MAA OMWATI DEGREE COLLEGE, HASSANPUR (PALWAL)

NOTES

SUBJECT : Organic Chemistry

CLASS : B.SC 5th Sem

SESSION : 2021-2022

Section-D

Spectroscopy-II
Vibrational spectrum
Infrared spectrum: Energy levels of simple harmonic oscillator, selection rules, pure vibrational spectrum, intensity, determination of force constant and qualitative relation of force constant and bond energies, effects of anharmonic motion and isotopic effect on the spectra., idea of vibrational frequencies of different functional groups.

Raman Spectrum:
Concept of polarizibility, pure rotational and pure vibrational Raman spectra of diatomic molecules, selectin rules, Quantum theory of Raman spectra.

B. Sc Vth Semester

Paper XIX (Theory) Organic Chemistry **Marks: 30**

CH-503 **Time: 3 Hrs.**

Note: Examiner will set nine questions and the candidates will be required to attempt five questions in all. Question number one will be compulsory containing six short answer type questions covering the entire syllabus and will be of six marks. Further, examiner will set two questions from each section and the candidates will be required to attempt one question from each section which will be of six marks each.

Section-A

NMR Spectroscopy-I
Principle of nuclear magnetic resonance, the PMR spectrum,number of signals, peak areas, equivalent and nonequivalent protons positions of signals and chemical shift,shielding and deshielding of protons, proton counting,splitting of signals and coupling constants, magnetic equivalence of protons.

Section-B

NMR Spectroscopy-II
Discuss ion of PMR spectra of the molecules: ethyl bromide, npropyl bromide, isopropyl bromide, 1,1-dibromoethane, 1,1,2-tribromoethane, ethanol, acetaldehyde, ethyl acetate, toluene, benzaldehyde and acetophenone..Simple problems on PMR spectroscopy for structure determination of organic compounds.

SECTION – C

Carbohydrates-I

Classification and nomenclature. Monosaccharides, mechanism of osazone formation, inte rconversion of glucose and fructose, chain lengthening and chain shortening of aldoses. Configuration of monosaccharides. Erythro and threo diastereomers. Conversion of glucose in to mannose. Formation of glycos ides, ethers and esters. Determination of ring size of glucose and fructose. Open chain and cyclic structure of D(+)-glucose & D(-) fructose. Mechanism ofmutarotation. Structures of ribose and deoxyribose.

SECTION – D

1. Carbohydrates-II

An introduc tion to disaccharides (maltose, sucrose and lactose) and polysaccharides (starch and cellulose) without involving structure determination.

2. Organometallic Compounds

Organomagnesium compounds: the Grignard reagents-formation, structure and chemical reactions. Organozinc compounds: formation and chemical reactions. Organolithium compounds: formation and chemical reactions.

ORGANIC CHEMISTRY

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Chapter → 1. Spectroscopy

* **Introduction** → We would now take up the study of nuclear magnetic resonance (NMR) spectroscopy. which was introduced by felix bloch & edward purcell in 1946 and is easily the most powerful tool for structure elucidation and identification of organic substance.

Nuclear magnetic resonance spectroscopy is now divided into proton magnetic resonance spectroscopy. (PMR or ^1H-NMR) and ^{13}C nuclear magnetic resonance spectroscopy (^{13}C-NMR). ^{13}C-NMR was introduced only around 1970.

* **Principle of NMR Spectroscopy.**

Like $e^{\ominus}$, the nuclear particles (i.e, proton & neutrons) are also considered to spin around their axis. If the particles in a particular nucleus do not have their spin paired, the nucleus as a whole will have a resultant spin designated as I.

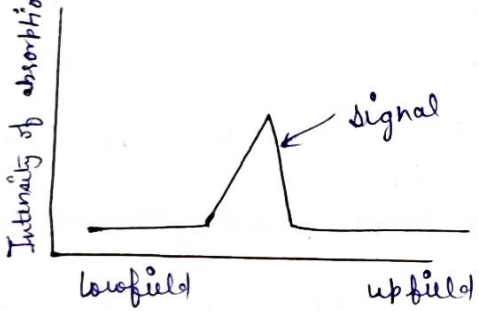
Nuclei having resultant nuclear spin. The nuclei must have either odd mass number or even mass number.

Mass number	Atomic number	Example
odd	odd or even	^1_1H, $^{13}_6C$, $^{15}_7N$, $^{19}_9F$, $^{31}_{15}P$
Even	odd	^2_1H, $^{10}_5B$, $^{14}_7N$

✱ PMR or ^1H-NMR - Spectrum : Origin of signals

In principle, a PMR-spectrum could be obtained by placing the substance containing hydrogen nuclei or protons in a magnetic field of constant strength and passing a radiation of varying frequency through the substance.

In actual practice, NMR-spectrometers usually operate by keeping the applied radio-frequency constant (generally maintained at 40, 60 or 100MHz) and varying the strength of applied magnetic field.



PMR spectra are recorded on charts which show the applied field strength from left to right. left of the chart is called low field (or down field) while right-side is called high field (or upfield)

"This is because the field strength at which absorption by a particular proton takes place is strongly influenced by the local environments of the proton such as e⊖ density around it & the presence of other protons in its neighbourhood.

✱ Number of signals : Equivalent & non-equivalent protons

A set of protons having identical environments are referred to as equivalent protons and all of them give rise to one signal. The proton with different environm are termed as non-equivalent protons and they give rise to different signals.

Imagine each hydrogen or proton in the molecule, to be substituted by some other atom 3.

a.) $CH_3-CBr_2-CH_3$ → All protons equivalent; only 1 PMR signal.

b.) $CH_3^a-CH^bCl-CH_3^a$ → Two kinds of protons 2 PMR signals.

c.) $CH_3^a-CH_2^b-CH_2^c-Cl$ → Three kinds of proton 3 PMR signals.

✱ Positions of signals and chemical shift

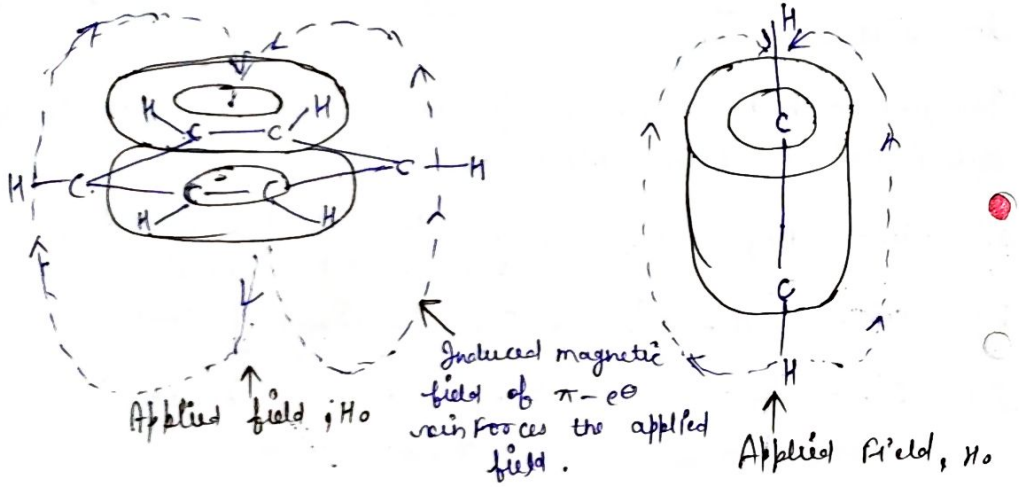
We have learnt above that the no. of signals in a PMR spectrum tells us about the no. of types of protons that a molecules has. At the same time, the position of the signals reveals the actual nature of protons. i.e, whether the protons are aromatic, aliphatic, vinylic, acetalynic, hydroxyl etc.

✱ Shielding & Deshielding of protons

If the induced field oppose the applied field, the effective field strength experienced by the protons decrease. This is called shielding of the proton. And if the induced field reinforce the applied field, the effective field strength experienced by proton increased. This called deshielding of the

proton. A deshielding proton naturally requires only a smaller applied field to give a signal i.e, it absorbs downfield.

Whether the induced field oppose or reinforce the applied field depends upon the manner in which π-e$^{\ominus}$ circulate under the influence of applied field.

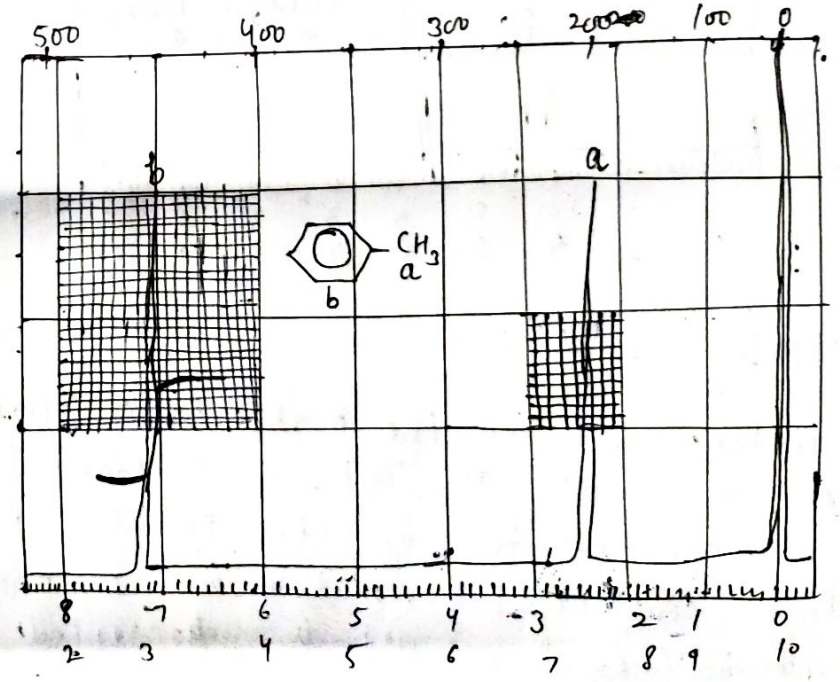


(*) Shielding & deshielding of proton.

(*) Peak Area & Proton counting

It is also possible to estimate the number of protons giving rise to a particular signal by measuring the relative intensities of the signals. The intensity of the peak means the area under the peak and nearly the height of the peak the area under a particular peak is directly proportional to the number of equivalent protons which give rise to that signals. The relative area under the different peaks would thus reveal the relative number of protons of different kinds present in a molecule of the given sample

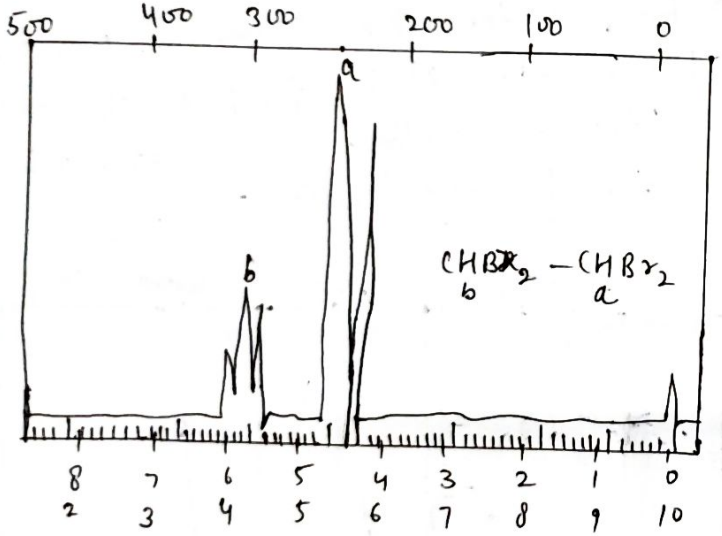
The peak areas of different signals are measured by an automatic integrator. and are generally shown on the spectrum in the form of a stepped up curve integral curve. for example, in the PMR spectrum of toluence shown below the step hights of the respective signals due to methyl and aromatic ring protons are in the ratio 3:5.



PMR spectrum of toluece  $-CH_3$

* Splitting of Signals : Spin-spin Coupling

This implis that the individual signal which we expect form of a equivatent protons must be appearing not a signal peak but as a group of peak. This is known as spitting of the PMR signals.



* Coupling Constant

The distance between the peaks in a given multiplet is known as coupling constant. Coupling constants are denoted by the symbles J and coupling constant between two protons marked a and b (i.e. H^a and H^b) is represented as J_{ab} The value of coupling constant is expressed in hertz (Hz and it is a quantitative measure of the magnitude of splitting effect. Unlike chemical shift, the value of J depends only on internal forces and is independent of the applied feild strength

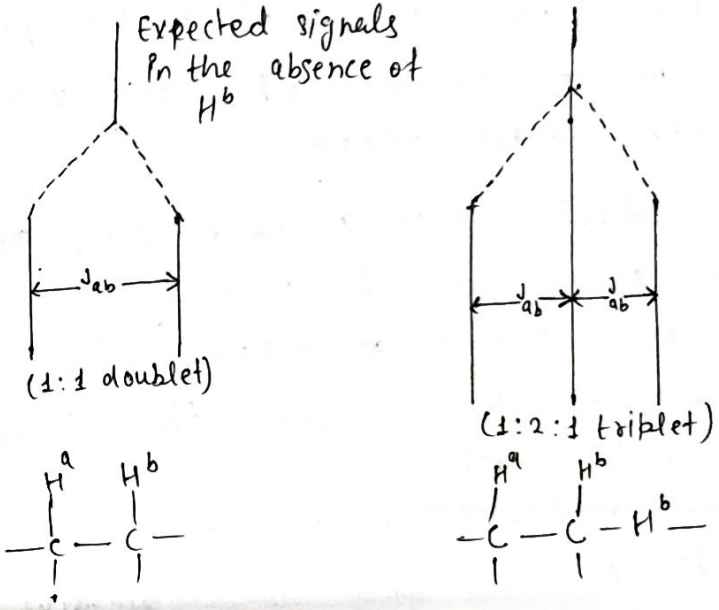


fig. 11.3 Theoretical representation of coupling constant.

* Magnetice Equivalent of protons

The magnatic equavatence of protons in many molecules depends upon the rate of certain molecular changes such as rotation aroud single bonds and proton exchange in alcohols and amines

To understand this aspect of PMR spectroscopy, let us compare a PMR spectrosmeter to a slow speed automatic camera If such a camera is used to photograph a rotating spoked wheel, the nature of photographs obtained would depends upon the rate at which the wheel rotates.

(1) If the wheel rotates somewhat fast, only blurred spokes will be seen.
(2) If the wheel rotates at a very slow speed, the photograph would show the Individual spoken quite sharply.
(3.) Lastly if the whed rotates very fast, the Photograph does not show the individual spoken at all only a, circular smeared out cloud would be seen.

Chapter → 2

Carbohydrates

* Classification

→ The carbohydrates or Saccharides may be broadly divided into sugars and non-sugers. The Sugurs like glucose, fructose, are crystallin water soluble and sweet subtance. Non-sugurs which include starch, cellulose, etc are amouphous, insoluble in water and tasteless subtances. Accordingly they are divided into three classes. monosaccharides, oilgosaccharides, and Polyccaharides as discribed below.

(1.) **Monosaccharides.** ⁰⁄₀ These are the simples carbohydrates which cannot be hydrolsed to smaller molecules. A monosaccaharides which contains an aldehide group is called an aldose while the one which contains a keto group is called a ketos.

(2.) **Oilgosaccharides** ⁰⁄₀ (Greek oilgoes = a few) which can be hydralyed These are carbohydrates to yeild two to nine monosaccharieles molecules (genrally hexoses.)

(ii.) Disaccharides :→ $C_{12}H_{22}O_{11}$, such as sucrose, lactose, maltose.

(iii) Trisaccharides :→ $C_{18}H_{32}O_{16}$, such as raffinose.

(iii) Tetrasaccharides :→ $C_{24}H_{42}O_{21}$, such as stagyose.

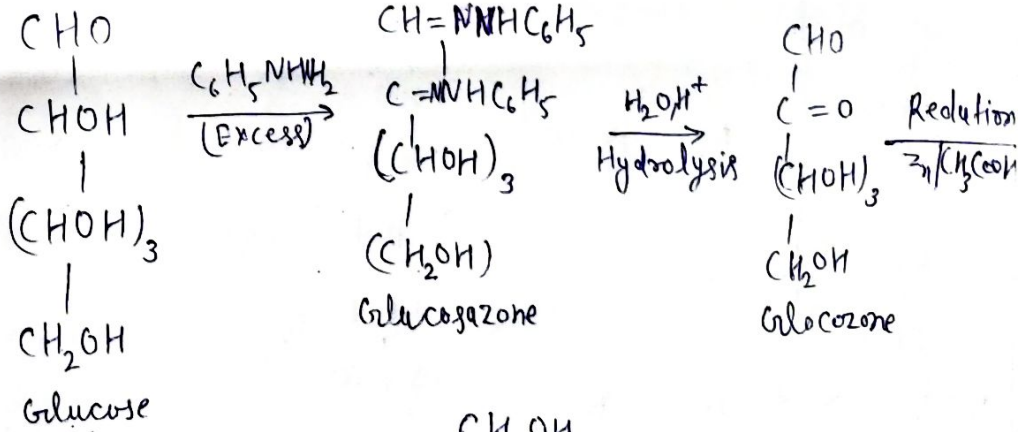
(3.) Polysaccharides :→ These are carbohydrates can be hydralyes to yeild a very large number of monosaccharides molecules. The most commonly occuring Polysaccharides. have the genral formula $(C_6H_{10}O_5)_n$ disaccharides (a prominant exception being sucroes) reduce fehling sollution and tollen. a regent and are, therfore, also reffered to as reducing saccharides, such as sucrose with do not reduce. fesling solution are Tollen's are called non - reducing saccharides.

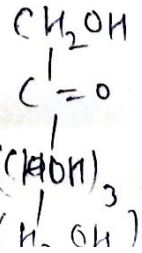
* Nomenclature :→ The names of most of the carbohydrates end - in - ose.

* Monosaccharides → Monosaccharides are simplest, the important saccharides which contain 3-8 carbon atoms in their molecules. It may be stated that much of what can be said about glocose, can also be said about the other monosaccharides.

* Interconversion of Glucose and fructose

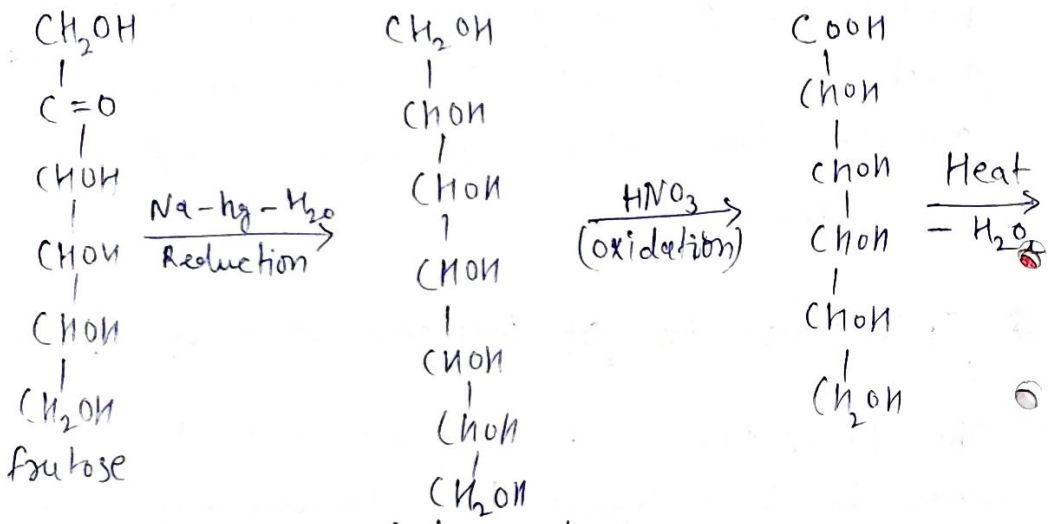
The Procedure employed for this purpose may be illustrated by considering the conversion glucose into fructose.



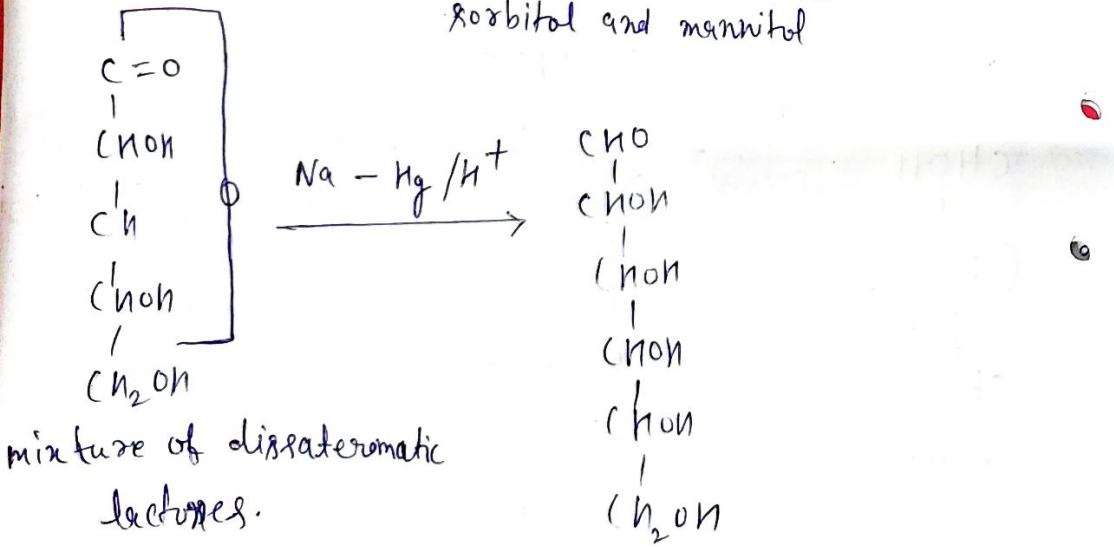


fructose.

The Procedure employed in this illustrated by condering the conversion of fructose to a mixture of epimetic aldoes, glecoes and mannose.



mixture of disaterometric sorbitol and mannitol



mixture of dissateromatic lactones.

mixture of epimetice glecose and mannose

The Process Involed four steps as shown below:-

(i) Reaction of given aldose with hydrogen cyainide when a mixture of two diasteromeric cyanohydeins is obtained. This is beacause cyanohydrins formation given rise to a new stereocentre.

(ii) Hydrolysis of cyonydein mixture of obtain a corresponding acids which are seperated from other each.

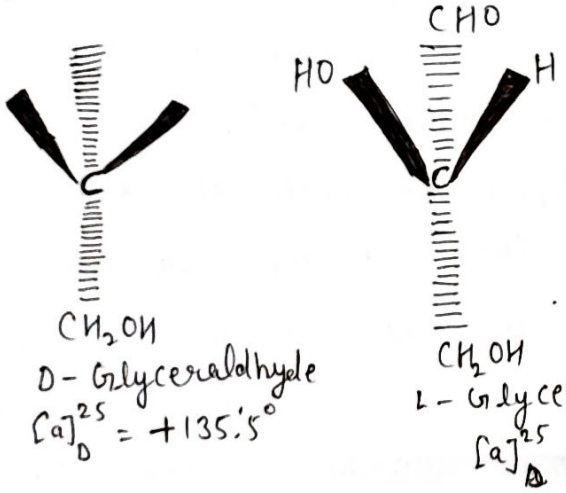
(iii) Action of heat on each of acids to form the corresponding lactones.

(iv) Reduction of the lactons by sodium amalgam to get the higher aldose. Containning one carbom atom more than the stating aldose.

* Configurations of monosaccharides :-

It has been already stated that with the exception of simplest ketone, dihyroxyaceton all other monosaccharides are optacally active processing one of more stereocentres in their molecules.

Dibending upon the number of stereocentres present in the molecule, they exist different stereosometic form having different configurations. The determination of absolute configurations of various stariosomeric was a very challenging task.



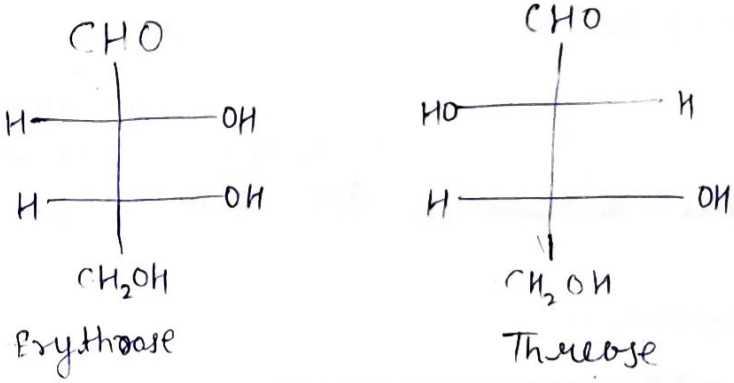
D - Glyceraldhyde
$[a]_D^{25} = +135.5°$

L - Glyceraldehyde
$[a]_D^{25} = -13.5°$

* Erytro and Threo Diastereomers :-

Erythrose and threoses are Diastereomeric aldotetroses two adjacent steriocentres. In erythrose, the -OH groups on its steriacentres are situated on the same sides of the fischer projection while in threoses, the -OH groups are opposite sides of the fischer projections.

This has been given rise to a system of denoting diastereomers with two adjecent steriocentres in which at least one atom of group attached to the one steriocentres is same as the atom on group attached to the other steriocentres.

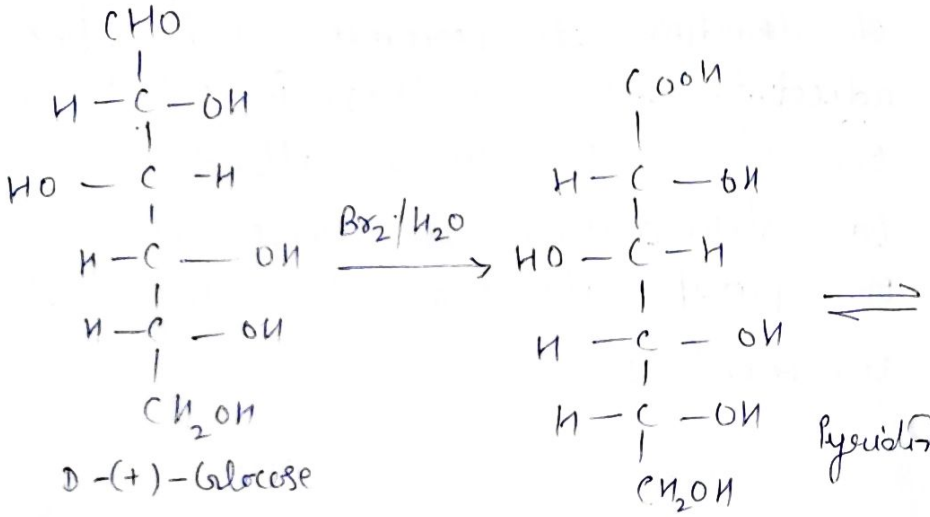


Erythrose

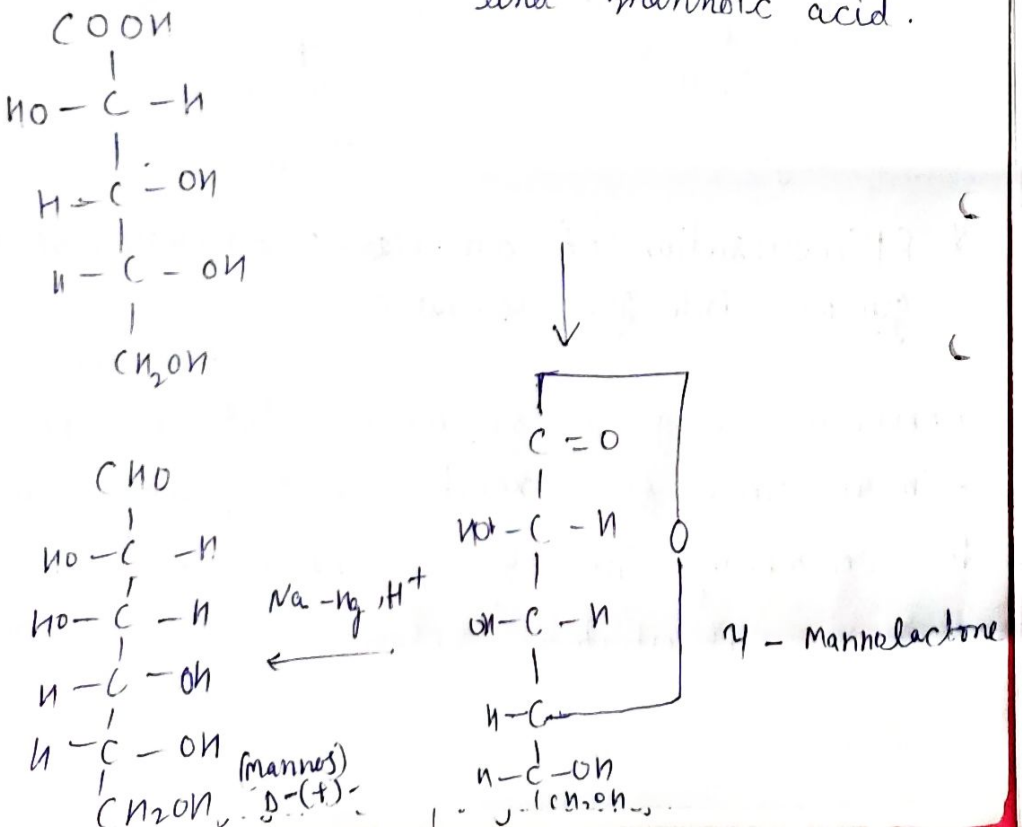
Threose

* Epimerisation of an aldose : Conversion of D-glucose into D-mannose :-

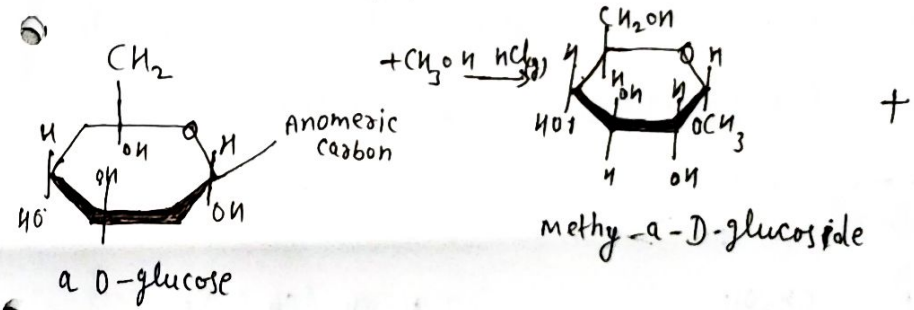
The process of converting a given saccharide into its known as epimerisation. for example → D-glucose may be converting into by adopting the produre illustrated below.

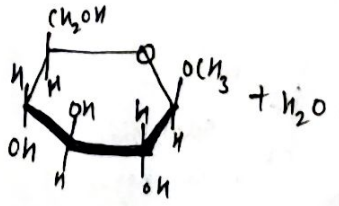


Equilibrium mixture of epimeric acids gluconic and mannoic acid.



* **Glycosides** :→ When monosaccharides are treated with alcohols in the presence of traces of acid catalyst, they are converted into cyclic acetals by the replacement of –OH group at the anomeric carbon an alkoxy group. Such cyclic acetals derived from monosaccharides are called glycosides.

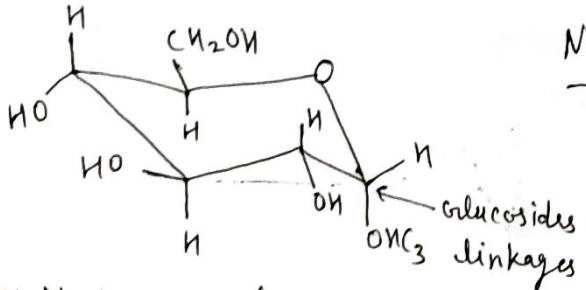




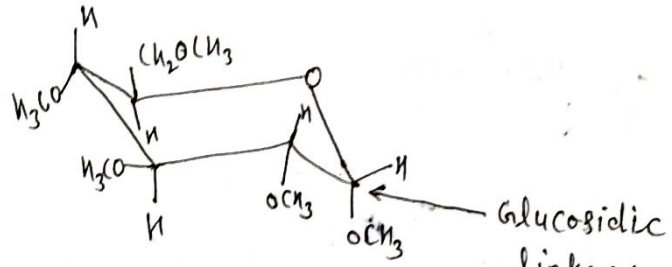
Methy-β-D-glucoside

* formation of ethers :-

We have seen that when a monosaccharides is treated with an alcohol in the presence of acids catalyst, a mixture of α- and β-glucosides is obtained by reaction at the anomerice carbon of the monosaccarides. it is also possible to convert the remanning -OH groups into alkly derivatives having ordinary ether (-O-C linkages.



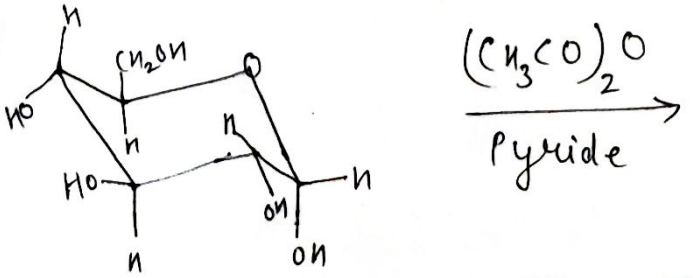
Methyl α-D-glucosides



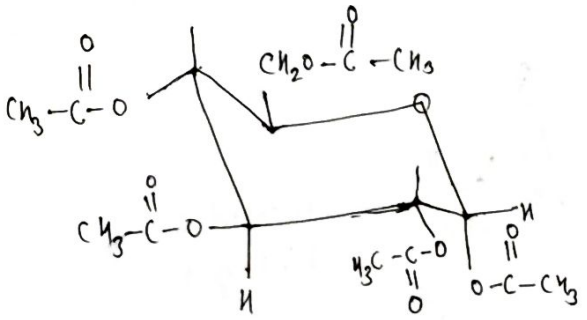
(D-glucopyranoside)

* formation of esters :-

Monosaccharides can be easily converted into esters derivatives with are very useful crystalline compounds.



(α-D-glucopyranose)



(Petna – O – acetly – α – D – glucopyranoside)

Organometallic Compounds

Chapter → 3

* Organomagnesium Compounds : the grignard reagents

Organomagesium halides, bopularly known as Grignard reagents, are the most important of all organometallic compounds, they were discovered by victor Grignard who recived the Nobel Prize in 1912 for this discovery.

Where R = alkyl, alkenyl, alkynyl or aryl group and X = Cl, Br or I

Organomagnesium fluorides are practically Unown.

* Preperation of grignard reagent :-

A Grignard reagent can be prepared in the laboratory by the action of Alkyl or aryl, halide on megnesium metal in the

Presence of dry ether:

$$R-X + Mg \xrightarrow{\text{Dry ether}} RMgX$$

Alkyl halide → Alkyl magnesium halide

for example → $C_2H_5Br + Mg \xrightarrow{\text{Dry ether}} C_2H_5MgBr$

Ethyl bromide → Ethyl magnesium bromide

If an a particular case, formation of grignard reagent does not take place easily addition of one or two drops of Methyl iodide helps in intanning the reaction. (this is called entertainment technique.)

* Reaction with compounds containing active hydroge

An active hydrogen means a hydrogen which is more acidic than the hydrogens in alkanes.)

$$R-MgX + H-A \rightarrow R-H + MgAX$$

compound having active hydrogen

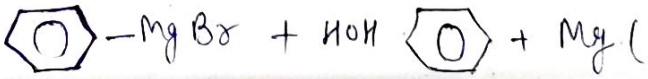
* (1) Some reaction involving the formation of Alkanaes are given below.

$$C_2H_5-MgBr + H_2O \longrightarrow C_2H_6 + Mg(OH)Br$$

(2.) Alkynyl magnesium halide (such as $CH_3-C\equiv C-MgI$ formed in the last reaction can be further used for preperation of higher alkynes by reaction with alkyl halide. for example:

$$CH_3-C\equiv CMgI + C_2H_5I \longrightarrow CH_3-C\equiv C-C_2H_5 + MgI_2$$

(3.) Aryl magnesium halides also undergo similar reactions to form aromatic hydrocarbon.



* ORGANOLITHUM COMPONDS

Organolithium compouns are the most important of organometallic compounds drived form alkali metals. they may be represented by the general formula R-Li where R may be an alkyl or aryl group. Some of the more commonly used organolithicum compounds are:-

CH_3-Li Methyl lithium

C_2H_5-Li Ethyl lithium

$CH_3-CH_2-CH_2-CH_2-Li$ n-Butyl lithium


Phenyl lithium

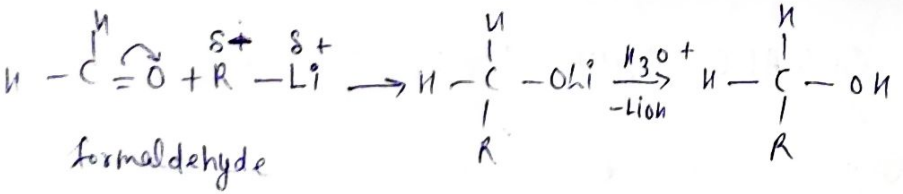
* Chemical properties: Synthetic application

(1.) Reaction with substances containing active hydrogen (formation of hydrocarbon). for example:

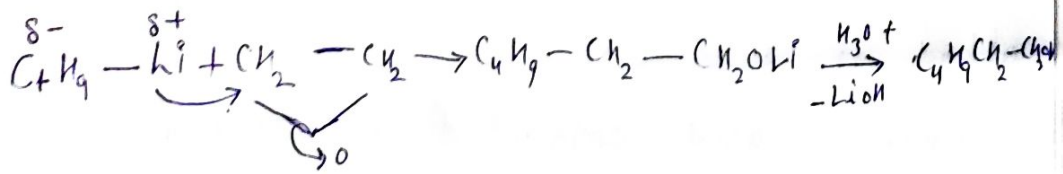
$$R-Li + H_2O \longrightarrow RH + LiOH$$

(2) Reaction with carbony compounds (formation of alcohols). like Grignard reagent organolithium compounds react with carbonyl compounds to form primary, secondary and tertiary alcohols.

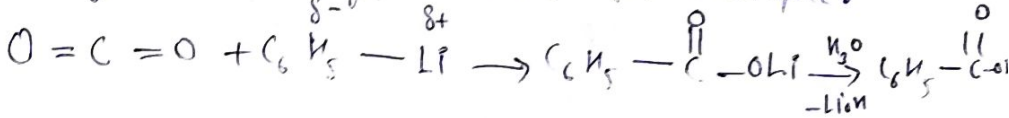
(i) formation of primary alcohols.



(3.) Reaction with epoxides (formation of Primary alcohol alcohols). They react with ethyene epioxide to give primary alcohols. for examlole:



(4.) Reaction with carbon dioxide (formation of carboxylic acids and ketone. Organolithium react with equimolecular proportions of CO_2 to yeild carboxylic acids. for example:



* Organozine compounds

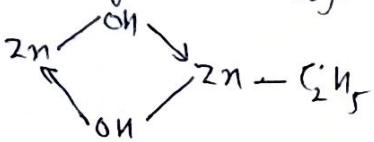
Organozine compounds were the first organometallic compounds to be prepared in the laboratary. they are milder reagent are compared to organolithium compounds or Grignard reagents. Some of the commenly used organozinc compounds are:—

$(CH_3)_2Zn$ Dimethyl zinc

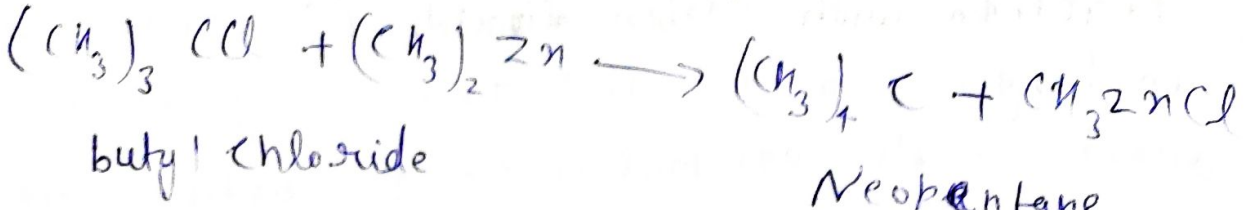
$(C_2H_5)_2Zn$ Diethyl zinc

$(C_6H_5)_2Zn$ Diphenyl zinc

(1.) Reaction with water (formation of hydrocarbons).

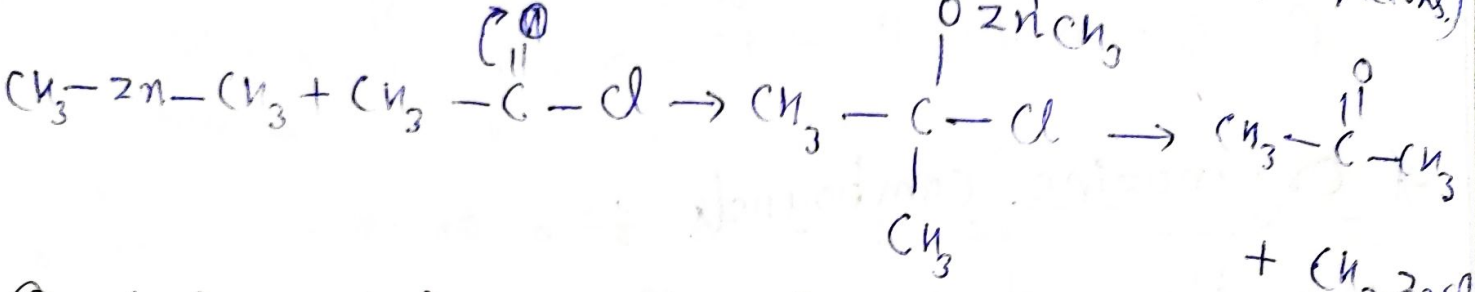


(2) Reaction with alkyl halides (formation of hydrocarbons) Containing carbon atom.) organozinc compounds react with tertiary alkyl halides (not with Primary or Secondary alkyl halides) to form hydrocarbons Containing quaternary carbon atom.



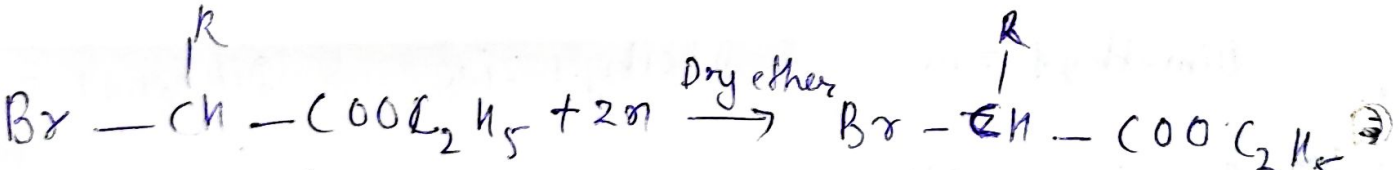
tert-butyl chloride — Neopentane

(3.) Reaction with acid chlorides (formation of ketones)



(4) Reformatsky reaction (formation of β-hydroxyesters)

This reaction consists in treating an aldehyde or a ketone with an α-bromoester and metallic zinc in the presence of dry ether or benzene.



α-Bromoester — organozinc compounds