrom (Å) and nanometer (nm). Ultraviolet light can be detected by photoelectric cell and infrared light can be detected by

photographically. In some techniques like ultraviolet and infrared spectroscopy. The common unit is wavelength.

2. Wave number: (ν):

It is the reciprocal of wavelength and it is expressed in per centimeter. In other words, it is defined as the total number of waves which can pass through a space of one cm. it is denoted by (ν). It is frequently used in Infrared technique.

3. Frequency:

It is defined as the number of waves which can pass through a point in one second.

It is expressed as ($\bar{\nu}$).

4. The velocity (c):

The distance traveled by the waves in one second is called the velocity of the waves. It is expressed in cm per second.

In the infrared region, the commonly used unit is wavenumber (ν), which gives the number of waves per centimeter. Thus

$$1 \text{ cm} = 10^7 \text{ nm} = 10^8 \text{ \AA}$$

$$1 \text{ \AA} = 10^{-1} \text{ nm} = 10^{-8} \text{ cm}$$

The four quantities wavelength, wavenumber, frequency and velocity can be related to each other by following relationships

$$\text{Wavelength } (\lambda) = c/\nu$$

$$\text{Wave-number } (\nu) = 1/\lambda = \nu/c$$

$$\text{Frequency } (\nu) = c/\lambda = c \nu$$

$$\text{Velocity } (c) = \nu \lambda = \nu/\nu$$

Absorption of Different Electromagnetic radiations by Organic Molecules

In absorption spectroscopy, though the mechanism of absorption of energy is different in the ultraviolet, infrared and nuclear magnetic resonance regions, the fundamental process is the absorption of a discrete amount of energy. The energy required for the transition from a state of lower energy (E_1) to state of higher energy (E_2) is exactly equivalent to the energy of electromagnetic radiation that causes transition.

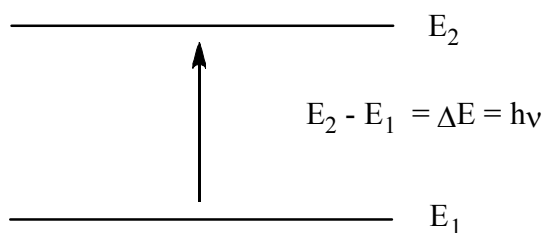


Figure 2: Energy transition for the absorption of any electromagnetic radiation

$$E_2 - E_1 = \Delta E = h \nu = h c / \lambda,$$

Where ΔE is energy of electromagnetic radiation being absorbed, h is the universal Planck's

constant, 6.624×10^{-27} erg sec and ν is the frequency of incident light in cycles per second (cps or hertz, Hz), c is velocity of light 2.998×10^{10} cm s⁻¹ and λ = wavelength (cm). Therefore, higher is the frequency, higher would be the energy and longer is the wavelength, lower would be the energy. As we move from cosmic radiations to ultraviolet region to infrared region and then radio frequencies, we are gradually moving to regions of lower energies.

A molecule can only absorb a particular frequency, if there exists within the molecule an energy transition of magnitude $E = h\nu$. Although almost all parts of electromagnetic spectrum are used for understanding the matter, in organic chemistry we are mainly concerned with energy absorption from only ultraviolet and visible, infrared, microwave and radiofrequency regions.

Ultraviolet – visible spectroscopy (200 - 800 nm) studies the changes in electronic energy levels within the molecule arising due to transfer of electrons from p- or non-bonding orbitals. It commonly provides the knowledge about p-electron systems, conjugated unsaturations, aromatic compounds and conjugated non-bonding electron systems etc.

Infrared spectroscopy (400-4000 cm) studies the changes in the vibrational and rotation -1 movements of the molecules. It is commonly used to show the presence or absence of functional groups which have specific vibration frequencies viz. C=O, NH, OH, CH, C-O etc.

Nuclear magnetic resonance (radiofrequency 60-600 MHz) provides the information about changes in magnetic properties of certain atomic nuclei. ¹H and ¹³C are the most commonly studied nuclei for their different environments and provide different signals for magnetically non-equivalent nuclei of the same atom present in the same molecule.

ULTRAVIOLET SPECTROSCOPY

1. Introduction:

The absorption of radiant energy in U.V and Visible region causes electronic excitation of the molecule such an excitation are known as U.V –Visible spectrum and it is also called as electronic spectra. The U. V region of electronic spectrum extend from 4 to 400 nm (40 to 4000 Å) the U.V region is obtained into two region.

- Near U.V region 200 to 400 nm.
- Far U.V region 4 to 200 nm.

Organic chemist interest to work in the U.V region 200to 400 nm in wave length. U.V radiations provide energy for promoting electrons of a molecule from ground state to excited state.

When U.V electromagnetic radiation passed through a molecule containing double or triple bonds, a part of incident radiation gets absorbed by a molecule . these absorption radiation energy causes promotion of electrons in σ (sigma), π (pi), and n (nonbonding) non bonding molecular orbital i.e. ground state molecular orbit to higher energy level antibonding molecular orbitals and amount of UV radiations absorbed can be depends upon structure of compounds and wavelength of radiations and it is measured with the help of U.V spectrophotometer.

Principles of Absorption Spectroscopy:

Beer's and Lambert's Law

The greater the number of molecules that absorb light of a given wavelength, the greater the extent of light absorption and higher the peak intensity in absorption spectrum. If there are only a few molecules that absorb radiation, the total absorption of energy is less and consequently lower intensity peak is observed. This makes the basis of Beer-Lambert Law.

Which states that the fraction of incident radiation absorbed is proportional to the number of absorbing molecules in its path.

When the radiation passes through a solution, the amount of light absorbed or transmitted is an exponential function of the molecular concentration of the solute and also a function of length of the path of radiation through the sample. Therefore,

$$\text{Log } I_0 / I = \epsilon c l$$

Where I_0 = Intensity of the incident light (or the light intensity passing through a reference cell)

I = Intensity of light transmitted through the sample solution

c = concentration of the solute in mol^{-1}

l = path length of the sample in cm

ϵ = molar absorptivity or the molar extinction coefficient of the substance whose light absorption is under investigation. It is a constant and is a characteristic of a given absorbing species (molecule or ion) in a particular solvent at a particular wavelength. ϵ is numerically equal to the absorbance of a solution of unit molar concentration ($c = 1$) in a cell of unit length ($l = 1$) and its units are $\text{liters.moles}^{-1}.\text{cm}^{-1}$. However, it is customary practice among organic chemists to omit the units. The ratio I / I_0 is known as transmittance T and the logarithm of the inverse ratio I_0 / I is known as the absorbance A .

Therefore

$$\begin{aligned} & -\text{Log } I / I_0 = -\log T = \epsilon c l \\ \text{and} \quad & \text{Log } I_0 / I = A = \epsilon c l \\ \text{or} \quad & A = \epsilon c l \end{aligned}$$

For presenting the absorption characteristics of a spectrum, the positions as λ_{max} (in nm) values and the absorptivity is expressed in parenthesis.

Types of electronic transitions

The total energy of a molecule is the sum of its electronic, its vibrational energy and its rotational energy. Energy absorbed in the UV region produces changes in the electronic energy of the molecule. As a molecule absorbs energy, an electron is promoted from an occupied molecular orbital (usually a non-bonding n or bonding π orbital) to an unoccupied molecular orbital (an antibonding π^* or σ^* orbital) of greater potential energy (figure 3). For most molecules, the lowest-energy occupied molecular orbitals are σ orbitals, which correspond to σ bonds. The π orbitals lie at relatively higher energy levels than σ orbitals and the non-bonding orbitals that hold unshared pairs of electrons lie even at higher energies. The antibonding orbitals (π^* and σ^*) are orbitals of highest energy. The relative potential energies of these orbitals and various possible transitions have been depicted in figure 3.

The saturated aliphatic hydrocarbons (alkanes) exhibit only $\sigma \rightarrow \sigma^*$ transitions but depending on the functional groups the organic molecules may undergo several possible transitions which can be placed in the increasing order of their energies viz. $n \rightarrow \pi^* < n \rightarrow \sigma^* < \pi \rightarrow \pi^* < \sigma \rightarrow \pi^* < \sigma \rightarrow \sigma^*$. Since all these transitions require fixed amount of energy (quantized), an ultraviolet or visible spectrum of a compound would consist of one or more well defined peaks, each corresponding to the transfer of an electron from one electronic level to another. If the differences between electronic energy levels of two electronic states are well defined i.e. if the nuclei of the two atoms of a diatomic molecule are held in fixed position, the peaks accordingly should be sharp. However, vibrations and rotations of nuclei occur constantly and as a result each electronic state in a molecule is associated with a large number of vibrational and rotational states.

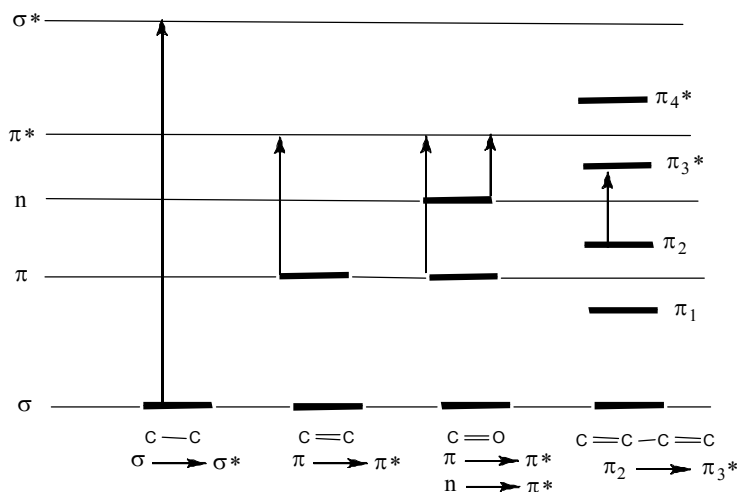


Figure 3 : Relative energies of orbitals most commonly involved in electronic spectroscopy of organic molecules

1. $\sigma \rightarrow \sigma^*$ transition:

A transition in which a bonding σ electron is excited into an antibonding orbital is referred to as a $\sigma \rightarrow \sigma^*$ transition.

σ -bonds are very strong hence high energy is required for this electronic transition this electronic transition occurs at wave length shorter than 165 nm. For ex. In saturated hydrocarbons, like CH_4 this transition takes place due to absorption of radiation of 150 nm in wavelength.

2. $n \rightarrow \sigma^*$ transition:

A transition in which the transition of one electron of lone pair (i.e non bonding pair of electron) to an antibonding σ orbital.

$n \rightarrow \sigma^*$ transition are of low energy than $\sigma \rightarrow \sigma^*$ transition it associated with energy less than 150 kcal/mole and occurs at wave length around greater than 175 nm. Alcohols, aldehydes, ketones, ethers, halides, amines etc. Undergo this type of transition.

CH₃-OH Absorb at 174 nm due to n→σ* transition.

3. π→π* transition:

A transition in which transition of a bonding π electron to an antibonding π*.

This transition occurs in aromatic compounds, compounds containing double or triple bonds for ex. Carbonyl compounds, cyanides etc. shows π→π* transition.

This transition requires less energy than that of n→σ* transition.

4. n→π* transition:

It represents the transition of one electron of a lone pair to an antibonding π* orbital.

This transition requires still less energy than π→π* transition and hence absorption occurs at longer wave length. For ex. Saturated aldehydes show two transitions.

i) n→σ* transition at 290 nm (less intense R-band) and

ii) π→π* transition at 180 nm (more intense K-band)

n→π* and π→π* transitions are most useful to organic chemists for establishing the structure of a molecule.

Terms used in U.V spectroscopy / Concept of chromophore and auxochrome, Bathochromic, Hypsochromic, Hyperchromic, Hypochromic shift.

Chromophore: The energy of radiation being absorbed during excitation of electrons from ground state to excited state primarily depends on the nuclei that hold the electrons together in a bond. The group of atoms containing electrons responsible for the absorption is called chromophore. Most of the simple un-conjugated chromophores give rise to high energy transitions of little use. Some of these transitions have been listed below.

Absorption maxima of simple un-conjugated chromophores

<u>Chromophore</u>	<u>Transition</u>	<u>ε_{max}</u>	<u>λ_{max} (nm)</u>
σ – bonded electrons			
(C-C, C-H etc.)	σ → σ*		~ 150
Lone pair electrons			
-O-, -N-, -S-	n → σ*	100-1000	~ 190
C=O, C=N	n → π*	15	~300
	<u>π→π*</u>	500	~190
R-C≡N	n → π*	5	~ 170
R-COOH, RCONH ₂ , RCOOR	n → π*	50	~ 210
π- bonded electrons			
C=C	<u>π→π*</u>	14000	~ 190
C≡C	<u>π→π*</u>	2000	~ 195
C=O	<u>π→π*</u>	500	~ 180

For example, alkanes contain only single bonds with only possible $\sigma \rightarrow \sigma^*$ type electronic transitions. These transitions absorb radiations shorter than wavelengths that are experimentally accessible in usually available spectrophotometers. In saturated molecules with heteroatom bearing non-bonding pairs of electrons, $n \rightarrow \sigma^*$ transitions become available. These are also high energy transitions. In unsaturated compounds, $\pi \rightarrow \pi^*$ transitions become possible. Alkenes and alkynes absorb ~ 170 nm but the presence of substituents significantly affects their position. The carbonyl compounds and imines can also undergo $n \rightarrow \pi^*$ transitions in addition to $\pi \rightarrow \pi^*$. Amongst these, the most studied transitions are $n \rightarrow \pi^*$ as these absorb at relatively longer wavelength 280-300 nm. These are low intensity (ϵ 10-100) transitions.

(ii) Auxochrome: An auxochrome is a functional group of atoms with non bonded electrons which, when attached to a chromophore, alters both the wavelength and intensity of absorption. If these groups are in direct conjugation with the pi-system of the chromophore, they may increase the wavelength at which the light is absorbed and as a result intensify the absorption. A feature of these auxochromes is the presence of at least one lone pair of electrons which can be viewed as extending the conjugated system by resonance.

For example, benzene does not display color as it does not have a chromophore; but nitrobenzene is pale yellow color because of the presence of a nitro group ($-\text{NO}_2$). Para-hydroxynitrobenzene exhibits a deep yellow color. Here an auxochrome ($-\text{OH}$) is conjugated with the chromophore $-\text{NO}_2$. Similar behavior is seen in azobenzene which has a red color, but para-hydroxy azobenzene is dark red in color. The substituents like methyl, hydroxyl, alkoxy, halogen, amino group etc. are some examples of auxochromes.

(a) Bathochromic Shift or Red shift: A shift of an absorption maximum towards longer wavelength or lower energy.

(b) Hypsochromic Shift or Blue Shift: A shift of an absorption maximum towards shorter wavelength or higher energy.

(c) Hypochromic Effect: An effect that results in decreased absorption intensity.

(d) Hyperchromic Effect: An effect that results in increased absorption intensity.

Effect of conjugation on position of U.V and visible bonds.

The wave length of absorption is shifted to higher values (Bathochromic shift), if two or more chromophore group are present in a molecule.

For ex. Ethylene (one double bond) absorb at 170 nm ($\pi \rightarrow \pi^*$ transitions), while butadiene (two double bonds in conjugation) absorb at 217 nm.

The bathochromic shift is more pronounced if the double bonds are in conjugation as compared to the isolated double bonds in which there is a little interaction between them. The absorption maxima is usually shifted 15-45 nm towards higher wave length in conjugated system. The value of extinction coefficient also increases. In conjugated dienes $\pi \rightarrow \pi^*$ transitions results in the formation of a band, called k-band.

Brief Information Regarding U.V spectroscopy:

A spectrophotometer is a device which detects the percentage transmittance of light radiation. When light of certain intensity and frequency range is passed through the sample, thus the instruments compares the intensity of the transmitted light with that of the incident light.

U. V spectrophotometer is made up of three basic components.

- i) A source of radiation ii) A monochromator
- i) A detector and measuring assembly.

I] now days, visible- ultraviolet spectrophotometer are built together, containing two different sources of radiation. (a) Tungsten lamp for scanning in the visible region (400-800) and (b) deuterium discharge lamp for scanning in the near UV region(200-400)

II] These radiation passed through a monochromator which automatically select the required wavelengths. The monochromatic beam is split up into two parallel beams (i) one of which is passes through a cell containing very dilute solution of organic compound it is called as sample beam. (ii) the another beam is passed through a cell containing solvents only. It is termed as reference beam.

III] The spectrophotometer electronically subtract the absorption of solution in the sample beam. "A plot of absorbance against wavelength is auto record through detector in the form of UV spectrum."

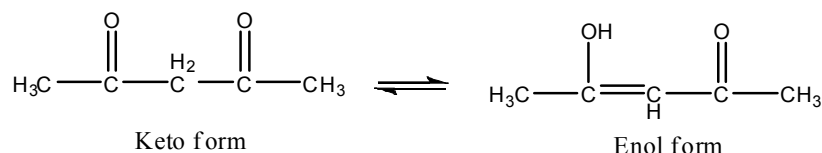
Application of U.V spectrophotometer:

1. For determining the structure of a compound:-

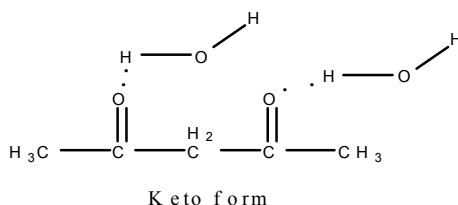
U.V spectroscopy is useful in determining the presence or absence of chromophores. Characteristic UV absorptions for some of the chromophores are as in table no. 1

2. Tautomerism:

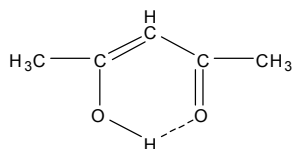
We can determine the presence of tautomerism in a molecule by Scanning UV spectra in different solvents. Ex. Acetylacetone can under go tautomeric changes.



In aqueous polar solvent, keto form this compound predominates due to stability by means, of intermolecular hydrogen bonding with polar solvent. It shows absorption band at λ_{max} 274 nm ($\epsilon_{\text{max}} = 2050$)



On the other hand in non-polar solvents, such as iso-octane, intermolecular hydrogen bonding is not possible. In this situation, the enol form can gain stability by means of intramolecular hydrogen bonding. Thus in nonpolar solvent iso-octane, a strong absorption band at λ_{max} 272 nm ($\epsilon_{\text{max}} = 12000$) indicates the predominance of the enol form.



Since the band intensities in the UV spectra are the function of the concentration of the keto and enol forms by the UV spectroscopy and also calculate the equilibrium constants.

III] Conjugated System:

If two or more chromophore groups are presents in a molecule and they are separated by two or more single bonds, there is less effects on the spectrum ex. $\text{CH}_2=\text{CH}_2$ absorb at λ_{max} 165 nm

($\epsilon_{\text{max}} = 15000$). While 1,4-pentadiene $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$ absorb at nearly the same position as the single ethylinic chromophore i.e. at λ_{max} 175 nm. ($\epsilon_{\text{max}} = 15000$).

However, if two chromophore groups are separated by only one single bond (a conjugated system),

A large effects on the absorption band results because IT electros get delocalised over four carbon atoms. Absorption band is generally shifted to 15-45 nm to longer wavelength with respect to the simple conjugated chromophore with high intensity ex. Ethylene shows absorption band at

λ_{max} 165 nm. ($\epsilon_{\text{max}} = 15000$).while 1,3- butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ shows absorption band at λ_{max} 217 nm. ($\epsilon_{\text{max}} = 21000$).

UV spectroscopy is especially applicable for determining the presence of conjugation system in an unknown compound.

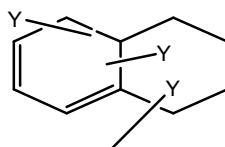
Table no. 1: Characteristic UV absorption for some of the chromophores.

Chromophore group	Example	λ_{max}	E max	Transition
$\begin{array}{c} \text{---C=C---} \\ \quad \end{array}$	ethylene	165	15000	Pi-Pi*
$\text{---C}\equiv\text{C---}$	Acetylene	190	8000	Pi-Pi*
$\begin{array}{c} \text{---C=O} \\ \end{array}$	Acetone	190	900	n- σ^*
		270	30	n- Pi*
$\begin{array}{c} \text{HC=O} \\ \end{array}$	Aldehyde	210	1200	Pi-Pi*
		290	16	n- Pi*
benzenoid ring	Benzene	180	60000	Pi- Pi* E ₁ -band
		200	8000	Pi- Pi* E ₂ -band
		255	215	Pi- Pi* B-band
Aromatic hydroxy compounds	Phenol	210	6200	Pi- Pi* E ₂ -band
		270	1450	Pi- Pi* B-band
	methoxy benzene	217	600	
		269		
	Aceto-phenone	245.5	9800	

Woodward Fieser Rules for predicting λ_{max} can be summarised as follows.

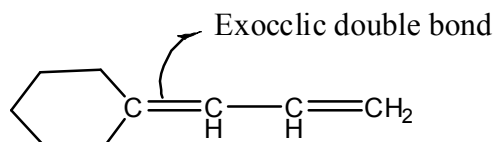
- 1, 3-butadiene system is considered as the parent chain and alicyclic dienes. Its base value is considered as 214 nm. (217 nm)
- Each alkyl group or ring residue, attached to the parent 1,3-butadiene system, shift the absorption 5 nm towards the longer wavelength region.

A part of the carbocyclic ring directly linked to the diene moiety is called ring residue and is denoted by "Y" ex.

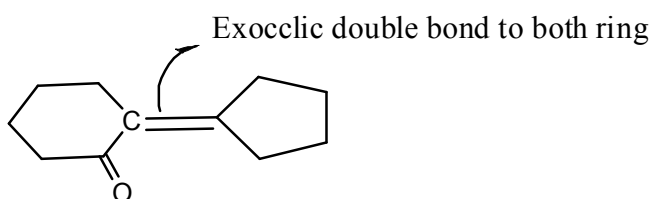


This compound contains 3 ring residues, hence, increment of three ring residues $5 \times 3 = 15$ nm is added to base value.

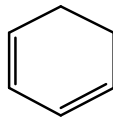
3. Increments for extended conjugation of parent diene system is calculated as 30 nm, which is then added to base value of parent diene.
4. When one carbon atom of the double bonded carbon atom is in the ring with the double bond extending outside of the ring. It is said to be an exocyclic double bond. Each exocyclic double bond causes an additional 5 nm increment to the base value of parent diene.



If the double bond is exocyclic to two rings, additional becomes 10nm.

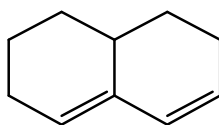


5. When both of the conjugated double bonds are present in same ring, the system is known as homo-annular diene.



Its base value is considered as 253 nm.

6. When both of the conjugated double bonds are not present in same ring, the system is known as hetero-annular diene.



Its base value is considered as 214 nm.

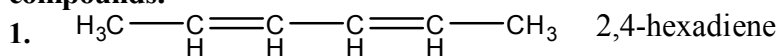
1. Increments are also considered for substituents like OAc, OR, Cl, Br, SR, NR₂, etc. On parent diene system.

The base value for conjugated diene system and increments for substituent's and ring residues, as per Woodward Fieser's rules, are given in the following table no. 2.

Table no. 2

Base value for butadiene system	214 nm
Parent open chain or hetero-annular diene	214 nm
Homo-annular diene	253 nm
Increments for	
(a) Each alkyl substituent or ring residue	5 nm
(b) Double bond extending conjugation	30 nm
(c) Exocyclic double bond	5 nm
(d) Lone pair conjugation	
(i) O-C(=O)-R	0 nm
(ii) O-alkyl	6 nm
(iii) S-alkyl	30 nm
(iv) -Cl, -Br	5 nm
(v) NR ₂	60 nm

Applications of Woodward Fieser rules to calculate λ_{max} of the following compounds:



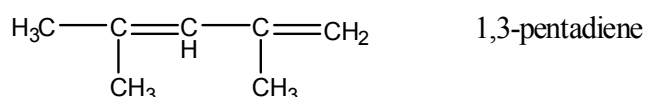
Basic unit in this compound is butadiene and two $-\text{CH}_3$ groups are substituents.

Base value for 1,3-butadiene 214 nm

Increments for two alkyl groups ($2 \times 5 = 10$) + 10

$$\lambda_{\text{max}} = \underline{\underline{224 \text{ nm}}}$$

2.



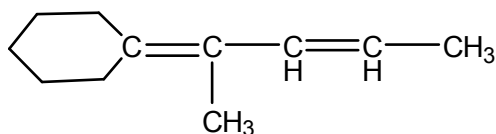
Basic unit in this compound is butadiene and two $-\text{CH}_3$ groups are substituents.

Base value for 1,3-butadiene 214 nm

Increments for three alkyl groups ($3 \times 5 = 15$) + 15

$$\lambda_{\text{max}} = \underline{\underline{229 \text{ nm}}}$$

3.



Basic unit in this compound is butadiene and two $-\text{CH}_3$ groups are substituents.

Base value for 1,3-butadiene 214 nm

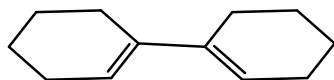
Increments for two alkyl groups ($2 \times 5 = 10$) + 10

Increments for two ring residue ($2 \times 5 = 10$) + 10

One exocyclic double bond + 05

$$\Lambda_{\text{max}} = \underline{\underline{239 \text{ nm}}}$$

4.



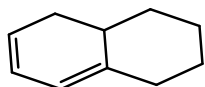
It is hetero-annular diene having four ring residues.

Base value for hetero-annular diene 214 nm

Increments for four ring residue ($4 \times 5 = 20$) + 20

$$\Lambda_{\text{max}} = \underline{\underline{234 \text{ nm}}}$$

5.



It is homo-annular diene having three ring residues.

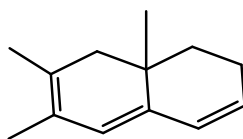
Base value for hetero-annular diene 253 nm

Increments for three ring residue ($3 \times 5 = 15$) + 15

One exocyclic double bond + 05

$$\Lambda_{\text{max}} = \underline{\underline{273 \text{ nm}}}$$

6.



It is homo-annular diene having five ring residues, one exocyclic double bond and one extended double bond.

Base value for homo-annular diene 253 nm

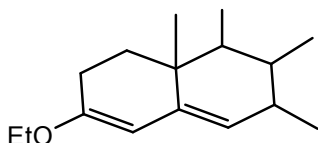
Increments for five ring residue ($5 \times 5 = 25$) + 25

One exocyclic double bond + 05

One extended double bond + 30

$$\Lambda_{\text{max}} = \underline{\underline{313 \text{ nm}}}$$

7.



It is hetero-annular diene having three ring residues, one exocyclic double bond and one alkoxy group.

Base value for hetero-annular diene	214 nm
Increments for three ring residue (3x5=15)	+ 15
One exocyclic double bond	+ 05
One alkoxy group substituted	+ 06
λ_{max} =	240 nm

Woodward Fieser rules for calculating absorption maxima in α, β -unsaturated ketones and aldehydes .

Woodward and Fieser framed certain empirical rules for estimating the absorption maxima for α, β -unsaturated ketones and aldehydes. The rules were later modified by Scott and are as follows.

- a) The basic value of α, β -unsaturated ketones is taken as 215 mu. The α, β -unsaturated ketones may be cyclic or six membered.
For compound, $=\text{CH}-\text{COX}$, basic value is 215 mu, if x is an alkyl group.
If x=H, basic value becomes 207 mu. If x=OH or OR basic value becomes 193 mu.
- b) If the double bond and the carbonyl group are in a five member ring (cyclopentenone), then for such α, β -unsaturated ketones, the basic value becomes 200 mu. The ϵ_{max} for such compounds is generally above 10,000.
The structural increments for estimating λ_{max} for a given α, β -unsaturated carbonyl compounds are as follows.
 - i) For each exocyclic double bond +5 mu
 - ii) For each double bond endocyclic in five or seven Member ring except cyclopentenone. +5 mu
 - iii) For each alkyl substituent or ring residue at the

α ,- position	+10 mu
β - position	+12 mu
γ or δ or higher position	+18 mu
 - iv) For each double bond extending conjugation + 30mu
 - v) For a homoannular conjugated diene 039 mu

Empirical rules for calculating absorption maxima in α, β -unsaturated ketones

and aldehydes.

Parent acyclic ketone or six-membered	215 nm
Parent α , β -unsaturated pentenone	202 nm
Parent α , β -unsaturated aldehyde	207 nm

Increments for

(a) A double bond extending conjugation	30 nm
(b) Each alkyl group or ring residue	

α	10 nm
β	12 nm
or higher	18 nm

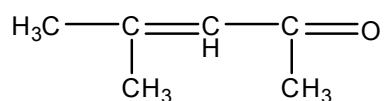
(c) *auxochrome*

(i) -OH	α	35 nm
	β	30 nm
	δ	50 nm
(ii) -OCOR	α , β , δ	6 nm
(iii) -OCH ₃	α	35 nm
	β	30 nm
	γ	17 nm
	δ	31 nm
(iv) -Cl	α	15 nm
	β	12 nm
(v) -Br	α	25 nm
	β	30 nm
(vi) NR ₂	β	95 nm

(d) Exocyclic double bond	5 nm
(e) Homocyclic diene	30 nm

Examples:

1. Calculate the $\lambda_{\max}$ for given structure.

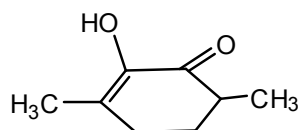


The basic value for a cyclic α , β -unsaturated ketone is
Two β -alkyl substituent.

213 mu.
(2x 12= 24) + 24 mu

$\lambda_{\max} = 239 \text{ mu}$

2. Calculate the $\lambda_{\max}$ for given structure.

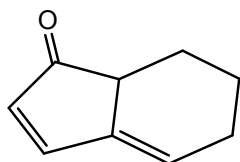


Basic value for α, β -unsaturated ketone is
 One $-\text{OH}$ group substituent at α ,
 One β -alkyl substituent and
 one ring residue at β -position.

215 mu.
 + 35
 + 12 mu
 + 12 mu

$$\lambda_{\text{max}} = 274 \text{ mu}$$

3. Calculate the λ_{max} for given structure.

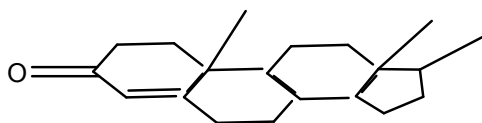


Basic value for α, β -unsaturated ketone is
 One β -alkyl substituent and
 One γ and one δ ring residue (18 + 18)
 One exocyclic double bond
 One double bond extending conjugation

215 mu.
 + 12 mu
 + 36 mu
 + 05 mu
 + 30 mu

$$\lambda_{\text{max}} = 274 \text{ mu}$$

4. Calculate the λ_{max} for given structure.



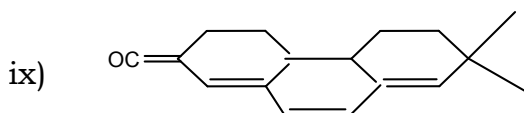
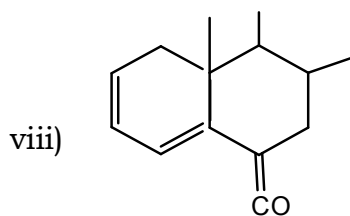
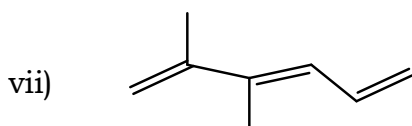
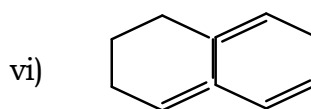
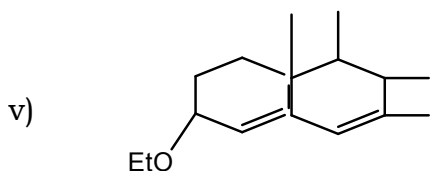
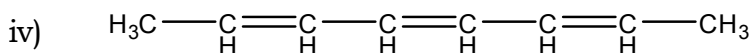
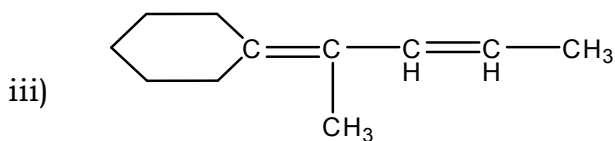
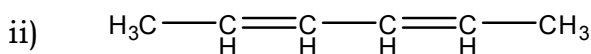
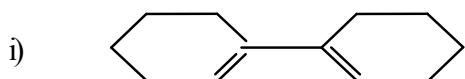
Basic value for α, β -unsaturated ketone is
 Two β -ring residues
 exocyclic double bond

215 mu.
 + 24 mu.
 + 05 mu

$$\lambda_{\text{max}} = 274 \text{ mu}$$

Question Bank

- Q1. Define the following terms
i) Wavelength ii) Wavenumber iii) Frequency iv) Velocity
- Q2. Explain Lamberts and Beers law
- Q3. Explain the following terms
i) $\sigma \rightarrow \sigma^*$ transition ii) $n \rightarrow \sigma^*$ transition
iii) $\pi \rightarrow \pi^*$ transition iv) $n \rightarrow \pi^*$ transition
- Q4. Define the following terms with suitable examples
i) Chromophore ii) Auxochrome
iii) Bathochromic shift iv) Hypsochromic shift
v) Hyperchromic effect vi) Hypochromic effect
- Q5. Give the brief information regarding U. V. spectrophotometer.
- Q6. Give the applications of U. V. spectrophotometer.
- Q7. Calculate the λ_{max} of following compounds



Infrared Absorption Spectroscopy

Introduction:

At ordinary temperatures, organic molecules are in a constant state of vibrations, each bond having its characteristic stretching and bending frequencies. When infrared light radiations between **4000–400 cm⁻¹** (the region most concerned to an organic chemist) are passed through a sample of an organic compound, some of these radiations are absorbed by the sample and are converted into energy of molecular vibrations. The other radiations which do not interact with the sample are transmitted through the sample without being absorbed. The plot of % transmittance against frequency is called the infrared spectrum of the sample or compound.

This study of vibrations of bonds between different atoms and varied multiplicities which depending on the electronegativity, masses of the atom and their geometry vibrate at different but specified frequencies; is called infrared spectroscopy.

The presence of such characteristic vibrational bands in an infrared spectrum indicates the presence of these bonds in the sample under investigation. The infrared radiation expressed in terms of wavelength (λ) or wave number (ν).

This is one of the most widely used Spectroscopic techniques for the detection of Functional group in pure unknown compounds.

The region from 0.5 μ to 2.5 μ of IR radiation is called near IR.

The region from 2.5 μ to 15 μ of IR radiation is called middle IR.

The region from 15 μ to 200 μ of IR radiation is called far IR (1 μ = 10⁻⁴ cm) the most important region for organic chemist is 2.5 μ to 15 μ (4000 to 667 cm⁻¹) in which molecular vibrations can be detected and measured in IR spectrum.

Bond intensity is either expressed in terms of absorbance (A) or transmittance (T)

$$A = \log_{10} 1/T$$

Fundamental modes and types of vibrations: Hooks law;

The two atoms joined together by a chemical bond (may be single, double or triple bond), macroscopically can be composed as two balls joined by a spring. The application of a force like

- i) Stretching of one or both the balls (atoms) away from each other or closer to each other
- ii) Bending of one of the atoms either vertically or horizontally and then release of the force results in the vibrations on the two balls (atoms). These vibrations depend on the strength of the spring and also the mode (stretching or bending) in which the force is being applied.

iii) Modes of molecular vibrations

- iv) Molecules with large number of atoms possess a large number of vibrational frequencies.

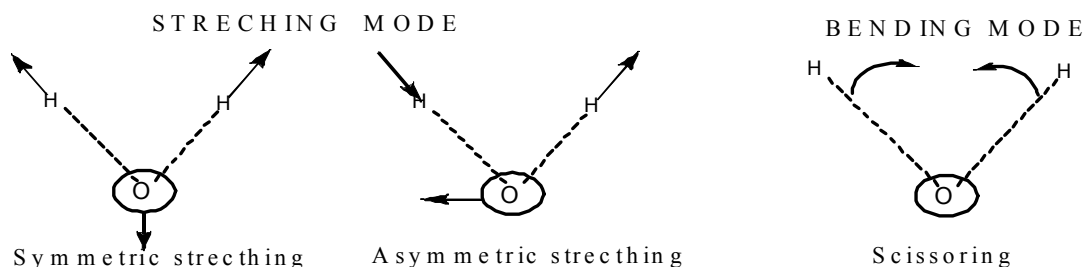


Figure 1 : Vibrational modes for water molecule

- i) For a non-linear molecule with n atoms, the number of fundamental vibrational modes is $(3n-6)$; linear molecules have $3n-5$ fundamental vibrational modes. Therefore, water - a non-linear molecule theoretically possesses **3** fundamental vibrations – two stretching and one bending (figure-1); whereas carbon dioxide - a linear molecule possess **4** fundamental absorption bands involving two stretching and two bending modes (figure-2).

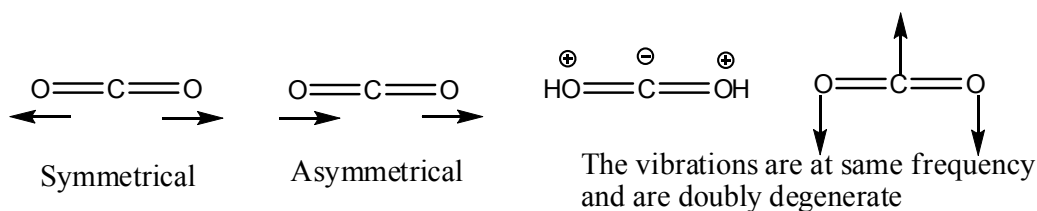


Figure 2 : Vibrational modes for carbon dioxide molecule (IR inactive)

- ii) The various stretching and bending modes can be represented by considering an AX_2 group
- iii) Appearing as a portion of molecule, for example, the $-CH_2-$ group in a hydrocarbon molecule (figure-3). Any atom joined to two other atoms will undergo comparable vibrations for example $-NH_2$ or $-NO_2$. Each of different vibration modes may give rise to a different absorption band so that $-CH_2-$ groups give rise to two C-H stretching bands i.e. ν_{sym} and $\nu_{antisym}$. Some of vibrations may have the same frequency i.e. they are degenerate and their absorption bands will appear at same position (for CO_2 , see figure-2).

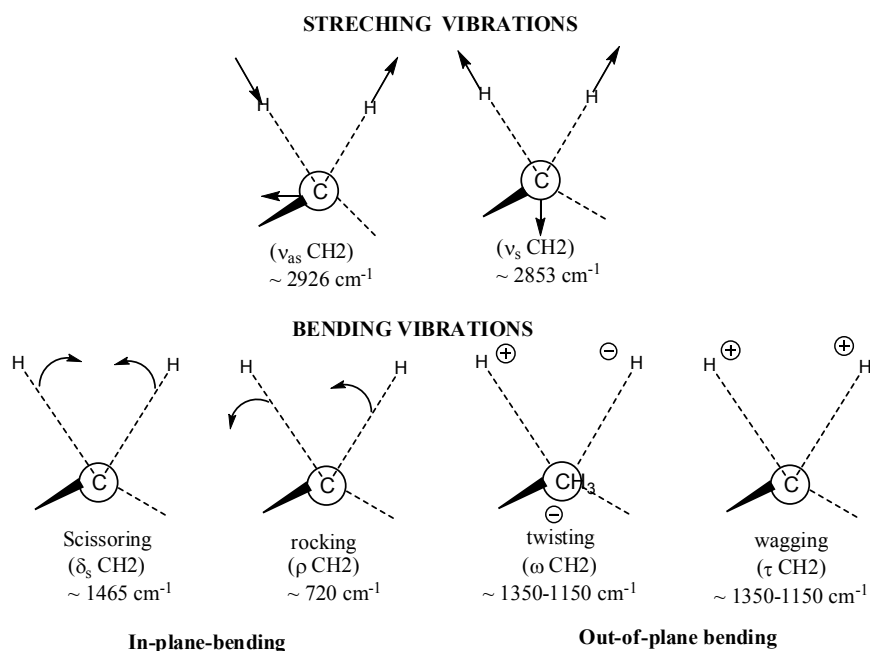


Figure-3: Vibrational modes of a CH₂ group.
[⊕ and ⊖ indicate movement above and below the plane of page]

Hooke's law and Absorption of radiations

The band positions in the IR spectrum are presented in wave number (ν) whose unit is the reciprocal centimeter (cm⁻¹). ν is proportional to the energy of vibration.

$$E = h \nu = hc / \lambda = hc \nu$$

Therefore, in principle, each of absorption of radiation in the infrared region is quantized and should appear as sharp line. However, each vibrational transition within the molecule is associated with number of rotational energy changes and thus appears as combination of vibrational-rotational bands.

The analogy of a chemical bond with two atoms linked through a spring can be used to rationalize several features of the infrared spectroscopy.

The approximation to vibration frequency of a bond can be made by the application of Hooke's law. In Hooke's law, two atoms and their connecting bond are treated as a simple harmonic oscillator composed of two masses joined by a spring and frequency of vibration is stated as

$$\bar{\nu} \propto \frac{\text{bond strength}}{\text{mass}}$$

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{m_1 m_2 / (m_1 + m_2)}} \quad \text{----- equation (1)}$$

Where,

ν = the vibrational frequency (cm)⁻¹
 c = velocity of light (cm/s)
 K = force constant of the bond (dyne/cm)
 m_1 and m_2 = masses of the two atoms

The quantity $(m_1 \times m_2) / (m_1 + m_2)$ is often expressed as μ , the reduced mass of the system.

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \quad \text{----- equation (2)}$$

Since according to equation (2) ———

$$\bar{\nu} \propto \sqrt{k}$$

Therefore, the vibrational frequency of a bond would increase with the increase in bond strength. Consequently, we can expect that C=C and C=O stretching will have higher frequencies than C-C and C-O stretching, respectively. Also,

$$\bar{\nu} \propto \sqrt{\frac{1}{\mu}}$$

Therefore, the vibrational frequency of a bond would increase with the decrease in reduced mass of the system. It implies that C-H and O-H stretching absorptions should appear at higher frequencies than C-C and C-O stretching frequencies. Similarly, O-H stretching should appear at higher frequency than O-D stretching. Further, the stretching of the spring requires more energy than to bend it, the stretching absorption of a band always appear at higher energy than the bending absorption of the same band.

Brief information regarding IR Spectroscopy:

IR Spectrophotometer consists of following components.

1. A source of radiations
2. A monochromator
3. Recording assembly.

1. A source of radiations:

IR Spectrophotometer is a globular rod or Nernst filaments.

Globular rod: is a rod of silicon carbide, and Nernst filament is a mixture of the oxides of

Zr, Y, Ce, and Th. These are electrically heated at 1500°C.

2. A Monochromator:

- The output from the source can be divided and focussed by the two mirrors to produce two beams. Reference beam and sample beam.
- Sample beam passes through NaCl cell containing sample and the reference beam passes through reference cell containing only solvent.
- These two beams pass through rotating segmented mirror, it alternately allows light from each of the two beams to enter the monochromator.
- A monochromator is made up of crystals of NaCl, CaF₂ OR LiF i.e glass or quartz as they strongly absorb IR RADIATIONS.

3. Recording assembly:

- These two beams alternatively pass through electronic amplifier and fall on the detector, which scan the range of IR frequencies.
- Moving a pen along the corresponding frequencies on the x-axis of chart paper.
- Higher frequencies (shorter wavelength) appear towards left of paper. Detector signal is proportional to the difference in the intensity of light in sample and reference beam. Detector signal controls movement of pen along y-axis with 100 % transmittance (no absorption) at the top of the paper and 0 % transmittance (absorption of all the light) at the bottom.

Sampling method:

IR Spectra of gaseous and liquid sample can be directly obtained. The spectrum of a solid sample is often best determined as an alkali halide pellet.

About 1-3 mg of the substance and 100-200 mg KBr are ground together, dried to remove moisture and passes at room temperature. Under high pressure into a small disk. Since KBr does not absorb infrared radiation in the region 4000 cm⁻¹ - 667 cm⁻¹ (2.5 μ to 15 μ) a complete spectrum of sample is obtained.

The spectrum of a solid is also determined in a mull. The most commonly used mulling agent is Nujol. It is a mixture of high molecular weight liquid paraffin. In this method 2.5 mg of sample is ground together with Nujol. In IR spectrum Nujol gives absorption band at 2920 cm⁻¹ - 2860 cm⁻¹ due to C-H stretching and at 1460 cm⁻¹ and 1380 cm⁻¹ due to C-H bending. Hence, when Nujol is used as mulling agent no information can be derived about absorption of the sample in this region.

Another mulling agent is hexachloro-butadiene which does not contain any C-H bond. And hence in IR spectrum of the sample, hexachloro-butadiene does not exhibit any absorption bands due to C-H bond.

Conditions for IR absorption: Let us consider how the radiations are being absorbed. At normal temperature, molecules are in constant state of vibrations. The change in dipole moment during vibration of the molecule produces a stationary alternating electric field. When the frequency of incident electromagnetic radiations is equal to the alternating electric field produced by changes

in the dipole moment, the radiation is absorbed and vibrational levels of the molecule are excited. Once in the vibrational levels are excited state, the molecules can lose the extra energy by rotational, collision or translational processes etc. and come back to ground state.

Therefore, only those vibrations which result in a rhythmic change in the dipole moment of the molecule absorb infrared radiations and are defined as IR active. The others which do not undergo change in dipole moment of the molecule are IR inactive e.g. the stretching of a symmetrically substituted bond, viz. $C \equiv C$ in acetylene and symmetrical stretching in carbon dioxide (figure-2) – a linear molecule, produce no change in the dipole moment of the system and these vibrations cannot interact with infrared light and are IR inactive. In general, the functional groups that have a strong dipole give rise to strong absorption bands in the IR.

IR Spectrum: Functional group region and Finger print region:

An infrared spectrum of an organic compound comprises many bands and assigning each band to a particular mode of vibration is practically impossible but two non-identical molecules generally have different IR spectra. An IR spectrum, therefore, is a fingerprint of the molecule.

Fingerprint region:

The region most useful for the purpose of “fingerprinting” of the compound is $650\text{--}1350\text{ cm}^{-1}$. This region comprises a large number of bands due to skeletal vibrations and when the spectrum we are studying coincides exactly with the spectrum of a known compound, it can be safely assumed that the two compounds are identical.

Functional group region:

The region above 1350 cm^{-1} to 4000 cm^{-1} often provides easily recognizable bands of various functional groups and thus known as functional group region.

Functional region is related with vibrational changes in the functional groups in the molecule by observing absorption in this range, we can draw some conclusions regarding the functional groups present in the molecule. Hence this region is called the functional group region.

The region from 1400 to 1430 cm^{-1} to the left in an IR spectrum is useful for identification of functional groups.

Fundamental bands:

When molecule absorb IR radiant energy which is equal to the difference between two vibrational energy levels ($\Delta E\text{-vib}$). Vibrational transition in a molecule takes place. Transition from vibrational ground state to the first excited state give rise to intense bands, called as Fundamental bands.

Overtone:

Transition from the ground state to the second excited state with the absorption of infrared radiation gives rise to weak bands, called overtones.

Characteristics Infrared absorption bands of some common functional groups:-

sr. no.	Functional group	compound	wavenumber cm^{-1}
01	O-H	Alcohol, Carboxylic acids	3600-3200
02	$\begin{array}{c} \text{—NH} \\ \end{array}$	Amines, Amides	3600-3200
03	$\equiv\text{CH}$	Acetylene	3600-3200
04	$\begin{array}{c} =\text{CH} \\ \end{array}$	Alkene	3100-3000
	Ar-H	Aromatic	3100-3020
05	$\begin{array}{c} \\ \text{—CH} \\ \end{array}$	Alkanes	3000-2800
06	C-H band -CHO	Aldehydes	2900-2700 (two bands, fermiresonance)
07	—S-H	Thiols	2950-2550
08	—C $\equiv$ C—	Alkynes	2200-2100
09	—C $\equiv$ N	Nitriles	2280-2240
10	$\begin{array}{c} \text{—C=O} \\ \end{array}$	Aldehydes, Ketones, acids, esters, amides	1870-1650
11	$\begin{array}{c} \text{—C=C—} \\ \quad \end{array}$	Alkenes	1680-1620
12	$\begin{array}{c} \text{—C} \cdots \text{C—} \\ \quad \end{array}$	Aromating ring	1600-1400 (4-bands)
13	—NO ₂	Nitrocompounds	1560-1515 and 1385-1345 (2-bands)
14	$\begin{array}{c} \quad \\ \text{—C—O—C—} \\ \quad \end{array}$	Ethers	1270-1050
15	$\begin{array}{c} \\ \text{—C—X} \\ / \end{array}$	Haloalkanes	750-500

Interpretation of IR Spectra of following organic compounds:

Following points are to be observed while interpreting IR spectrum.

1. Always start interpreting from high frequency and of the spectrum (shorter wavelength 4000 cm^{-1}) use the finger print region 1400 cm^{-1} - 667 cm^{-1} only for confirmation.
2. Absorption bands due to main functional groups give much information about the structure of the molecule. Total interpretation of IR spectrum is not required.
3. Always take into consideration negative evidence. Absence of an absorption band due to certain functional groups indicates that molecule does not contain that functional group. Ex. If spectrum does not show absorption band in 1870 cm^{-1} - 1650 cm^{-1} region. The sample does not contain carbonyl group.
4. A strong broad band in 3600 cm^{-1} - 3200 cm^{-1} region indicates the presence of -OH group.
5. Aromatic compounds show characteristic band due to Ar-H stretching at 3030 cm^{-1} , due to $\text{C}=\text{C}$ Stretching in 1600 cm^{-1} - 1400 cm^{-1} region. and due to C-H bending in 710 cm^{-1} - 690 cm^{-1} region.

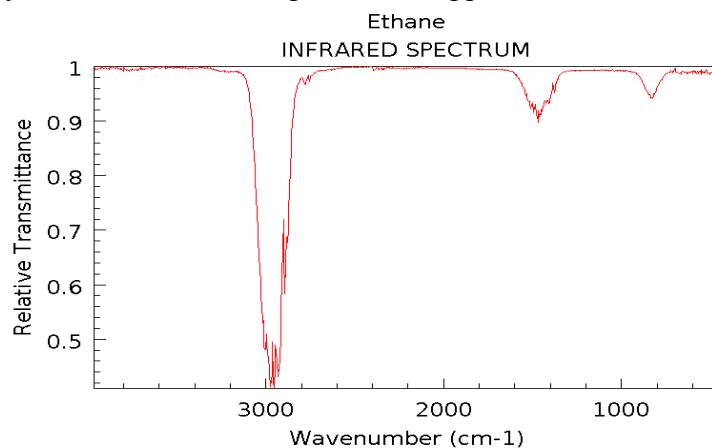
Absence of these bands in IR spectrum indicates that compound is aliphatic.

Examples:

1. Alkanes (ethane) :

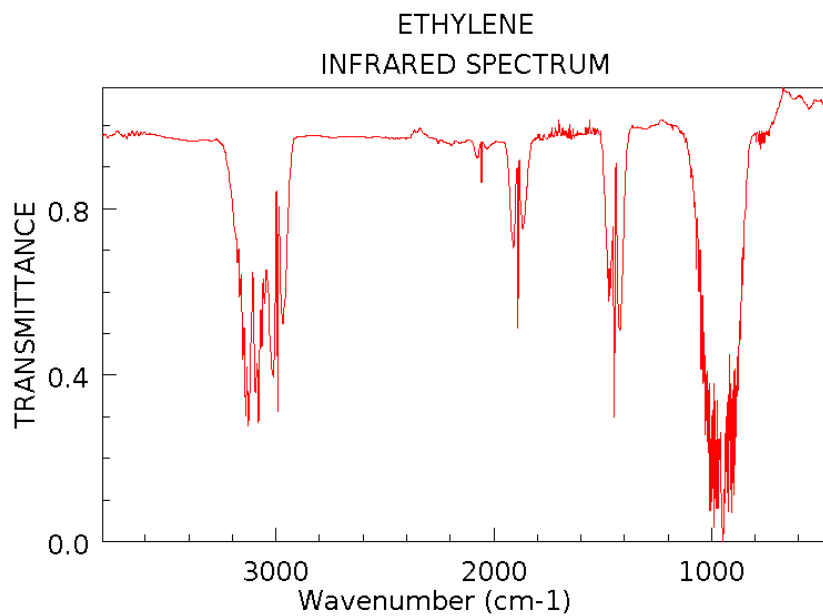
Ethane gives two strong absorption bands in high frequency region.

- i) One band at 2940 cm^{-1} due to -C-H asymmetric stretching.
- ii) Another band at 2880 cm^{-1} symmetric stretching.
- iii) Asymmetric -C-H bending vibrations appears at 1465 cm^{-1} while
- iv) Symmetric -C-H bending vibrations appears at 1380 cm^{-1} .



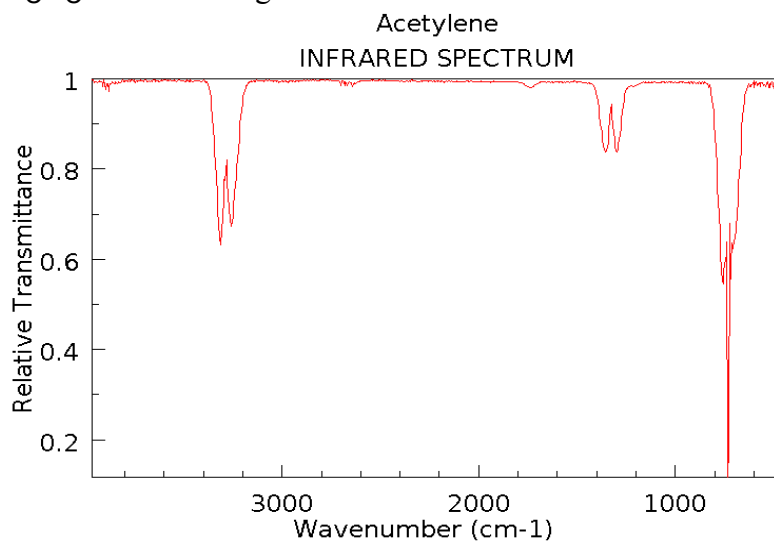
2. Alkene [ethylene]

- i) —C=C—H
| |
Stretching strong absorption band appears in the region 3100 cm^{-1} - 3000 cm^{-1}
- ii) $\text{C}=\text{C}$ Stretching band appears in the region 1680 cm^{-1} - 1620 cm^{-1} .



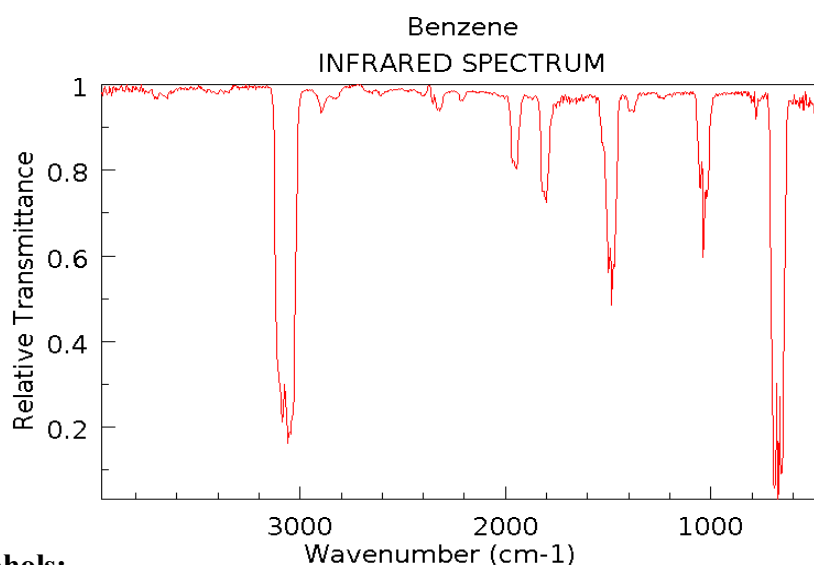
3. Alkynes [Ethyne]:

- i) In acetylene, a strong band for $\text{—C}\equiv\text{CH}$ stretching appears at about 3300 cm⁻¹ - 3300 cm⁻¹.
- ii) And $\text{—C}\equiv\text{C—}$ stretching occurs at 2200 cm⁻¹ - 2100 cm⁻¹.



4. Benzene:

- i) In IR Spectrum of benzene, aromatic C-H stretching band occurs in 3100 cm^{-1} region.
- ii) Absorption bands due to $\text{C}=\text{C}$ Stretching occurs
 - at 1600 cm^{-1} .
 - 1580 cm^{-1}
 - 1500 cm^{-1}
 - 1450 cm^{-1}
- iii) In plane C-H bending absorption bands appears in 1300 cm^{-1} - 1000 cm^{-1} region and out of plane.
- iv) A C-H bending absorption band appears in 900 cm^{-1} - 675 cm^{-1} region.



5. Alcohols:

The characteristic bands observed in the IR spectra of alcohol result from O-H and C-O stretching.

These vibrations are sensitive to hydrogen bonding. OH group of alcohol is not involved in hydrogen bonding gives sharp band at 3640 cm^{-1} - 3610 cm^{-1} region.

A strong broad band appears in 3600 cm^{-1} - 3200 cm^{-1} region due to -OH stretching involved in hydrogen bonding.

A primary alcohol shows characteristic strong broad band at 1050 cm^{-1} .

Secondary alcohols shows characteristic strong broad band at 1100 cm^{-1} .

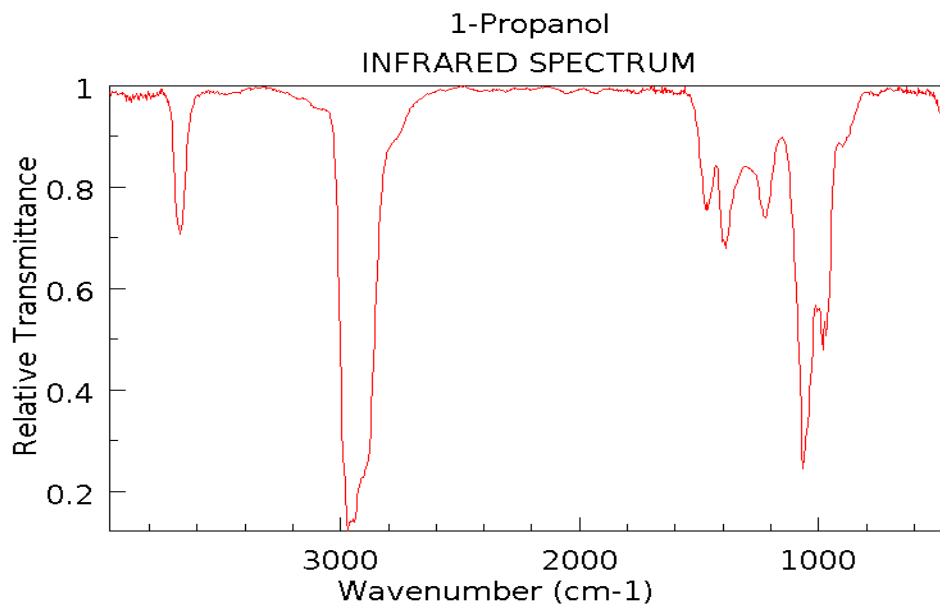
Tertiary alcohols shows characteristic strong broad band at 1150 cm^{-1} due to C-O stretching.

On the basis of these bands, primary, secondary and tertiary alcohols can be distinguished.

1-Propanol:

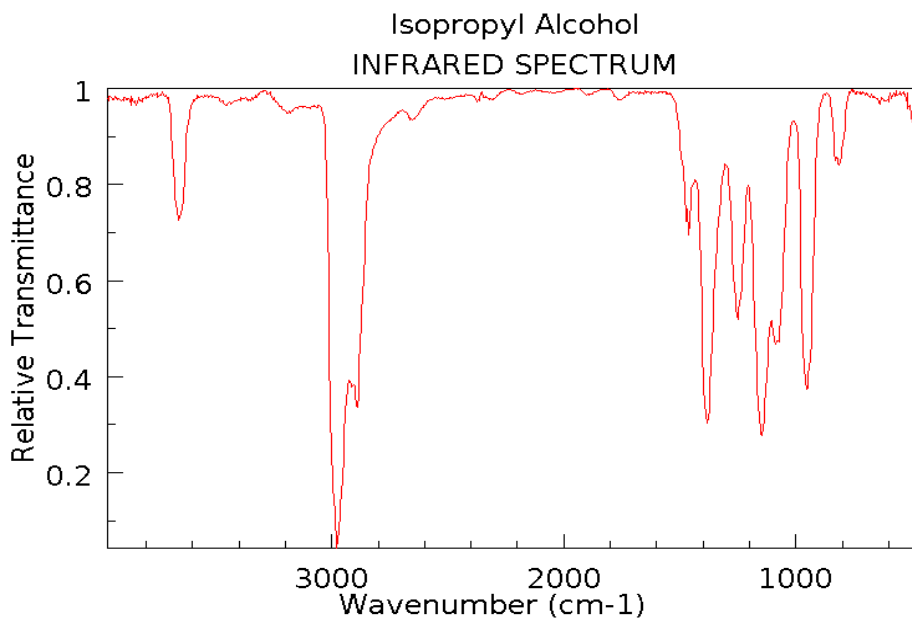
A strong broad band appears in 3640 cm^{-1} - 3610 cm^{-1} region due to -OH stretching.

Characteristic strong broad band at 1050 cm^{-1} due to C-O stretching.



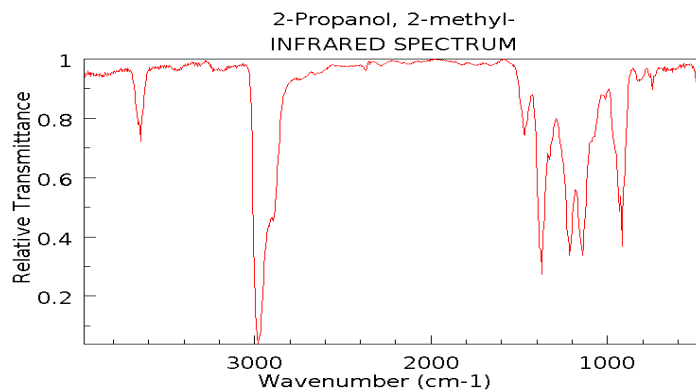
2-Propanol:

A strong broad band appears in 3640 cm⁻¹ - 3610 cm⁻¹ region due to -OH stretching. Characteristic strong broad band at 1050 cm⁻¹ due to C-O stretching.



2-methyl-2-propanol :

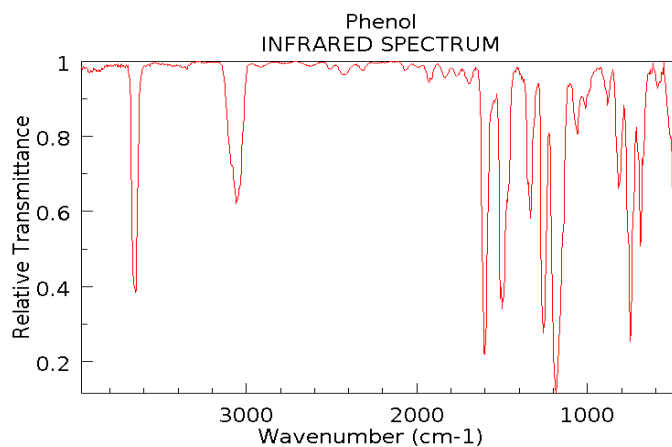
A strong broad band appears in 3640 cm^{-1} - 3610 cm^{-1} region due to -OH stretching.
Characteristic strong broad band at 1150 cm^{-1} due to C-O stretching.



6. Phenol:

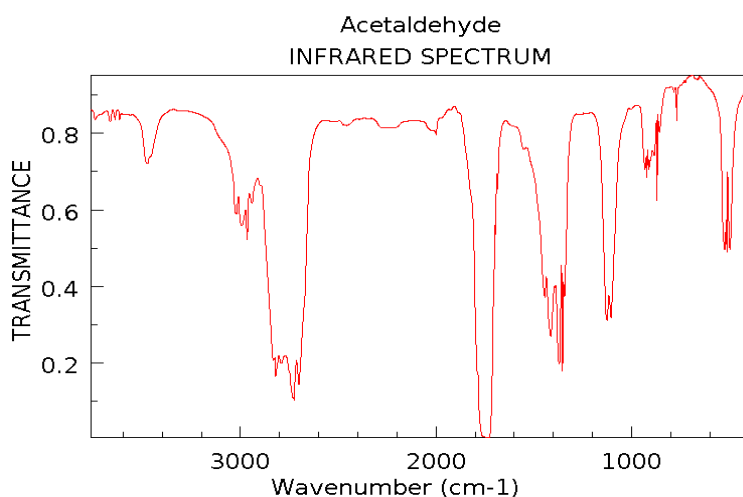
In IR spectrum of phenol,

- i) Aromatic C-H stretching bands occurs in 3100 cm^{-1} - 3000 cm^{-1} region.
- ii) Absorption bands due to $\text{C}=\text{C}$ STRETCHING occurs
at 1600 cm^{-1} ,
 1580 cm^{-1} ,
 1500 cm^{-1} ,
 1450 cm^{-1}
- iii) A strong broad band appears in 3640 cm^{-1} - 3610 cm^{-1} region due to -OH stretching.
- iv) Out of plane C-H bending absorption bands appears in 900 cm^{-1} - 675 cm^{-1} region.



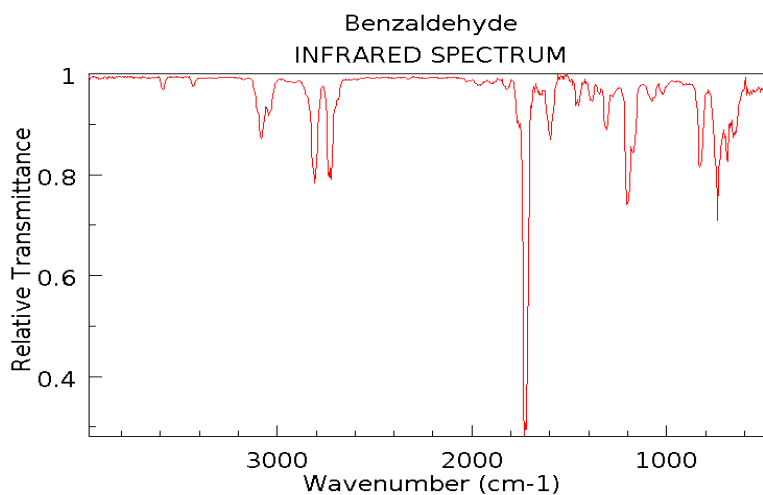
7. Acetaldehyde :

- i) The C=O stretching absorption for acetaldehyde 1745 cm^{-1}
- ii) C-H stretching in methyl group at 2850 cm^{-1} - 2950 cm^{-1} .



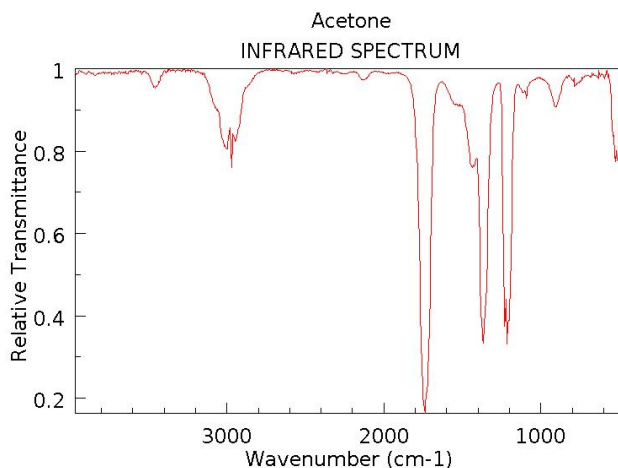
8. Benzaldehyde:

- i) The C=O stretching absorption for benzaldehyde 1700 cm^{-1} .
- ii) Aromatic C-H stretching at 3080 cm^{-1} .
- i) C=C STRETCHING of aromatic ring 1595 cm^{-1} .
- ii) Characteristic bands of aromatic substitution 745 cm^{-1} .
- iii) C-H stretching in aldehyde at 2860 cm^{-1} - 2775 cm^{-1} .



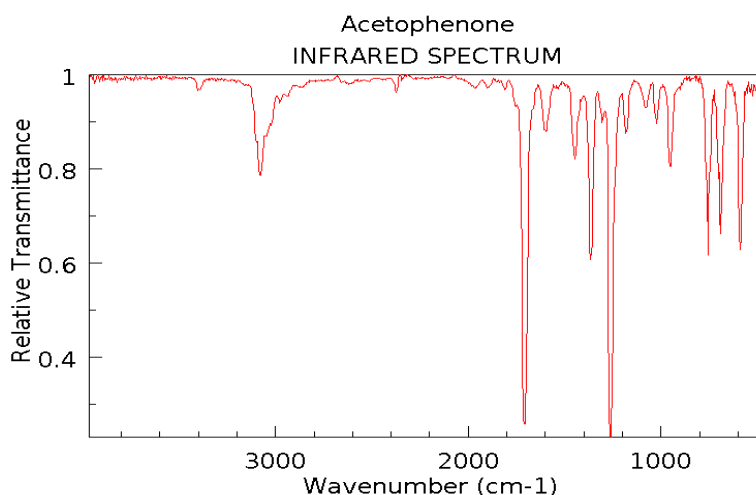
9. Acetone :

- i) The C=O stretching absorption for acetone 1718 cm⁻¹.
- ii) Two weak bands:
C-H stretching (asymmetric) absorption band at 2820 cm⁻¹.
And other C-H stretching (symmetric) absorption band near 2720 cm⁻¹.



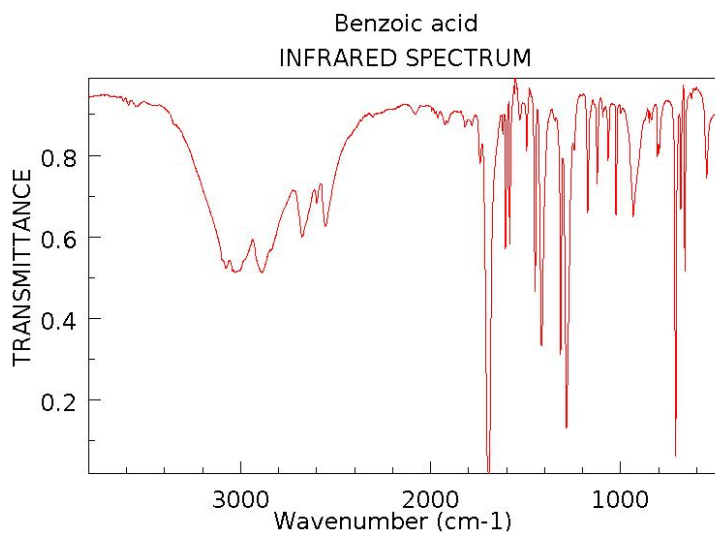
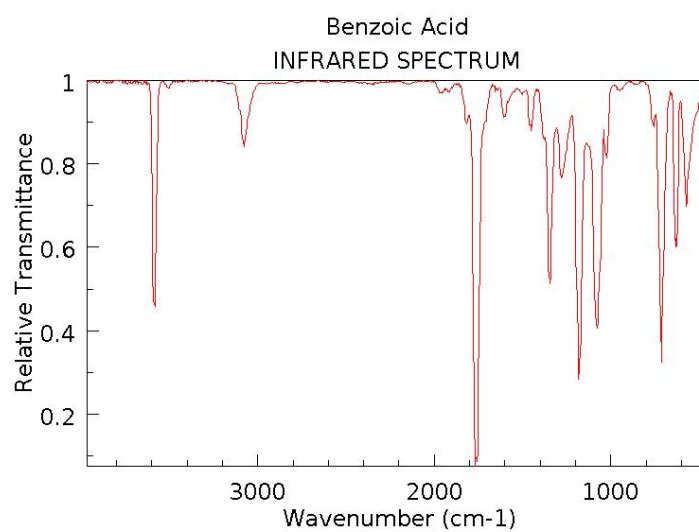
10. Acetophenone:

- i) The C=O stretching absorption for acetophenone 1690cm⁻¹.
- ii) Aromatic C-H stretching at 3080 cm⁻¹.
- iii) C=C STRETCHING of aromatic ring 1595 cm⁻¹.
- iv) Characteristic bands of aromatic substitution 745 cm⁻¹.
- v) C-H stretching in methyl group at 2850 cm⁻¹ - 2950 cm⁻¹.



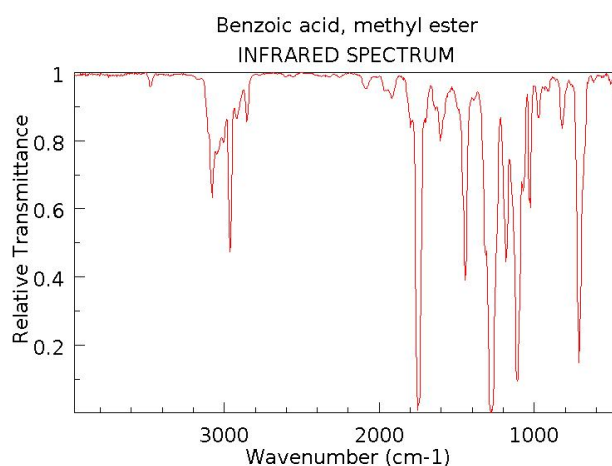
11. Benzoic acid:

- i) Aryl carboxylic acid, C=O stretching at 1700 cm^{-1} - 1680 cm^{-1} .
- ii) Carboxylic acid, O-H stretching 3000 cm^{-1} - 2500 cm^{-1} .
- iii) C=C STRETCHING of aromatic ring 1600 cm^{-1} - 1400 cm^{-1} .
- iv) Aromatic C-H stretching 3080 cm^{-1} .
- v) Characteristic bands of aromatic substitution 745 cm^{-1} .



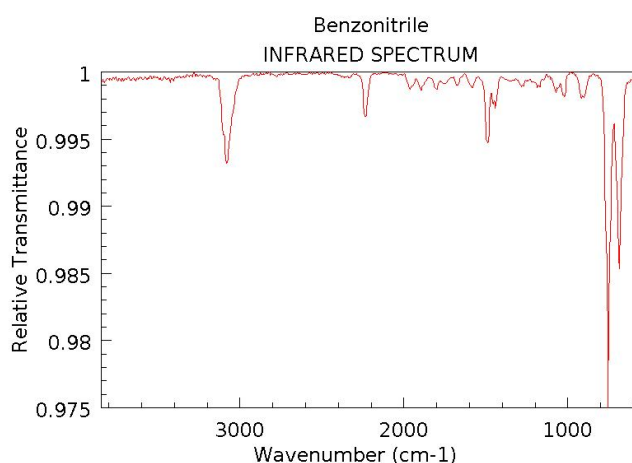
12. Methyl benzoate:

- i) Aryl ester, C=O stretching at 1730 cm^{-1} - 1715 cm^{-1} .
- ii) Carboxylic acid, O-H stretching 3000 cm^{-1} - 2500 cm^{-1} .
- iii) C=C STRETCHING of aromatic ring 1600 cm^{-1} - 1400 cm^{-1} .
- iv) Aromatic C-H stretching 3080 cm^{-1} .
- v) Characteristic bands of aromatic substitution 745 cm^{-1} .



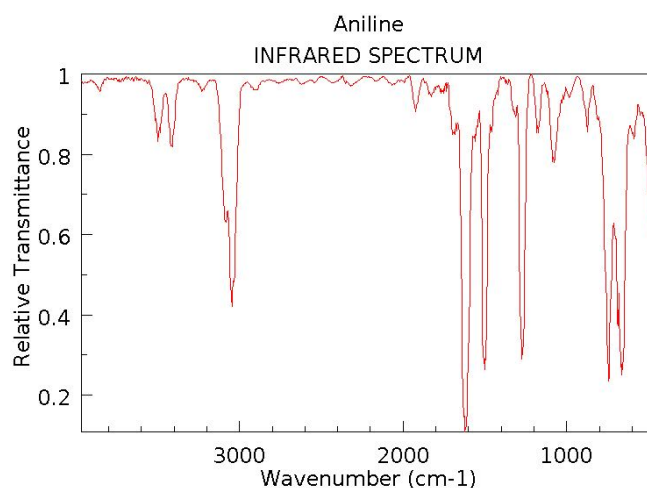
13. Phenyl cyanide: [Benzonitrile]

- i) Benzonitrile, $\text{—C}\equiv\text{N}$ stretching at 2230 cm^{-1} .
- ii) C=C STRETCHING of aromatic ring 1600 cm^{-1} - 1400 cm^{-1} .
- iii) Aromatic C-H stretching 3080 cm^{-1} .
- iv) Characteristic bands of aromatic substitution 745 cm^{-1} .



14. Aniline:

- i) N-H stretching at 3600-3200.
- ii) $\text{C}=\text{C}$ Stretching of aromatic ring 1600 cm^{-1} - 1400 cm^{-1} .
- iii) Aromatic C-H stretching 3080 cm^{-1} .
- iv) Characteristic bands of aromatic substitution 745 cm^{-1} .



QUESTION BANK

- Q1. Explain the stretching and bending vibrations in I.R spectroscopy.
- Q2. State and explain the Hookes law.
- Q3. Give the brief information regarding I. R spectroscopy.
- Q4. Give the sampling method in I. R spectroscopy.
- Q5. Explain the following terms
 - 1. Functional group region
 - 2. Finger print region
 - 3. Fundamental bands
 - 4. Overtones
- Q6. How will you distinguish 1-propanol, 2-propanol and 2-methyl-2-propanol?
- Q7. How will you interpret I.R. spectra of following compounds?
 - i) Benzene
 - ii) Phenol
 - iii) Acetophenone
- Q8. How will you interpret I.R. spectra of following compounds?

- i) Ethane
- ii) Ethane
- iii) Ethyne

Q9. How will you interpret I.R. spectra of following compounds?

- i) Acetaldehyde
- ii) Acetone
- iii) 1-propanol

Q10. How will you interpret I.R. spectra of following compounds

- i) Benzaldehyde
- ii) Benzoic acid
- iii) Methyl benzoate.

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Introduction

NMR or Nuclear Magnetic Resonance spectroscopy is a powerful and theoretically complex analytical tool. The chemical environment of specific nuclei is gathered from information obtained about the nuclei. NMR is a technique used to determine a compound's unique structure. It identifies the carbon-hydrogen (^1H -NMR), carbon- carbon (^{13}C -NMR) framework of an organic compound. Using this method and other instrumental methods including infrared and mass spectrometry, scientists are able to determine the entire structure of a molecule.

Principles of NMR spectroscopy

Nuclear spin and the splitting of energy levels in a magnetic field

Subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axis. In many atoms (such as ^{12}C) these spins are paired against each other, such that the nucleus of the atom has no overall spin. However, in some atoms (such as ^1H and ^{13}C) the nucleus does possess an overall spin. The rules for determining the net spin of a nucleus are as follows;

1. If the number of neutrons **and** the number of protons are both even, then the nucleus has **no spin**.
2. If the number of neutrons **plus** the number of protons is odd, then the nucleus has a half-integer spin (i.e. $1/2$, $3/2$, $5/2$)
3. If the number of neutrons **and** the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

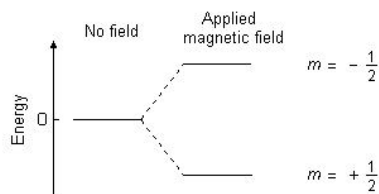
The overall spin, I , is important. Quantum mechanics tells us that a nucleus of spin I will have $2I + 1$ possible orientations. A nucleus with spin $1/2$ will have 2 possible orientations. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a *magnetic quantum number*, m .

The atomic nucleus is a spinning charged particle, and it generates a magnetic field. Without an external applied magnetic field, the nuclear spins are random and spin in random directions. But, when an external magnetic field is present, the nuclei align themselves either with or against the field of the external magnet.

Spin state: Protons that align with the external magnetic field. They are in a lower energy state.

Spin state: Protons that align against the external magnetic field. They are in a higher energy state.

Energy levels for a nucleus with spin quantum number 1/2



When the nucleus is in a magnetic field, the initial populations of the energy levels are determined by thermodynamics, as described by the Boltzmann distribution. This is very important, and it means that **the lower energy level will contain slightly more nuclei than the higher level**. It is possible to excite these nuclei into the higher level with electromagnetic radiation. The frequency of radiation needed is determined by the difference in energy between the energy levels.

Calculating transition energy

The nucleus has a positive charge and is spinning. This generates a small magnetic field. The nucleus therefore possesses a magnetic moment, μ , which is proportional to its spin, I .

$$\mu = \frac{\gamma I h}{2 \pi}$$

The constant, γ , is called the *magnetogyric ratio* and is a fundamental nuclear constant which has a different value for every nucleus. h is Planck's constant.

The energy of a particular energy level is given by;

$$E = - \frac{\gamma h}{2 \pi} m B$$

Where B is the strength of the magnetic field **at the nucleus**.

The difference in energy between levels (the transition energy) can be found from

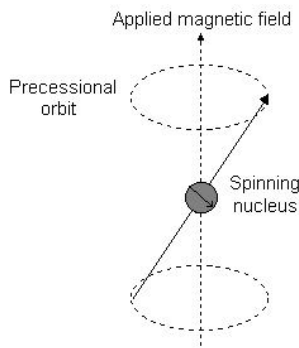
$$\Delta E = \frac{\gamma h B}{2 \pi}$$

This means that if the magnetic field, B , is increased, so is ΔE . It also means that if a nucleus has a relatively large magnetogyric ratio, then ΔE is correspondingly large.

The absorption of radiation by a nucleus in a magnetic field

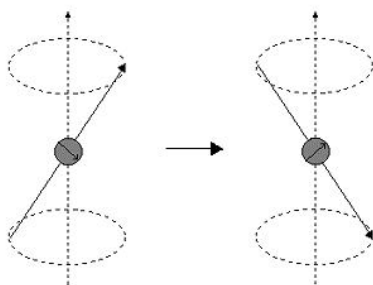
In this discussion, we will be taking a “classical” view of the behaviour of the nucleus - that is, the behaviour of a charged particle in a magnetic field.

Imagine a nucleus (of spin 1/2) in a magnetic field. This nucleus is in the lower energy level (i.e. its magnetic moment does not oppose the applied field). The nucleus is spinning on its axis. In the presence of a magnetic field, this axis of rotation will *precess* around the magnetic field;



The frequency of precession is termed the *Larmor frequency*, which is identical to the transition frequency. The potential energy of the precessing nucleus is given by; $E = -\mu B \cos \theta$ Where θ is the angle between the direction of the applied field and the axis of nuclear rotation.

If energy is absorbed by the nucleus, then the angle of precession, θ , will change. For a nucleus of spin $1/2$, absorption of radiation “flips” the magnetic moment so that it **opposes** the applied field (the higher energy state).



It is important to realize that only a small proportion of “target” nuclei are in the lower energy state (and can absorb radiation). There is the possibility that by exciting these nuclei, the populations of the higher and lower energy levels will become equal. If this occurs, then there will be **no** further absorption of radiation. The spin system is *saturated*. The possibility of saturation means that we must be aware of the relaxation processes which return nuclei to the lower energy state.

Relaxation processes

How do nuclei in the higher energy state return to the lower state? Emission of radiation is insignificant because the probability of re-emission of photons varies with the cube of the frequency. At radio frequencies, re-emission is negligible. We must focus on non-radiative relaxation processes (thermodynamics!).

If the relaxation rate is fast, then saturation is reduced. If the relaxation rate is too fast, line-broadening in the resultant NMR spectrum is observed.

There are two major relaxation processes;

- Spin - lattice (longitudinal) relaxation
- Spin - spin (transverse) relaxation

Spin - lattice relaxation:

Nuclei in an NMR experiment are in a sample. The sample in which the nuclei are held is called the *lattice*. Nuclei in the lattice are in vibrational and rotational motion, which creates a complex magnetic field. The magnetic field caused by motion of nuclei within the lattice is called the *lattice field*. This lattice field has many components. Some of these components will be equal in frequency and phase to the Larmor frequency of the nuclei of interest. These components of the lattice field can interact with nuclei in the higher energy state, and cause them to lose energy (returning to the lower state). The energy that a nucleus loses increases the amount of vibration and rotation within the lattice (resulting in a tiny rise in the temperature of the sample).

The relaxation time, T_1 (the average lifetime of nuclei in the higher energy state) is dependant on the magnetogyric ratio of the nucleus and the mobility of the lattice. As mobility increases, the vibrational and rotational frequencies increase, making it more likely for a component of the lattice field to be able to interact with excited nuclei. However, at extremely high mobility, the probability of a component of the lattice field being able to interact with excited nuclei decreases.

Spin - spin relaxation:

Spin - spin relaxation describes the interaction between neighboring nuclei with identical precessional frequencies but differing magnetic quantum states. In this situation, the nuclei can exchange quantum states; a nucleus in the lower energy level will be excited, while the excited nucleus relaxes to the lower energy state. There is no **net** change in the populations of the energy states, but the average lifetime of a nucleus in the excited state will decrease. This can result in line-broadening.

Instrumentation and Experimental procedure:

NMR Spectrophotometer consists of following four parts.

1. Powerful Magnet
 2. Sweep Generator
 3. Radio frequency oscillator.
 4. Radio frequency detector.
1. Powerful magnet:
A powerful magnet generate a very strong homogenous field, order about 14,000 gauss is generally used.
 2. Sweep generator:
It is used to supply D.C current to secondary small magnet. It also helps to vary the total applied field over a small range.
 3. Radio frequency oscillator:

This coil is kept perpendicular to magnetic field and transmits radio-waves of some fixed frequency in the order of 60 or 1000 or 220MHz.

4. Radio frequency detector:

This coil is kept perpendicular to both the magnetic and oscillator coil. When the precessional frequency matches with radio frequency, the nuclei induce an e.m.f in the detector coil. The signal is amplified and sends to the detector, where graph is plotted.

Procedure:

The substance (20-25 mg) is dissolved in proper solvent [solvent are used CCl_4 , CS_2 , CDCl_3 , pyridine, trifluoroacetic acid, dimethyl sulphoxide etc. most ideal solvent is CCl_4] is placed in sample tube. The tube is kept between two magnet faces, which supply a strong magnetic field, at certain field strength. The energy require to flip the proton matches the energy of radiation absorption of energy is detected by appearances of signal in the spectrum. i.e. NMR spectrum.

Equivalent and non-equivalent protons

Chemically Equivalent Protons are protons that are in the same environment, and they must be identical in every way. They experience is the same magnetic force, and therefore, will create overlapping signals on the spectrum. Each group of chemically equivalent protons gives rise to a signal. Therefore, we can determine how many sets of equivalent protons there are in a molecule by looking at the number of signals (peaks) in its ^1H -NMR spectrum.

How do we determine how many equivalent protons there are?

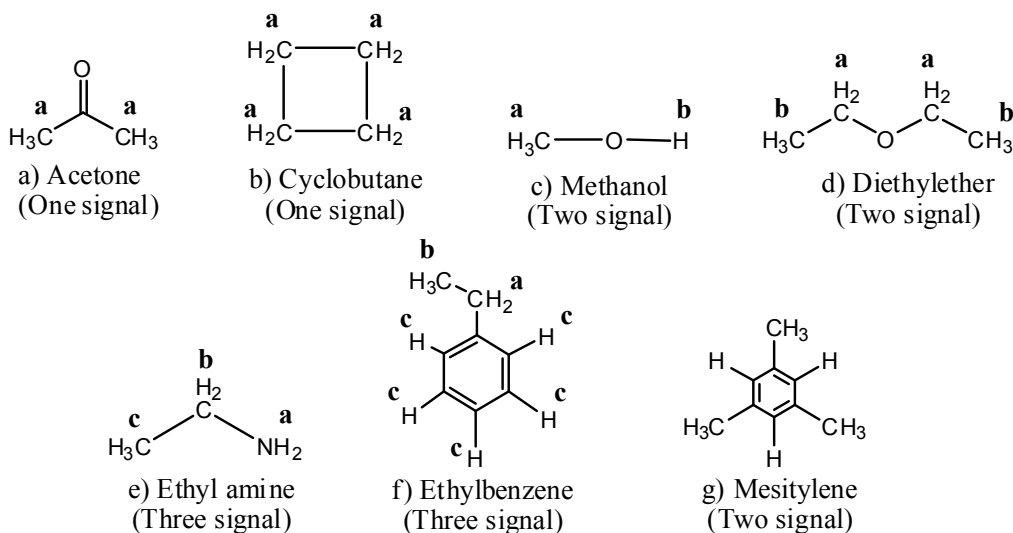
Protons that are aligned on a line of symmetry are equivalent. Another way is to replace the proton with deuterium to form two molecules, and if the two molecules are the same, then the two protons are equivalent. The third way to determine how many equivalent protons there are is to look at the atom attached to the proton (usually a carbon) and observe what that atom is bonded to, and then the atom bonded to that, all the way until a difference is observed. If there is no difference, the protons are equivalent. If there is a difference, the protons are not equivalent.

Are protons on the same carbon always equivalent?

No. Usually, protons on the same carbon are equivalent. But, sometimes, they are not equivalent because they are not in the same environment. One proton could be trans and the other proton could be cis. This would create two different signals.

How many different absorption (signals) in the following compounds:

- | | | |
|--------------|-----------------|---------------|
| a) Acetone | b) Cyclobutane | |
| c) Methanol | d) Diethylether | |
| e) Ethyamine | f) Ethylbenzene | g) Mesitylene |



Number of absorption (signals) of a) Acetone b) Cyclobutane c) Methanol
d) Diethylether e) Ethylamine f) Ethylbenzene g) Mesitylene

Position of Signals

The positions of the signals in an NMR spectrum are based on how far they are from the signal of the reference compound. This information tells us the kind of proton or protons that are responsible for the signal. Reference compound - Tetramethylsilane (TMS) is usually used as the reference compound because it can easily be removed from the sample by evaporation due to its volatile properties. TMS is at a lower frequency than most other signals because its methyl protons are in a more electron dense environment than most protons are because silicon is less electronegative than carbon (which is a significant component of organic molecules). The position of the signals depends on the chemical shift.

Chemical Shift:

It is a measure of how far the signal produced from the proton is from the reference compound signal, and it is usually measured using the δ (delta) scale. The TMS or reference compound is at the zero position on the very left of the spectrum, and as it moves toward the left, the ppm values become larger. Ppm stands for parts per million, and it is the unit used to measure chemical shift. Proton chemical shifts cover a range of over 30 ppm, but the vast majorities appear in the region δ 0-10 ppm, where the origin is the chemical shift of tetramethylsilane. The chemical shift is identical for a specific proton regardless of the spectrometer used. The formula for the chemical shift is

$$\delta = \frac{[\nu_o(H) - \nu_o(TMS)]}{[\text{Spectrometer Frequency in MHz}]}$$

Chemical shifts of all nuclei should be reported using δ values, with frequency and δ increasing from right to left. Many early papers on proton and multinuclear NMR used the opposite convention (not to mention other references) - in particular the τ scale was used in the early days on which tetramethylsilane (TMS) is taken as 10.0 ppm. Most τ values lie between '0' and '10' but there are some nuclei having negative τ values related by expression $\delta = 10 - \tau$.

What is shielding and how does it affect the chemical shift?

As mentioned before, ΔE is determined by the strength of the magnetic field. The nucleus of the molecule is found within a cloud of electrons that partly shields it from the applied magnetic field. This shielding is different for different protons in a molecule, and that is why there are many signals in the H NMR spectrum, instead of just one. In a magnetic field, electrons go around the nuclei and induce a local magnetic field that opposes the applied magnetic field.

Effective Magnetic Field: This is what the nuclei sense through its electron filled environment.

$$B_{\text{effective}} = B_{\text{applied}} - B_{\text{induced}}$$

B_{applied} is the magnetic field supplied by the applied external magnetic force (NMR spectrometer) and the magnetic fields supplied by the earth. This number is the same of all the nuclei in the molecule. B_{local} is the magnetic field supplied by the surrounding electrons around the nuclei. This number varies between nuclei in the molecule. According to this formula, the greater the electron density is around the nuclei, the larger the B_{induced} will be, and the more the proton is shielded from the applied magnetic field. This is called diamagnetic shielding.

Protons in electron dense (rich) environments sense a smaller effective magnetic field because they are more shielded by the large amount of electrons, and therefore, will require a lower frequency to come into resonance because the ΔE is smaller. The δ (ppm) will be smaller, and lower frequencies are located on the right side of the spectrum.

Up field: farther to the right hand side of the spectrum

Protons in electron poor environments sense a larger effective magnetic field because they are less shielded due to fewer electrons, and therefore, they require a higher frequency to come into resonance because the ΔE is larger. The δ (ppm) will be larger, and higher frequencies are located on the left side of the spectrum.

Downfield: farther to the left side of the spectrum.

How does electronegativity affect chemical shift?

The electron cloud shields the nucleus from the applied magnetic field, and electronegativity is defined as the tendency of an atom to pull electrons toward itself. Therefore, electronegative atoms remove electron density from the proton. This causes the proton to have less electron density, and this leads to less shielding. If the proton has less shielding, it will feel the applied magnetic field more, and this leads to a higher ΔE and a higher chemical shift. Protons that are

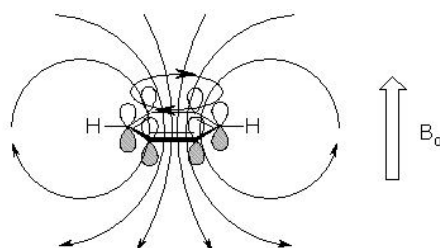
closer to the electronegative atom are in a less electron dense environment, which means that their chemical shifts will be larger.

What is magnetic anisotropy and how does it influence chemical shifts?

Magnetic anisotropy is the magnetic field created by pi electrons or rings. This describes an environment where different magnetic fields are found at different points in space. π electrons are held less strongly than sigma electrons, so π electrons are more able to move in response to the magnetic field. How this affects the chemical shift depends on the direction of the induced magnetic field relative to the direction of the applied magnetic field.

Aromatic Rings

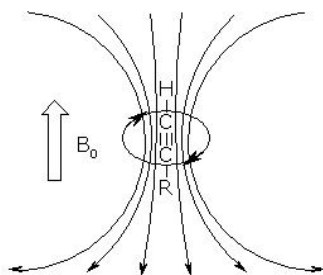
The π electrons in an aromatic ring are induced to circulate around the ring in response to an applied magnetic field. This “ring current” generates a local magnetic field which opposes the applied magnetic field. However, on the periphery of the ring, the flux lines are in the direction of the applied magnetic field. Consequently, protons attached to the aromatic ring “feel” a larger magnetic field than protons elsewhere in the molecule. Aromatic ring protons will therefore resonate at higher frequency and exhibit a downfield shift (7 - 8 ppm).



Magnetic anisotropy of an aromatic ring.

Acetylenic Hydrogens

The π electrons in a triple bond circulate around the bond axis to produce a magnetic field directly opposing the applied magnetic field. The acetylenic hydrogen is shielded by this induced field, and will therefore resonate at lower frequency (2 - 3 ppm).

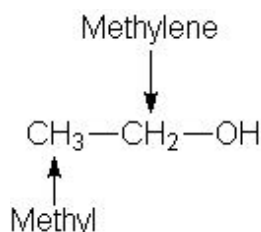


Magnetic anisotropy of a C,C-triple bond.

3. Integration or intensity of NMR Signals

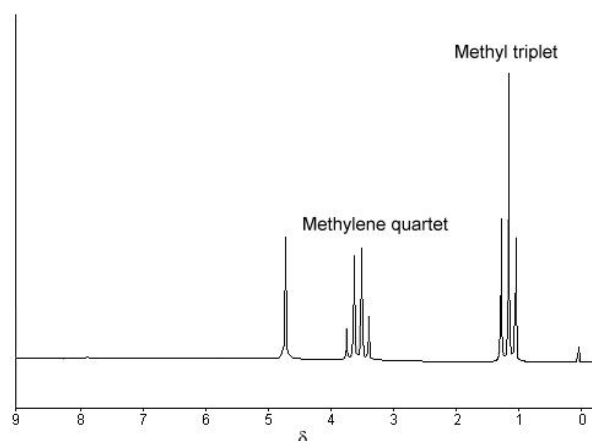
Integration is the area measurement that tells us the relative number of protons that give rise to each signal. Beer's Law says that the amount of energy absorbed or transmitted is proportional to a certain number of moles present. The area under each signal is proportional to the amount of radio energy and number of equivalent protons that give rise to that signal. The numbers do not always correspond to the exact or absolute number of protons. Instead, it tells us the relative number or ratio of the amount of equivalent protons.

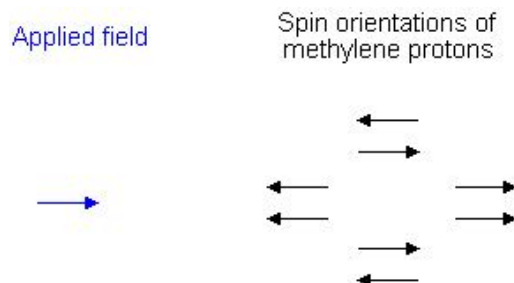
Spin - spin splitting (coupling): Consider the structure of ethanol;



The ^1H NMR spectrum of ethanol (below) shows the methyl peak has been split into three peaks (a *triplet*) and the methylene peak has been split into four peaks (a *quartet*). This occurs because there is a small interaction (*coupling*) between the two groups of protons. The spacing between the peaks of the methyl triplet are equal to the spacing between the peaks of the methylene quartet. This spacing is measured in Hertz and is called the *coupling constant, J*.

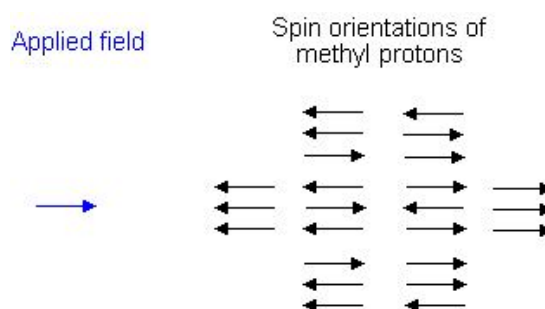
To see why the methyl peak is split into a triplet, let's look at the **methylene** protons. There are two of them, and each can have one of two possible orientations (aligned with or opposed against the applied field). This gives a total of four possible states;





In the first possible combination, spins are paired and opposed to the field. This has the effect of reducing the field experienced by the **methyl** protons; therefore a slightly higher field is needed to bring them to resonance, resulting in an upfield shift. Neither combination of spins opposed to each other has an effect on the methyl peak. The spins paired in the direction of the field produce a downfield shift. Hence, the methyl peak is split into three, with the ratio of areas 1:2:1.

Similarly, the effect of the methyl protons on the methylene protons is such that there are eight possible spin combinations for the three methyl protons;



Out of these eight groups, there are two groups of three magnetically equivalent combinations. The methylene peak is split into a quartet. The areas of the peaks in the quartet have the ratio 1:3:3:1.

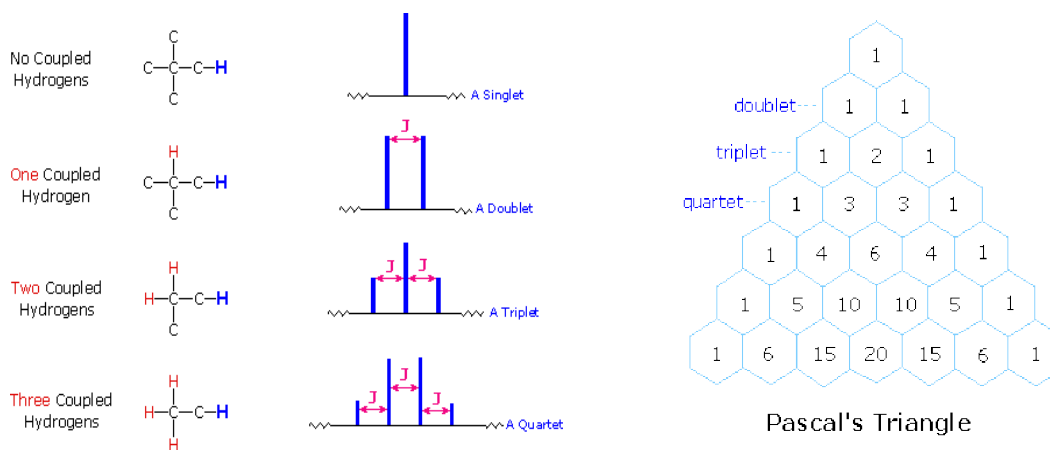
In a *first-order* spectrum (where the chemical shift between interacting groups is much larger than their coupling constant), interpretation of splitting patterns is quite straightforward;

- The multiplicity of a multiplet is given by the number of equivalent **protons** in **neighbouring** atoms (n) plus one, i.e. *the $n + 1$ rule*
- Equivalent nuclei do not interact with each other. The three methyl protons in ethanol cause splitting of the neighboring methylene protons; they do not cause splitting among themselves
- The coupling constant is not dependant on the applied field. Multiplets can be easily distinguished from closely spaced chemical shift peaks.

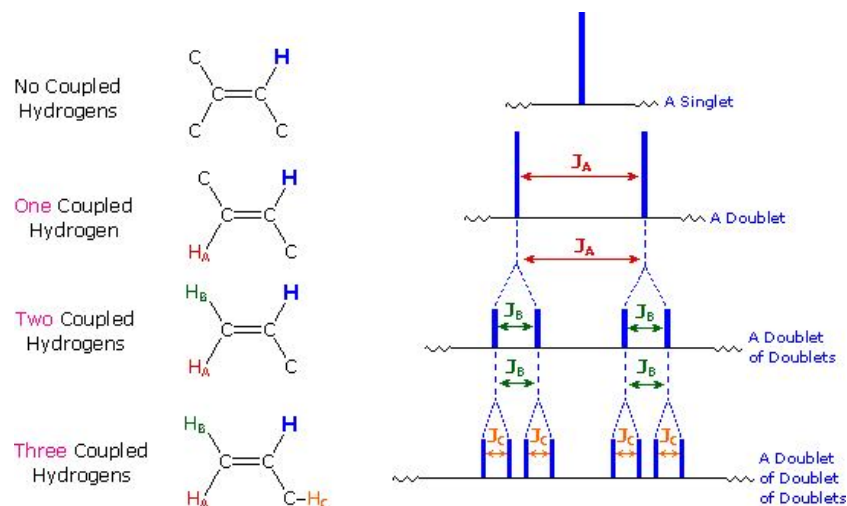
The following general rules summarize important requirements and characteristics for spin 1/2 nuclei:

- 1) Nuclei having the same chemical shift (called **isochronous**) do not exhibit spin-splitting. They may actually be spin-coupled, but the splitting cannot be observed directly.
- 2) Nuclei separated by three or fewer bonds (e.g. vicinal and geminal nuclei) will usually be spin-coupled and will show mutual spin-splitting of the resonance signals (same J's), provided they have different chemical shifts. Longer-range coupling may be observed in molecules having rigid configurations of atoms.
- 3) The magnitude of the observed spin-splitting depends on many factors and is given by the coupling constant **J** (units of Hz). J is the same for both partners in a spin-splitting interaction and is independent of the external magnetic field strength.

The splitting pattern of a given nucleus (or set of equivalent nuclei) can be predicted by the **n+1 rule**, where n is the number of neighboring spin-coupled nuclei with the same (or very similar) Js. If there are 2 neighboring, spin-coupled, nuclei the observed signal is a triplet ($2+1=3$); if there are three spin-coupled neighbors the signal is a quartet ($3+1=4$). In all cases the central line(s) of the splitting pattern are stronger than those on the periphery. The intensity ratio of these lines is given by the numbers in Pascal's triangle. Thus a doublet has 1:1 or equal intensities, a triplet has an intensity ratio of 1:2:1, a quartet 1:3:3:1 etc. See how the numbers in Pascal's triangle are related to the Fibonacci series.



If a given nucleus is spin-coupled to two or more sets of neighboring nuclei by different J values, the n+1 rule does not predict the entire splitting pattern. Instead, the splitting due to one J set is added to that expected from the other J sets. Bear in mind that there may be fortuitous coincidence of some lines if a smaller J is a factor of a larger J.



Magnitude of Some Typical Coupling Constants

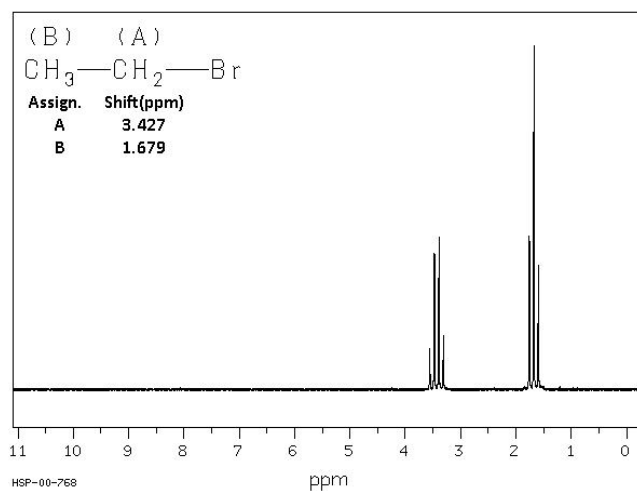
Structural Type	J (Hz)	Structural Type	J (Hz)
$\text{H}-\text{C}-(\text{C})_n-\text{C}-\text{H}$	0 (unless in a rigid ideal orientation)	$\text{H}-\text{C}=\text{C}-\text{H}$	12 to 18
$\text{H}_3\text{C}-\text{CH}_2-\text{X}$	6 to 8	$\text{H}-\text{C}=\text{C}-\text{H}$	7 to 12
$\text{H}_3\text{C}-\text{CH}-\text{X}$	5 to 7	$\text{C}=\text{C}-\text{H}$	0.5 to 3
$\text{H}-\text{C}-\text{C}-\text{H}$	2 to 12 (depends on dihedral angle and the nature of X and Y)	$\text{C}=\text{C}-\text{C}-\text{H}$	3 to 11 (depends on dihedral angle)
$\text{C}-\text{C}(=\text{O})-\text{H}$	0.5 to 3	$\text{C}-\text{C}\equiv\text{C}-\text{H}$	2 to 3
$\text{C}-\text{H}$	12 to 15 (must be diastereotopic)	C_6H_6	o 6 to 9 m 1 to 3 p 0 to 1

Spin 1/2 nuclei include ^1H , ^{13}C , ^{19}F & ^{31}P . The spin-coupling interactions described above may occur between similar or dissimilar nuclei. If, for example, a ^{19}F is spin-coupled to a ^1H , both nuclei will appear as doublets having the same J constant. Spin coupling with nuclei having spin other than 1/2 is more complex and will not be discussed here.

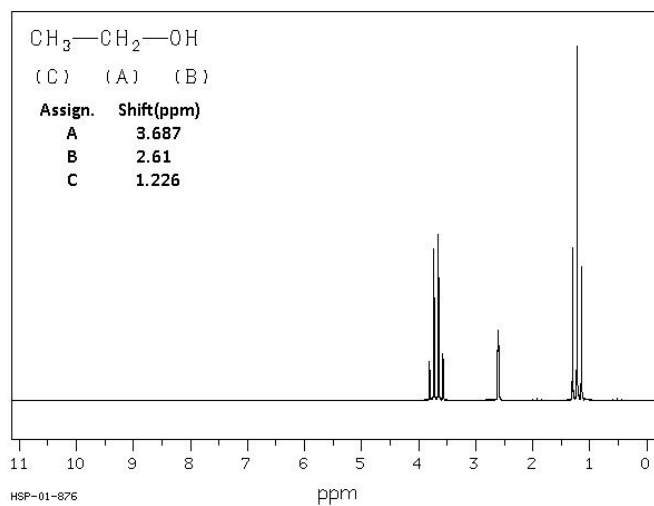
Table of Characteristic Proton NMR Shifts

<i>type of proton</i>	<i>type of compound</i>	<i>chemical shift range, ppm</i>
RCH_3	primary aliphatic	0.9
R_2CH_2	secondary aliphatic	1.3
R_3CH	tertiary aliphatic	1.5
$\text{C}=\text{C}-\text{H}$	vinyllic	4.6-5.9
$\text{C}=\text{C}-\text{H}$	vinyllic, conjugated	5.5-7.5
$\text{C}(\text{triple bond})\text{C}-\text{H}$	acetylenic	2-3
$\text{Ar}-\text{H}$	aromatic	6-8.5
$\text{Ar}-\text{C}-\text{H}$	benzylic	2.2-3
$\text{C}=\text{C}-\text{CH}_3$	allylic	1.7
$\text{HC}-\text{F}$	fluorides	4-4.5
$\text{HC}-\text{Cl}$	chlorides	3-4
$\text{HC}-\text{Br}$	bromides	2.5-4
$\text{HC}-\text{I}$	iodides	2-4
$\text{HC}-\text{OH}$	alcohols	3.4-4
$\text{HC}-\text{OR}$	ethers	3.3-4
$\text{RCOO}-\text{CH}$	esters	3.7-4.1
$\text{HC}-\text{COOR}$	esters	2-2.2
$\text{HC}-\text{COOH}$	acids	2-2.6
$\text{HC}-\text{C}=\text{O}$	carbonyl compounds	2-2.7
RCHO	aldehydic	9-10
ROH	hydroxylic	2-4
ArOH	phenolic	4-12
$\text{C}=\text{C}-\text{OH}$	enolic	15-17
RCOOH	carboxylic	10.0-13.2
RNH_2	amino	1-5

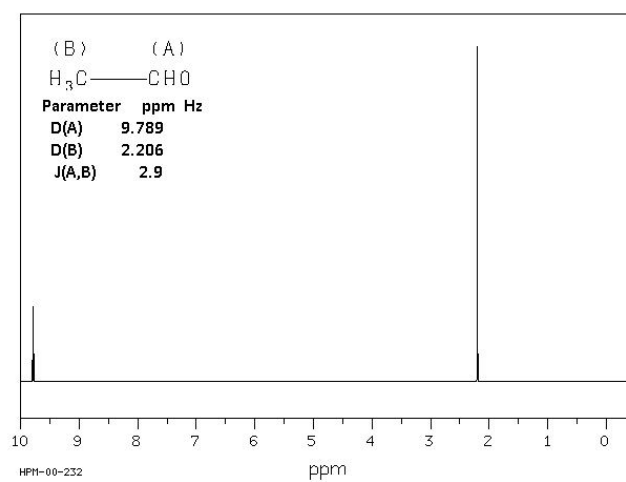
1. Ethyl Bromide -



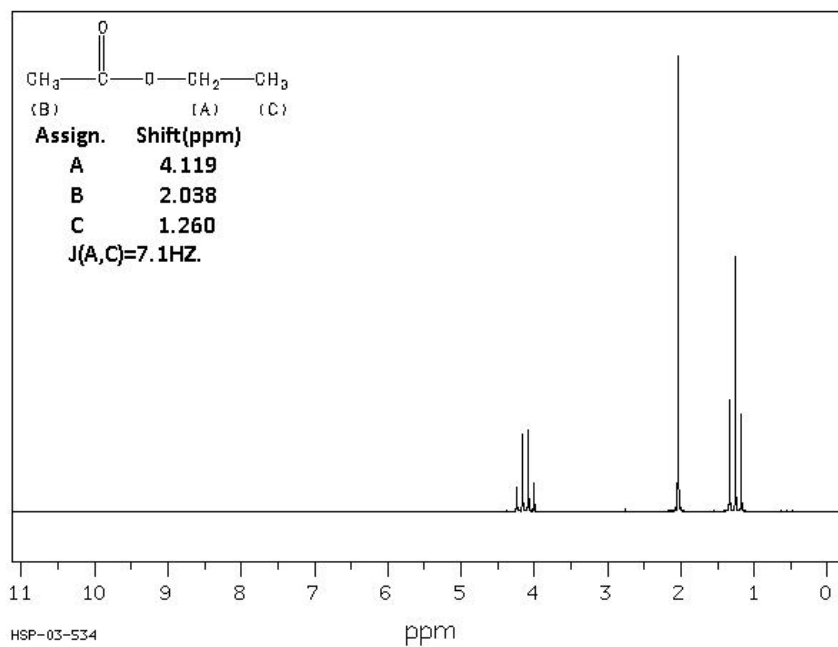
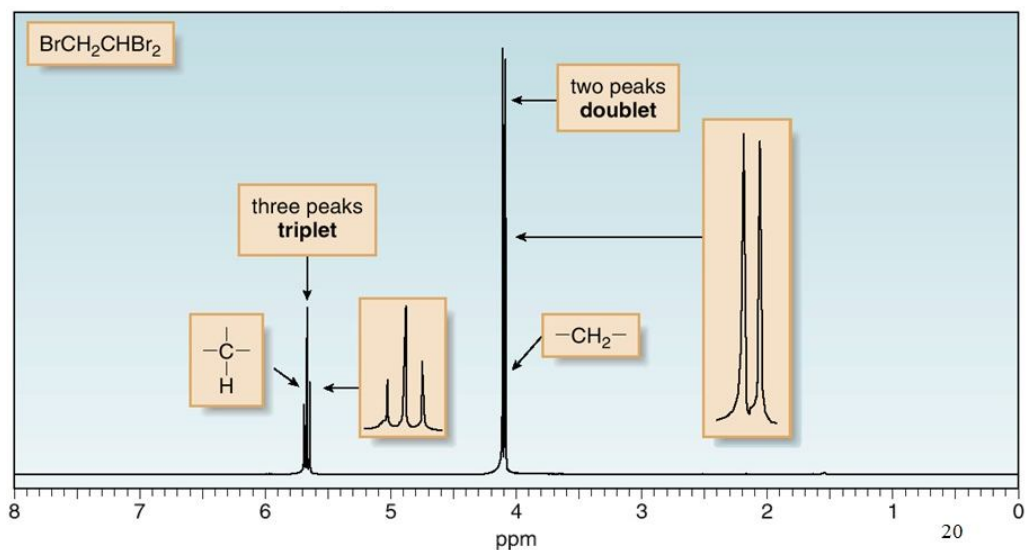
2. Ethanol -



3. Acetaldehyde -

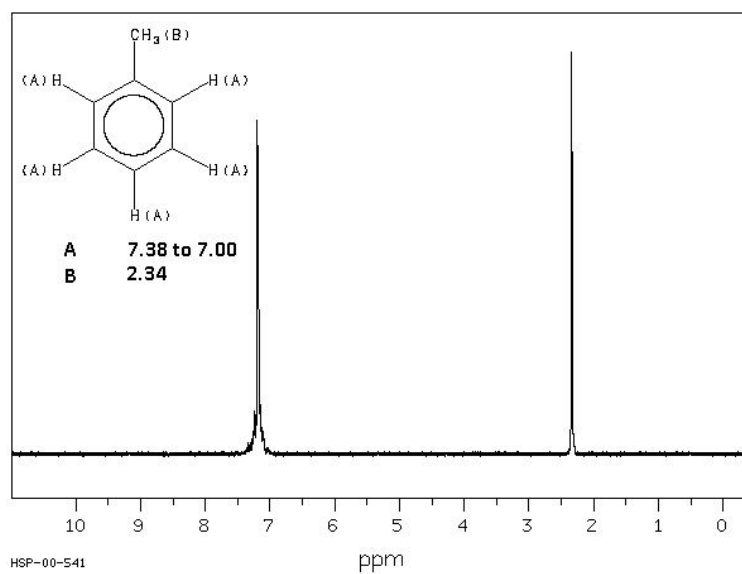


4. ^1H NMR of 1, 1, 2 - tribromoethane

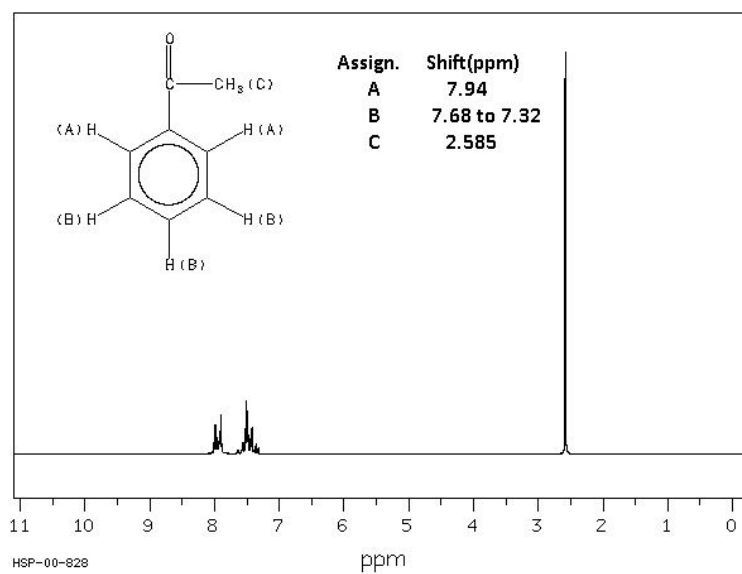


5. Ethylacetate -

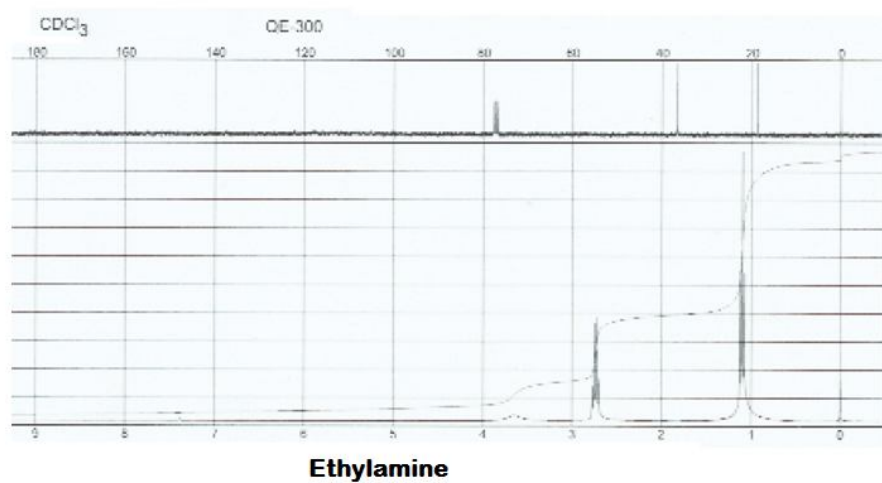
6. Toluene -



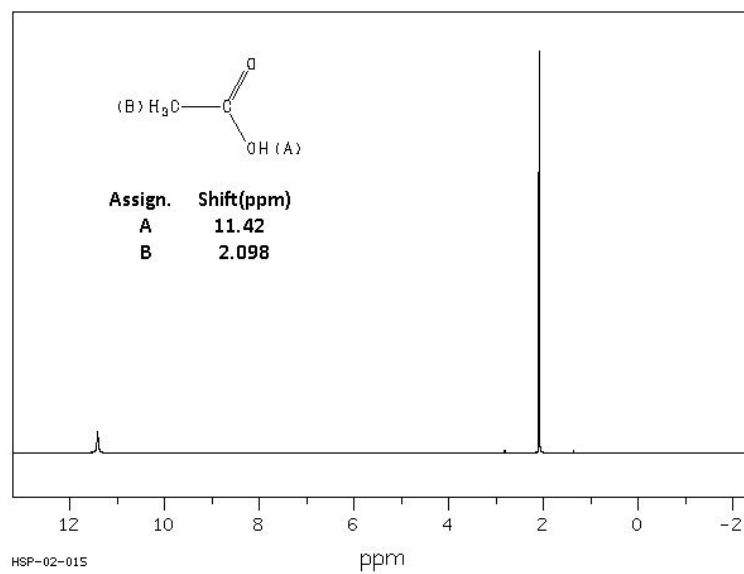
7. Acetophenone -



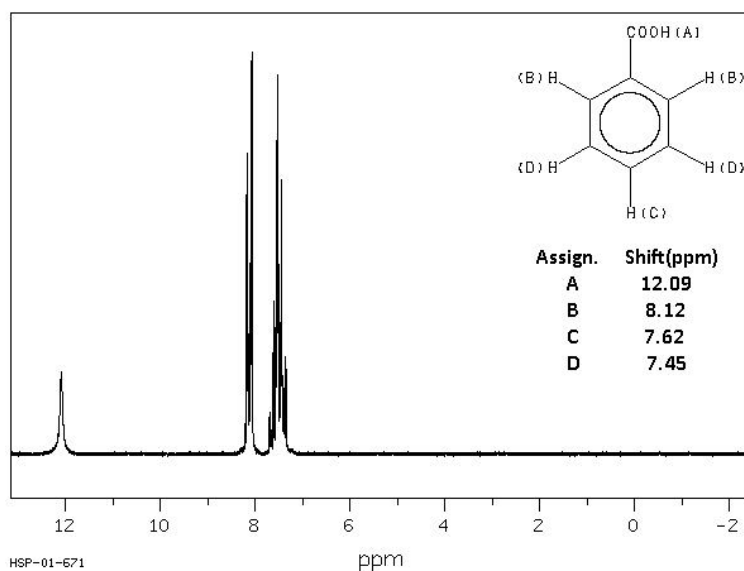
8. Ethylamine -



9. Acetic Acid -



10. Benzoic Acid -



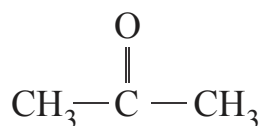
Deduce the structure of following compounds :

01. Molecular formula : C_3H_6O .

PMR (δ ppm) : δ 2.05 (5, 6H)

Ans :-

In the given molecular formula contains three carbon atoms. and in PMR spectrum, there is only singlet ($-CH_3$) and these two $-CH_3$ groups attached with electron withdrawing group $-C=O$. Therefore structure of compounds.



02. Molecular formula : C_8H_{10}

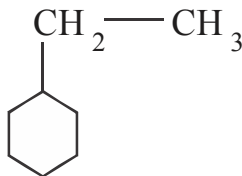
**PMR (δ ppm) : δ 2.3 (Q, $J = 7Hz$, 2H), 1.0 (t, $J = 7Hz$, 3H)
 δ 7.3 (5, 5H)**

Ans :-

δ 7.3 peak for 5H as singlet indicates the compound contains monosubstituted benzene ring. i.e. C_6H_5 .

δ 2.3 peak as quartet for 2H indicates the presence of $-CH_2$ group attached to CH_3 group.

δ 1.0 peak as triplet for 3H indicates the presence of $-\text{CH}_3$ group attached to $-\text{CH}_2$ group. Hence monosubstitution is $-\text{CH}_2-\text{CH}_3$
Therefore Structure of compound is

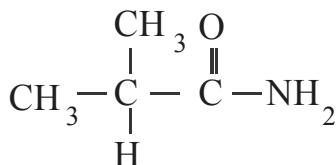


03. Molecular formula : $\text{C}_4\text{H}_9\text{NO}$.

**PMR (δ ppm) : δ 1.10 (septet, $J = 8\text{Hz}$, 1H), 2.1 (d, $J=8\text{Hz}$, 6H)
 δ 9.1 (5, 2H exchangeable with D_2O)**

Ans :-

Peak at δ 1.0 as septet for 1H indicate that $-\text{CH}-\text{OS}$ adjacent to two $-\text{CH}_3$ groups and it is supported by another peak at 2.1 as doublet for 6H with the same coupling constant. Hence compound must contain



04. Molecular formula : $\text{C}_5\text{H}_{10}\text{O}$

PMR (δ ppm) : 1.05 (t, $t = 6\text{Hz}$, 6H), 2.4 (q, $J=6\text{Hz}$, 4H)

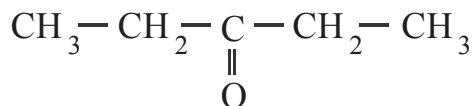
Ans :-

Peak with same coupling constant (J) indicates that both groups are adjacent.

Peak at δ 1.05 triplet for 6H indicates that compound must contain two $-\text{CH}_3$ groups.

Peak at δ 2.4 quartet for 4H indicates that compound must contain two $-\text{CH}_2-$ is split up by neighbouring three protons in the form of $-\text{CH}_3$ groups.

$-\text{CH}_2-$ Protons are more deshielded (δ 2.4) than $-\text{CH}_3$ protons (δ 1.5) i.e. $-\text{CH}_2-$ electron withdrawing $\text{C}=\text{O}$ group. Hence structure of compound is.



05. Molecular formula : C_8H_8O .

**PMR (δ ppm) : δ 2.8 (d, $J = 6.5\text{Hz}$, 2H), δ 7.2 - 7.6 (m,s, 5H)
 δ 9.78 (t, $J=6.5\text{Hz}$, 1H)**

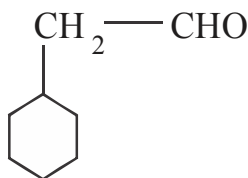
Ans :-

Peak 7.2 - 7.6 multiplet for 5H indicates that compound contains monosubstituted benzene ring.

Peak δ 9-10 triplet for 1H indicate -CHO proton appears in the down field region.

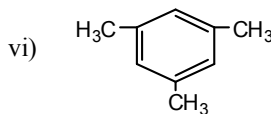
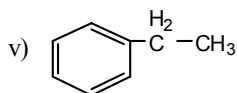
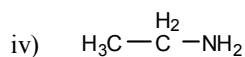
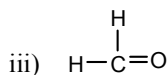
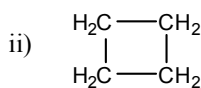
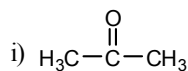
Peak at δ 9.8 triplet indicate the presence of $-CH_2-CHO$ group & is supported by peak 2.8 doublet with the same coupling constant.

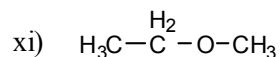
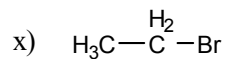
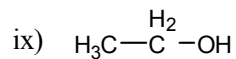
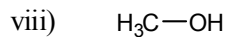
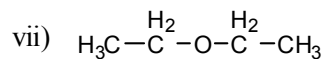
Hence structure of compound is



QUESTION BANK

- Q1. Explain the principal of NMR spectroscopy.
Q2. Write note on Orientation of hydrogen nucleus.
Q3. Give the instrumentation and experimental procedure for NMR spectroscopy.
Q4. Explain Shielding and Deshielding protons with suitable examples.
Q5. Explain Shielding effect by taking example of acetylene.
Q6. Explain Deshielding effect by taking example of acetylene.
Q7. What is Chemical shift? Explain with suitable example.
Q8. How many signals are obtained for the following compounds.

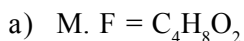




Q 9. Explain the terms (i) Spin-Spin Coupling (ii) Coupling Constant.

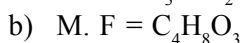
Q10. Based on PMR spectral data given below. Deduce the structure of the following compound.

Justify the PMR spectral data.



PMR(δ ppm): δ 1.1(t, $j=7$ Hz, 3H), δ 2.3(q, $j=7$ Hz, 2H), δ 3.8(s, 3H)

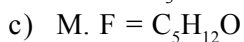
Ans: $\text{CH}_3-\text{CH}_2\text{COOCH}_3$



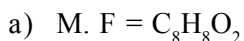
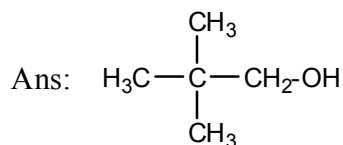
PMR(δ ppm): δ 2.12(s, 3H), δ 2.6(t, $j=6$ Hz, 2H), δ 2.82(t, $j=6$ Hz, 2H),

δ 11.0(s, H exchangeable with D_2O),

Ans: $\text{CH}_3-\text{O}-\text{CH}_2\text{CH}_2-\text{COOH}$

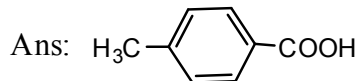


PMR(δ ppm): δ 1.12(s, 9H), δ 3.4(s, 2H), δ 5.0(s, H exchangeable with D_2O),



PMR(δ ppm): δ 2.35(s, 3H), δ 7.10(d, $j=9$ Hz, 2H), δ 7.95(d, $j=9$ Hz, 2H),

δ 11.0(s, H exchangeable with D_2O),



Numerical problems on UV, IR and NMR

General spectral data given in table – 1, 2 and 3 is useful to solve the problems based on U.V, IR and NMR spectroscopy:

Table no.1

Chromophore group	Example	λ max	E max	Transition
$\begin{array}{c} \text{---C=C---} \\ \quad \end{array}$	ethylene	165	15000	Pi-Pi*
$\text{---C}\equiv\text{C---}$	Acetylene	190	8000	Pi-Pi*
$\begin{array}{c} \text{---C=O} \\ \end{array}$	Acetone	190	900	n- σ^*
		270	30	n- Pi*
$\begin{array}{c} \text{HC=O} \\ \end{array}$	Aldehyde	210	1200	Pi-Pi*
		290	16	n- Pi*
benzenoid ring	Benzene	180	60000	Pi- Pi* E ₁ -band
		200	8000	Pi- Pi* E ₂ -band
		255	215	Pi- Pi* B-band
Aromatic hydroxy compounds	Phenol	210	6200	Pi- Pi* E ₂ -band
		270	1450	Pi- Pi* B-band
	methoxy benzene	217	600	
		269		
	Aceto-phenone	245.5	9800	
-O-	ether	210		n - σ^*
-N=O	Nitrobutane	302	100	
---N=N---	Azomethane	348	04	pi- pi *
	Acetonitrile	160	05	pi- pi*
-NO ₂	Nitromethane	200	5000	pi- pi*

Table no. 2: IR group frequency bands-region.

sr. no.	Functional group	compound	wavenumber cm^{-1}
01	O-H	Alcohol, Carboxylic acids	3600-3200
02	$\begin{array}{c} \text{—NH} \\ \end{array}$	Amines, Amides	3600-3200
03	$\equiv\text{CH}$	Acetylene	3600-3200
04	-COOH	Carboxylic acids	3600-2500
05	$\begin{array}{c} =\text{CH} \\ \end{array}$	Alkene	3100-3000
	Ar-H	Aromatic	3100-3020
06	$\begin{array}{c} \\ \text{—CH} \\ \end{array}$	Alkanes	3000-2800
07	C-H band -CHO	Aldehydes	2900-2700 (two bands, fermiresonance)
08	—S-H	Thiols	2950-2550
09	—C $\equiv$ C—	Alkynes	2200-2100
10	—C $\equiv$ N	Nitriles	2280-2240
11	$\begin{array}{c} \text{—C=O} \\ \end{array}$	Aldehydes, Ketones, acids, esters, amides	1870-1650
12	$\begin{array}{c} \text{—C=C—} \\ \quad \end{array}$	Alkenes	1680-1620
13	$\begin{array}{c} \text{—C} \cdots \text{C—} \\ \quad \end{array}$	Aromating ring	1600-1400 (4-bands)
14	—NO ₂	Nitrocompounds	1560-1515 and 1385-1345 (2-bands)
15	$\begin{array}{c} \quad \\ \text{—C—O—C—} \\ \quad \end{array}$	Ethers	1270-1050
16	$\begin{array}{c} \\ \text{—C—X} \\ / \end{array}$	Haloalkanes	

Table .3: PMR Chemical shift data. (δ ppm)

<i>type of proton</i>	<i>type of compound</i>	<i>chemical shift range, ppm</i>
RCH_3	primary aliphatic	0.9
R_2CH_2	secondary aliphatic	1.3
R_3CH	tertiary aliphatic	1.5
$\text{C}=\text{C}-\text{H}$	vinyllic	4.6-5.9
$\text{C}=\text{C}-\text{H}$	vinyllic, conjugated	5.5-7.5
$\text{C}(\text{triple bond})\text{C}-\text{H}$	acetylenic	2-3
$\text{Ar}-\text{H}$	aromatic	6-8.5
$\text{Ar}-\text{C}-\text{H}$	benzylic	2.2-3
$\text{C}=\text{C}-\text{CH}_3$	allylic	1.7
$\text{HC}-\text{F}$	fluorides	4-4.5
$\text{HC}-\text{Cl}$	chlorides	3-4
$\text{HC}-\text{Br}$	bromides	2.5-4
$\text{HC}-\text{I}$	iodides	2-4
$\text{HC}-\text{OH}$	alcohols	3.4-4
$\text{HC}-\text{OR}$	ethers	3.3-4
$\text{RCOO}-\text{CH}$	esters	3.7-4.1
$\text{HC}-\text{COOR}$	esters	2-2.2
$\text{HC}-\text{COOH}$	acids	2-2.6
$\text{HC}-\text{C}=\text{O}$	carbonyl compounds	2-2.7
RCHO	aldehydic	9-10
ROH	hydroxylic	2-4
ArOH	phenolic	4-12
$\text{C}=\text{C}-\text{OH}$	enolic	15-17
RCOOH	carboxylic	10.0-13.2
RNH_2	amino	1-5

Double bond and/or ring equivalent:

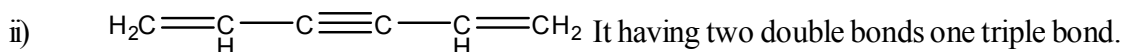
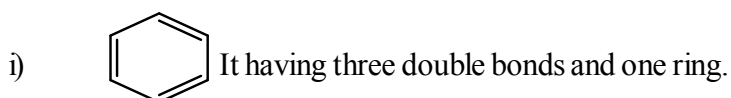
If the molecular formula of the compound is given, then the number of bonds or/ and ring equivalent DBE can be easily calculated.

I] Type A: If the compound is hydrocarbon with general formula C_xH_y , then

$$DBE = X+1 - Y/2 \quad \text{OR} \quad C+1 - H/2$$

For ex. C_6H_6 the number of DBE in it

$DBE = 6+1 - 6/2 = 4$ and possible structure for given molecular formula



A triple bond may be regarded as equivalent to two double bonds. The presence of triple bond. $[C \equiv C, C \equiv N]$

III Type B: if the compound contains one or more divalent atoms (sulphur, oxygen) in addition to the elements carbon and hydrogen. Then the presence of divalent atom can be ignored, while calculating DBE.

$$DBE = X+1 - Y/2 \quad \text{OR} \quad C+1 - H/2$$

For ex. Organic compound with molecular formula. (i) $C_3H_8O_3$ (ii) $C_6H_6O_2$

I) $DBE = 3+1 - 8/2 = 0$ i.e. it does not contains double bond or ring.

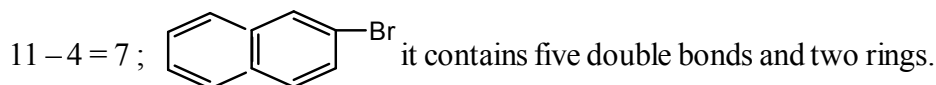
II) $DBE = 6+1 - 6/2 = 7 - 3 = 4$. It contains three double bonds and one ring.

III Type C: if molecular formula of compound contains some monovalent element like halogens [Cl, Br, I etc.] then for calculating the number of DBE in its structural formula.

$$DBE = x+1 - y+z/2; \quad \text{or} \quad DBE = C+1 - H + X/2$$

For ex. consider a compound with molecular formula $C_{10}H_7Br$. The number of DBE in the compound is equal to,

$$10+1 - 7+1/2;$$



IV Type D: If compound contains nitrogen atom or some trivalent phosphorous atom. The number of trivalent atoms subtracted from number of hydrogen atoms present in molecular formula.. $C_xH_yN_z$.

$$DBE = x+1 - y-z/2 \quad \text{or} \quad DBE = C+1 - H - N/2$$

for ex. 1. $C_{12}H_{12}N_2$ 2. $C_6H_8O_3N_2$
 1. $DBE = 12+1 - 12 - 2/2 = 13 - 5 = 8$.
 2. $DBE = 6+1 - 8 - 2/2 = 7 - 3 = 4$.

Solved combined problems based on UV, IR, and NMR data:

1] An organic compound contains C_4H_8O . In UV it gives a characteristic band at 275 nm,

ϵ_{max} 17. In IR band are formed at 2941-2857(m)

1715(s) and

1460 (m).

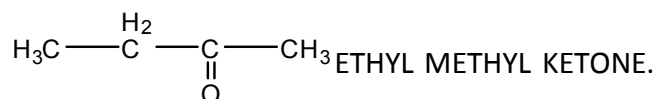
In NMR, three signals appears at i) 7.5 τ or 2.5 quartet, (2H)

ii) 7.88 τ singlet (3H)

iii) 8.93 τ triplet, (3H) determine the structural formula.

Ans:-

1. Absorption at 275 μ , ϵ_{max} 17 is characteristic of a carbonyl group. Due to $n \rightarrow \pi^*$ transition.
2. a) the absorption at 2941-2857(m) in IR spectrum is due to C-H stretching.
b) at 1715(s) is characteristic of saturated ketonic group.
c) at 1460 (m) may be due to C-H bending.
3. i) The presence of triplet at 8.93 τ triplet, (3H) and quartet at 7.5 τ or 2.5 quartet, (2H) is characteristic of $\text{H}_3\text{C}-\text{CH}_2$ group in the compound.
ii) The singlet at 7.88 τ singlet (3H) is due to methyl group adjacent to a carbonyl group. Hence the structure of compound is



- 2] An organic compound with molecular mass 69 and molecular formula $\text{C}_4\text{H}_7\text{N}$.

It transparent above 200 nm

The absorption bands in IR spectrum, are

a) 2941 cm^{-1} (m).

b) 2273 cm^{-1} (m). and

c) 1460 cm^{-1} (m).

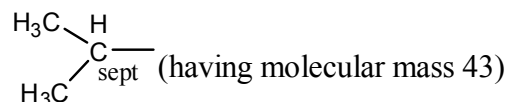
in NMR, two signals are formed, a) one is septet at 7.28 τ ($J=6.7\text{cps}$, 4.2 square)

b) doublet at 8.67 τ ($J=6.7\text{cps}$, 2.8 square).

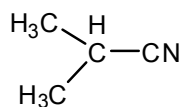
determine the structural formula.

Ans:-

1. The UV spectrum is transparent above 200 nm. shows absence of conjugation and carbonyl group.
2. In IR spectrum, a) the signal at 2941 cm^{-1} (m) indicate C-H stretching and 1460 cm^{-1} (m) indicate C-C stretching. And b) signal at 2273 cm^{-1} (m) indicate the presence of CN group.
3. In NMR one signal septet at 7.28 τ is a part of structure



Remaining 26 mass unit corresponds to CN group, there fore structure of compound is



3] A hydrocarbon containing molecular formula C_4H_8 .

i) it transparent above 210 nm, in UV spectrum

ii) in its infra red spectrum, bands are formed at a) 3022cm^{-1} , 1676cm^{-1} and at 965cm^{-1} .

iii) Two signals appears in its NMR spectrum a) 8.40τ doublet and 4.45τ quartet in the integral area ratio at 3:1 respectively, determine structural formula of the compound.

Ans:-

1. The UV spectrum is transparent above 210 nm, shows the absence of conjugation and carbonyl group.

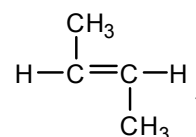
2. In IR, a) absorption at 3022cm^{-1} C-H stretching in aromatic compound or $=\text{CH}$ stretching. Since carbonyl group is absent.

b) and bond at 1676cm^{-1} may be due to $\text{C}=\text{C}$ stretching. Thus the hydrocarbon must be unsaturated.

c) bond at 965cm^{-1} , indicate trans alkenes.

3. In NMR, two signals are formed 8.40τ doublet indicate methyl group attached to $=\text{CH}$ and second signal due to one proton quartet i.e.

$\text{H}_3\text{C}-\underset{\text{H}}{\text{C}}=$ and its molecular mass is 28. The molecular formula is double of it. Hence probable structure is



4] A compound with molecular mass 71.

i) is transparent in UV spectrum.

ii) In IR bands are formed at a) $2941-2857\text{cm}^{-1}$,

b) 2247cm^{-1} and

c) 1460cm^{-1} .

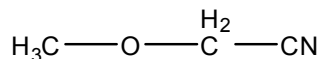
iii) Two signals are formed at i) 5.78τ (16.8square) and 6.51τ (23.9 square)

Ans:-

1. In IR spectrum band at 2941cm^{-1} (m) indicate $-\text{C}-\text{H}$ stretching and 1460cm^{-1} (m) indicate $\text{C}-\text{C}$ stretching. and band at 2247cm^{-1} indicate the presence of CN group.

2. Two signal formed in NMR are, two sets of protons are in the ratio 2:3 thus, CH_3 and CH_2 may be part of structure. Thus, CH_3 , CH_2 and CN are the part of structure. And mole. Mass 55 and total mass given is 71. Remaining mass 16 corresponding to an atom of oxygen.

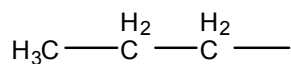
3. Thus the probable structure of compound is



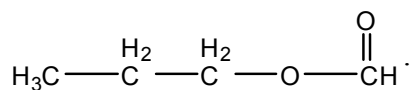
- 5] An organic compound with molecular mass 88 absorb at 206 nm, ϵ_{max} 50, In IR medium absorb at on bands formed at
- 3049-2924 and
 - 1445 cm^{-1} . also strong absorption band at 1736 cm^{-1} and following signals are formed in its NMR spectrum.
- 1.93 τ singlet (5.9 sq.)
 - 5.88 τ triplet ($J=7.0$, 12.2 sq.)
 - 8.33 τ sextet ($J=7.0$, 11.6 sq.) and
 - 9.05 τ triplet ($J=7.0$, 18.6 sq.).

Ans:-

- In UV an absorption band at 206 nm, ϵ_{max} 50 does not gives any definite information/ presence of $\text{C}=\text{O}$ group.
- In IR, i) formation of strong absorption band 1736 cm^{-1} shows the presence of an ester.
ii) The bands at 3049-2924 and 1445 cm^{-1} due to C-H stretch, and c-c stretch and $\text{C}=\text{O}$ stretch respectively.
- The set of protons with different chemical shift are in the ratio 1:2:2:3. The formation of triplet, sextet and triplet with the same coupling constant ($J=7.0$) shows that



as the part of structure. A one proton singlet at very low field suggest as $-\text{CH}$ also as a part of structure. This amount to 56 mass units.



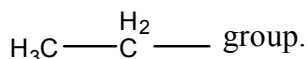
[56+32=88]

[$\text{C}=\text{O}$ structure for acid appears at 1715-1720 cm^{-1}]

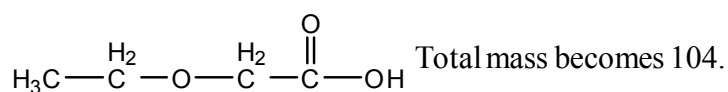
- 6] A compound with molecular formula $\text{C}_4\text{H}_8\text{O}_3$ and having mass 104. Is transparent below 210nm.
- In IR spectrum, the medium bands formed are i) 3125- 2857 cm^{-1} and 1449 cm^{-1} (s). A strong band formed at 1718 cm^{-1} and also weak bands at 2695 cm^{-1} and 2625 cm^{-1} .
 - In NMR spectrum following signals are observed
- 0.95 τ singlet (5.4 sq.),
 - 5.87 τ singlet (11.2 sq.),
 - 6.34 τ quartet ($J=7.1$, 10.6 sq.) and
 - 8.73 τ triplet ($J=7.1$, 16.2 sq.),

Ans:-

1. In UV, absorption band transparent below 210nm indicates $n \rightarrow \pi^*$ transition i.e. C=O gr.
2. a) The broad band 3125- 2857 cm^{-1} appears due to O-H stretching. And strong bond formed at 1718 cm^{-1} results presence of C=O group.
3. In NMR spectrum, -0.95 τ singlet (5.4 sq.) results the formation -COOH group, and 6.34 τ quartet ($J = 7.1, 10.6$ sq.) and 8.73 τ triplet ($J = 7.1, 16.2$ sq.) indicate the formation of



5. 87 τ singlets (11.2 sq.) indicate the presence of -CH₂- group.
There fore possible structure is

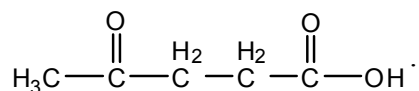


- 7] A compound with molecular weight 116 gave the following spectral information.
i) UV, 283 μ , ϵ max 50.
ii) IR, a) 3000-2500 b) 1715(s) c) 1345(w) cm^{-1} .
iii) NMR, 7.88 τ singlet, (3H), 7.40 τ triplet (2H), 7.75 τ triplet (2H), and 1.1 τ singlet (1H).

Ans:-

1. In UV, absorption at 283 μ , ϵ max 50 of low intensity indicates presence of -C=O group.
2. In IR, a) the presence of -C=O group is confirmed by a strong band at 1715 cm^{-1} .
b) A very broad band at 3000-2500 cm^{-1} is most characteristic of acid (O-H stretching) and it appears as a result of hydrogen bonding.
3. In NMR, a) the presence of an acid group is also shown by NMR which gives signal singlet at -ve τ value. Thus compound contains -C=O and -COOH groups.
b) 7.88 τ singlet (3H) indicates presence of -CH₃ group.
c) 7.40 τ triplet (2H), 7.75 τ triplet (2H) indicates the presence of -CH₂-CH₂-.

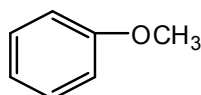
Hence compound with this structure is



8. Molecular formula: C₇H₈O.
Uv: 230 nm (ϵ max 1000), 270 nm (ϵ max 600).
IR: 3100, 2950, 1600, 1500, 1250, 750, AND 700 cm^{-1} .
NMR: (δ ppm), δ 3.8 (s, 3H), δ 6.8-7.2 (m, 5H).

Ans:-

- a) In UV; absorption bands at 230 nm (ϵ max 1000), 270 nm (ϵ max 600) indicates the presence of E_2 band and B- band of benzene ring.
- b) In IR spectrum the band at 3100 cm^{-1} due to C-H stretching of benzene ring, band at 2950 cm^{-1} is due to C-H stretching of aliphatic alkyl group. 1600, 1500 cm^{-1} indicate the C=C - benzene ring. And band at 1250 cm^{-1} is due to C-O-C asymmetric stretching of aromatic ether. 750, AND 700 cm^{-1} bands indicates the presence of monosubstituted benzene.
- c) In NMR, δ 3.8 (s, 3H), peak due to OCH_3 protons. And the presence of oxygen atom in molecular formula accounts for OCH_3 group.
- d) As CH_3 group attached to electronegative oxygen atom. δ 6.8-7.2 (m, 5H) represent multiplet for 5H in benzene ring. Hence the structure of the compound is



9. Molecular formula: $\text{C}_6\text{H}_{12}\text{O}$
 UV: 282nm (ϵ max 221)
 IR: 2950-2840 cm^{-1} , 1710 cm^{-1} .
 PMR: (δ ppm), δ 1.2 (s, 3H), δ 2.1 (s, 9H).

Ans: -

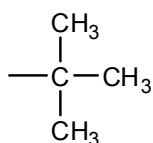
In UV spectrum absorption band at 282nm (ϵ max 221) indicates the presence of carbonyl group.

In IR spectrum the absorption band at 2950-2840 cm^{-1} , due to C-H stretching of alkyl group.

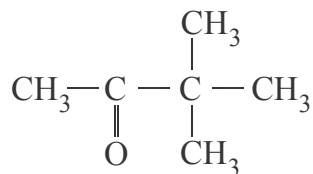
And the band at 1710 cm^{-1} due to C=O group present.

In PMR: spectrum, the peak at δ 1.2 (s, 3H), as singlet for 3H indicate the presence of CH_3 group.

And the presence of singlet peak at δ 2.1 (s, 9H) indicate the presence of three CH_3 group at same carbon atom, i.e.



Hence the presence of CH_3 , C=O and in the structure, there fore possible structure is.



10. Molecular formula: $C_8H_8O_2$

In UV: 202nm (ϵ max 7900), 255nm (ϵ max 215),

IR: broad band between 3300- 2700 cm^{-1} , 1700 cm^{-1} , 1600, 1500, 750, 700 cm^{-1} .

PMR: (δ ppm) , δ 3.5 (s, 12 mm), δ 7.2 (s, 30mm), δ 12.3 (s, 6 mm exchangeable with D_2O),

Ans:

In UV:

Spectrum absorption band at 202 nm and 255 nm indicate the presence of E_2 band and B band of benzene ring.

In IR:

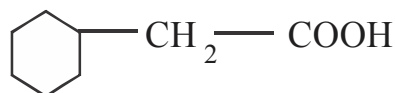
Broad band between 3300- 2700 cm^{-1} indicate the presence of O-H stretching of -COOH group.

1700 cm^{-1} this band indicate the presence of -C=O group in -COOH..

Band at 1600, 1500 cm^{-1} indicate the presence of benzene ring. -C-H deformation bands at 750, 700 cm^{-1} indicate the presence of mono-substituted benzene.

In PMR: singlet peak at δ 3.5 (s, 12 mm), indicate the presence of two protons, which represent s - CH_2 group. Singlet peak at δ 7.2 (s, 30mm), indicate the presence of 5H of benzene ring with mono-substitution. Singlet peak with exchangeable D_2O confirms the presence of O-H of COOH group.

Hence, the presence of - CH_2 group, -COOH group and one benzene ring gives possible structure.



11. Molecular formula: C_3H_8O

In UV: transparent above δ max 210.

IR: broad band 3400 cm^{-1} , 2890 cm^{-1} , 1050 cm^{-1} .

PMR: (δ ppm), δ 1.2 (t, J= 7.5 Hz, 3H), δ 2.6 (sextet, 7.5 Hz, 2H), δ 3.5 (t, J=7.5 Hz, 2H), δ 4.5 (s, 1H, exchangeable with D_2O).

Ans:

In UV:

Spectrum absorption band above 210 nm indicate the absence of carbonyl group and conjugation.

In IR:

Absorption band at broad band 3400 cm^{-1} due to -OH stretching. Band at 2890 cm^{-1} , indicate the -CH stretching of alkyl group. And 1050 cm^{-1} . indicate the -CO stretch of - CH_2OH group.

In PMR:

Triplet at δ 1.2 (t, J= 7.5 Hz, 3H), δ 2.6 (sextet, 7.5 Hz, 2H), δ 3.5 (t, J=7.5 Hz, 2H) indicate the presence of group.

Singlet at δ 4.5, exchangeable with D_2O indicate the presence of -OH group.

Hence, the presence of group and -OH group gives possible structure.

12. Molecular formula: C_3H_8O

In UV: transparent above δ max 210.

IR: broad band 3500 cm^{-1} , 2910 cm^{-1} , 1100 cm^{-1} .

PMR: (δ ppm), δ 1.2 (d, $J = 6\text{ Hz}$, 6H), δ 3.8 (septet, 6 Hz, 1H), δ 4.3 (s, 1H, exchangeable with D_2O).

Ans:

In UV:

Spectrum absorption band above 210 nm indicate the absence of carbonyl group and conjugation.

In IR:

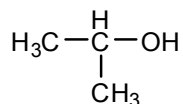
Absorption band at broad band 3350 cm^{-1} due to -OH stretching. Band at 2910 cm^{-1} , indicate the -CH stretching of alkyl group. And 1100 cm^{-1} is a characteristic of -CO stretch of secondary alcohol i.e. -CHOH group.

In PMR:

doublet at δ 1.2 (d, $J = 6\text{ Hz}$, 6H), and δ 3.8 (septet, 6 Hz, 1H), indicate the presence of $H_3C-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-$ group.

Singlet at δ 4.3, exchangeable with D_2O indicate the presence of -OH group.

Hence, the presence of $H_3C-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-$ group and -OH group gives possible structure.



13. Molecular formula: $C_4H_{10}O$

In UV: transparent above δ max 210.

IR: broad band 3300 cm^{-1} , 2970 cm^{-1} , 1150 cm^{-1} .

PMR: (δ ppm), δ 1.3 (s, 9H), δ 4.2 (s, 1H, exchangeable with D_2O).

Ans:

In UV:

Spectrum absorption band above 210 nm indicate the absence of carbonyl group and conjugation.

In IR:

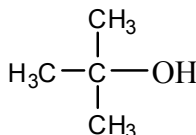
Absorption band at broad band 3300 cm^{-1} due to -OH stretching. Band at 2970 cm^{-1} , indicate the -CH stretching of alkyl group. And absorption band at 1150 cm^{-1} is a characteristic of -CO stretch of tertiary alcohol i.e. -C-OH group.

In PMR:

Singlet at δ 1.3 (S, 9H) indicate the presence of $\text{H}_3\text{C}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-$ group.

Singlet at δ 4.2, exchangeable with D_2O indicate the presence of $-\text{OH}$ group.

Hence, the presence of $\text{H}_3\text{C}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-$ group and $-\text{OH}$ group gives possible structure.



14. **Molecular formula: $\text{C}_2\text{H}_4\text{O}_2$**

In UV: ϵ max 204 (ϵ max 50).

IR: broad band $3100\text{--}2700\text{ cm}^{-1}$, 1720 cm^{-1} .

PMR: (δ ppm), δ 2.1 (S, 3H), δ 11.8 (s, 1H, exchangeable with D_2O).

Ans:

In UV:

Spectrum absorption band at 204 nm indicate the presence of carbonyl group of $-\text{COOH}$ group and due to $n\text{--}\pi^*$ transition.

In IR:

broad band $3100\text{--}2700\text{ cm}^{-1}$ due to $-\text{OH}$ stretching of $-\text{COOH}$ group. and band at 1720 cm^{-1} .

indicate the presence of $-\text{C}=\text{O}$ stretching of $-\text{COOH}$ group.

In PMR:

Singlet at δ 2.1 (S, 3H) indicate the presence of $-\text{CH}_3$ group and its protons are deshielded as attached with electron withdrawing group. and

Singlet at δ 11.8 (s, 1H, exchangeable with D_2O) indicate the presence of H of $-\text{COOH}$ group.

Hence, the presence of $-\text{CH}_3$ group and $-\text{COOH}$ group gives possible structure.



15. **Molecular formula: $\text{C}_2\text{H}_5\text{Cl}$**

In UV: transparent above ϵ max 210.

IR: 2980 cm^{-1} , 750 cm^{-1} .

PMR: (δ ppm), δ 1.48 (t, 3H, $J=7\text{ Hz}$), δ 3.57 (q, 2H, $J=7\text{ Hz}$).

Ans:

In UV:

Spectrum absorption band above 210 nm, indicate the absence of carbonyl group and conjugation.

In IR:

Absorption at 2980 cm⁻¹ due to -CH stretching of alkyl group. and band at 750 cm⁻¹ indicate the -C-Cl stretching.

In PMR:

Triplet at δ 2.1 δ 1.48 (t, 3H, J= 7Hz) indicate the presence of -CH₃ group and Quartet at δ 3.57 (q, 2H, J= 7Hz). indicate the presence of CH₂ group. peaks have same coupling constant which indicate that group are adjacent to one another. Hence, the presence of -CH₃ group, -CH₂ group and -Cl gives possible structure.



16. Molecular formula: C₂H₅O₂N

In UV: ϵ max 274 (ϵ max 15).

IR: band at 2980 cm⁻¹, 1530 cm⁻¹, 1350 cm⁻¹.

PMR: (δ ppm), δ 1.0 (t, 3H, J= 7Hz), δ 4.3 (q, 2H, J= 7Hz).

Ans: -

In UV:

Spectrum absorption band at 274 nm indicate the presence of -NO₂ group due to n-pi* transition.

In IR:

Absorption at 2980 cm⁻¹ due to -CH stretching of alkyl group. and band at 1530 and 1350 cm⁻¹ due to asymmetric and symmetric stretching of -NO₂ group resply.

PMR:

Triplet at δ 1.0 (t, 3H, J= 7Hz), indicate the presence of -CH₃ group and Quartet at δ 4.3 (q, 2H, J= 7Hz). indicate the presence of CH₂ group. peaks have same coupling constant which indicate that group are adjacent to one another. Hence, the presence of -CH₃ group, -CH₂ group and -NO₂ group gives possible structure.



17. Molecular formula: C₄H₈O

In UV: ϵ max 283 (ϵ max 20).

IR: band at 2940 cm⁻¹, 1710 cm⁻¹.

PMR: (δ ppm), δ 1.05 (t, 3H, J= 7Hz), δ 2.4 (q, 2H, J= 7Hz) δ 2.1 (s, 3H,).

Ans:-

In UV:

Spectrum absorption band at 283nm indicate the presence of carbonyl group of aldehyde or ketone.

In IR:

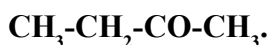
broad band 2940 cm^{-1} due to C-H stretching of alkyl group. And band at 1710 cm^{-1} indicate the presence of C=O stretching of aliphatic keto group band is due to C=O .

PMR:

Triplet at δ 1.05 (t, 3H, $J = 7\text{Hz}$), indicate the presence of -CH_3 group and

Quartet at δ 2.4 (q, 2H, $J = 7\text{Hz}$) indicate the presence of CH_2 group. Peaks have same coupling constant which indicate that group are adjacent to one another i.e. $\text{CH}_3\text{-CH}_2\text{-}$ group. δ 2.1 (s, 3H,) for 3H indicate the presence of -CH_3 group. Proton are shielded as -CH_3 group is attached to electron withdrawing group

Hence, the presence of $\text{CH}_3\text{-CH}_2\text{-}$ group -CH_3 group and C=O group gives possible structure.



18. Molecular formula: $\text{C}_2\text{H}_6\text{O}_2$

In UV: ϵ max 290 (ϵ max 20).

IR: band at 2980 cm^{-1} , 2720 cm^{-1} , 1740 cm^{-1} .

PMR: (δ ppm), δ 1.1 (t, 3H, $J = 6\text{Hz}$), δ 2.5 (quintet, 2H, $J = 6\text{Hz}$) δ 9.6 (t, 1H,).

Ans:-

In UV:

Spectrum absorption band at 290nm indicate the presence of carbonyl group of aldehyde or ketone.

In IR:

Absorption band 2980 cm^{-1} due to C-H stretching of alkyl group, band at 1740 cm^{-1} indicate the presence of C=O stretching of aliphatic keto group band is due to C=O and band at 2720 cm^{-1} indicate strong absorption of C=O group.

PMR:

Triplet at δ 1.1 (t, 3H, $J = 6\text{Hz}$), indicate the presence of -CH_3 group and

Quintet at δ 2.5 (quintet, 2H, $J = 6\text{Hz}$) indicate the presence of CH_2 group. Peaks have same coupling constant which indicate that group are adjacent to one another i.e. $\text{CH}_3\text{-CH}_2\text{-}$ group. δ 9.6 (t, 1H,) for 1H indicate the presence of -CHO group adjacent to -CH_2 group.

Hence, the presence of $\text{CH}_3\text{-CH}_2\text{-}$ group and -CHO group gives possible structure.



19. Molecular formula: $\text{C}_2\text{H}_6\text{O}_2$

In UV: ϵ max transparent above 210.

IR: Broad band at 3400 cm^{-1} , 2970 cm^{-1} ,

PMR: (δ ppm), δ 2.5 (s, 2H, exchangeable with D_2O), δ 3.68 (t, 4H).

Ans:-

In UV:

Spectrum absorption band at 210nm indicate the absence of carbonyl group and conjugation.

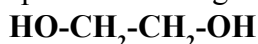
In IR:

Absorption of broad band at 3400 cm⁻¹ due to -O-H stretching. Band at 2970 cm⁻¹ indicate the presence of -C-H stretching.

PMR:

δ 2.5 (s, 2H, exchangeable with D₂O) indicate the presence of two -OH groups and triplet at δ 3.68 (t, 4H) indicate the presence of two CH₂ groups.

Hence, the presence of CH₂-CH₂- group and two -OH groups gives possible structure.



20.

Molecular formula: C₃H₆N

In UV: ε max transparent above 210.

IR: band at 2980 cm⁻¹, 2250 cm⁻¹,

PMR: (δ **ppm**), δ 1.1 (t, 3H, J= 6Hz), δ 3.5(q, 2H, J= 7Hz).

Ans:-

In UV:

Spectrum absorption band at 210nm indicate the absence of carbonyl group and conjugation.

In IR:

Absorption band 2980 cm⁻¹ due to -C-H stretching of alkyl group and 2250 cm⁻¹ indicate the presence of -C≡N group.

PMR:

Triplet at δ 1.1 (t, 3H, J= 6Hz), indicate the presence of -CH₃ group and

Quartet at δ 3.5(q, 2H, J= 7Hz) indicate the presence of CH₂ group, protons are deshielded as -CH₂ group attached to electron withdrawing group.

Hence, the presence of -CH₃ group, -CH₂ group and group gives possible structure.

AMINO ACID, PEPTIDES AND PROTEINS

Introduction

There are mainly three groups of biological polymers:

1) Polysaccharides: Functions primarily as energy reserves and in plants as structural materials.

2) Nucleic acids: Serve two major purposes; storage and transmission of information.

3) Proteins: They are substances of life. Of all chemical compounds, proteins must be ranked first. Proteins make up a large part of animal body they hold it together and they run it. Only nucleic acids which control heredity can challenge the position of protein. And nucleic acids are important because they direct synthesis of proteins.

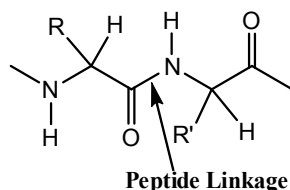
Proteins can be broken down by various chemical and enzymatic methods into smaller and smaller fragments until the final products are the amino acids.



There is no sharp dividing link between peptides and proteins.

Mol. Wt.	>	10,000	– proteins
Mol. Wt.	<	10,000	– poly peptides

In proteins, amino acids are joined in a linear fashion by peptide linkage. Carboxyl groups of one amino acid forms an amide by combination with the amino group of the next amino acid. Thus protein molecule may be represented as a linear polymer of amino acid molecule.



Amino Acids

Amino acids are building blocks of proteins. More than 100 amino acids have been isolated and identified but only 25 are obtained upon hydrolysis of typical proteins. All 25 except 2 are α -amino acids; the two exceptions are proline and hydroxyl proline, which are imino acids. Only 20 amino acids are of general occurrence because they are usually found in all proteins. Ten of the amino acids are essential amino acids i.e. a deficiency in any one prevent growth in young animals, and may even cause death. They must be furnished in the diet, as they are not synthesized in the body.

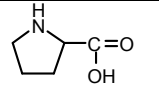
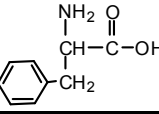
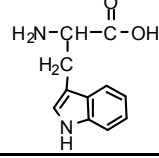
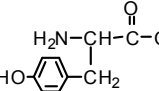
Classification of Amino Acids

Classification:

There are 20 amino acids which are obtained by the complete hydrolysis of proteins. All these amino acids are classified in to three groups.

- Acidic amino acids:** These contains one amino group and two carboxyl groups. For ex. Aspartic acid, Glutamic acid.
- Basic amino acids:** These contains two amino group and one carboxyl groups. For ex. Lysine, Histidine.
- Neutral amino acids:** These contains one amino group and one carboxyl groups. For ex. Glycine, Alanine.

1: Neutral Amino Acids

S.No	Amino acid	abbrev- iation	Systamatic name	IUPAC name	Structure
1.	Glycine	[gly (G)]	aminoacetic acid	2-aminoethanoic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$
2.	Alanine	[Ala(A)]	α -amino propionic acid	2-aminopropanoic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$
3.	Valine	[Val (V)]	α -aminoisocaproic acid	2-amino-3- methylbutanoic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$
4.	Isoleucine	[Ile (I)]	α -amino- β -methyl (-n-Valeric acid)	2-amino-3- methylpentanoic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}-\text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$
5.	Proline	[Pro (P)]	pyrrolidine- α - carboxylic acid	pyrrolidine-2- carboxylic acid	
6.	Phyenyl alanine	[Phe(F)]	α -amino- β -phenyl propionic acid	2-amino-3- phenylpropanoic acid	
7.	Tryptophan	[Trp(W)]	α -amino- β - indolepropionic acid	2-amino-3-(1 <i>H</i> - indol-3-yl)propanoic acid	
8.	Cysteine	[Cys(C)]	α -amino- β -mercapto propionic acid	2-amino-3- mercaptopropanoic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{H}_2\text{C}-\text{SH} \end{array}$
9.	Methionine	[Met(M)]	α -Amino- γ - methylthio-n-butyric acid	2-amino-4- (methylthio)butanoic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{H}_3\text{C}-\text{S}-\text{CH}_2 \end{array}$
10.	Serine	[Ser(S)]	α -amino- β - hydroxypropionic acid	2-amino-3- hydroxypropanoic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{CH}_2 \end{array}$
11.	Threonine	[Thr(T)]	α -amino- β -hydroxy- n-butyric acid	2-amino-3- hydroxybutanoic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{H}_3\text{C}-\text{CH}-\text{OH} \end{array}$
12.	Tyrosine	[Tyr(Y)]	α -amino- β -[p- hydroxyphenyl]propi onic acid	2-amino-3-(4- hydroxyphenyl)propan oic acid	

2: Acidic Amino Acids

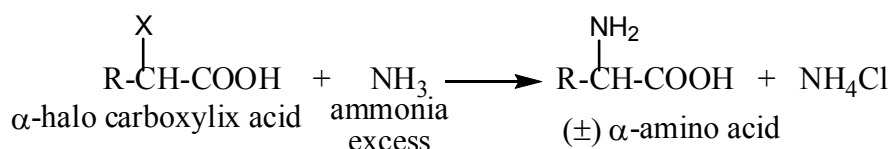
S.No	Amino acid	abbrev- iation	Systamatic name	IUPAC name	Structure
1.	Aspartic Acid	[Asp(D)]	α -aminosuccinic acid	2-aminobutandioic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{H}_2\text{C}-\text{C}-\text{OH} \\ \parallel \\ \text{O} \end{array}$
2.	Asparagine	[Asp(D)]	α -amino aminosuccinamic acid	2,4-diamino-4-oxobutanoic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{H}_2\text{C}-\text{C}-\text{NH}_2 \\ \parallel \\ \text{O} \end{array}$
3.	Glutamic acid	[Gla(E)]	α -aminoglutaric acid	2-aminopentanedioic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{H}_2\text{C} \quad \parallel \\ \quad \text{O} \\ \text{H}_2\text{C}-\text{C}-\text{OH} \end{array}$
4.	Glutamine	[Glu(Q)]	α -aminoglutaramic acid	2,5-diamino-5-oxopentanoic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{H}_2\text{C} \quad \parallel \\ \quad \text{O} \\ \text{H}_2\text{C}-\text{C}-\text{NH}_2 \end{array}$

3: Basic Amino Acids

S.No	Amino acid	abbrev- iation	Systamatic name	IUPAC name	Structure
1.	Lysine	[Lys(K)]	α -, δ -diamino-n-caproic acid	2,6-diaminohexanoic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ (\text{CH}_2)_4 \\ \\ \text{NH}_2 \end{array}$
2.	Arginine	[Arg(R)]	α -amino- δ -guanidino-n-valeric acid	2-amino-5-guanidino pentanoic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ (\text{CH}_2)_3 \\ \\ \text{HN}-\text{C}=\text{NH} \\ \\ \text{NH}_2 \end{array}$
3.	Histidine	[His(H)]	α -Amino- β -imidazole propionic acid	2-amino-3-(1 <i>H</i> -imidazol-4-yl) propanoic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{Imidazole ring} \end{array}$

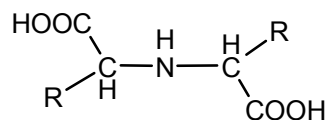
Synthetic Methods of preparation of Amino Acids

1) Amination of α -halogen substituted Acids (Perkins et al, 1958): Amination of α -halo (chloro or bromo) acids, obtained by direct halogenation of carboxylic acids, with aqueous or liquid ammonia gives the respective amino acid.



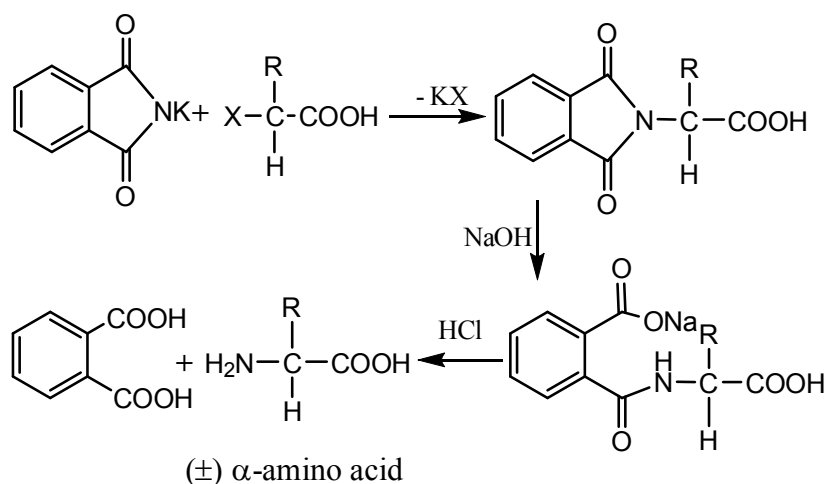
This amination may, however, be applied for the synthesis of alanine, glycine, serine, threonine, valine, leucine and norleucine. All amino acids obtained in this method, are in the form of ($\pm$) racemic mixture.

Since the method requires an excess of ammonia and also forms side products like-



In order to prevent the formation of primary and secondary amines ammonia may be replaced by hexamethylenetetramine.

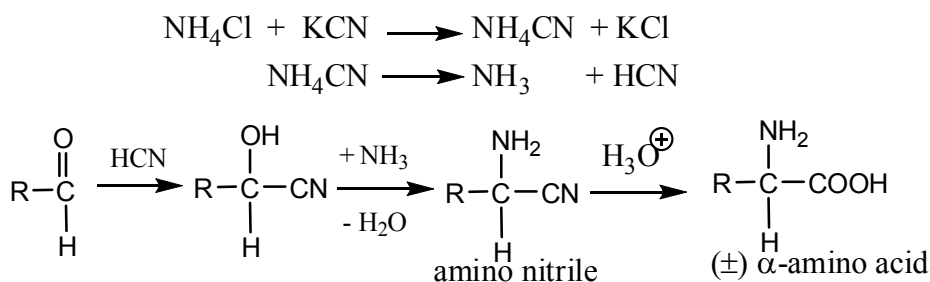
2) Gabriel's Phthalimide Synthesis (1889): This synthesis involves the treatment of α -halogenated ester with potassium salt of phthalimide and subsequent hydrolysis of the product.



Better yield is obtained in this method than the process of amination of α -halo acids. It may also be used for acidic amino acids e.g. synthesis of aspartic acid.

3) Strecker's synthesis (1850): In this synthesis, a cyanohydrin, obtained from aldehyde and hydrogen cyanide, is treated with concentrated ammonia and the resulting amino nitrile is then

hydrolysed with an acid. Aminonitrile may also be prepared in one step by taking a mixture of ammonium chloride and potassium cyanide and treating it with oxo compound.

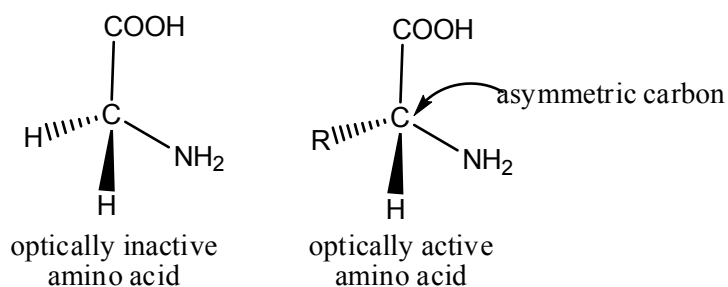


his method is useful for the preparation of glycine, alanine, serine, valine, methionine, leucine, isoleucine, norleucine, phenylalanine and glutamic acid.

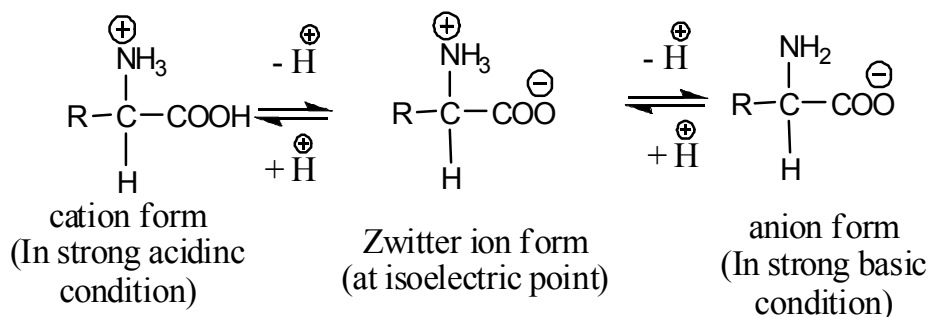
General properties of Amino acids

1) Physical properties:

- i) Amino acids are colourless, crystalline, stable, high melting solids having sweet taste. They Melt with decomposition at high temperature, but a few have tendency to sublime.
- ii) They are generally soluble in water but sparingly soluble in organic solvents such as petroleum ether, ethanol and benzene.
- iii) All α -amino acids contain at least one asymmetric carbon (except glycine) and are optically active.

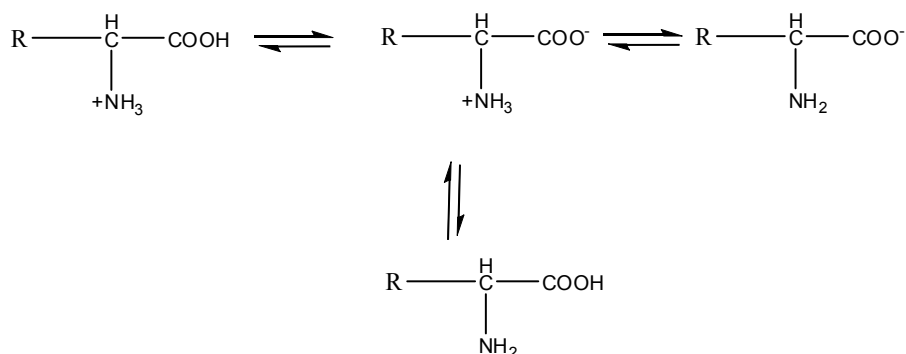


iv) Zwitter ion: When the dipole moment of glycine is measured in aqueous solution, this value is found to be very large. To account for this large value it has been suggested that glycine consists, in solution, as an inner salt, as it has both basic -NH_2 group and acidic -COOH group, it exists as double charged ion which is known as Zwitter ion or dipolar ion. Finally X-ray analysis has shown that all amino acids exist as dipolar ions.



In neutral solution an amino acid will be present in the following species, which are in equilibrium

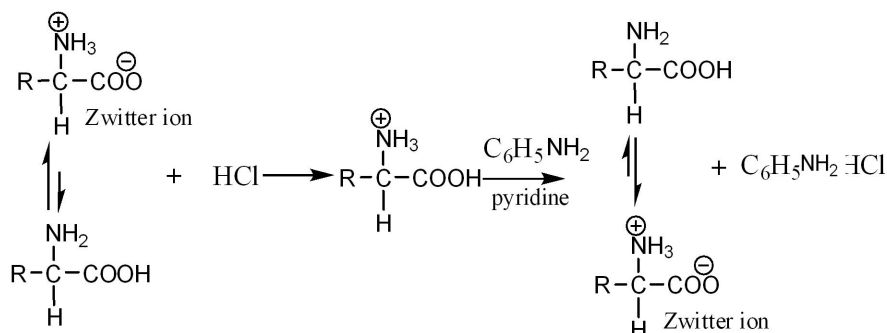
Isoelectric point: The position of above equilibrium depends on the pH of the solution, in acid solutions the conjugated acid predominates and in alkaline solution the conjugate base predominates. For each amino acid there is a particular pH value at which the concentration of the dipolar ion is maximum since the net charge is zero, the dipolar ion is electrically neutral and consequently, in this condition the amino acid does not migrate when placed in an electric field. The pH at which migration does not occur is called the isoelectric point of that amino acid.



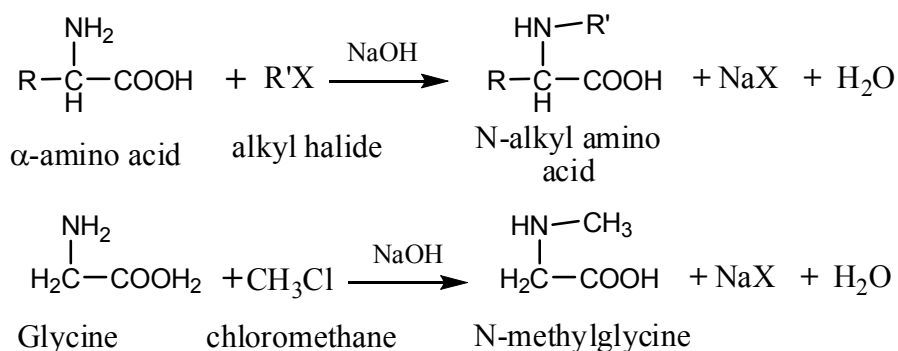
2) Chemical properties:

a) Reaction due to $-\text{NH}_2$ group:

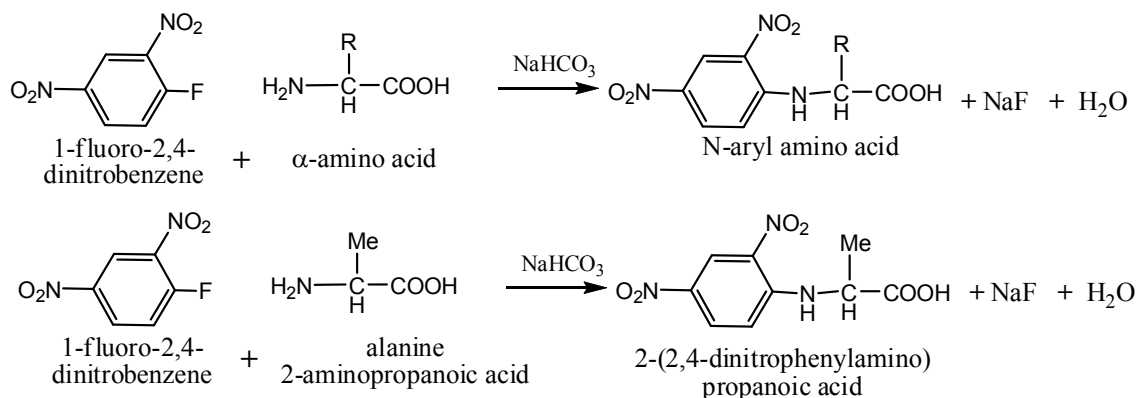
i) Salt formation with strong acids: Amino acids form salt with strong mineral acids. These salts are usually less soluble in water. However, solution becomes strongly acidic. Free amino acids may be liberated from these salts by means of strong bases like pyridine .



ii) Alkylation: In basic solution amino group can displace the halogen of alkyl halides.

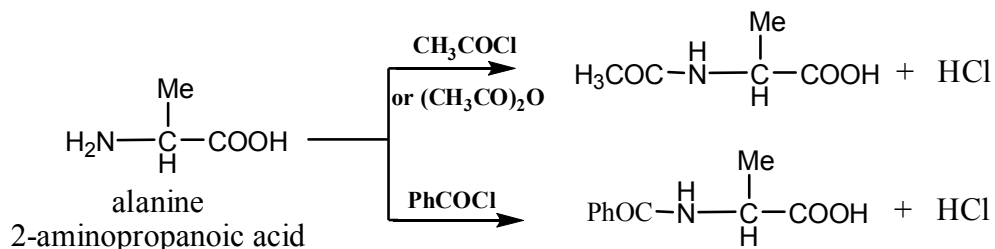


iii) Arylation: In solution the amino group can also displace halogen of acyl halide. For example amino acids form DNP derivative with 2,4-Dinitrofluorobenzene. This reaction is useful for the determination of N-terminal amino acid.

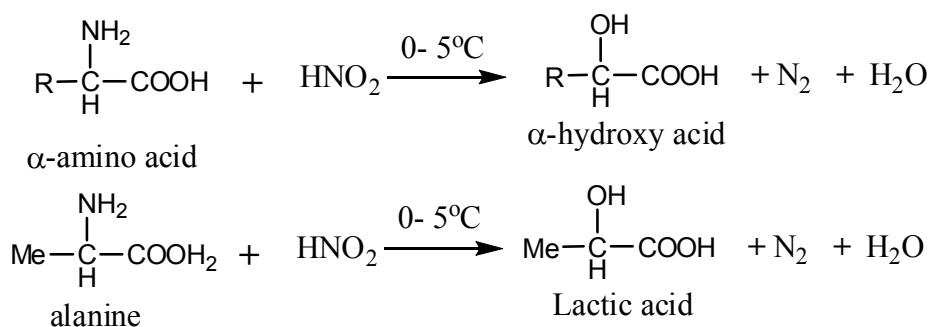


iv) Acylation and Benzoylation: Amino acids may be acylated with acid chloride or

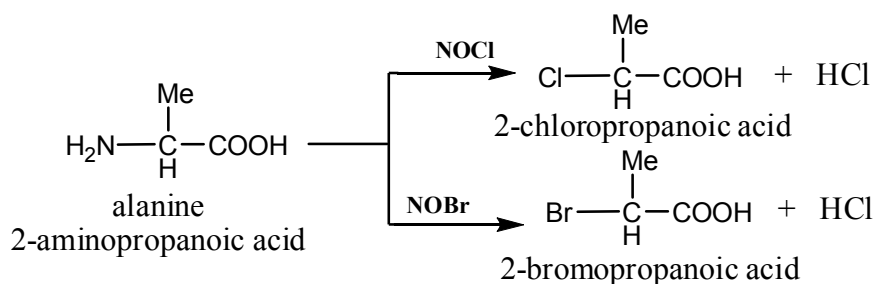
anhydride which blocks the amino group and acylated amino group behaves as typical organic acid. Similarly with benzoyl chloride amino acids yield benzoyl derivatives.



v) Reaction with Nitrous Acid: By the action of nitrous acid amino acid is converted to hydroxyl acid with the liberation of nitrogen. Measurement of the nitrogen evolved is the basis of Van slyke method of estimation of amino acids.

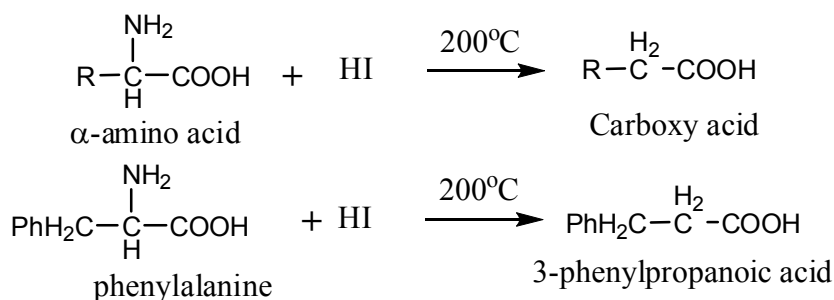


vi) Reaction with Nitrosyl Chloride or Bromide: Amino acids with this reagent give chloro or bromo acids.

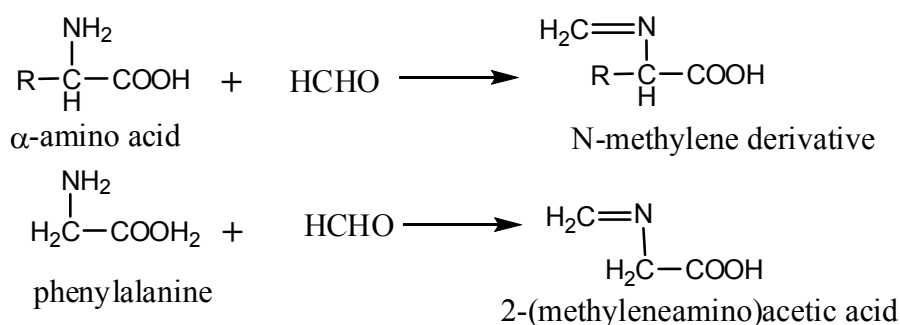


viii) Reaction with hydroiodic acid: When heated with hydroiodic acid at about 200° C the

amino group is eliminated to produce the corresponding fatty acid.



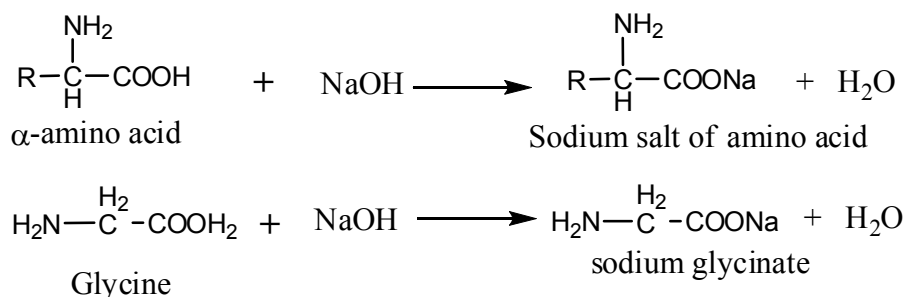
viii) Condensation with Formaldehyde: They form N-methylene derivative with formaldehyde.



Since N- methylene derivative thus formed containing a free COOH group can be titrated against standard alkali. This reaction is used for the estimation of amino acids and known as Sorenson formal titration method.

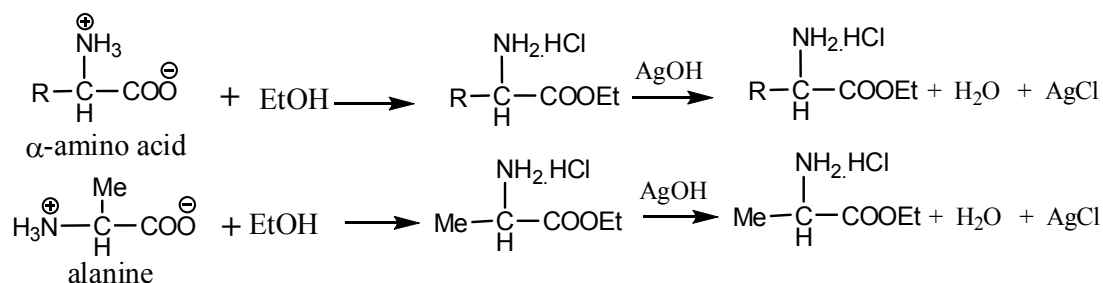
B) Reaction due to –COOH group:

i) Formation of salt with bases: Amino acids forms salts with strong bases.

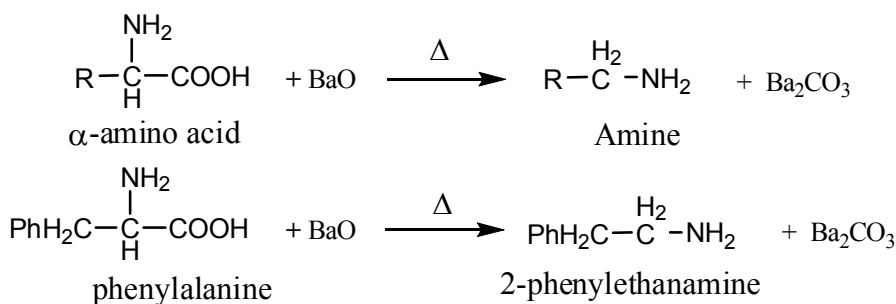


ii) Ester formation: When heated with an alcohol in the presence of dry hydrogen

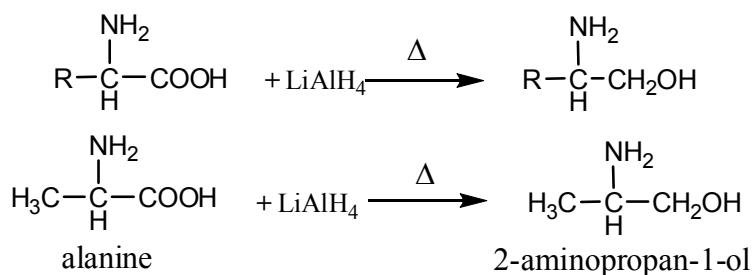
chloride they form their ester hydrochloride. Free ester is obtained by the action of silver hydroxide or aqueous sodium carbonate solution on them.



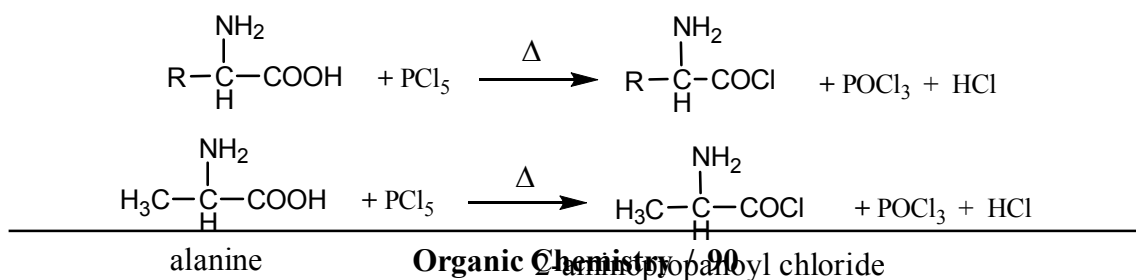
iii) Decarboxylation: Amino acids may be decarboxylated by dry distillation with acids, bases, barium oxide or specific enzymes to give corresponding amine.



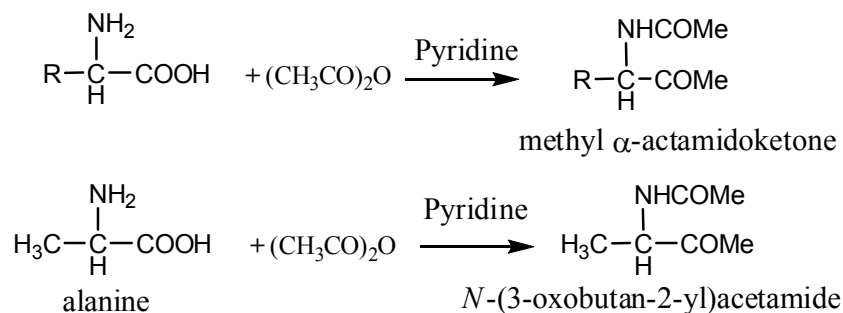
iv) Reduction: Amino acids on reduction with LiAlH_4 give corresponding amino alcohols.



v) Formation of Acid Chloride: In this reaction amino group of amino acid is treated with phosphorous penta chloride to give corresponding acid chloride.



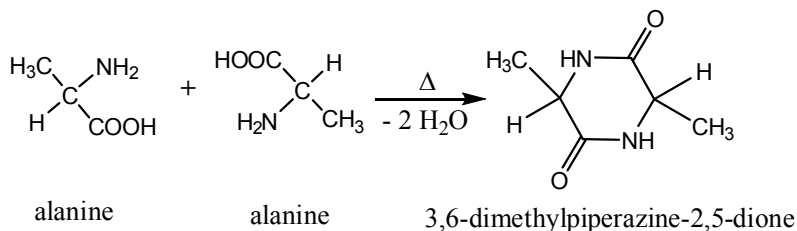
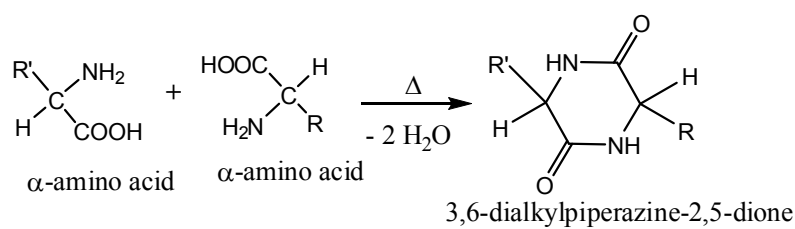
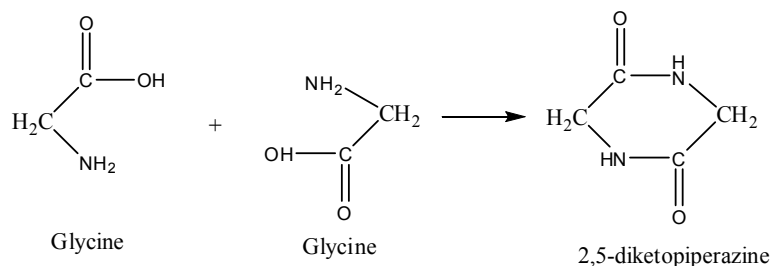
vi) Dakin-West reaction: When acids are treated with acid anhydride in pyridine solution, they are converted to methyl α -acetamidoketone. The reaction is referred to as the Dakin-West reaction.



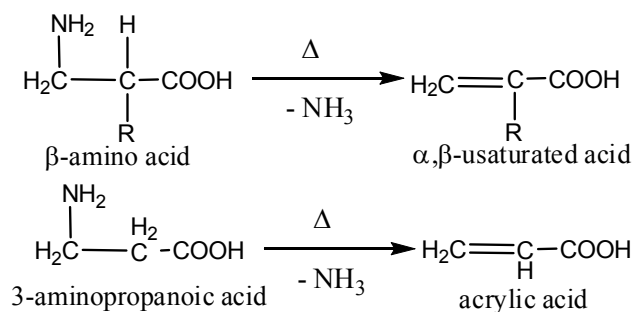
3) Reactions due to both Amino and Carboxyl groups:

i) Action of heat: On heating amino acids behaves as hydroxyl acids.

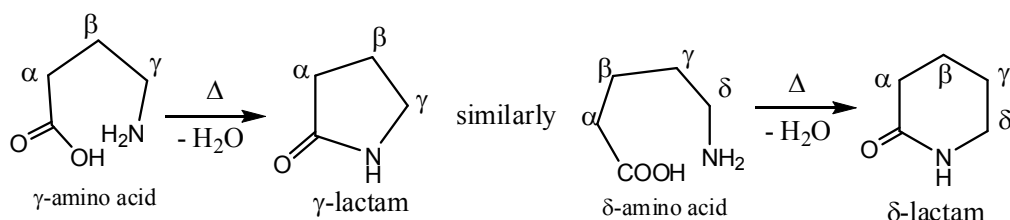
a) α -Amino acids lose two molecules of water between two molecules of amino acids and give cyclic amides known as Diketopiperazine.



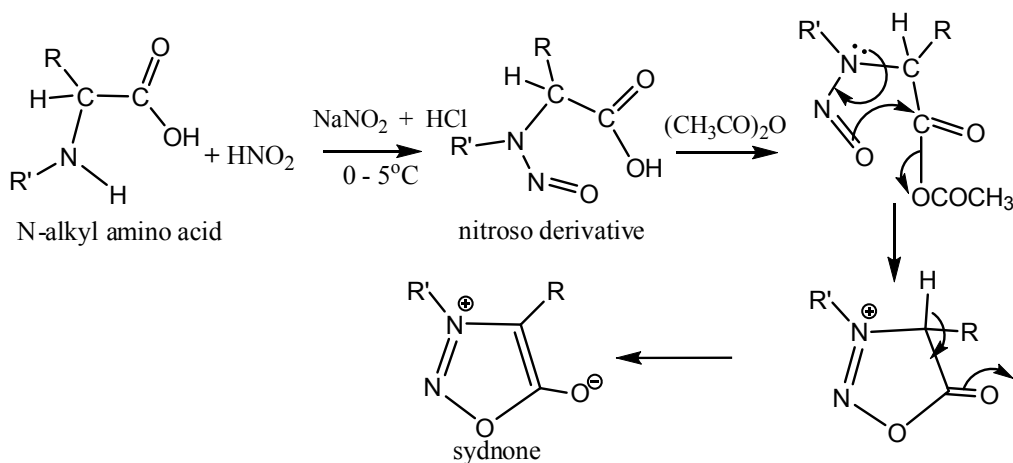
b) β -Amino acids eliminate a molecule of ammonia and yield α,β -unsaturated acids.



c) γ and δ - amino acids by losing one molecule of water within a molecule form cyclic amides called lactams.

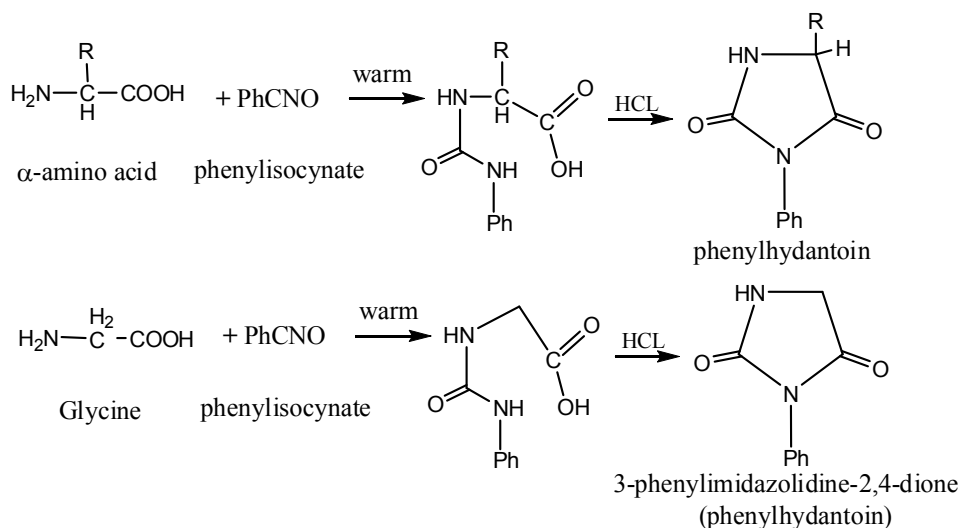


ii) **Action of Nitrous acid:** N-alkyl or N-aryl amino acids form N-nitroso derivatives with nitrous acid and these derivatives dehydrate in presence of acetic anhydride to give “sydnones”

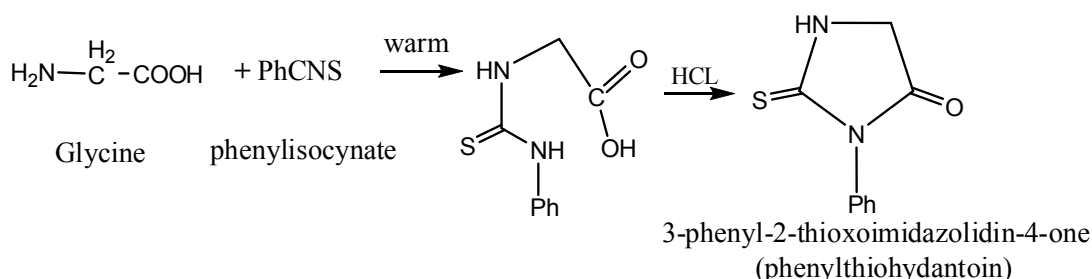


3) Reaction with phenyl isocyanate and phenyl thiocyanate: Amino acids with phenyl isocyanate form phenyl hydantoic acids which on treatment with hydrochloric acid easily form

hydantoins.



Phenylisocyanate yields thiohydantoin



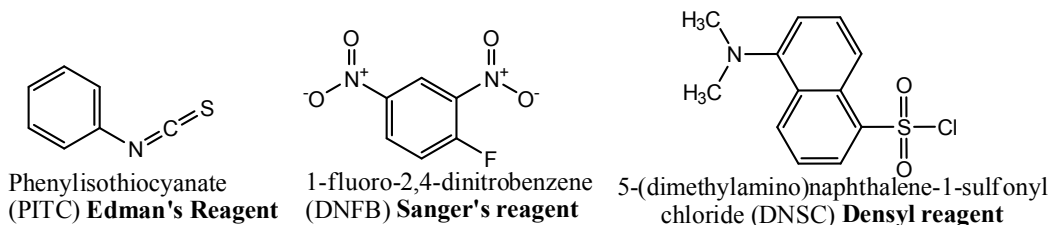
Reagents used for identification of amino acids

Phenylisothiocyanate (PITC) also known as Edman's Reagent. PITC enables the sequential degradation of amino acids in a polypeptide chain, yielding primary structural information. PITC reacts readily with amino acids at alkaline pH. Precolumn derivatization results in phenylthiocarbamyl derivatives (PTC-amino acids) that can be separated and quantified using reverse-phase HPLC. This method produces stable products with all amino acids, including proline.

Sanger's reagent or **1-fluoro-2,4-dinitrobenzene** (commonly called **dinitrofluorobenzene** or **DNFB**), is a chemical used for polypeptide sequencing. Dinitrofluorobenzene reacts with the amine group in amino acids to produce dinitrophenyl-amino acids. These DNP-amino acids are moderately stable under acid hydrolysis conditions that break peptide bonds. The DNP-amino acids can then be recovered, and the identity of those amino acids can be discovered through chromatography.

Dansyl chloride or **5-(dimethylamino) naphthalene-1-sulfonyl chloride** is a reagent that reacts with primary amino groups in both aliphatic and aromatic amines to produce stable blue- or blue-green-fluorescent sulfonamide adducts. Dansyl chloride is widely used to modify amino acids, specifically, protein sequencing and amino acid analysis. Dansyl chloride may also

be denoted DNSC. Dansyl chloride is unstable in dimethyl sulfoxide, which should never be used to prepare solutions of the reagent.



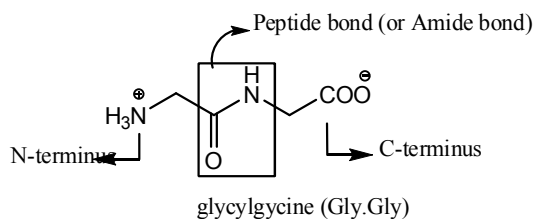
PEPTIDES

The Peptide Linkage

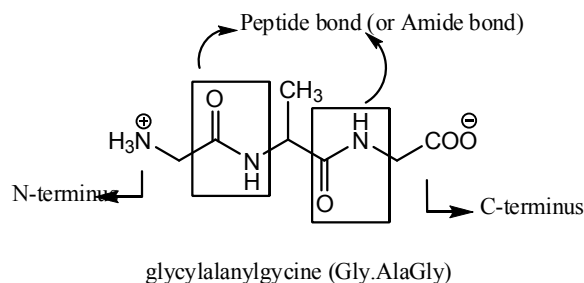
Peptides bond is formed by the condensation of amino group of an amino acid with the carboxylic group of the other amino acid. They are in fact secondary amides having -CO-NH- linkage commonly referred to as peptide linkage. Depending upon the number of amino acid residues per molecule they are referred to as dipeptides, tripeptides, tetrapeptides and polypeptides. The term polypeptide is reserved only for those compounds which have molecular weight of 10,000 or less while that molecule which has molecular weight higher than 10,000 are proteins.

The main structural features of the peptides are that they have a free amino group on one end which is called the N-terminus and a free carboxylic group on the other which is called the C-terminus. They are named from N-terminus to C-terminus through the sequential listing of the names of amino acids. This is done by replacing the ending -ine by -yl in the names of all amino acids excepting the C-terminus. Quite often the names of the peptides are abbreviated by using three letter abbreviations for amino acids. This is well explained from following examples.

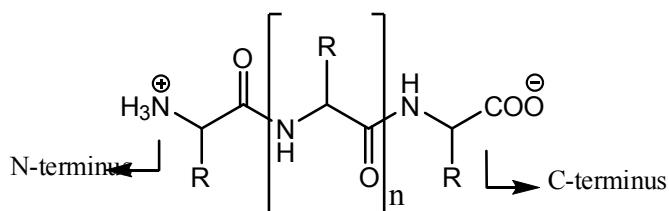
A Dipeptide



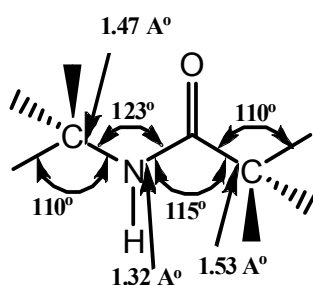
A Tripeptide



A polypeptide



Studies on the structure determination of peptides have revealed that the amide group is flat and the carbonyl and amino groups lie in one plane having H (of NH) and O (of CO) *trans* with respect to each other. Further the pioneering work by Linus Pauling on the X-ray studies of peptides has revealed that the C-N bond length of -CO-NH- is 1.32 Å which is shorter than the usual 1.47 Å showing slight double bond character.



The double bond character of the C—N bond may be rationalized on the basis of resonance and because of this there is restricted rotation about amide bond, thus giving rise to *cis*, *trans* isomerism in which the *trans* isomer predominates.

Peptide Synthesis: Peptides are polyamides and are synthesized by the stepwise condensation in which the amino group of one amino acid is condensed with the carboxylic

group of a second amino acid until, after successive operations; the desired polypeptide chain is obtained. It is complicated by the fact that self condensation of the two molecules of the same amino acid is possible because of the presence of both the functionalities in each amino acid. Nevertheless, this difficulty can be overcome by converting the amino group of one amino acid into substituted amino group thus preventing it from condensation with the carboxylic group of the other. This amino group is now said to be protected or blocked from chemical reaction with carboxylic group and condensation of carboxylic group of the 'protected' amino acid with the amino group of a different amino acid can selectively take place. Alternatively, the carboxylic group of one amino acid may be suitably protected so that the selective condensation of the amino group of this acid with the carboxylic group of the other acid can occur.

As 'protection' of amino or carboxylic group is necessary the peptide synthesis consists of three steps.

- (i) Protection of amino or carboxylic group;
- (ii) Condensation; and
- (iii) Removal of the protecting group.

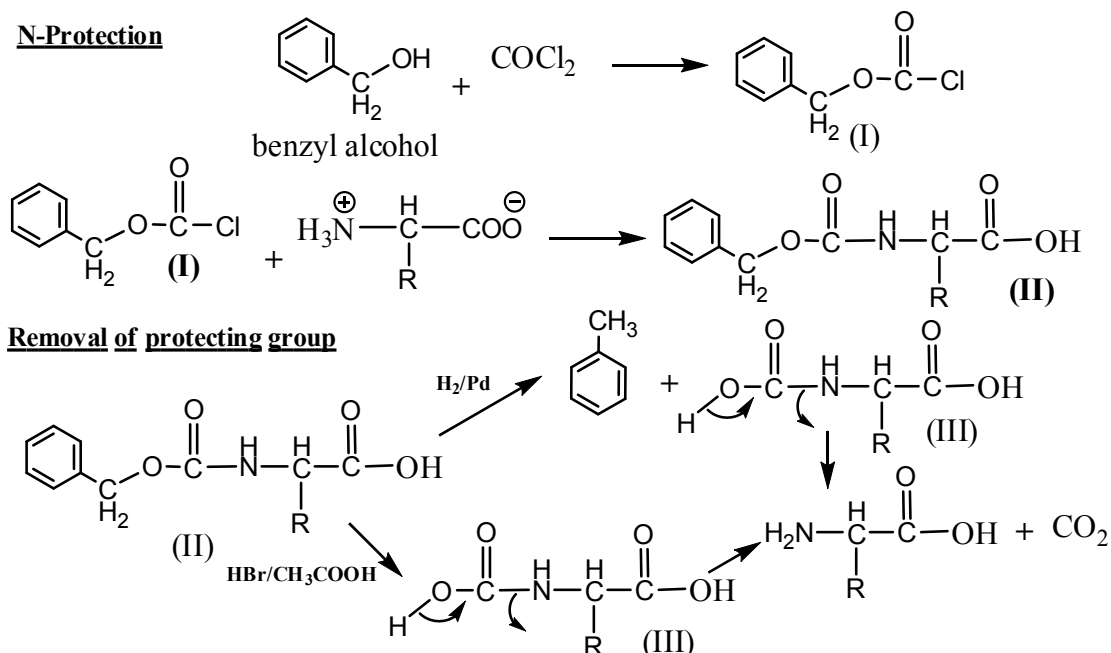
The Protecting Agents

Many protecting agents are used but a good protecting agent is characterized by the fact that it can react with the amino or carboxylic group easily and can be removed, at the end of the synthesis, without affecting the peptide bond. Some of the important protecting agents for both amino (N-terminus) and carboxylic (O-terminus) groups are -

(i) N-Terminus protecting agents: Acylation of the amino group is one of the most common methods for protecting this group. Almost all such reagents have been tried. But here we shall discuss only those which are commonly used in the peptide synthesis along with the methods of removing them:

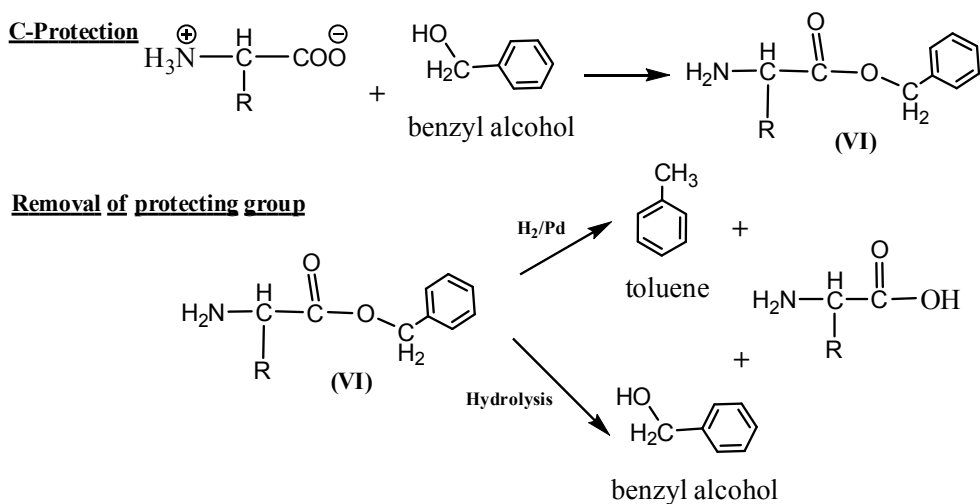
(a) Carbobenzoxy chloride (I): It is an ester as well as an acid chloride of carbonic acid and is obtained by treating benzyl alcohol with carbonyl chloride (phosgene). When treated with an amino compound, it forms the corresponding substituted amide (II) which, either on catalytic reduction or treatment with HBr in acetic acid, regenerates the amine via carbamic acid (III).

N-Protection



(ii) C-Terminus protecting agents: Esterification of the carboxylic group with benzyl alcohol is the most common method of protecting this group. The ester (LXIII) so obtained is readily converted into the free carboxylic acid either by catalytic reduction or hydrolysis with dilute alkali.

C-Protection



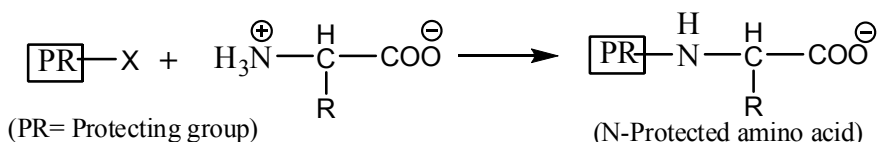
It is important to note that for the formation of a peptide bond, activation of the free carboxylic (or amino) group of the protected amino acid (or peptide) is necessary. This can be accomplished by converting the protected species into the corresponding acid chloride.

This may be a separate step prior to the condensation step.

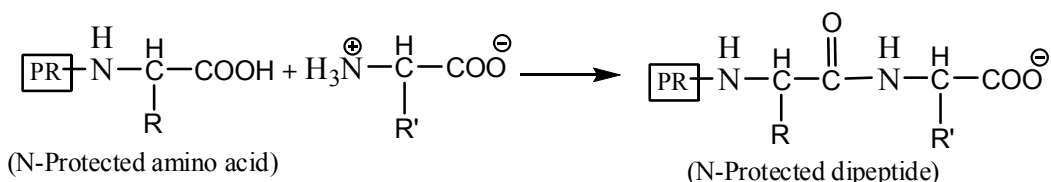
The following general sequences illustrate these steps.

(a) Peptide Synthesis by Protecting Amino Group

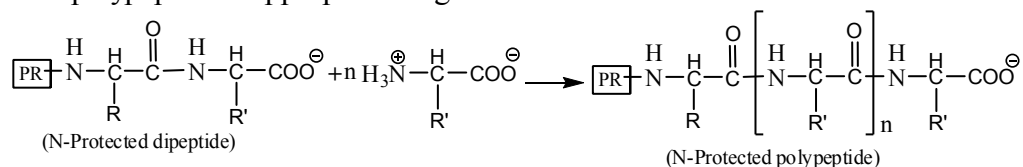
(i) Protection of the amino group of amino acid: This is done by treating the amino acid, which will form the N-terminus of the peptide with a suitable reagent, called protecting agent, that condenses with the amino group of this acid.



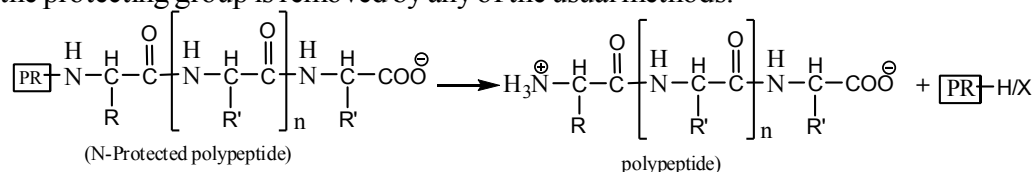
(ii) Condensation of the carboxylic group of the N-protected amino acid with the amino group of the second amino acid: This is done by using the usual methods of conversion of carboxylic acids into amides. This gives rise to a protected dipeptide



This step is repeated several times using the desired amino acids one by one till the protected polypeptide of appropriate length is formed.

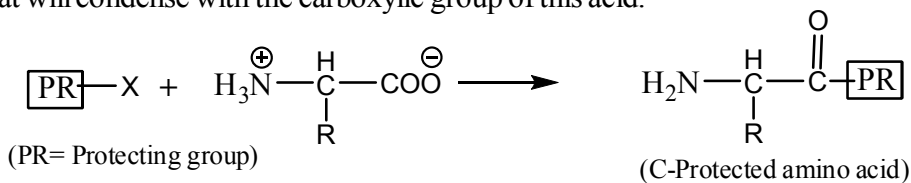


(iii) Removal of the protecting group: After the polypeptide chain of the desired length is built up, the protecting group is removed by any of the usual methods.

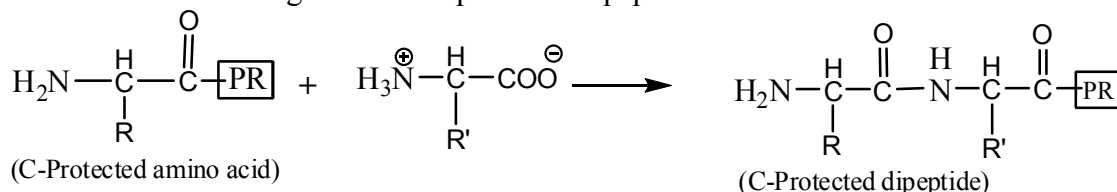


(b) Peptide Synthesis by Protecting Carboxylic Group

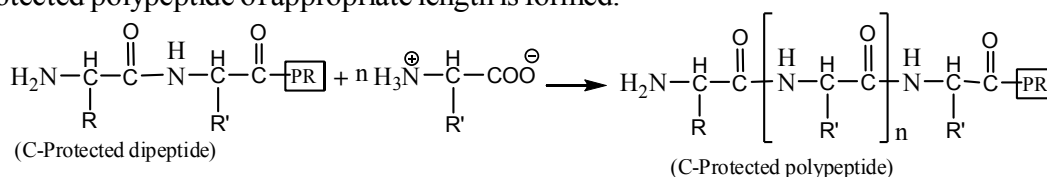
(i) Protection of the carboxylic group of one amino acid: This is done by treating the amino acid, which will form the C-terminus of the peptide, with a suitable reagent (the protecting agent) that will condense with the carboxylic group of this acid.



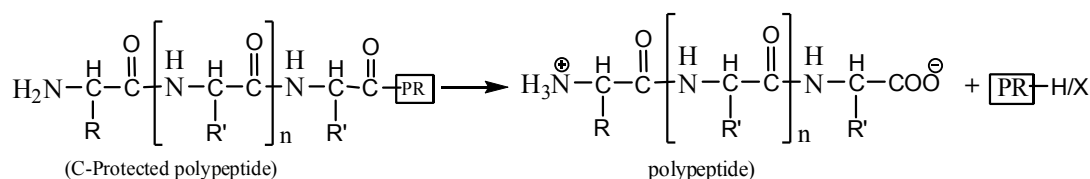
(ii) Condensation of the amino group of the C-protected amino acid with the carboxylic group of the second amino acid: This is done by using the usual methods of conversion of carboxylic acids into amides. This gives rise to a protected dipeptide



This step is repeated several times using the desired amino acids one by one when the protected polypeptide of appropriate length is formed.



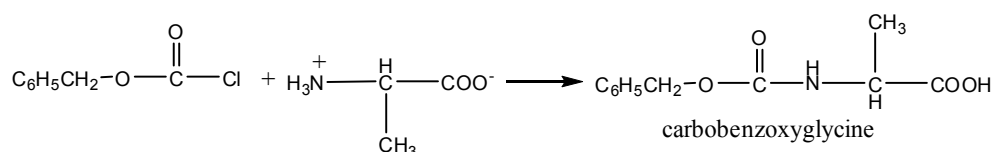
(iii) Removal of the protecting group: The protecting group is removed using any of the usual methods taking care to choose such reagents that do not disturb the peptide chain.



Use of DCC (Dicyclohexyl Carbodiimide) as reagent for peptide bond

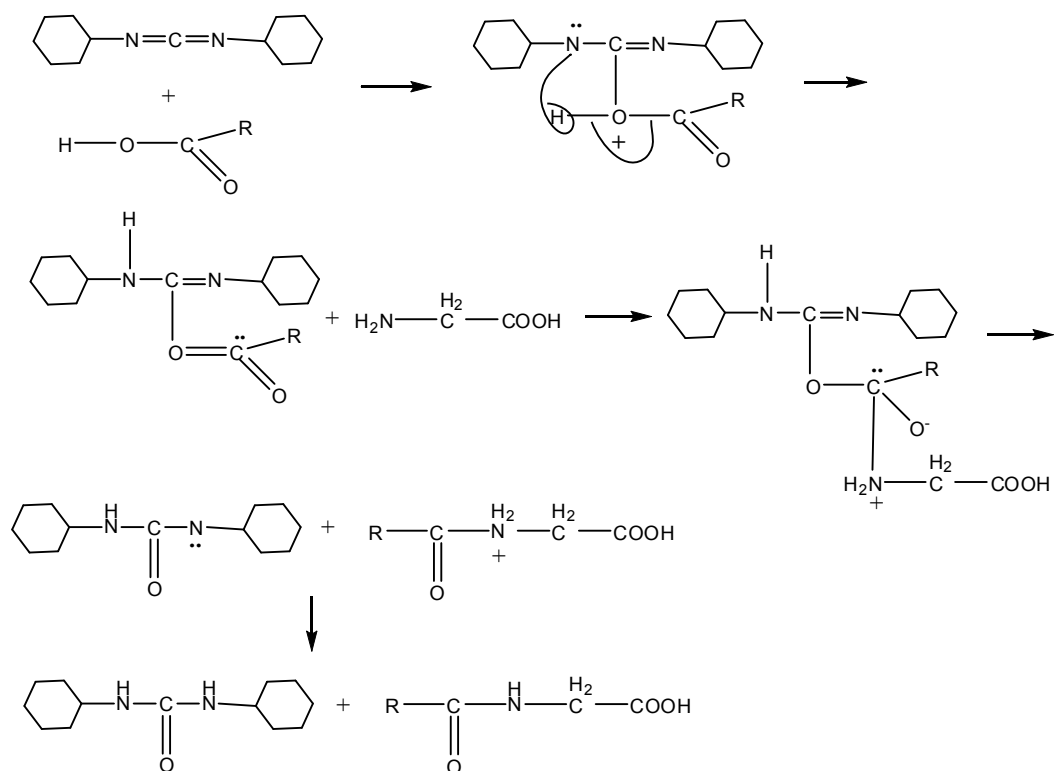
The use of carbodiimides such as dicyclohexylcarbodiimide (DCC) for the activation of a carboxylic acid together with the addition of an amine is a frequently used procedure for the peptide bond formation. DCC is probably the most utilized carbodiimide reagent that is relatively cheap and soluble in the solvents used in peptides synthesis. The following steps in the synthesis of alanylglycine along with mechanism, of DCC catalyzed condensation illustrates this process.

A]

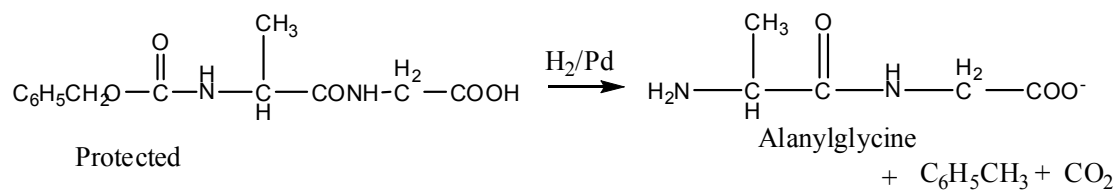


Protection of amino group of alanine.

B] Condensation of carbobenzoxyalanine with glycine in the presence of DCC:



C] Removal of protecting group:



PROTEINS

INTRODUCTION: Proteins are vital (necessary) for life. These are essential constituents of all living cells. It is found that two-third of the total dry weight of the cell is composed of proteins. They perform diverse biological functions in the living systems. They are highly important in human and animal nutrition. Proteins like Keratin (in hair) serves as structural materials, proteinic hormones like insulin (in pancreas) regulate metabolic process and proteins like haemoglobin (in

blood) transport oxygen within the body. Enzymes perform catalytic activity in biological reactions. Antibodies like gamma globins destroy antigens. (the foreign material released into the body by infectious agents and nucleoproteins transmit genetic messages in cells) The Dutch chemist, G.J. Mulder was the first scientist to recognize their importance and used the term protein (Greek, proteios meaning first) to describe these vital compounds.

The animals and human beings are dependent on plants for proteins which they get in the form of food. However, plants synthesize their own proteins in the presence of sunlight from carbon dioxide, water and mineral salts (like nitrates and ammonium salts) obtained from soil (absorbed by roots in solution form). The protein composition of some common food materials (obtained from animal and plant source) consumed by human beings is given in table below.

S. No.	Foodstuff (<i>Animal source</i>)	Protein in Percentage	S.No.	Foodstuff (<i>Plant source</i>)	Protein in Percentage
1.	Milk	5	7.	Peas	21
2.	Cheese	33	8.	Ground nut	26.7
3.	Meat	24-26	9.	Casheu nut	21.2
4.	Egg white	12-13	10.	Almonds	20.8
5.	Egg yolk	16	11.	Soyabean	43.2
6.	Wheat	14	12.	Maize	14

The term protein was introduced by Mulder (1839). Derived from the greek word proteious meaning first. Proteins are nitrogeaneous substances occuring in the protoplasm of all animal and plant cells. Their composition varies with the source; carbon, 45-46%;hydrogen, 6-9% ; oxygen, 12-30 %; nitrogen, 10-32%; sulphur, 0.2-0.3%. Other elements may also be present, e.g. Phosphorous (nucleoproteins), Iron (heamoglobin).

There is no sharp dividing line between peptide, poly peptides and proteins. In general they differ in physical and chemical properties which can be correlated with the difference in molecular size. Both groups often exhibit physiological activity, behaving as e.g., enzymes, hormones growth factor etc.

CLASSIFICATION OF PROTEINS

Several arbitrary classifications of the proteins are in use.

I: According to solubility:

a) Fibrous proteins: These are insoluble in common solvents but are soluble in concentrated acids and alkalies. These are highly resistant to digestion by proteolytic enzymes. These are proteins appearing as fibers made of linear molecules that are arranged roughly parallel to the fiber axis. The long linear molecules of proteins are held together by inter molecular hydrogen bonds. Examples: silk, wool, skin, hair, horn, nails, quills, connective tissue and bone.

b) Globular proteins: These are soluble in water and in dilute acids, alkali and salts. These proteins are more highly branched and cross linked condensation products of basic or

acidic amino acids. The polypeptide chains in this type of proteins are held together by cross linked groups. Example: enzymes, oxygen carrying proteins, protein hormones etc.

II: On the basis of increasing complexity into their structures: This is a more common method of classification according to which proteins may be divided into three main groups.

1) Simple proteins: These give amino acids or their derivatives on hydrolysis. These are including the following groups:

a) Albumins: Soluble in water, acids and alkalies, coagulated by heat and precipitated by saturated salt solution like ammonium sulphate and low in glycine. Some albumins are serum albumin, egg albumin and lactalbumin.

b) Globulins: These are insoluble in water, but are soluble in dilute salt solution and in dilute solutions of strong inorganic acids and alkalies and precipitated by ammonia solution, coagulated by heat. Some globulins are serum globulin, tissue globulins and vegetable globulin.

c) Prolamins: Insoluble in water, soluble in dilute acids and alkalies and contain large amount of proline. Example: zein from maize, gliadin from wheat, hordein from barley.

d) Glutelins: insoluble in water, soluble in dilute acid and alkalies coagulated by heat, rich in arginine, proline and glutamic acid. Example: glutenin from wheat, oryzenin from rice.

e) Scleroproteins(albuminoids): Insoluble in water, soluble in concentrated acids and alkalies. Not attacked by enzyme. Example: Keratin from hair, hoof, fibroin from silk.

Sub members of albuminoids are:

i) Collagens: Present in skin, tendons and bones, they form gelatins which is water soluble.

ii) Elastins: Present in tendons and arteries, not converted to gelatin.

f) Basic protein: They are strongly basic and fall into two groups:

i) Histones: These are soluble in water or dilute acid, not coagulated by heat, contain large amount of histidine and arginine, low in cystine or methionine. These are proteins of nucleic acid and haemoglobin etc.

ii) Protamins: Less basic than histones, soluble in water, dilute acids and dilute ammonia, not coagulated by heat, precipitated from ethanol. They contain large amount of arginine and occur in various nucleic acids.

2) Conjugated protein: They contain non-protein group attached to protein part, called prosthetic group. These groups may be separated from protein part by careful hydrolysis. **Some sub members are:**

i) Nucleoprotein: The prosthetic group is nucleic acid.

ii) Chromoproteins: The prosthetic group is chromophoric group called prosthetic group. E.g. chlorophyll and haemoglobin.

iii) Glycoproteins: They contain carbohydrate prosthetic group. They are also known as mucoproteins, e.g. egg albumin, serum albumin and certain serum globulin.

iv) Phosphoproteins: In these, prosthetic group possesses phosphoric acid in some form other than in nucleic acids.

v) Lipoproteins: Prosthetic groups are phospholipids and cholesterol.

3) Derived proteins: These are the degraded products obtained by the action of acids, alkalis or enzymes on proteins.

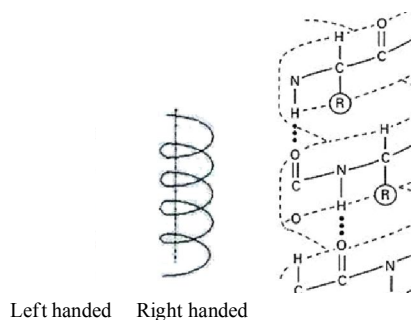
Primary structure of proteins: It is concerned with the sequence of amino acids in peptide chain. In every polypeptide, there is a specific sequence of amino acids. Biological activity of polypeptides depends on the sequence of amino acid. If only one amino acid in the sequence is changed, then total biological activity of amino acid may be changed. Bio synthesis of proteins is regulated by nucleic acids (DNA, RNA). In hemoglobin there is a specific sequence of 574 amino acids. If only one amino acid is replaced it becomes defective hemoglobin which produces sickle cell anemia disease.

$$\begin{array}{c} \text{H}_2\text{N}-\text{A}-\text{CONH}-\text{B}-\text{CONH}-\text{C}-\text{CONH}-\text{D}-\text{COOH} \\ \text{N-terminal} \left[\begin{array}{c} \text{H}_2\text{N}-\text{CH}(\text{R}_1)-\text{C}(=\text{O})-\text{NH}-\text{CH}(\text{R}_2)-\text{C}(=\text{O})-\text{NH}-\text{CH}(\text{R})-\text{C}(=\text{O})-\text{NH}-\text{CH}(\text{R}_4)-\text{C}(=\text{O})-\text{NH}-\text{CH}(\text{R}_5)-\text{C}(=\text{O})-\text{OH} \\ \text{R}_1 \qquad \qquad \qquad \text{R}_2 \qquad \qquad \qquad \text{R} \qquad \qquad \qquad \text{R}_4 \qquad \qquad \qquad \text{R}_5 \end{array} \right] \text{C-terminal} \end{array}$$

Secondary structure of Protein: Concerned with three dimensional arrangement of the polypeptide chain i.e. conformation of poly peptide chains which arise as a result of Hydrogen bonding.

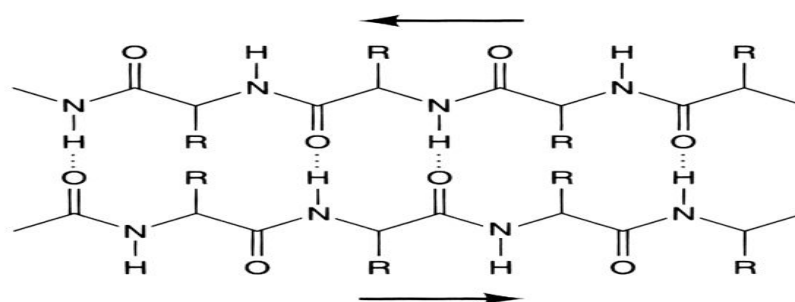
- i. Planarity of peptide bond.
- ii. The dihedral angles Ψ and Φ taken about $C^\alpha-C^1$ and $N-C^\alpha$ bonds, respectively, are close to those corresponding to potential minima in the system.
- iii. Conformation of the protein is stabilized by hydrogen bonding which is formed between $>C=O$ and $N-H$ group and the strength of this bond is a maximum of the atom concerned ($C=O-H-N$) are linear.
- iv. Maximum number of hydrogen bond.

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α -Helix structure of Protein

β -Pleated sheet structure: In this arrangement polypeptide chains are extended in a linear or zig-zag manner. Neighboring chains are bonded together by reciprocal inter chain hydrogen bonding. The result is a structure resembling pleated sheet.



β -Pleated sheet structure of Protein

PROPERTIES OF PROTEIN

Proteins are amphoteric; they behave as an anion or a cation depending on the pH of the solution. If some definite pH, characteristic for each protein, the positive and negative charge is exactly balanced, i.e. no net charge on the protein molecule, and the molecules will not migrate in an electric field. In this condition the protein is said to be at its isoelectric point and at this pH the protein has its least solubility i.e. it is most readily precipitated. The amphoteric nature of the proteins is due to the presence of a large number of free acidic and basic groups arising from the amino acid units in the molecule. The osmotic pressure and viscosity of the protein solution are also a minimum at the isoelectric point.

All proteins are optically active, may be coagulated and precipitated from aqueous solution by heat, addition of acids, alkali salts, organic solvents etc. Protein in this precipitated state are said to be denatured, and the process of reaching this state is known as Denaturation. Denaturation

occurs most readily near the isoelectric point. Denaturation is the result of changes in conformation or unfolding of the protein molecule. After denaturation loss of optical rotation and biological activity occurs e.g. enzymes becomes inactive when denatured.

Denaturation is generally irreversible, but in many cases the process has been reversed. This reversal of denaturation has been called renaturation or refolding. When denaturation is effected by heat, renaturation does not usually result on rapid cooling. If, however, cooling is carried out very slowly, renaturation often occurs. In these circumstances the process of renaturation has been referred to as annealing.

Colour reaction

Proteins exhibit a variety of colour reactions:

i) Biuret reaction: Alkaline solution of protein and dilute copper sulphate solution gives red or violet colour. (Due to coordination of Cu^{2+} with $-\text{CONH}-$ group at least two peptide linkages must be present (polypeptides do not give the test))

ii) Xanthoproteic reaction: Protein solution and concentrate nitric acid on warming gives a yellow precipitate which changes colour to orange at alkaline conditions due to nitration of aromatic groups present.

iii) Ninhydrin test: Protein on boiling with dilute ninhydrin solution gives violet colouration.

iv) Millon's test: Millon's reagent [mercuric nitrate in concentrated nitric acid having traces of nitrous acid] on adding to protein solution gives a white precipitate which on further heating produces a red precipitate due to the presence of phenolic group.

Importance of Proteins:

Importance of protein is pivotal in the growth and maintenance of your body's structures, including muscle and bones. Protein is a part of every cell in your body, and no other nutrient plays as many different roles in keeping you alive and healthy. The importance of protein for the growth and repair of your muscles, bones, skin, tendons, ligaments, hair, eyes and other tissues is proven since a very long time. Without it, one would lack the enzymes and hormones needed for metabolism, digestion and other important processes.

When anyone has an infection, then he/she should eat more protein because it helps create the antibodies your immune system needs to fight disease. Anyone injured, may need more, as well, to help his/her blood clot and make repairs. It helps regulate body processes (think hormones and antibodies) and provides a source of energy, four calories per gram to be exact. For athletes, adding a small amount of protein to a carbohydrate-rich post-workout meal can assist with muscle recovery.

Question Bank

- Q1. What are amino acids? How they are classified?
- Q2. Explain Acid base behavior of amino acids.
- Q3. Write note on Zwitter ion formation.

- Q4. Write note on Isoelectric point.
- Q5. How will you prepare Glycine from
- α -chloroacetic acid
 - Gabriel Phthalimide synthesis
 - Strecker's Synthesis
- Q6. What is the action of following on glycine
- Methyl iodide
 - Acetyl chloride
 - Nitrous acid
 - Formaldehyde
 - Sodium hydroxide
 - Ethyl alcohol
- Q7. Explain the following reactions of Glycine
- Reduction
 - Action of heat
 - Decarboxylation
- Q8. What are Proteins? Explain the classification of Proteins on the basis of chemical composition.
- Q9. What are Proteins? Explain the classification of Proteins on the basis of Molecular shape.
- Q10. Explain the Primary structure of Proteins.
- Q11. Give the general properties of proteins.
- Q12. Give the following tests of proteins
- Ninhydrin test.
 - Biuret test.
 - Millons test.
 - Xanthoprotic test.
- Q13. What are Peptides? Give the structure of dipeptide, tri-peptide, and Polypeptide.
- Q14. How will you prepare peptides by protecting $-\text{NH}_2$ group?
- Q15. How will you prepare peptides by protecting $-\text{COOH}$ group?
- Q16. Explain the following terms
- C-terminus protecting agent
 - N-terminus protecting agent
 - Use of DCC as reagent for peptide bond.

Synthetic polymers and Molecular Rearrangements

1. Synthetic polymers

INTRODUCTION

Natural polymers (from the Greek *poly* meaning “many” and *meros* meaning “parts”) are found in many forms in plants and animals. One of the most useful of the natural polymers was rubber, obtained from the sap of the *hevea* tree. (Rubber was named by the chemist Joseph Priestley who found that a piece of solidified latex gum was good for rubbing out pencil marks on paper. In Great Britain, erasers are still called “rubbers”.) The first synthetic polymer, a phenol-formaldehyde polymer, was introduced under the name “Bakelite”, by Leo Baekeland in 1909. Its original use was to make billiard balls. Rayon, the first synthetic fiber was developed as a replacement for silk in 1911.

Although many polymers were made in the following years, the technology to mass produce them was not developed until World War II, when there was a need to develop synthetic rubber for tires and other wartime applications and nylon for parachutes. Since that time, the polymer industry has grown and diversified into one of the fastest growing industries in the world. Today, polymers are commonly used in thousands of products as plastics, elastomers, coatings, and adhesives.

SYNTHETIC FIBERS Synthetic fibers are usually polyesters or polyamides. The most important synthetic fibers are dacron, nylon, orlon, and polypropylene (primarily used for upholstery).

Acrylic fibers are vinyl polymers valued for resistance to chemical and biological degradation. Acrylonitrile (or vinyl cyanide) forms a **homopolymer** that is used in filters and artificial wool, which is widely used in sweaters.

Condensation fibers such as nylon and polyethylene terephthalate are formed from two or more different monomers are called as **copolymers**

Classification of Polymers

There are several ways of classification of polymers based on some special considerations. The following are some of the common classifications of polymers:

Classification Based on Source

Under this type of classification, there are three sub categories.

1. Natural polymers

these polymers are found in plants and animals. Examples are proteins, cellulose, starch, resins and rubber.

2. Semi-synthetic polymers

Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate, etc. are the usual examples of this sub category.

3. Synthetic polymers

A variety of synthetic polymers as plastic (polythene), synthetic fibres (nylon 6,6) and synthetic rubbers (Buna – S) are examples of man-made polymers extensively used in daily life as well as in industry.

There are three different types based on the structure of the polymers.

Classification Based on Structure

1. Linear polymers on Structure: These polymers consist of long and straight chains. The examples of Polymers are high density polythene, polyvinyl chloride, etc. These are represented as:



2. Branched chain polymers: These polymers contain linear chains having some branches, e.g., low density polythene. These are depicted as follows:



3. Cross linked or Network polymers: These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains, e.g. bakelite, melamine, etc. These polymers are depicted as follows:



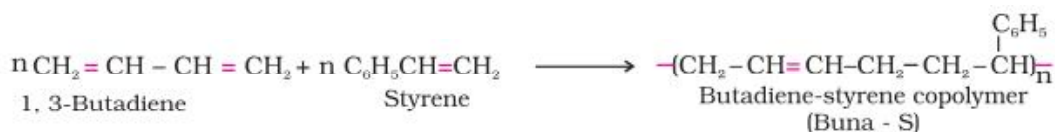
Classification Based on Mode of Polymerization

Polymers can also be classified on the basis of mode of polymerization into two sub groups.

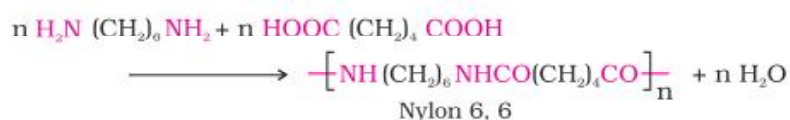
1. Addition polymers: The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds, e.g., the formation of polythene from ethene and polypropene from propene. However, the addition polymers formed by the polymerization of a single monomeric species are known as homopolymers, e.g. polythene.



The polymers made by addition polymerisation from two different monomers are termed as copolymers, e.g., Buna-S, Buna-N, etc.



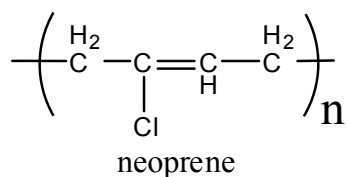
2. Condensation polymers: The condensation polymers are formed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units. In these polymerization reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. take place. The examples are terylene (dacron), nylon 6, 6, nylon 6, etc. For example, nylon 6, 6 is formed by the condensation of hexamethylene diamine with adipic acid.



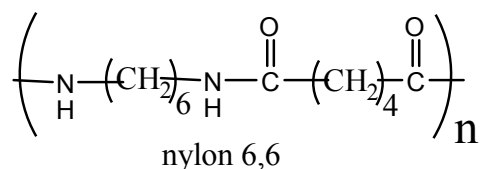
Classification Based on Molecular Forces

A large number of polymer applications in different fields depend on their unique mechanical properties like tensile strength, elasticity, toughness, etc. These mechanical properties are governed by intermolecular forces, e.g., van der Waals forces and hydrogen bonds, present in the polymer. These forces also bind the polymer chains. Under this category, the polymers are classified into the following four sub groups on the basis of magnitude of intermolecular forces present in them.

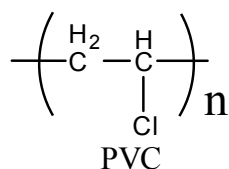
1. Elastomers: These are rubber – like solids with elastic properties. In these elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces permit the polymer to be stretched. A few ‘crosslinks’ are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber. The examples are buna-S, buna-N, neoprene, etc.



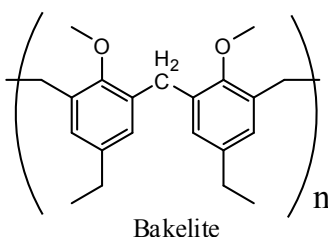
2. Fibers: Fibers are the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. The examples are polyamides (nylon 6, 6), polyesters (terylene), etc.



3. Thermoplastic polymers: These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.



4 Thermosetting polymers: These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldehyde resins, etc.

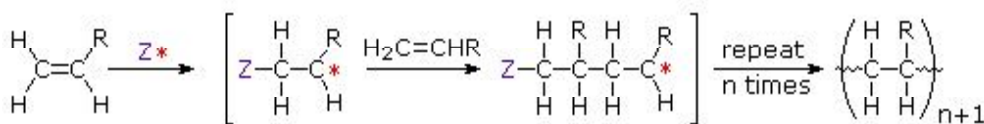


TYPES OF POLYMERIZATION REACTION: The process or reaction of making giant molecule (polymer) from a simple molecule (monomere) is described mainly into two types

1. **ADDITION POLYMERIZATION**
2. **CONDENSATION POLYMERIZATION**

ADDITION POLYMERIZATION

All the monomers from which addition polymers are made are alkenes or functionally substituted alkenes. The most common chemical transformations of alkenes are addition reactions. Many of these addition reactions proceed in a stepwise fashion by way of reactive intermediates, and this is the mechanism followed by most polymerizations. A general diagram illustrating this assembly of linear macromolecules, which supports the name **chain growth polymers**, is shown below. A pi-bond in the monomer is converted to a sigma-bond in the polymer.



Z* is an initiating species

* may be a radical, a cation or an anion

It is useful to distinguish four polymerization procedures fitting this general description.

1. **Radical Polymerization** The initiator is a radical, and the propagating site of reactivity (*) is a carbon radical.
2. **Cationic Polymerization** The initiator is an acid and the propagating site of reactivity (*) is a carbocation.
3. **Anionic Polymerization** The initiator is a nucleophile and the propagating site of reactivity (*) is a carbanion.
4. **Coordination Catalytic Polymerization** The initiator is a transition metal complex, and the propagating site of reactivity (*) is a terminal catalytic complex.

3] Types of Polymerization reactions

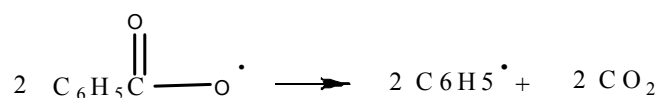
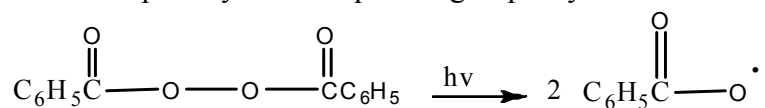
A] Addition (chain growth) polymerization reaction:

In which self addition of unsaturated molecules of one or more monomers without loss of any small molecules is called addition polymerization.

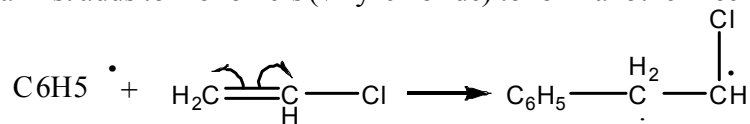
Addition polymerization reactions divided into three units/ parts.

a) Free radical polymerization:

In free radical polymerization organic peroxides are used as catalyst (initiators) Initiation step; benzoyl peroxide on photolysis decompose to give phenyl free radical.



Phenyl free radical first adds to monomers (vinyl chloride) to form another free radical.

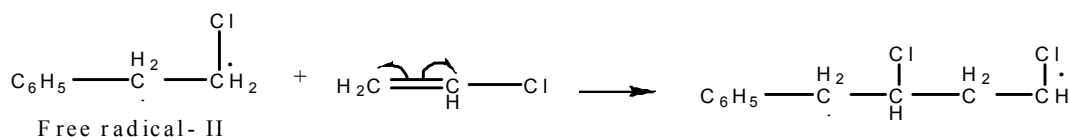


Free radical- I

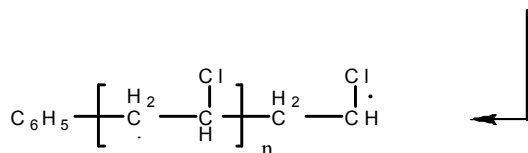
Free radical- II

Propagation step;

Free radical-II produced in initiation step adds to another monomer (vinyl chloride) molecule forming yet another free radical-III, successive addition of monomer to such radical leads to be the formation of long chain radical.



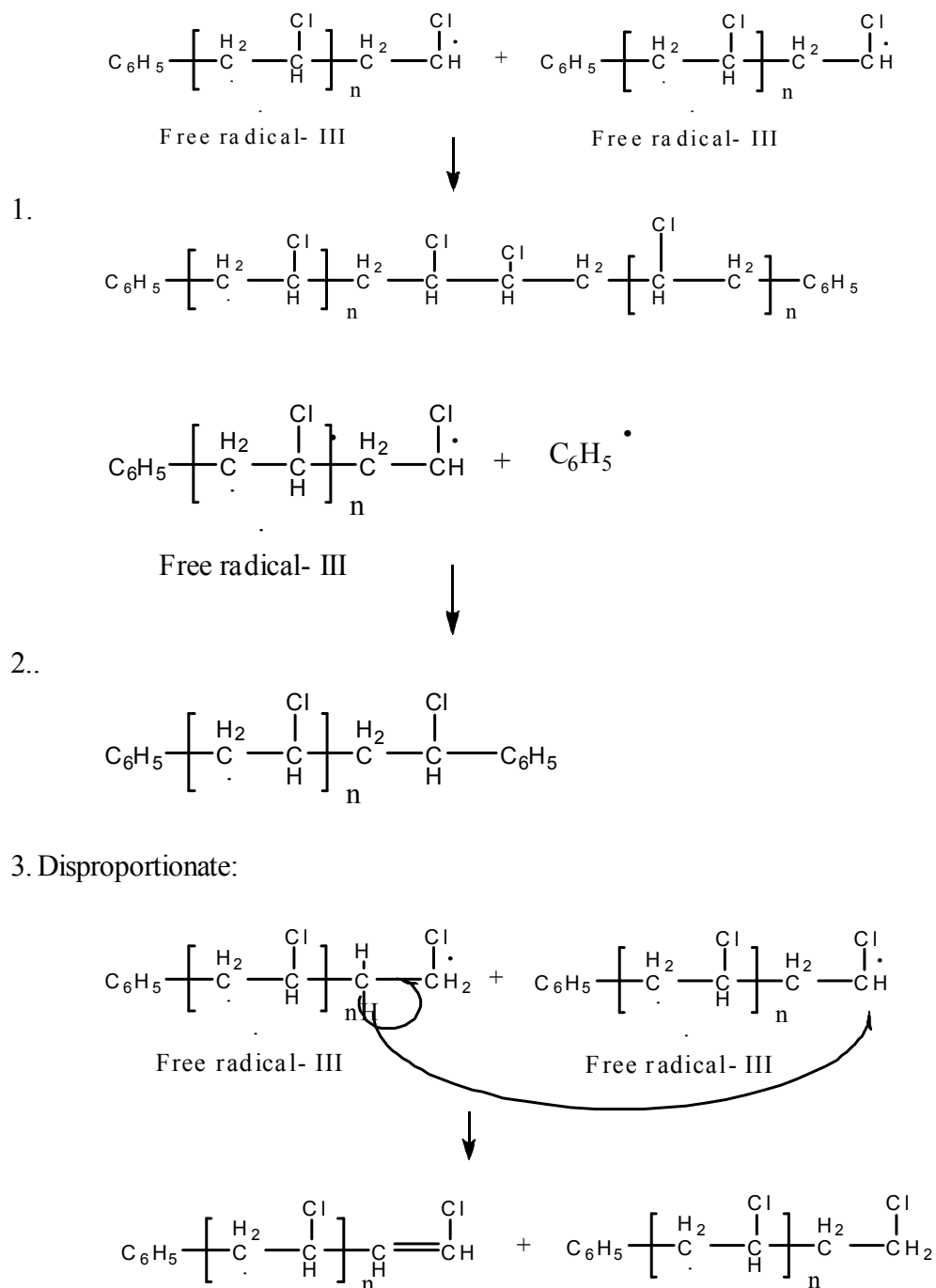
Free radical- II



Free radical- III

Termination step:

It occurs by any of the following processes.



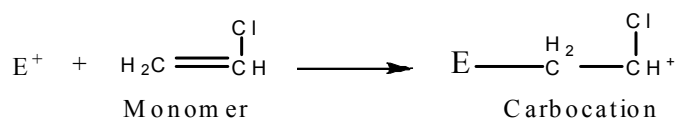
02] Ionic Polymerization:

These are classified into two steps.

i) **Cationic Polymerization:** these reactions are catalyzed by protonic acids such as halo acids, Sulphuric acids, Perchloric acid and Lewis acids like AlCl_3 , BF_3 , TiCl_4 and carbocation salts.

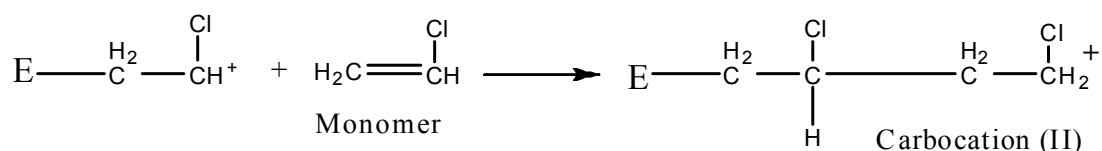
Cationic initiators act as electrophiles and they accept electron from double bond of monomer.

Initiation step:

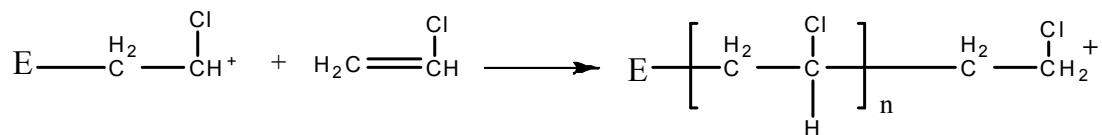


Propagation step:

Carbocation (I) combine with second molecule of monomer to form carbocation (II)

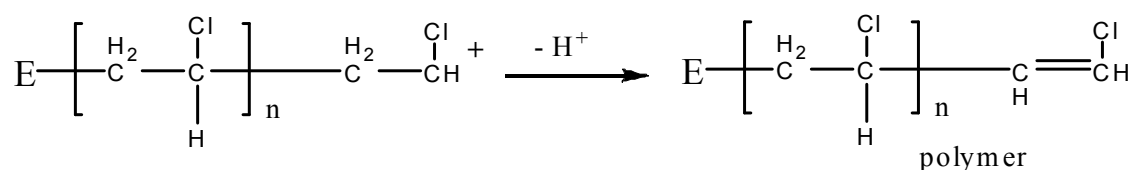


This step repeat several times to continue the polymer chain and form polymer.



Termination step:

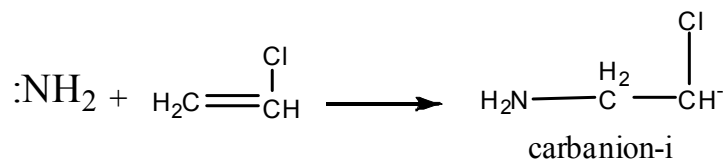
It usually occurs by abstraction of proton from growing polymerize carbocation.



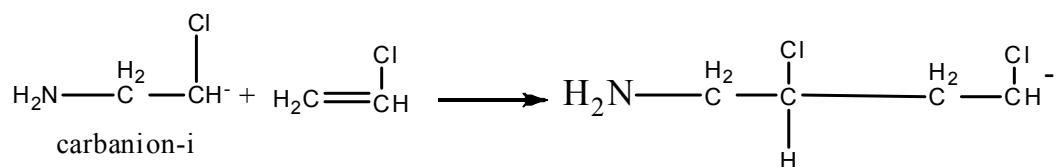
Anionic polymerization:

This type of polymerization takes place in the presence of strong electro donor base like soda amide (NaNH_2). In which electro pair is donated by base to monomer and forming carbanion.

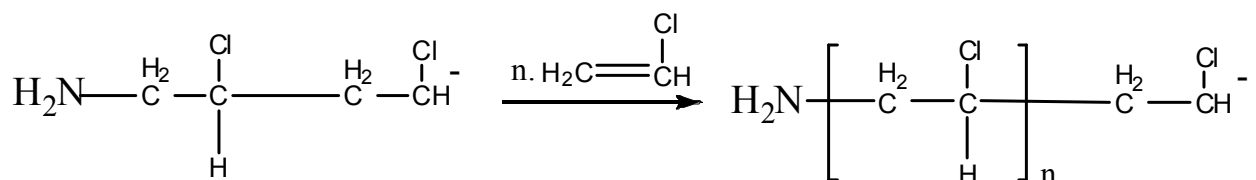
Initiation:



Propagation step:

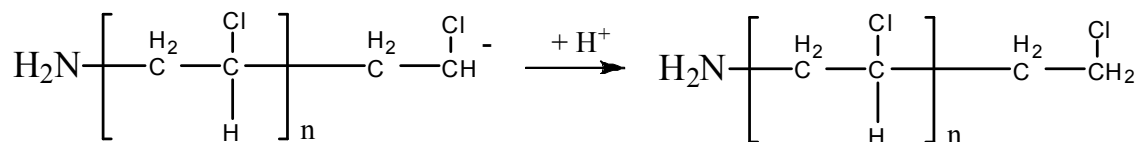


The carbanion attract the monomer successively to produce the long chain polymeric carbanion.



Termination:

It usually occurs by combination with a proton or some other Lewis acid in the reaction mixture.



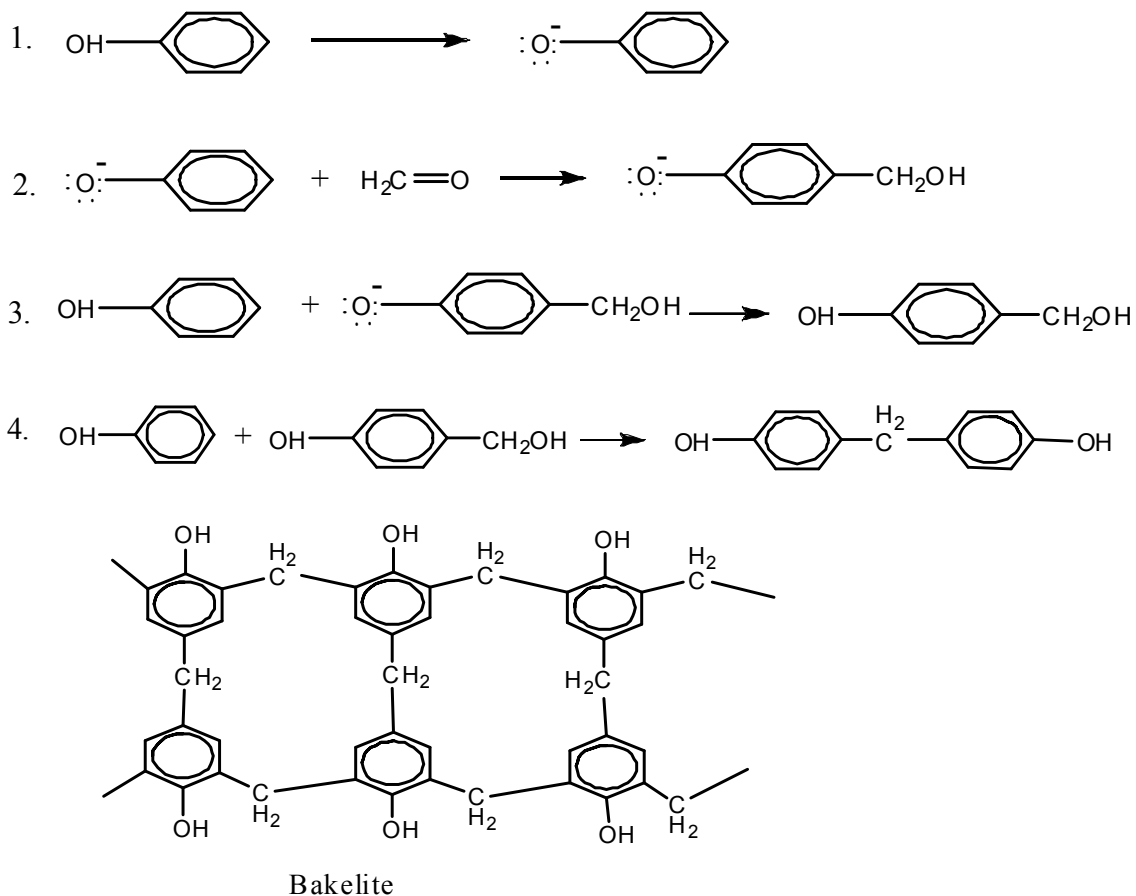
Condensation (Step growth) Polymerization Reaction:

This type of polymerization takes place by condensation of two or more monomers by the loss of small molecule like H₂O or HCl.

In which two monomers having different types of functional groups for ex. Bakelite [Phenol formaldehyde resin]

They represent important class of polymers produced by reaction between phenols and Formaldehyde in the presence of a basic catalyst.

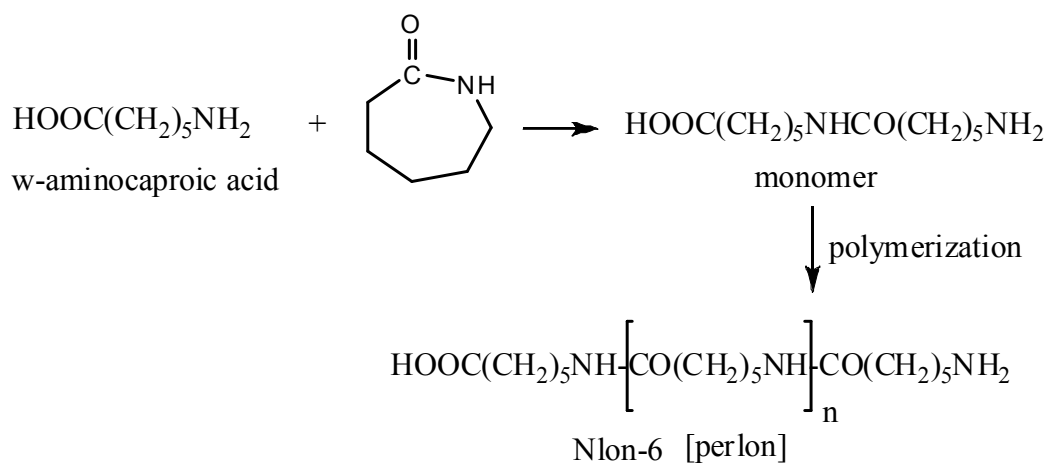
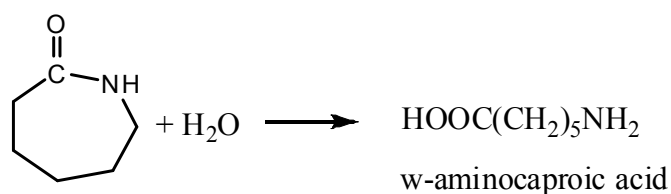
Polymer formed may be the low molecular weight branched polymer (Novolak) or high molecular weight cross-linked thermosetting resin (Bakelite) depending upon the experimental condition.



Synthesis and uses of following polymers:

1. Nylon-6:

Nylon-6 prepared from Caprolactum. the reaction is initiated by the hydrolysis of w-amino caproic acid, whose amino group attack the other molecule of caprolactum and the continuation of the process result in the formation of a polymer.



Uses:

- i) Nylon-6 is a polymer of major importance in synthetic fibre industries.
- ii) Nylon-6 is used in the manufacture of tyres and non-oven fabrics.
- iii) It is also used in molding process.

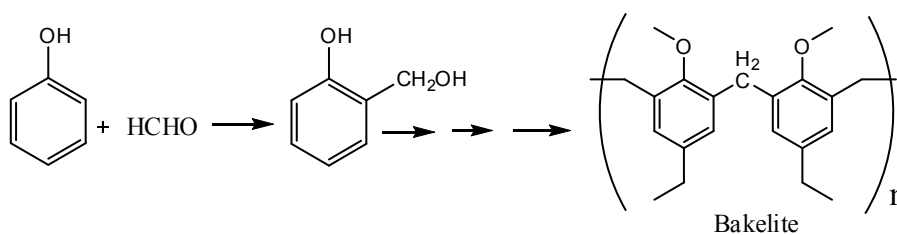
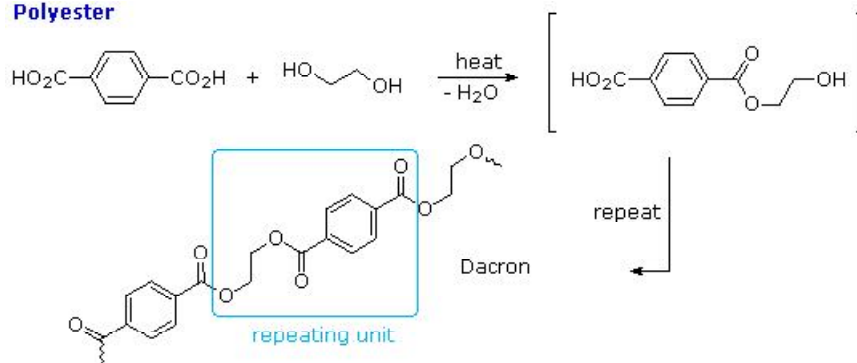
CONDENSATION POLYMERIZATION

A large number of important and useful polymeric materials are not formed by chain-growth processes involving reactive species such as radicals, but proceed instead by conventional functional group transformations of polyfunctional reactants. These polymerizations often (but not always) occur with loss of a small byproduct, such as water, and generally (but not always) combine two different components in an alternating structure. The polyester Dacron and the polyamide Nylon 66, shown here, are two examples of synthetic condensation polymers, also known as **step-growth** polymers. In contrast to chain-growth polymers, most of which grow by carbon-carbon bond formation, step-growth polymers generally grow by carbon-heteroatom bond formation (C-O & C-N in Dacron & Nylon respectively). Although polymers of this kind might be considered to be alternating copolymers, the repeating monomeric unit is usually defined as a combined moiety.

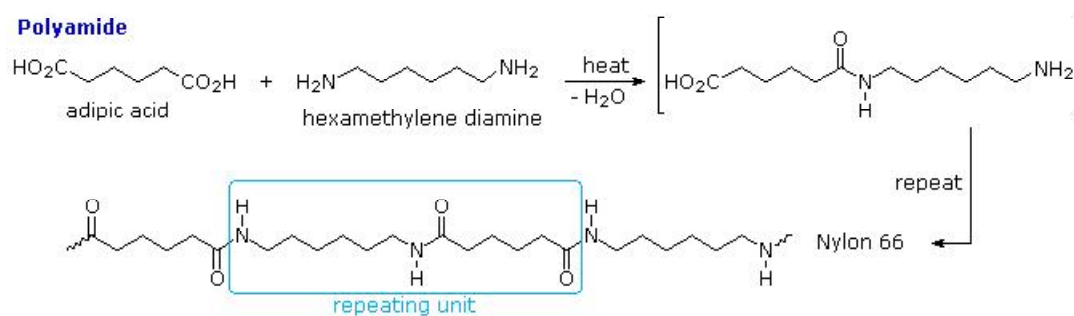
Examples of naturally occurring condensation polymers are cellulose, the polypeptide chains of proteins, and poly (β -hydroxybutyric acid), polyester synthesized in large quantity by certain soil and water bacteria.

Examples of Condensation Polymers

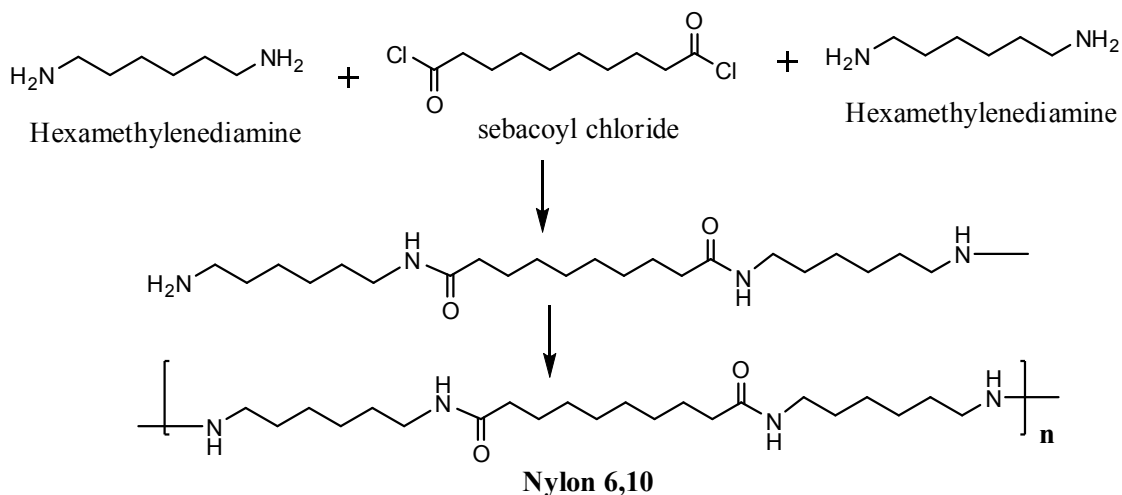
Polyester



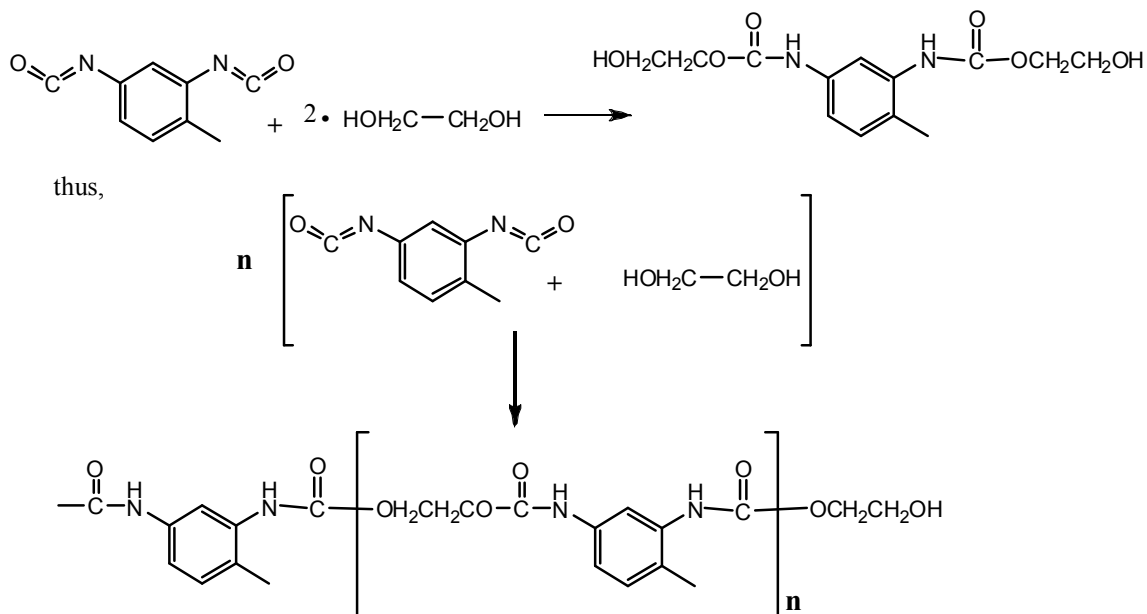
Polyamide



1) SYNTHESIS AND USES OF NYLON6,10: It is synthesized from hexamethylene diamine and sebacoyl chloride [$\text{ClOC}-(\text{CH}_2)_8-\text{COCl}$]



SYNTHESIS AND USES OF POLYURETHANE: This is condensation type of polymer. When ethylene glycol or any other diol is added to toluene diisocyanate, a rapid condensation results into formation of polyurethane. Low boiling liquids such as butane are often added to the reaction mixture. Heat evolved by the polymerization, vaporizes the volatile liquid (such as



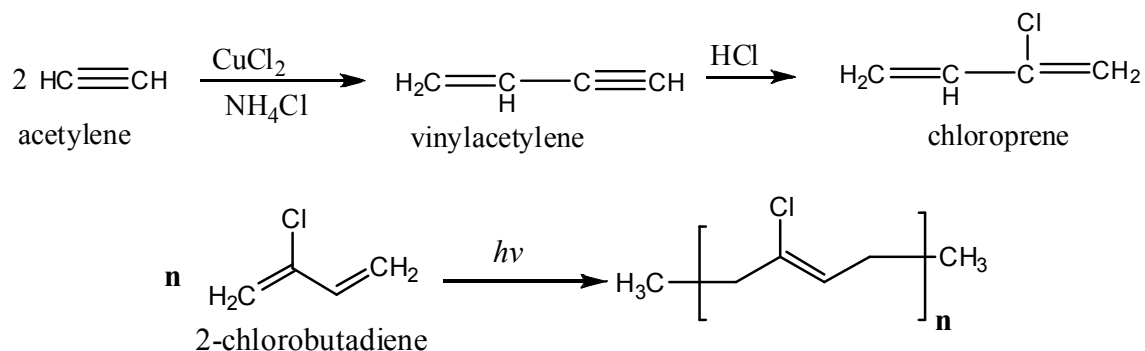
butane), producing bubbles that convert the viscous polymer to frothy mass of polyurethane foam.

Uses: Polyurethane materials are commonly formulated as paints and varnishes for finishing coats to protect or seal wood. Polyurethane is also used in making solid tires. polyurethane foam include furniture cushions, automotive seat cushions, carpet cushion, mattress padding and solid-core mattress cores. Flexible and semi-flexible polyurethane foams are used extensively for interior components of automobiles, in seats, headrests, armrests, roof liners, dashboards and instrument panels.

A thin film of polyurethane is added to a polyester weave to create polyurethane laminate, which is used for its waterproof and windproof properties in outerwear, diapers, shower curtains, and so forth. A still more popular use of polyurethane in textiles is in the form of spandex, also known as elastane or by DuPont's brand name Lycra. Polyurethane fibers in the form of spandex can stretch up to 600% and still return to their original shape. Spandex is spun with other fibers, such as cotton, nylon, or polyester, to create stretchable fibers essential for clothing for both sports and fashion.

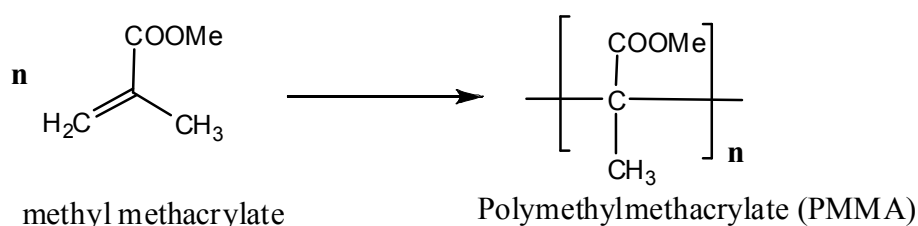
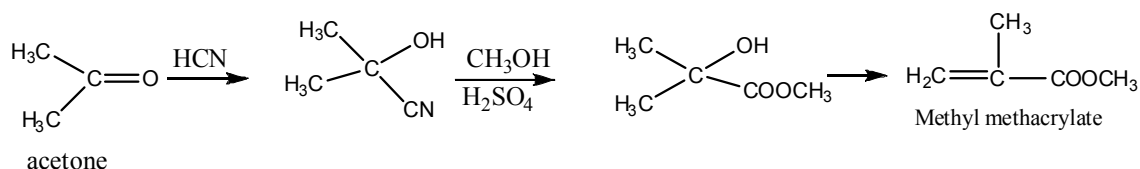
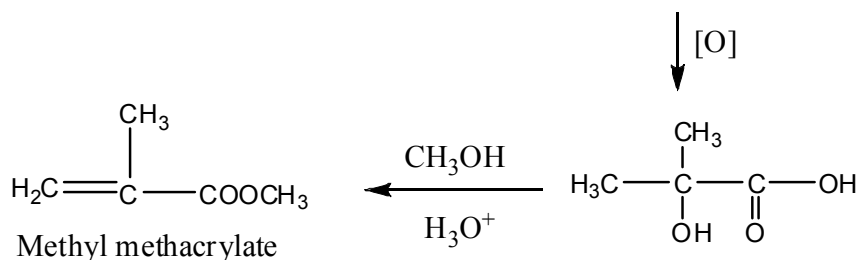
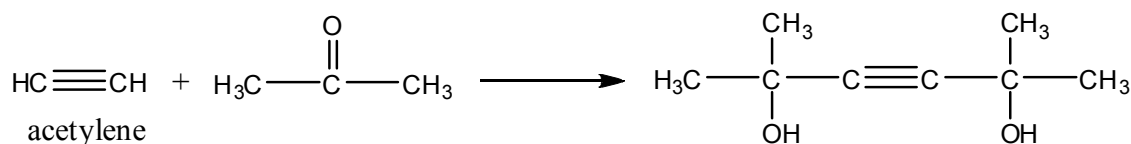
1) Synthesis and uses of Neoprene or polychloroprene is a family of synthetic rubbers that are produced by polymerization of chloroprene. Neoprene exhibits good chemical stability, and maintains flexibility over a wide temperature range.

Neoprene is synthesized by free-radical polymerization of 2-chlorobutadiene. In commercial production, this polymer is prepared by free radical emulsion polymerization. Polymerization is initiated using potassium persulfate, metal oxides (e.g. zinc oxide), and thioureas are used to crosslink individual polymer strands.



Uses: It is used in a wide variety of applications, such as laptop sleeves, orthopedic braces (wrist, knee, etc.), electrical insulation, liquid and sheet applied elastomeric membranes or flashings, and automotive fan belts.

1) Synthesis and uses of Polymethylmethacrylate (PMMA): It is a transparent thermoplastic, often used as a lightweight or shatter-resistant alternative to glass. Although it is not technically a type of glass, the substance has sometimes historically been called acrylic glass. **PMMA**, a synthetic resin produced from the polymerization of methyl methacrylate.

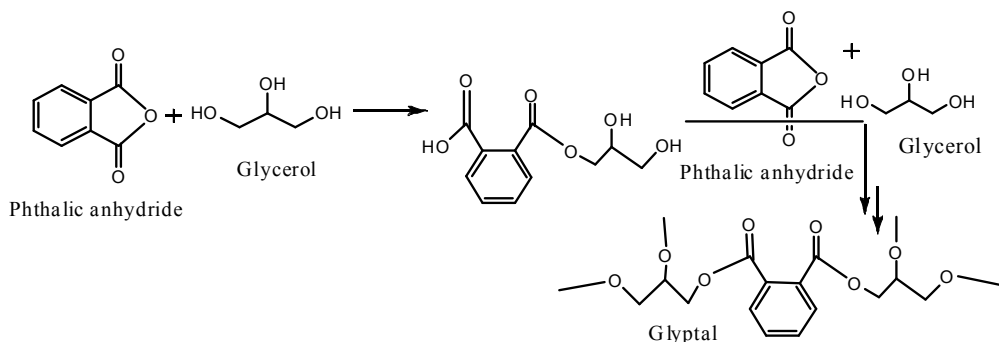


PMMA is a tactic (the substituents are placed randomly along the chain) polymer.

Uses: A transparent and rigid plastic, PMMA is often used as a substitute for glass in products such as shatterproof windows, skylights, illuminated signs, and aircraft canopies. It is sold under the trademarks Plexiglas, Lucite, and Perspex.

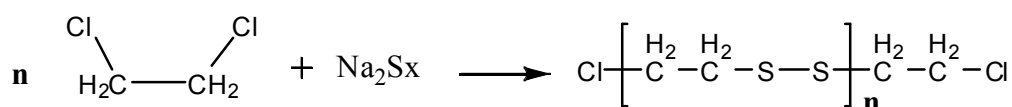
Synthesis and uses of Glyptal:

It is a polyester. **This is** cross-linked polymer to form a three-dimensional network. The polyester Glyptal is prepared from phthalic anhydride and a triol (glycerol) as follows. It is used as *adherent paints, lacquers and building materials like asbestos and cement.*



5) Synthesis and uses of Thiokol:

Polysulfide rubbers were among the first commercial synthetic rubbers produced. Two chemists, Joseph C. Patrick and Nathan Mnookin, were trying to invent inexpensive antifreeze in 1926. In an experiment involving ethylene dichloride and sodium polysulfide, they created a gum whose outstanding characteristic was a terrible odor. Trying to dispose of it, the substance clogged a sink in the laboratory, and none of the solvents used to remove it were successful. The chemists realized that the resistance of the material to any kind of solvent was a useful property. They had invented synthetic rubber, which they christened “Thiokol,” from the Greek words for sulfur (theion) and glue (kolla). Thiokol rubber is resistant to natural oxidants such as oxygen and ozone and to organic solvents such as oils and gasoline. This makes it useful for engine O-rings, gaskets, and hoses which may come in contact with oils. Thiokol can be prepared by the reaction of 1,2-dichloroethane and sodium polysulfide.

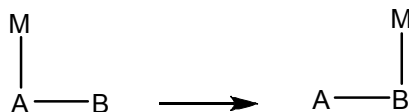


Uses: Some of the important Uses of Thiokol are It is used for making gaskets, seals and hard rubber products to be exposed to oil and pressure. Thiokol rubber mixed with oxygen releasing chemicals is used as a solid fuel in rocket engines. It is used for making hoses and linings of vessels used in the manufacture of chemicals.

2.Molecular Rearrangements:

Many organic reactions involve change at functional groups while the molecular skeleton of the reactants remains unchanged. We have, however, encountered some examples in which groups migrates within molecule and carbon skeleton are modified such transformation are known as molecular rearrangements.

The most common kinds of rearrangement involve migration of group from one atom to the next within the molecule, that is they are 1,2-rearrangements.



Molecular rearrangements are usually not considered as a separate class of organic reactions. They normally involve intramolecular substitutions with mechanistic features similar to those of their intramolecular counterparts.

Molecular rearrangements are two types.

1. Intramolecular rearrangements:

If rearrangement occurs within the same molecule they are said to be intramolecular. In these rearrangements the migrating group does not get detached completely from the system in which rearrangement is taking place.

2. Intermolecular rearrangements:

If rearrangement involve the migration of groups between two molecules. They are said to be intermolecular. In these rearrangements the migrating group is first detached and reattached at another site.

Types of molecular rearrangements:

The molecular rearrangement can be conveniently classified into following types.

a) Nucleophilic rearrangement:

These are the rearrangement reaction in which the migrating group (nucleophile) gets migrated to electron deficient centre. For ex. Pinacol-Pinacolone rearrangement reaction.

a) Electrophilic Rearrangement:

These are the rearrangement reaction in which the migrating group (electrophile) gets migrated to electron rich centre.

b) Free-radical Rearrangement:

These are the rearrangement reaction in which the migrating group moves to a free radical centre.

c) Aromatic Rearrangement:

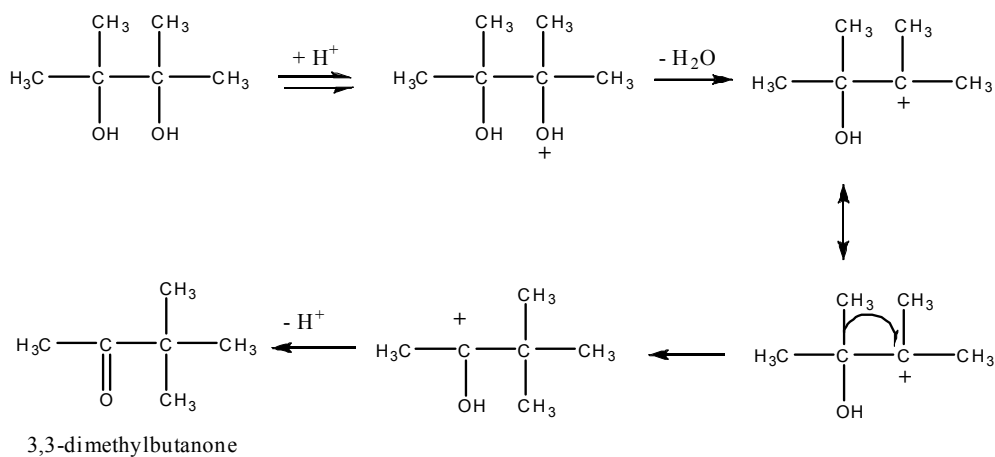
These are the rearrangement reaction in which the migrating group moves to aromatic nucleus.

The first three types of molecular rearrangements are intra-molecular, while the fourth type of molecular rearrangement may be intra-molecular, intermolecular or both.

Study of following rearrangements with Mechanism:

1. Pinacol-Pinacolone Reaction: (Nucleophilic rearrangement)

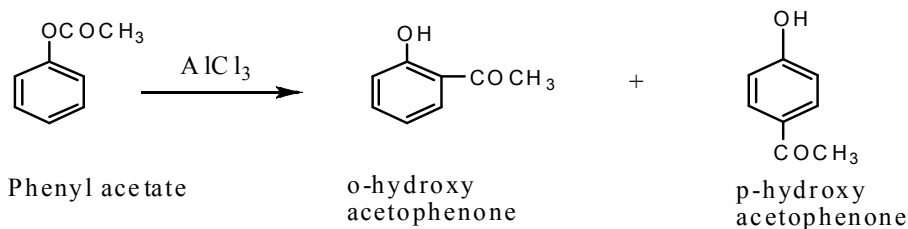
Conversion of 2,3-dimethylbutanediol to 3,3-dimethyl-2-butanone



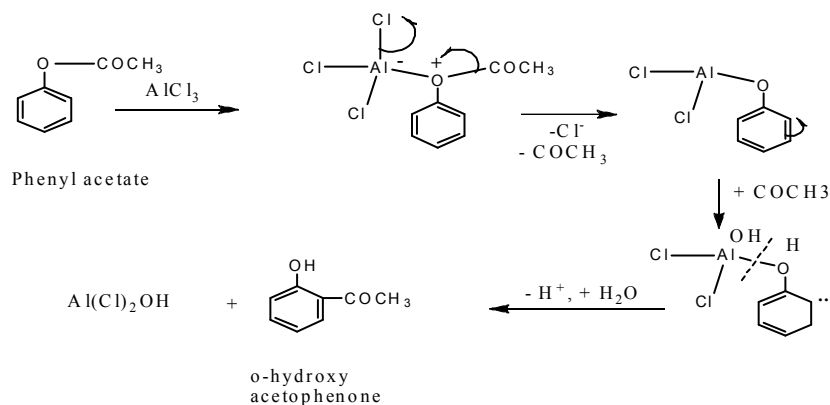
2. Fries Rearrangement: (Aromatic rearrangement)

Phenolic ester (phenyl acetate) when heated with anhydrous aluminium chloride, it undergoes a rearrangement reaction, in which acyl group migrated to aromatic ring to give principally ortho-phenolic ketone, this rearrangement is called Fries rearrangement.

If the ortho position is not vacant or the reaction is carried out at low temperature, the para product predominates.

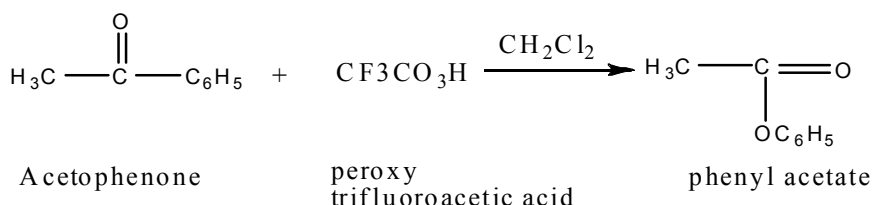


Mechanism:

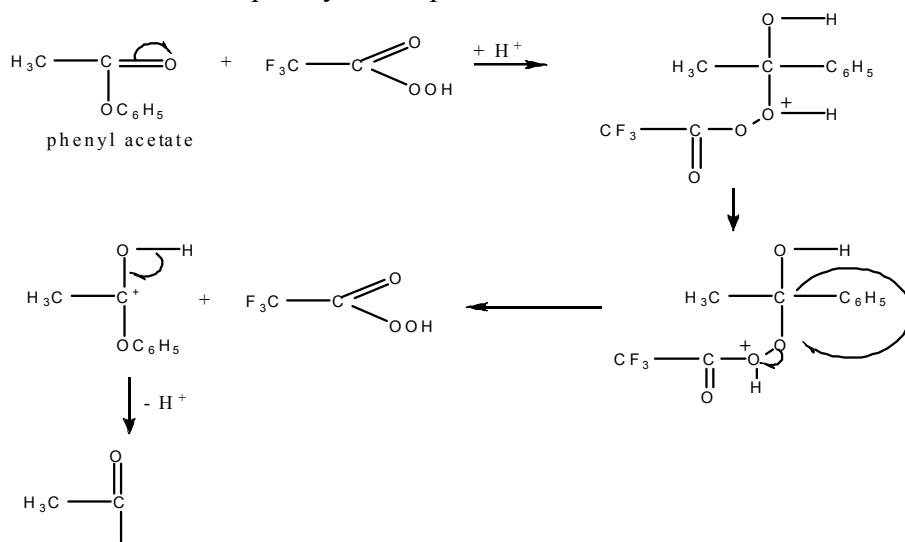


3. Baeyer-Villiger Rearrangement:

In the Baeyer-Villiger Rearrangement a ketone is converted into ester by reaction with peroxy acid. The reaction is an oxidation in which oxygen atom inserts between the ketone carbonyl and the migrating group. Peroxytrifluoroacetic acid is most often the reagent of choice, but other peroxy acids also have been employed.

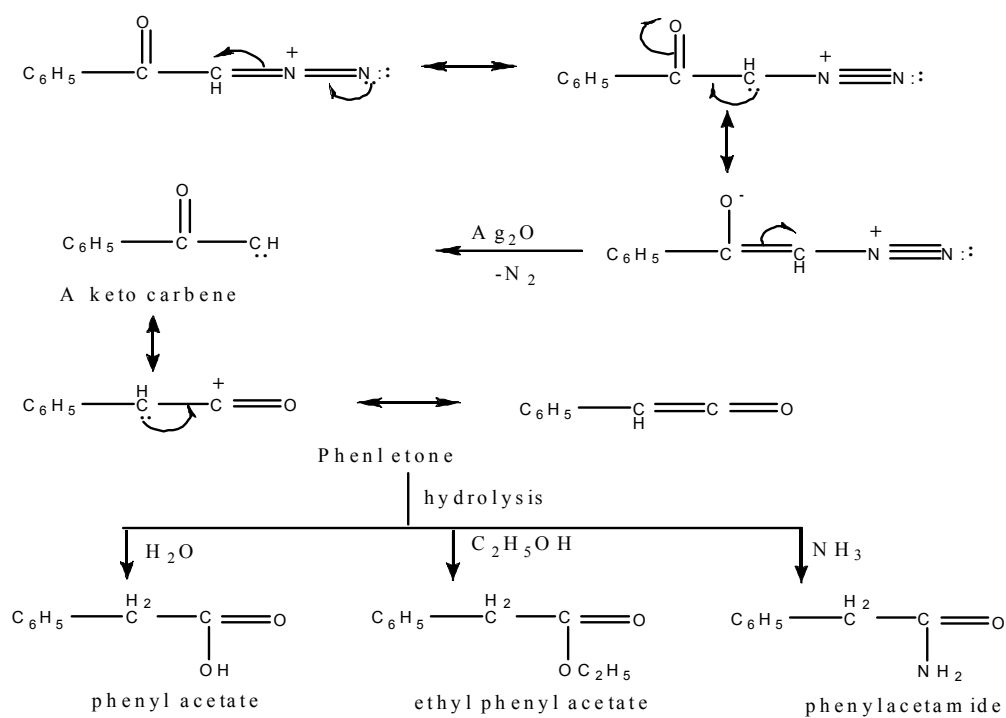


The reaction is believed to be initiated by formation of an adduct between the peroxy acid and the protonated ketone carbonyl group. Migration to oxygen then takes place as the carboxylate derived from the peroxy acid departs.



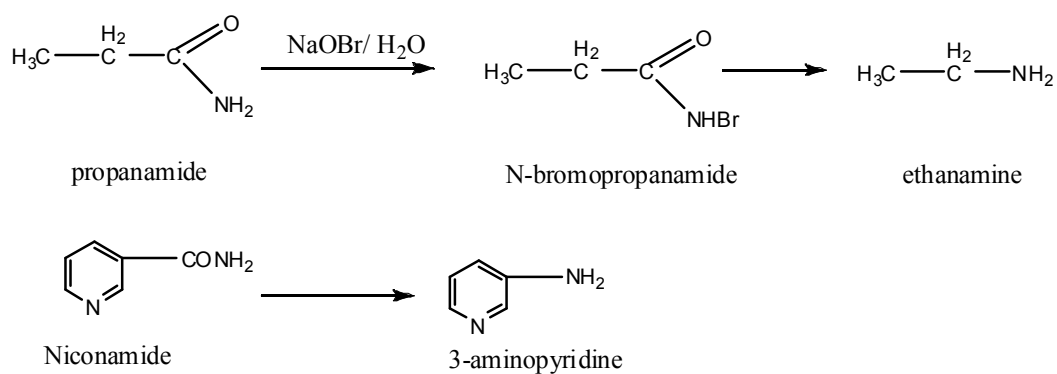
4. Wolff rearrangement:

In the Wolff rearrangement an α -diazoketone loses nitrogen by the action of silver oxide or irradiation with light to produce an intermediate carbene. Rearrangement of an adjacent group to that carbon atom leads to a ketene. Which rapidly reacts with the reactant solvent? When the solvent is water, alcohol, or an amine, the final product is a carboxylic acid, an ester, or an amide, respectively.



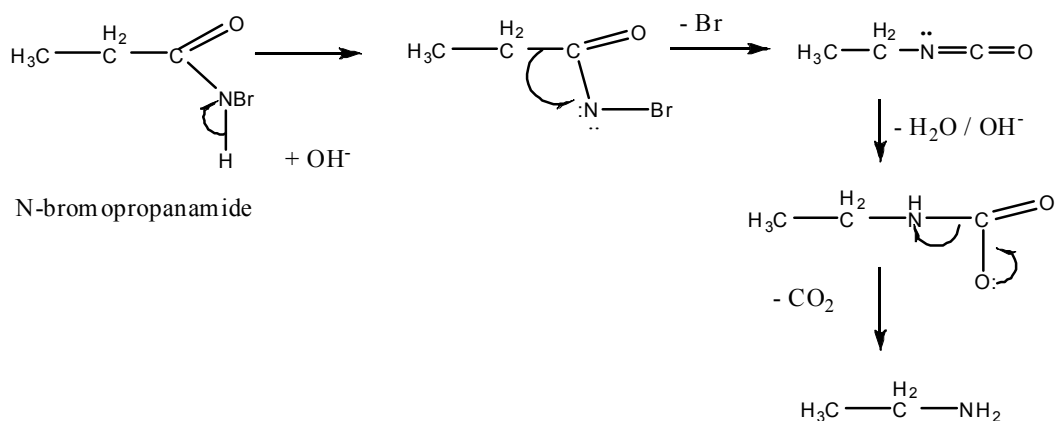
4. Hofmann Rearrangement:

This rearrangement involves migration of an electron deficient nitrogen atom. Hofmann rearrangement of N-haloamides is the most common rearrangement of the family, and it has been extensively studied since its discovery by Hofmann in 1882. Possessing one less carbon atom.



Mechanism:

The Hofmann rearrangement proceeds through formation of an N-haloamides anion that rearranges, with loss of bromide, to an isocyanate. Water adds to isocyanate to produce carbamic acid, which readily loses carbon dioxide to give the amine.



Question Bank

- Q1. Define the following terms
- Monomer
 - Polymer
 - Co-polymer
 - Homopolymer
 - Plastic
 - Elastomer
 - Thermoplastic polymer
 - Thermosetting polymer
- Q2. What is addition polymerization reaction? Explain Free radical Polymerization Reaction with mechanism.
- Q3. What is addition polymerization reaction? Explain Cationic Polymerization Reaction with mechanism.
- Q4. What is addition polymerization reaction? Explain Anionic Polymerization Reaction with mechanism.
- Q5. What is Condensation polymerization reaction? Explain with suitable example.
- Q6. Give the Synthesis and Uses of following reactions
- Bakelite
 - Nylon-6
 - Polyurethane
 - Neoprene
 - Thiokols

vi) Polymethyl methacrylates

vii) Glyptal

Q7. What is molecular rearrangement reaction? Explain the types of molecular rearrangement reactions.

Q8. Explain the following reactions with mechanism.

i) Pinacol- Pinacolone rearrangement

ii) Fries rearrangement

iii) Baeyer- Villiger rearrangement

iv) Wolff rearrangement

v) Hofmann rearrangement

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