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BIOMOLECULES

→ Carbohydrates / saccharides / sugars
↳ Poly hydroxy aldehyde or ketone

Classification:

1) On the basis of hydrolysis

→ monosaccharide $\xrightarrow{H_3O^+}$ no rxn

→ oligosaccharides $\xrightarrow{H_3O^+}$ monosaccharides
$n \leq 10$

→ Polysaccharide $\xrightarrow{H_3O^+}$ monosaccharide
$n > 10$.

Monosaccharide : Glucose / Fructose
Oligo : sucrose, maltose, lactose.
Poly : starch, cellulose

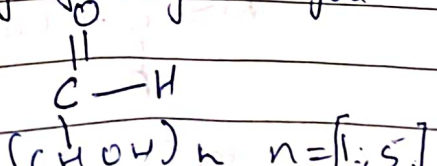
(2) On the basis of reducing nature.

→ Reducing sugar
: which give +ve Tollen's or Fehling test
(Somewhat hemiacetal due to Anomeric hydroxyl group)
↳ All monosaccharides & All disaccharides except sucrose

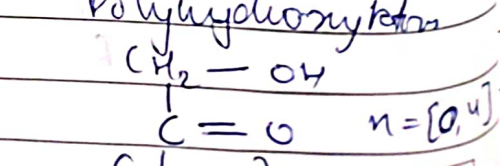
→ Non reducing sugar
Which do not give Tollen's or Fehling
. No anomeric hydroxyl group
Eg Sucrose + Trisaccharide to polysaccharide

MONOSACCHARIDE : Polyhydroxy aldehyde / ketone

Aldose
Poly hydroxy aldehyde



Ketose
Polyhydroxy ketone



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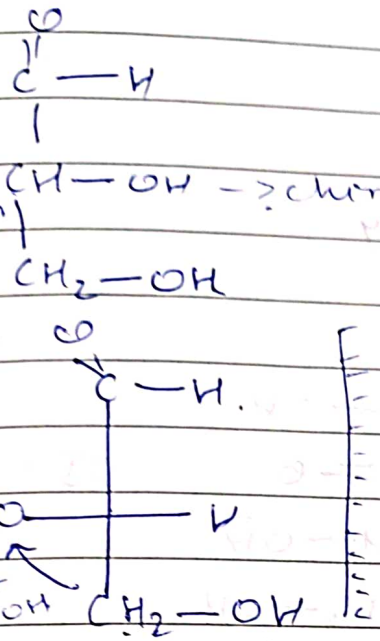
Aldose $n=1$



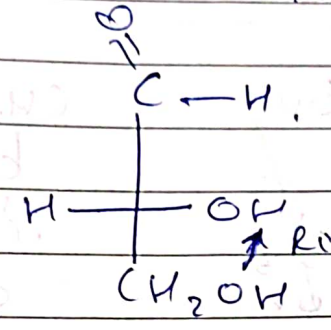
Trialdose, no. of DI $= 2^n = 2$

D L

All aldose are optically active.

L-glyceraldehyde

$\Rightarrow$ (−)



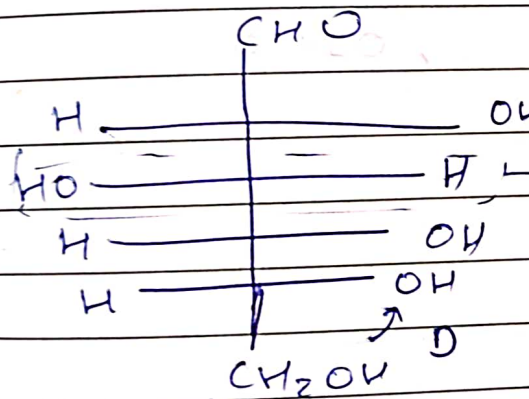
D-glyceraldehyde

(+) → experimentally

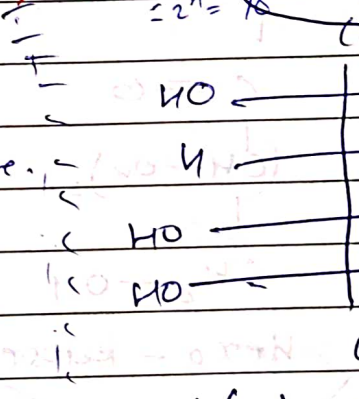
Special tetraldose

Glucose. $n = 4$ $= 2^n =$

D L for tetra aldose

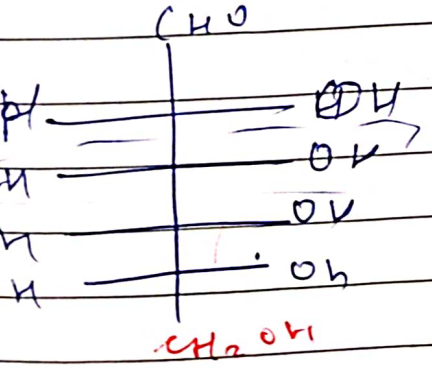


D(+) glucose



L(−) glucose.

theoretically



epimer of glucose w.r.t 3rd carbon

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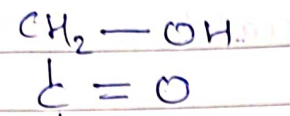
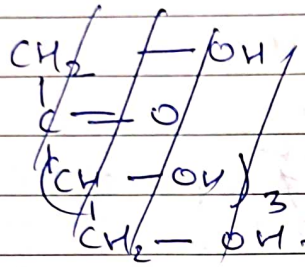
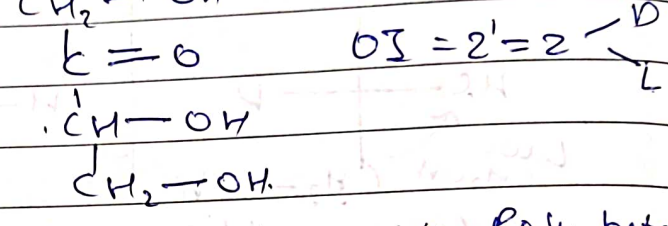
Ketose.



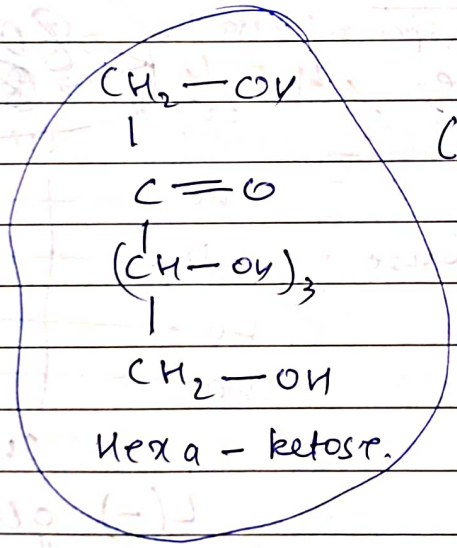
n = 0, 4



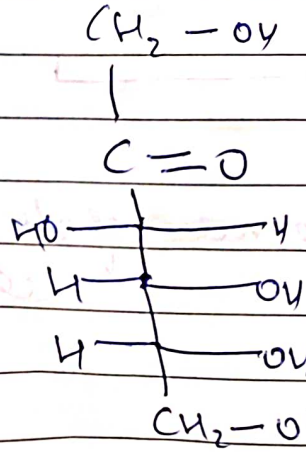


OI = 2' = 2

Tetra ketose to Poly ketose are optically active.



$C_6H_{12}O_6$, OI = 8



D(-) fructose.

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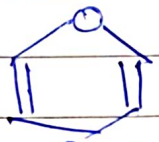
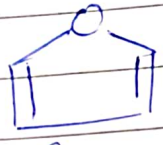
Cyclic structures.

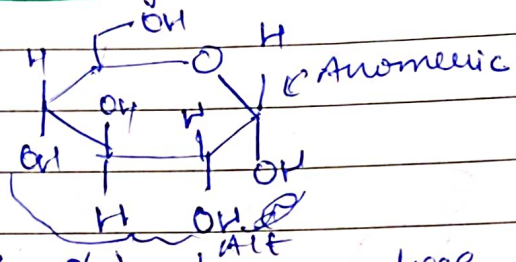


Pyrane



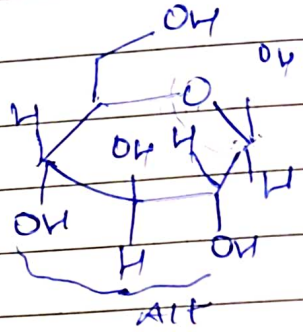
Furane

Glucose cyclic structs:



α D(+) gluco pyralose.

Derived from D

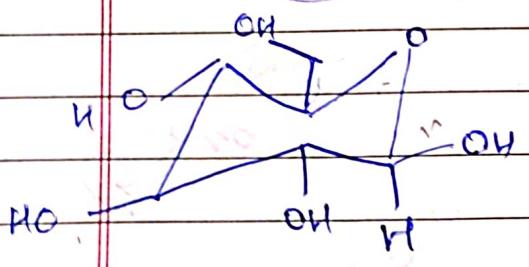


β – D(+) glucopyralos

D series : Anomeric OH down : α.
" " up : β

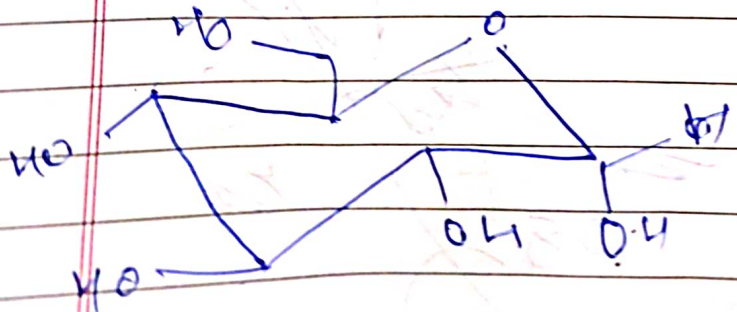
L series : Anomeric OH down : β
" " up : α.

Stability, β > α as in chair form



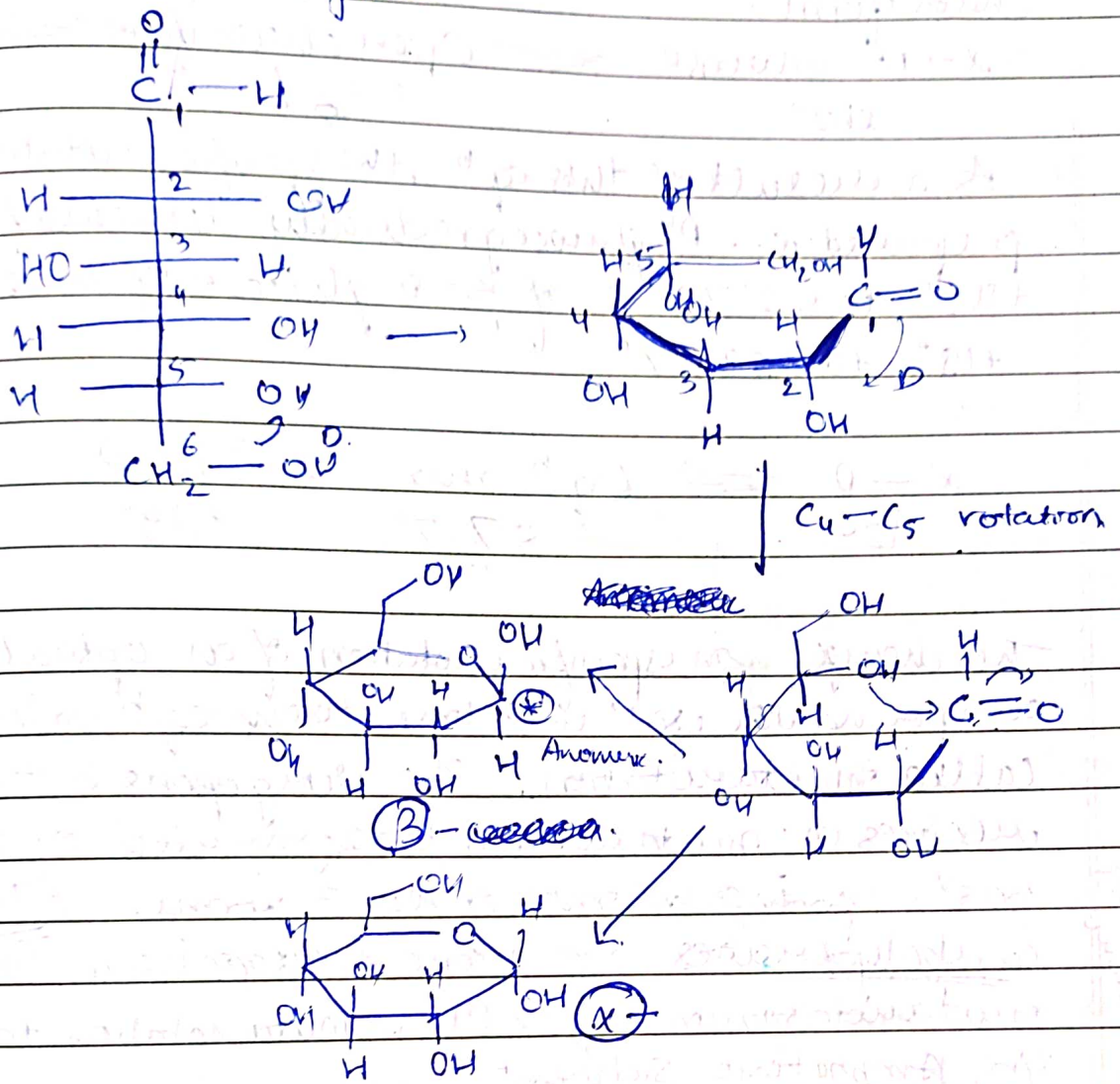
β – D(+) glucopyralose

more stable
as OH on equitorial



α – D+ glucopyralos
less stable
as an OH on axial

Chain ⟶ cyclic



↖ How and projection formulae

Mutarotation

The two stereoisomeric forms of glucose, i.e. α-D-glucose and β-D glucose exist in seperate crystalline forms and thus have different melting points and specific rotations for eg. α-D-glucose has an m.p of 419 K with specific rotation of +112° while β-D-glucose has a m.p of 424 K and has a specific rotation of +19°. However, when either of these two forms is dissolved in water and allowed to stand, it gets converted into an equilibrium mixture of α- and β- forms through through a small amount of the open

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chain form.

α-D-Glucose ⇌ Open chain form ⇌ β-D-Glucose
112° 0.02% 64%

As a result of this eqᵇ, the specific rotation of freshly prepared α-D glucose gradually decreases from +112° to 52.7° & of β-D-glucose increases from +19° to 52.7°

α-D ⇌ eqᵇ mix ⇌ β-D
112° 52.7° +19°

This change in specific rotation of an optically active compound with time to an eqᵇ value is called mutarotation. The ring opens & then recloses in mutarotation to the inverted or original position, giving a mix of α & β forms. All reducing carbohydrates i.e mono & disaccharides undergo mutarotation in aq soln. Mutarotation take place in Amphoteric Solvent.

Q Calculate how much of α & β anomers are present in eqᵇ mix of rotation 52.6
pure α-D: 112.2°, pure β-D: 19°

$x \cdot (112.2^\circ) + (100 - x)\, 18.7^\circ = 52.6 \times 100$

$\therefore x = 36\%$, $100 - x = 64\%$

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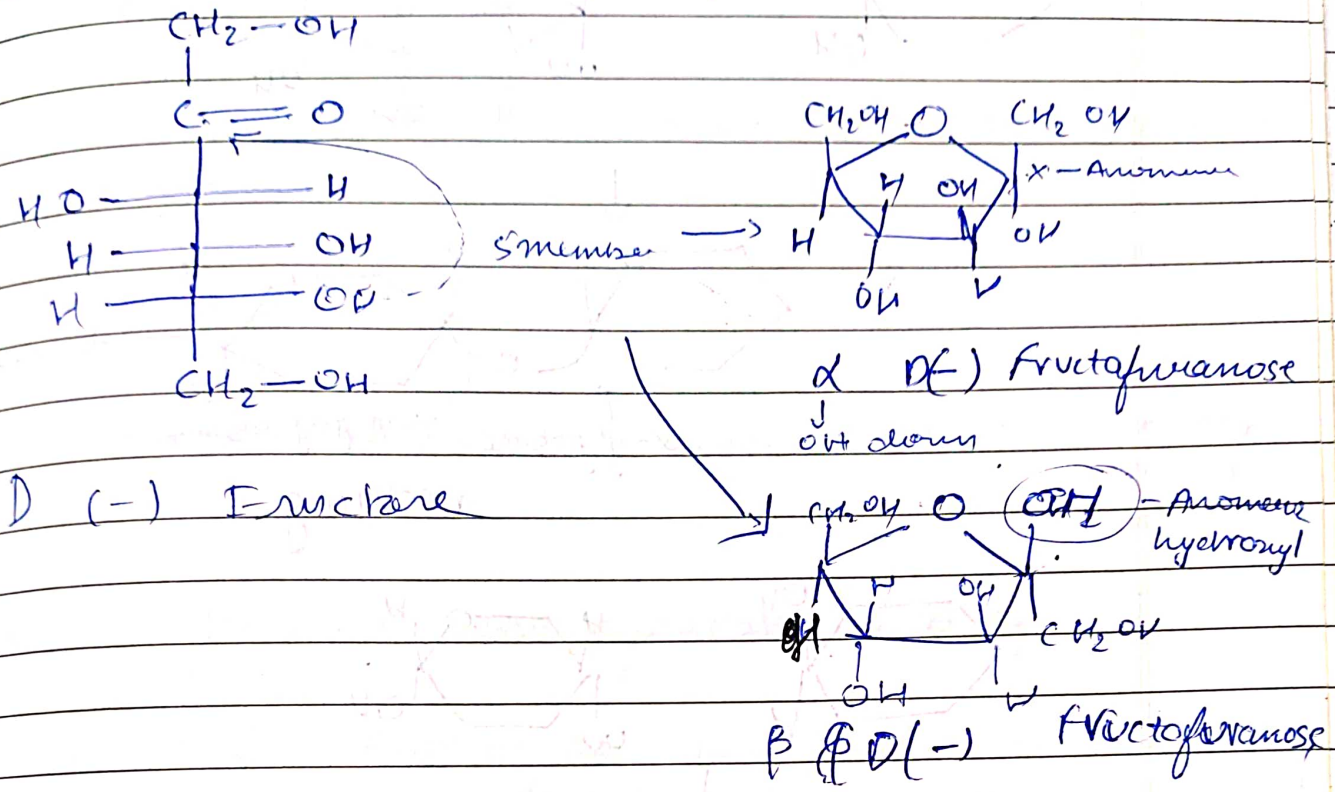
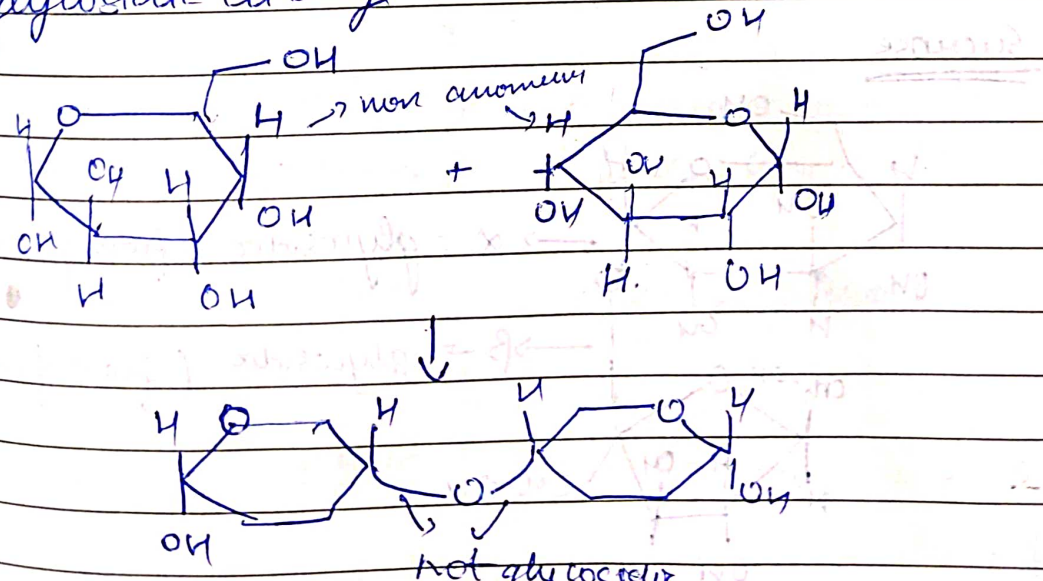
Fructose cyclic structures



Glycosidic linkage

When anomeric hydroxyl group of monosaccharide forms ~~ether~~ linkage by elimination of water, it is called glycosidic linkage



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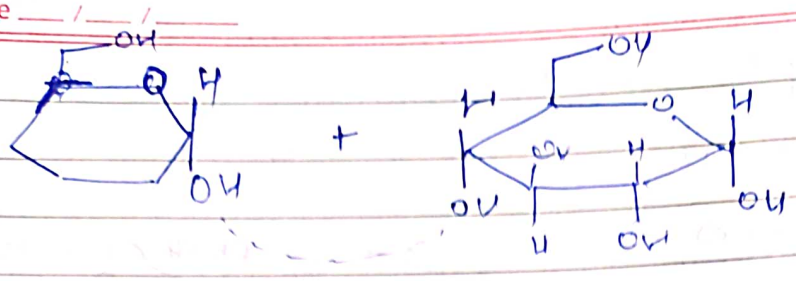
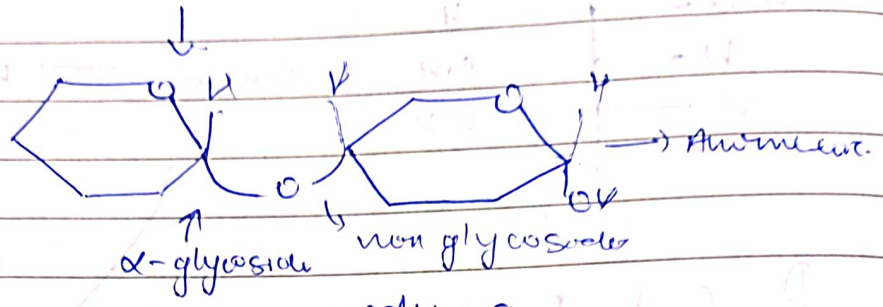
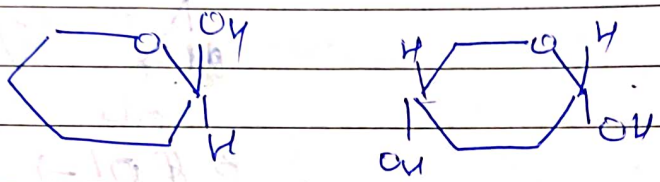
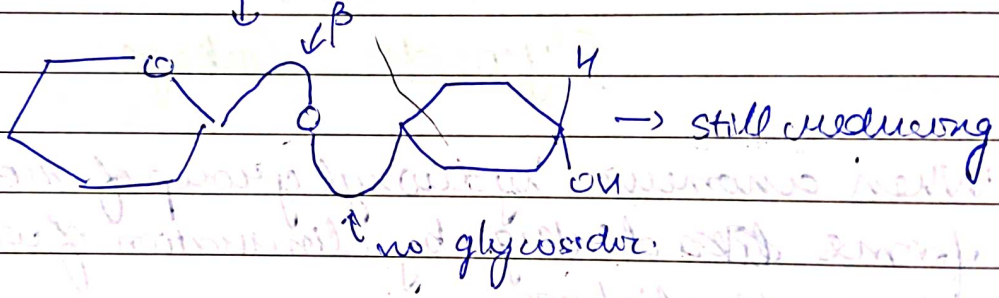


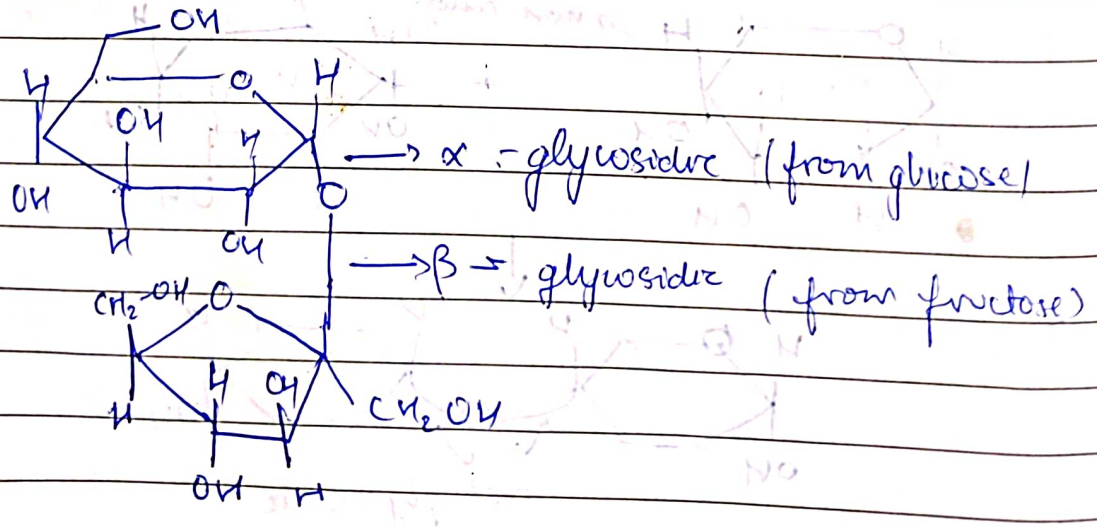


reducing





Sucrose



No anomeric

non reducing

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- Glucose does not form a furanose structure as five membered ring unstable.
- Ribose have furanose & pyranose struct but pyranose more stable
- α, β forms are called anomers.
- All reducing carbohydrates show mutarotation in aq sol^n.
- Fructose does not form pyranose structure
- Sucrose as also known as Cane sugar is crystalline colourless, sweet, & soluble in water
- Glycosidic linkage does not show mutarotation in basic medium.

Hydrolysis

Sucrose $C_{12}H_{22}O_{11}$ $\xrightarrow[\text{or invertase}]{H_3O^+}$ α-D glucose $C_6H_{12}O_6$ + β-D-fructose $C_6H_{12}O_6$

Maltose $C_{12}H_{22}O_{11}$ $\xrightarrow[\text{maltase}]{H_3O^+}$ 2 α-D glucose

Lactose $\xrightarrow{H_3O^+}$ β-D glucose + β-D galactose ($C_6H_{12}O_6$)

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Maltose:

- White crystalline solid soluble in water
- solution is dextrorotatory
- shows mutarotation
- Oxidized by Br_2/H_2O to form D-Maltobionic acid.

Glucose:

- Exists in 2 different crystalline forms α & β
- α- form is obtained by crystallization of conc glucose at 300K, while β-form is obtained from hot saturated aq soln at 371K
- Pentaacetate of glucose does not react with NH_2OH which indicates absence of free aldehyde group.
- Glucose & fructose do not give schiff's test, DNP test & grignard reagent, showing that they have cyclic structure and $NaHSO_3$ also

→ Glucose $\xrightarrow[OH^-]{\text{Tollen's/Fehling}}$ Aldonic acid.

Fructose $\xrightarrow[OH^-]{\text{Tollen's/Fehling}}$ Glucose + Mannose

Mannose $\xrightarrow{\text{Tollen's/Fehling}}$ Aldonic acid.

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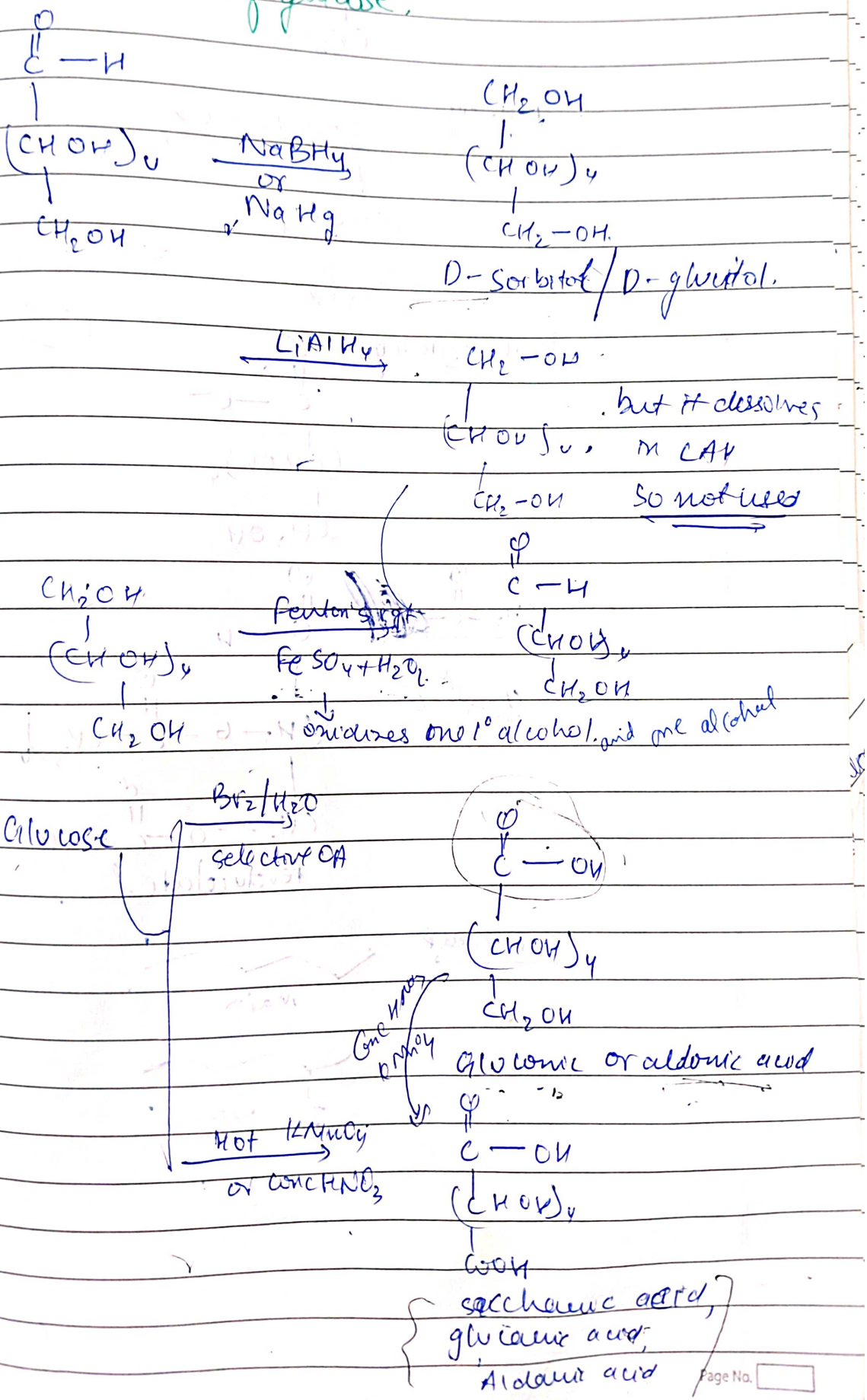
Note from pdf & NCERT

Polysaccharide.

Chemical reaction of glucose.



(B)

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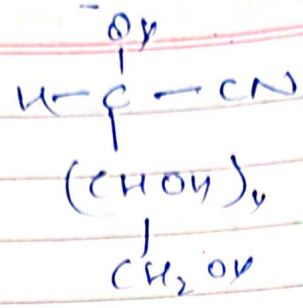
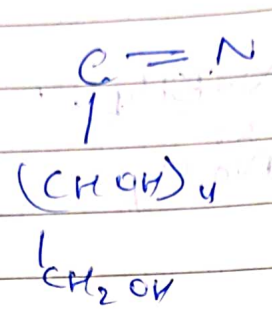
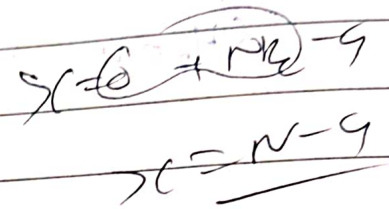
HCN →

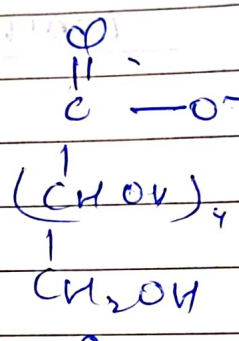


NH_2OH →

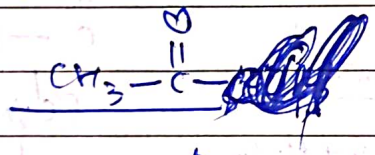


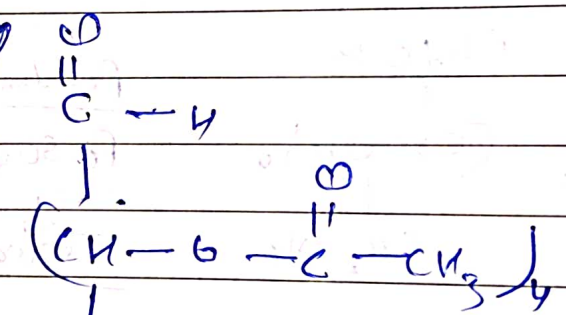


Tollens reagent →



$CH_3-C(=O)-$





Pentaacetate.

HI/red P →

Major

I minor.

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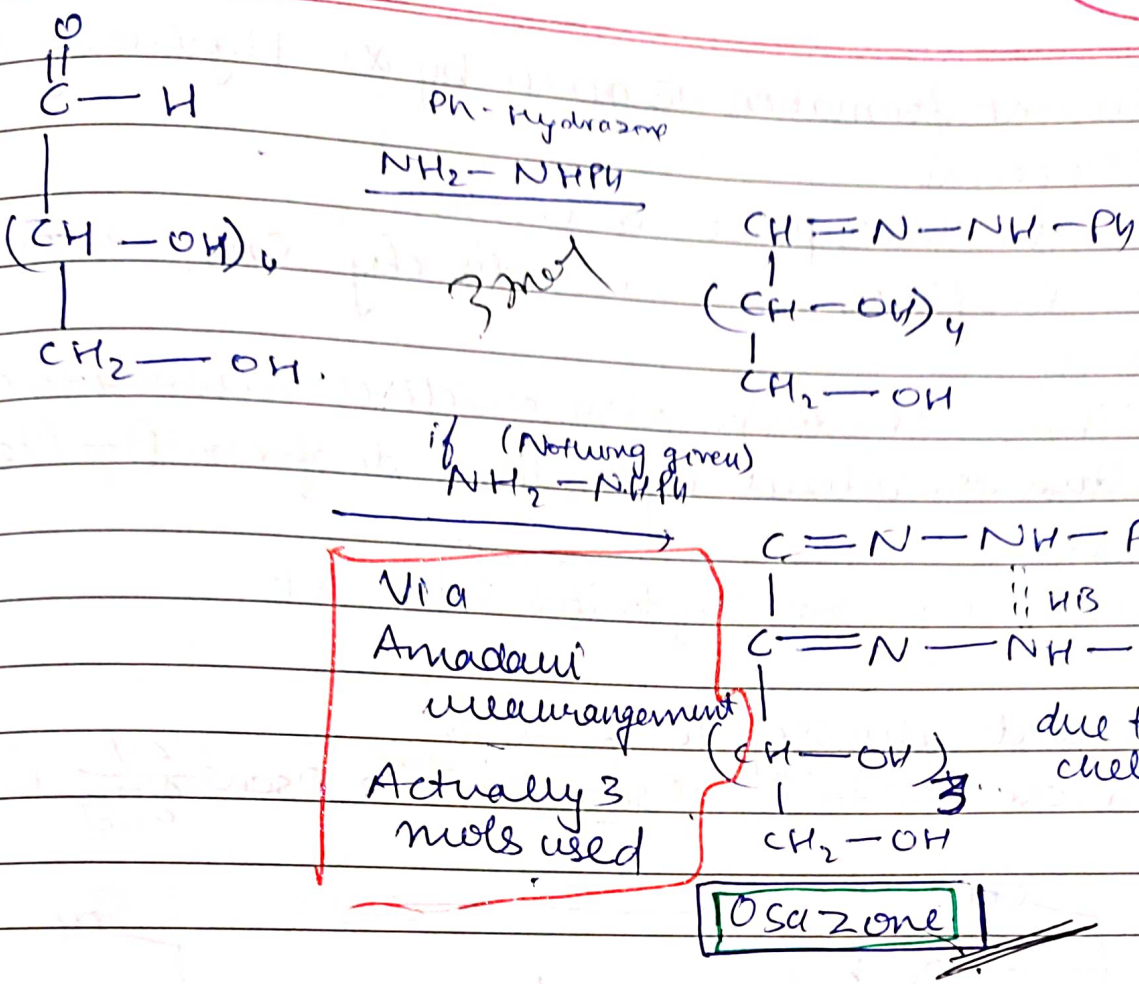
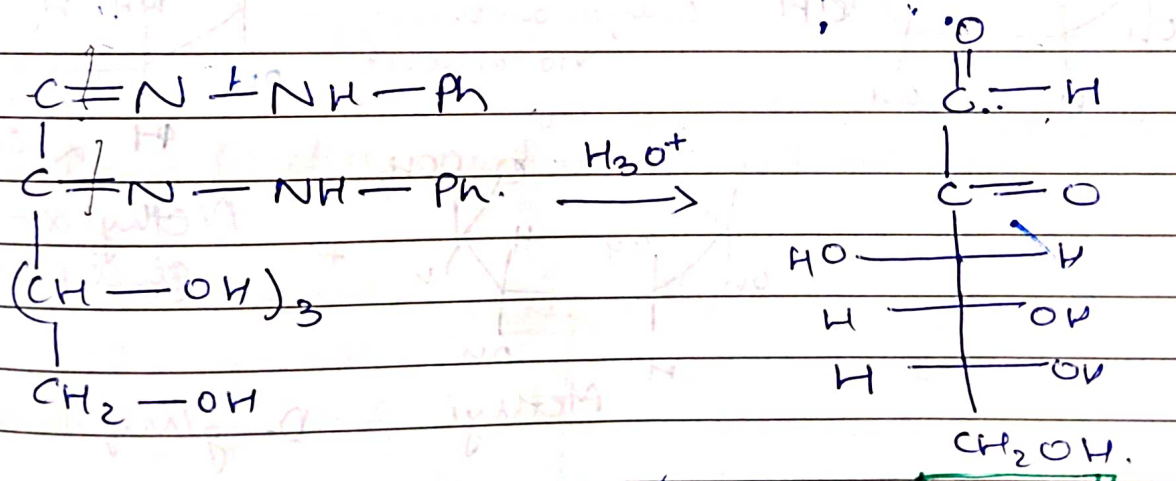
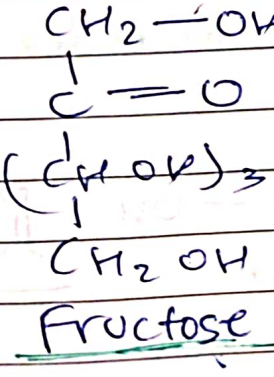


Fructose $\xrightarrow{NH_2-NH_2Ph}$ Osazone.





Fructose

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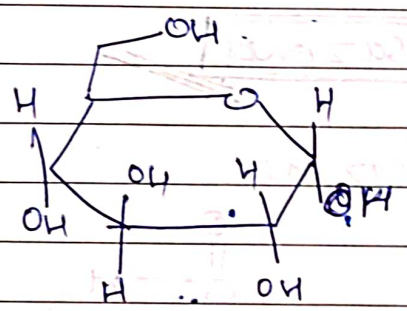
- Osazone formation is given by α-Hydroxy carbonyl compound
- It also takes place in fructose
- In Br_2/H_2O, it is a selectively OA, oxidises aldehyde only
- Fe^{2+}/H_2O_2 (Fenton) also oxidises secondary alcohol
- Maltose is oxidized by Br_2/H_2O to form D-Maltobionic acid.
- Maltose is a white crystalline solid

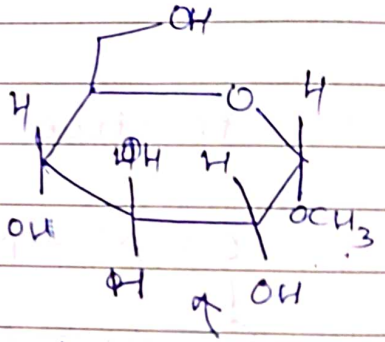
Q Convert glucose to fructose

Glucose $\xrightarrow{NH_2-NHPh}$ Osazone $\xrightarrow{H_2O^+}$ Osone $\xrightarrow[\text{Acetic acid}]{Zn/}$ Fructose



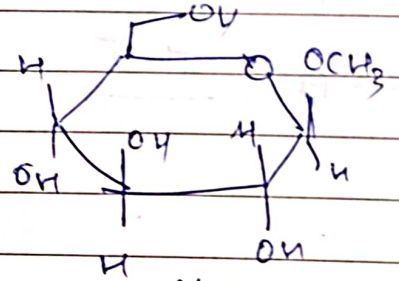
$\xrightarrow{CH_3OH/HCl}$

Only on anomeric via carbocat



Methyl α-D glucopyranoside

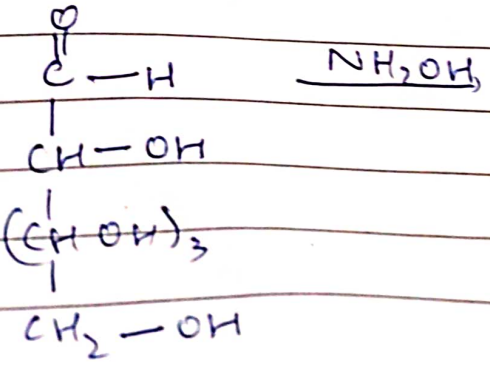
+



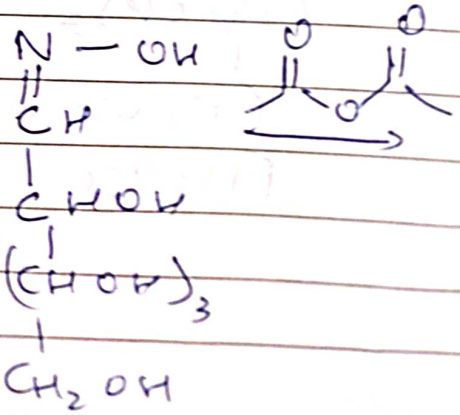
Methyl β-D-glucopyranoside.

Higher aldose to lower aldose

① Wohl method:



$\xrightarrow{NH_2OH}$



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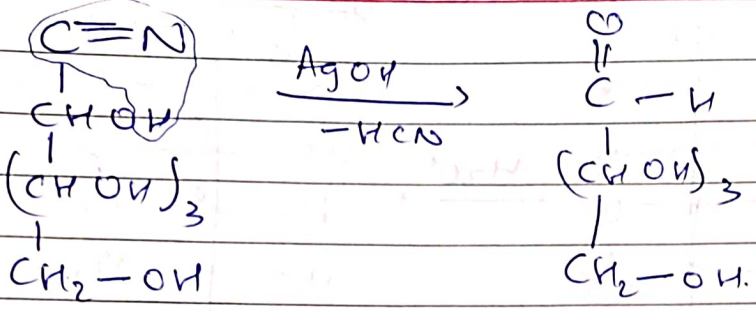
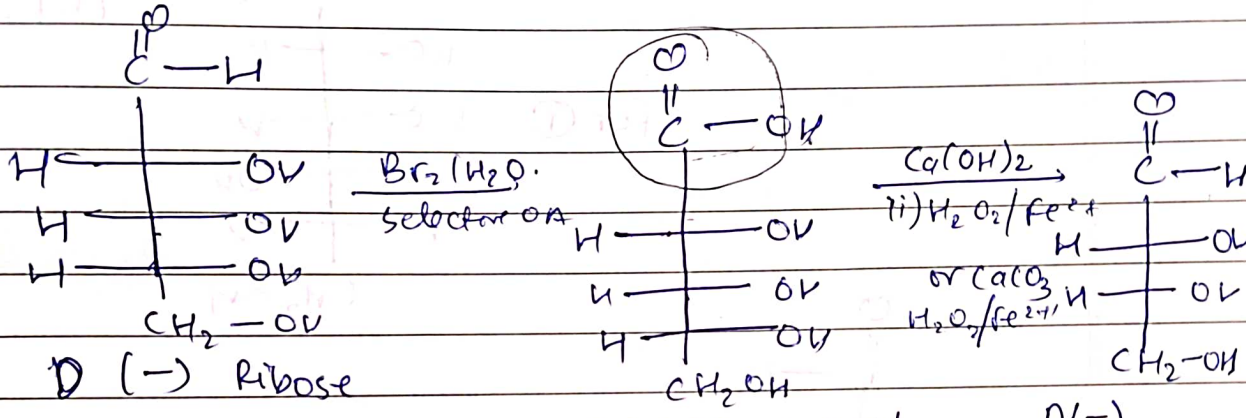
AgOH/Δ

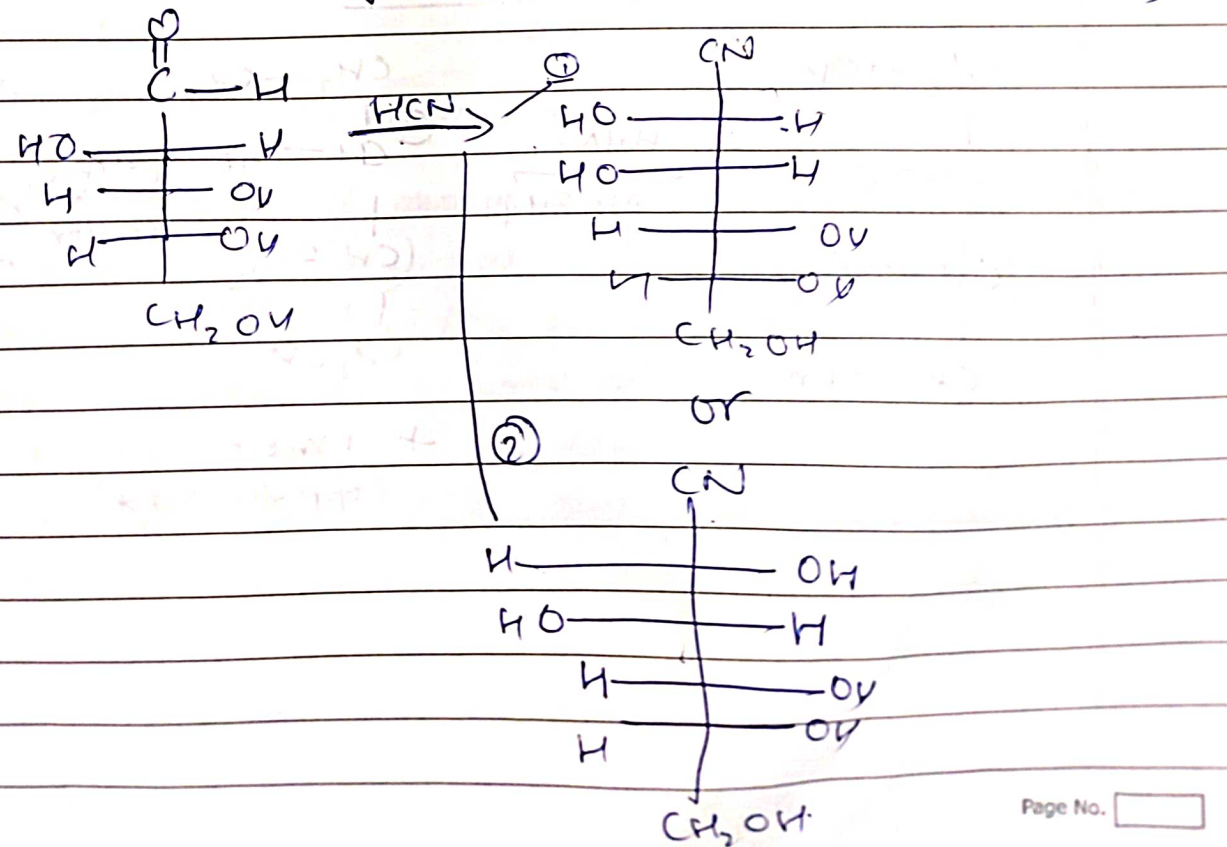


② Ruff degradation !



Lower aldose to higher aldose

① Kiliani - Fischer synthesis ! → ① HCN ② H_3O^+ ③ Δ/$-H_2O$ ④ Reduction (Na−Hg / $NaBH_4$)



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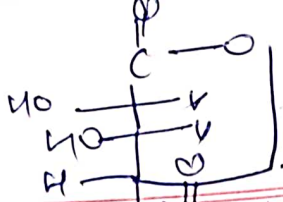
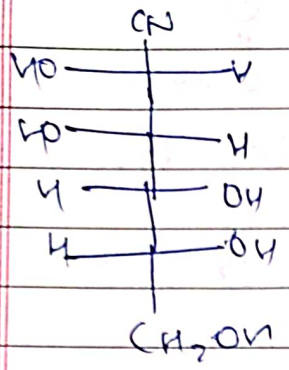
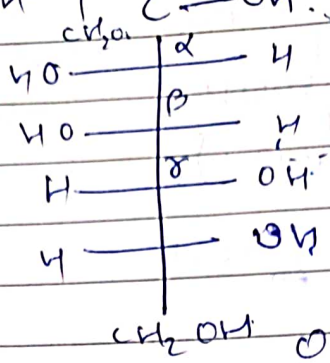
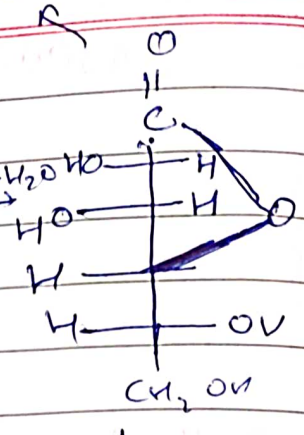
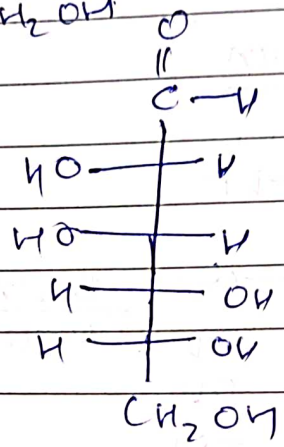


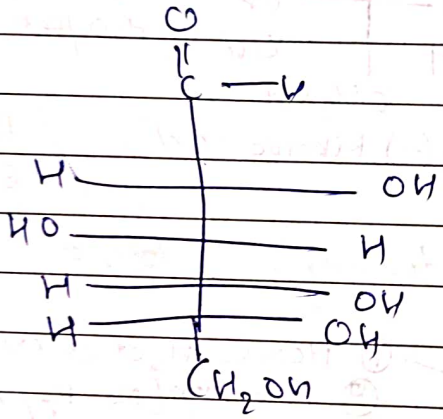




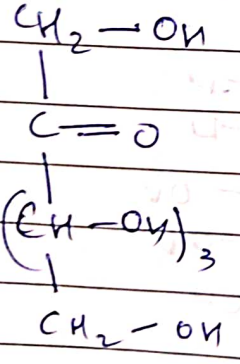


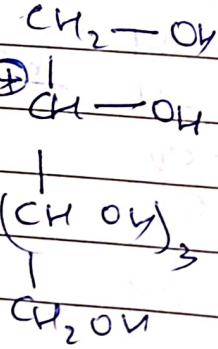
For ①



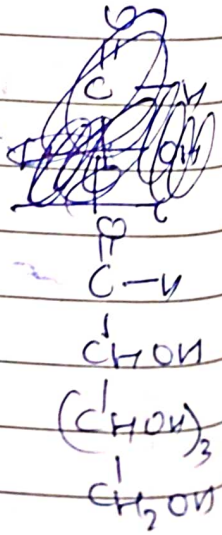


For ②





+ 1 more (epp stereo q*)



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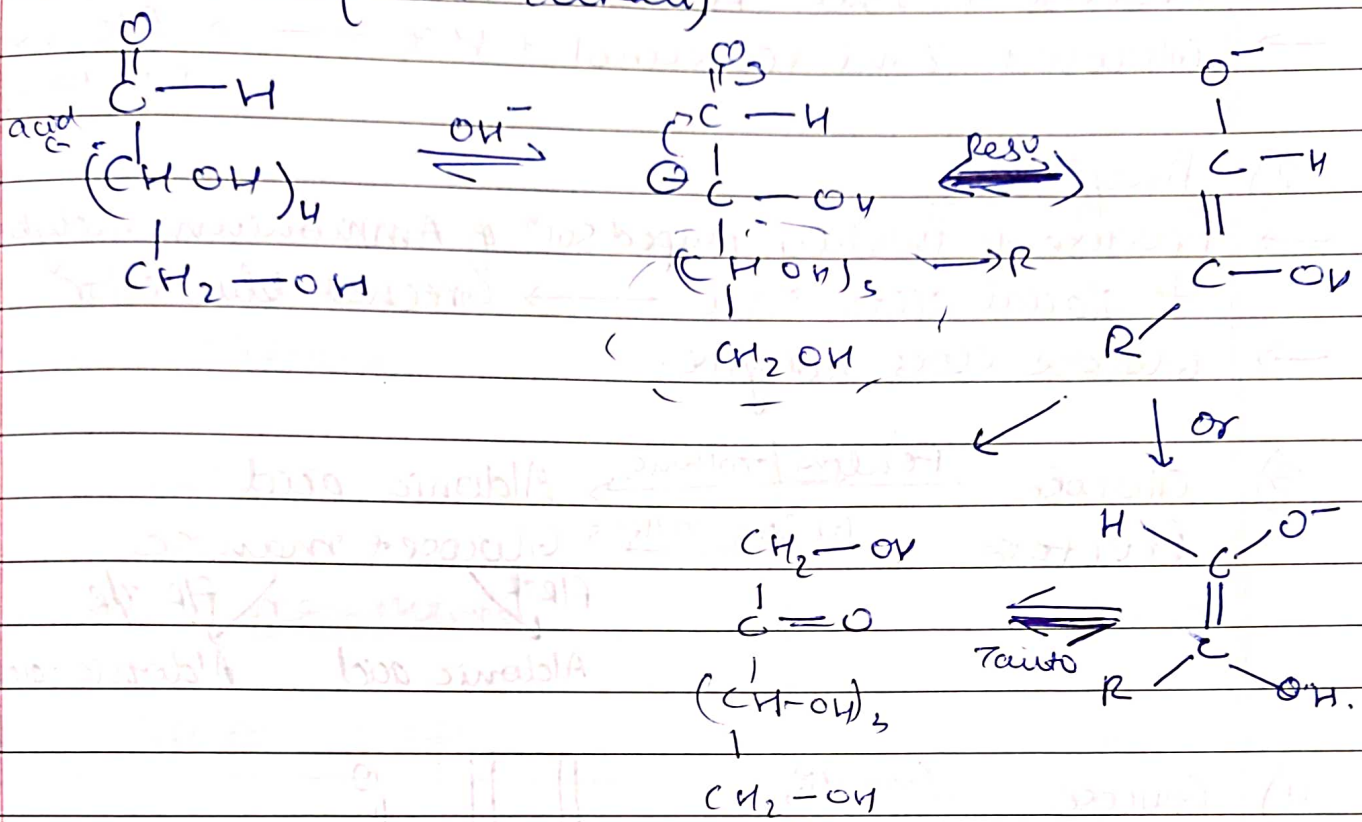
Glucose ⟶ Fructose

(Via alkali)



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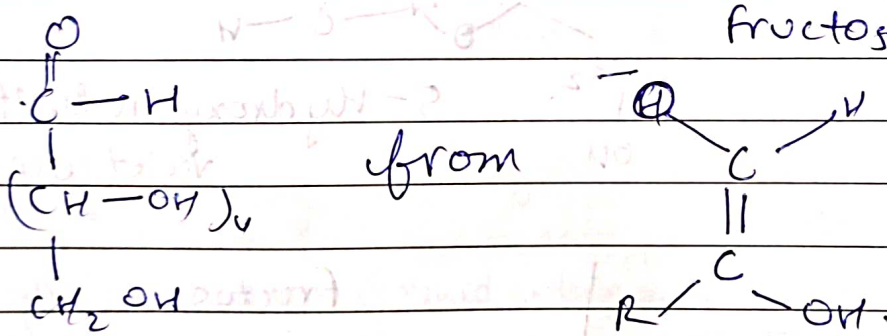


↕ Lobry de Bruyn van Ekenstein (Isomerization)

- Chemical reaction of monosaccharide should not be carried out in basic medium as isomerization takes place
- Aldose $\xrightarrow{\text{alkali}}$ 1 aldose + 1 ketose
- Ketose on treatment with OH^- gives 2 aldose which give Fehling and Tollen's test
- Lobry de Bruyn van Ekenstein rearrangement in formation aldose.

Test for glucose & fructose

1) Silver mirror test

Saathi

Date __/__/____

1) ~~Glucose test~~ Seliwanoff's test

→ Fructose + 2ml Resorcinol + HCl ⟶ Red color

→ Glucose + 2ml resorcinol + HCl ⟶ No rxn. No change

2) ~~Pinoff test~~ Fructose + freshly prepd sol^n of Ammonium molybdate + glacial acetic acid ⟶ Greenish blue color.

→ Glucose does not give.

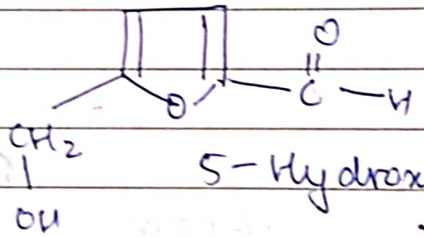
3) Glucose $\xrightarrow{\text{Fehling / Tollens}}$ Aldonic acid

Fructose $\xrightarrow{\text{Fehling / Tollens}}$ Glucose + mannose

Glucose: F/R T/R → Aldonic acid

Mannose: F/R T/R → Aldonic acid

4) Glucose $\xrightarrow{\text{Conc HCl}}$ 5-Hydroxy methyl furanol



Violet color with α-naphthol

Fructose also

	Glucose	Fructose
Melting pt	140°C	102°C
Optical rotation	d (+)	l (−)
Sol^n	Insoluble in C_2H_5OH	Soluble in C_2H_5OH
→	Oxidized with Br_2/H_2O ⟶ gluconic acid	No reaction
Reaction with HNO_3	Saccharic acid	Mixture of Tartaric acid, Trihydroxy glutaric acid, Glycolic acid

Date __/__/____

	Glucose	Fructose
Reaction with $Ca(OH)_2$	Forms calcium glucosate sol^b in H_2O	forms calcium fructose, insol^b in H_2O
Seliwanoff's	No rx^n	Red color
Barfoed	No rx^n	Greenish blue
Ph Hydrazine	Osazone	Osazone
Fehling	Red ppt	Red ppt
Tollen's	Silver mirror	silver mirror
Molisch rgt	Violet ring	Violet ring.

More from NCERT.

Polysaccharides

Polysaccharides are formed when a large no. (100s – 1000s) of monosaccharide molecules join together with the elimination of an H_2O molecule. They can be regarded as condensation polymers in which monosaccharides are joined by glycosidic linkages

Important polysaccharides:

- **Starch:**

Polymer of glucose, G.F: $(C_6H_{10}O_5)_n$, $n \in (200, 1000)$ depending on source.

Chief food reserve material or storage polysaccharide of plants & is found mainly in seeds, roots, tubers, etc

It is not a single compound but is a mixture of 2

Date __/__/____

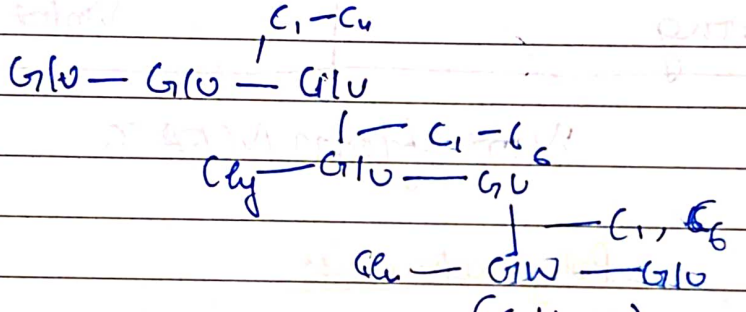
Components :- amylose (10–20%) & amylopecton (80–30%)
Both of them are polymers of α-D-glucose

Amylose is a linear polymer of α-D glucose with 200 glucose units linked by α linkage b/w C_1 & C_4 carbons of 2 glucose units

linear

$$\left[\text{Glucose} - \text{Glucose} - \text{Glucose}\right]_n$$

Amylopecton is a highly branched polymer, containing large no. of short chains containing 20–25 glucose units joined by α- linkage b/w $C_1 - C_4$. In terminal glucose units, C_1 of one terminal is linked to C_6 of another terminal.



$(C_6H_{10}O_5)_n$ $C_{12}H_{22}O_{11}$ $2C_6H_{12}O_6$

Starch $\xrightarrow[\text{enzyme}]{\text{not } H_3O^+/}$ dextrons $\longrightarrow$ maltose $\longrightarrow$ D-glucose

Does not reduce F.R/T.R.

Uses: food, in potatoes, bread, etc. used in coating paper. Production of textile, dextron, glucose, ethanol, starch nitrate (explosive)

$$\text{Starch} \xrightarrow{200-250^\circ C} \text{Dextron} \longrightarrow \text{charring}$$

$$2(C_6H_{10}O_5)_n + n\,H_2O \xrightarrow{\text{Diastase}} n\,C_{12}H_{22}O_{11}$$

Maltose

Starch + I_2 $\longrightarrow$ Blue color, disappears on heating, reappears on cooling

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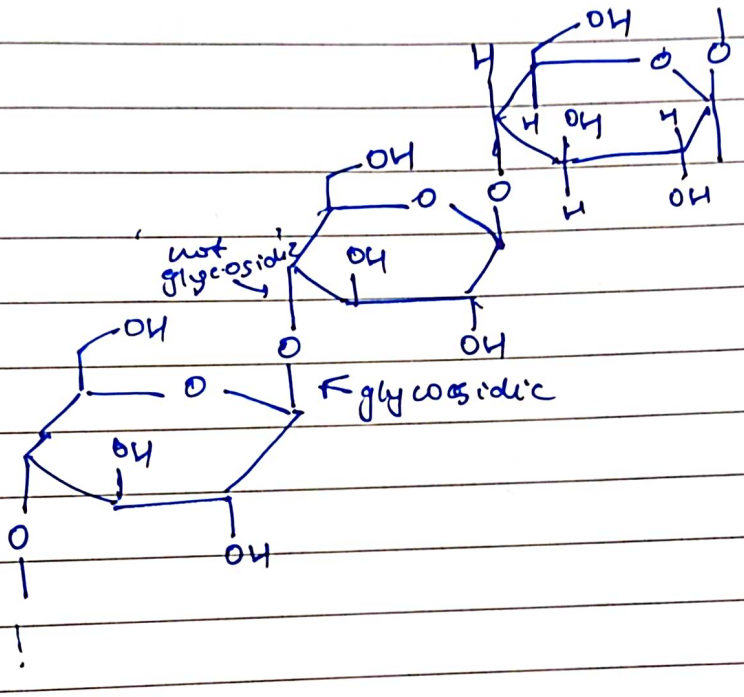
Saathi

Cellulose :

Occurs exclusively in plants, most abundant organic substance in plants. Predominant constituent of cell walls. It is a straight chain polysaccharide composed of β- D glucose units joined by glycosidic linkage b/w C_1 & C_4 of next



Saathi

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AMINO ACIDS

Introduction and Nomenclature

Amino ~~acid~~ acids are molecules, which contain two functional groups, one is carboxylic group and another is amino group. Amino acids are derivatives of carboxylic acids in which one hydrogen is substituted by Amino group.

Amino group may α, β, γ pos^{n} w.r.t carboxylic group.

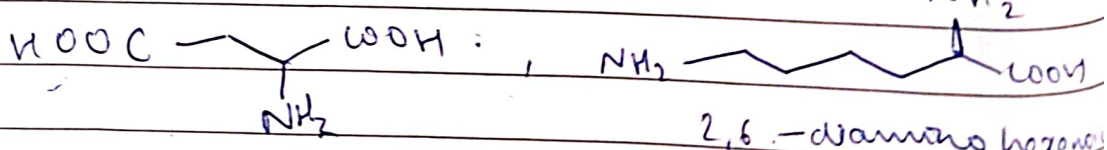
H_2N-CH_2-COOH, α-Amino acetic acid, or Glycine. → only amino acid, optically inactive.

$CH_3-\underset{\underset{NH_2}{|}}{CH}-COOH$, α-Amino propionic acid or Alanine.

$H_2N-CH_2-CH_2-COOH$, β-Amino propionic acid.

$H_2N-CH_2-CH_2-CH_2-COOH$, γ-Amino butyric acid.

Some amino acids contain a second carboxyl group or a potential carboxyl group in the form of carboxamide these are called acidic amino acid, some contain a second basic group which may be an amino group these are called basic amino acids.



2-amino succinic acid.

2,6-diamino hexanoic acid.

Physical properties and struct

(2)

$R-CH(NH_2)-COOH$, if $R=H$, $CH_2(NH_2)-COOH$ glycine. (Saathi)

Date __/__/__

is only α-Amino Acid

which is optically inactive.

$R = CH_3$, $CH_3-CH(NH_2)-COOH$ Analine

In aqueous medium.

$R-CH(\overset{\oplus}{N}H_3)-C(=O)-O^-$, zwitter ion, Dipolar ion

Net electrical charge = zero

There is no migration of amino acid in electric field.

In Acidic medium (like pH = 0)

$R-CH(\overset{\oplus}{N}H_3)-C(=O)-OH$.

(+ve) move towards -ve plate in EF (cathode)

In basic medium (like pH = 14)

$R-CH(NH_2)-C(=O)-O^-$

(-ve) , move towards anode

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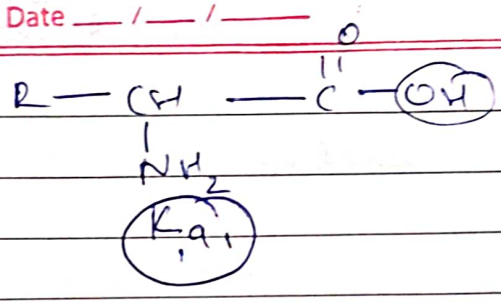
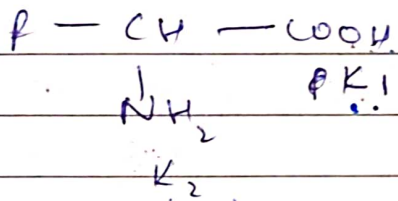


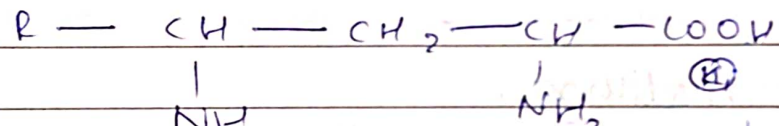
If K_b given, convert to K_2.
These are used in calculations.

Isoelectric point: That pH of the system in which conc of zwitterion is max, or that pH at which there is no migration of zwitterion in the electric field.

Amphoteric ions.



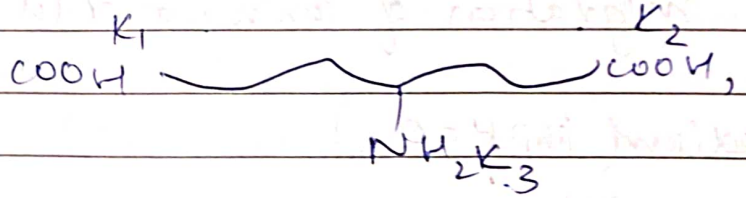
$pH = \frac{pK_1 + pK_2}{2}$



$pH = \frac{pK_2 + pK_3}{2}$

like group are added

$K_2 > K_3$



$pH = \frac{pK_1 + pK_2}{2}$

How?

Start from acidic medium (pH=0) & remove acidic H one by one. When Dipolar ion is first seen, take. $\frac{pK_{after\ DI} + pK_{before\ DI}}{2}$

Eg.

(4) K_1 always more than other

pK_1 pK_2 pK_3 = 1.8, 8.1, 8.10

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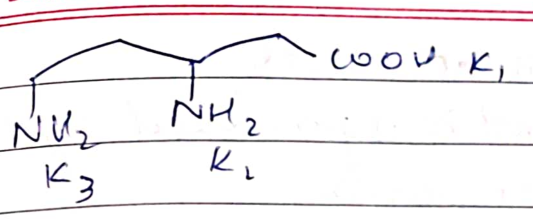


pK_1 pK_2 — cons

$\overset{+}{N}H_2 - CH_2 - CH - COOH$ 1.8

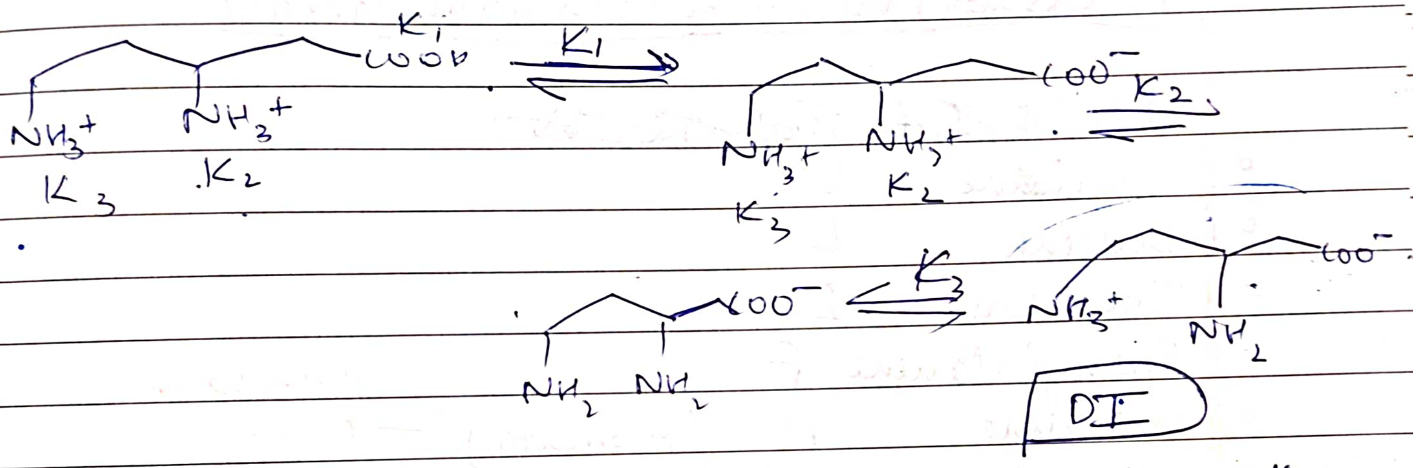
NH_3 10

8

$\frac{8+10}{2} = 9$

$K_2 > K_3$

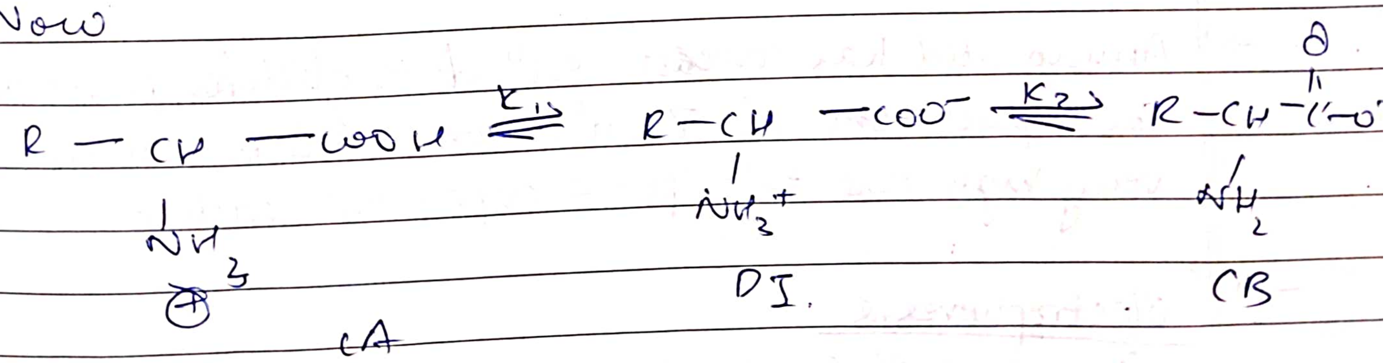
$pH = a$



For DI, $pH = \frac{pK_{after} + pK_{before}}{2} = \frac{pK_2 + pK_3}{2}$

Acidic ⟶ basic always

Now



we have $K_1 = \frac{[DI][H^+]}{[CA]}$, $K_2 = \frac{[CB][H^+]}{[DI]}$

$K_1 K_2 = [H^+]^2 \frac{[CB]}{[CA]}$, at isoelectric pt. $[CB] = [CA]$

$\Rightarrow pH = \frac{pK_1 + pK_2}{2}$

Date __/__/____

There are total 22 α-amino acids

Essential amino acids: Cannot be synthesized by an organism but are required for growth

Non essential: can be synthesized & are required for growth

10 essential amino acids for humans are:

~~(V, L, I, F, Histidine, W)~~

- Valine V
- Leucine L
- Isoleucine I
- Phenylalanine F
- Histidine H (Aromatic)
- Trypto phan W
- Threonine
- Methionine
- Lysine K
- Arginine R

phenylalanine
Tyrosine
Tryptophan
Histidine (non benzenoid)

→ Amino acid has lowest sol^b at isoelectric point as it has highest conc of Zwitter ion, & Lattice energy becomes very high due to dipole – dipole interaction

→ Electrophoresis

Separation of amino acids on the basis of their isoelectric points. A few drops of amino acid mixture are applied on the middle of a filter paper piece.
When it is placed in a buffer sol^n b/w 2 electrodes & applied E.F. If an amino acid with IEP > pH of sol^n will have an overall +ve charge & will migrate towards cathode.

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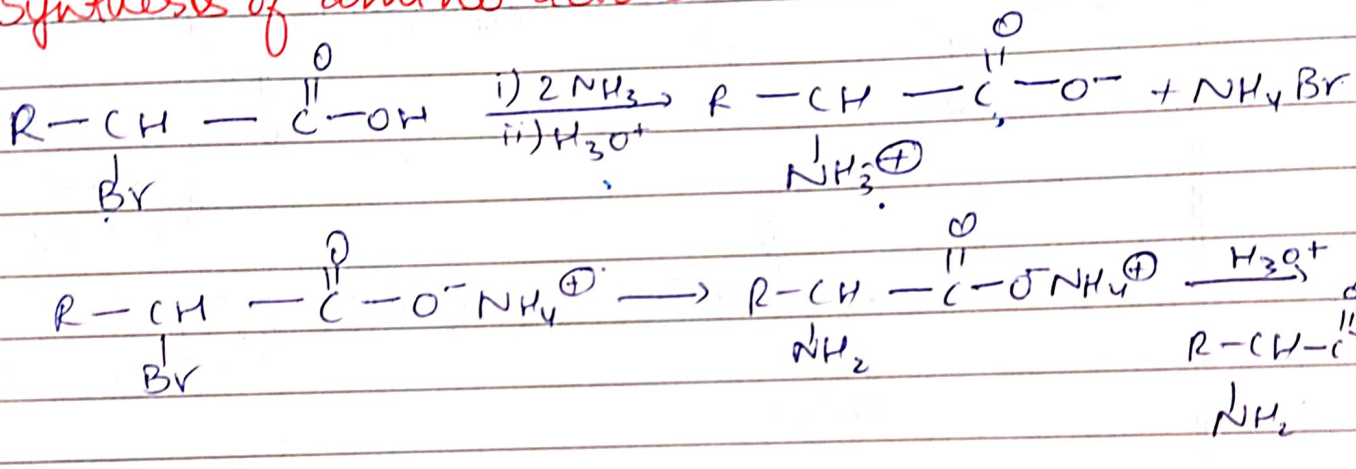
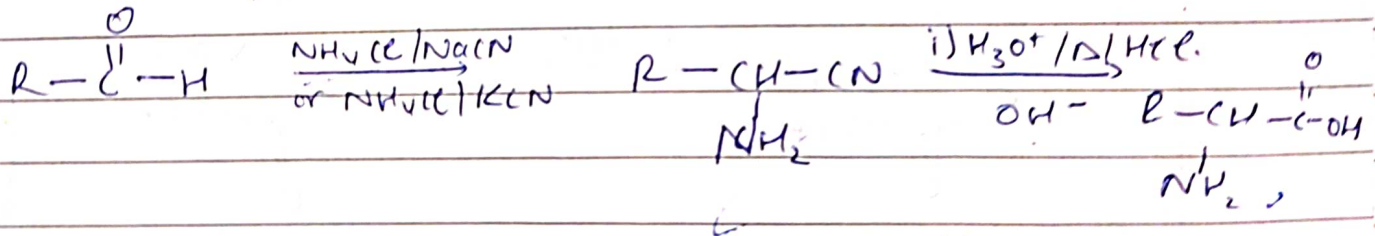
Further ~~to~~ its ~~~~ IEP ~~if~~ from pH of buffer, more ~~is~~ the charge & more migration

An amino acid with IEP < pH of sol^n will have ~~ve~~ -ve charge & will migrate towards anode. If 2 amino acids have equal charge, larger one will move slower during electrophoresis. Like thus, they can be seperated on filter paper

Synthesis of amino acids

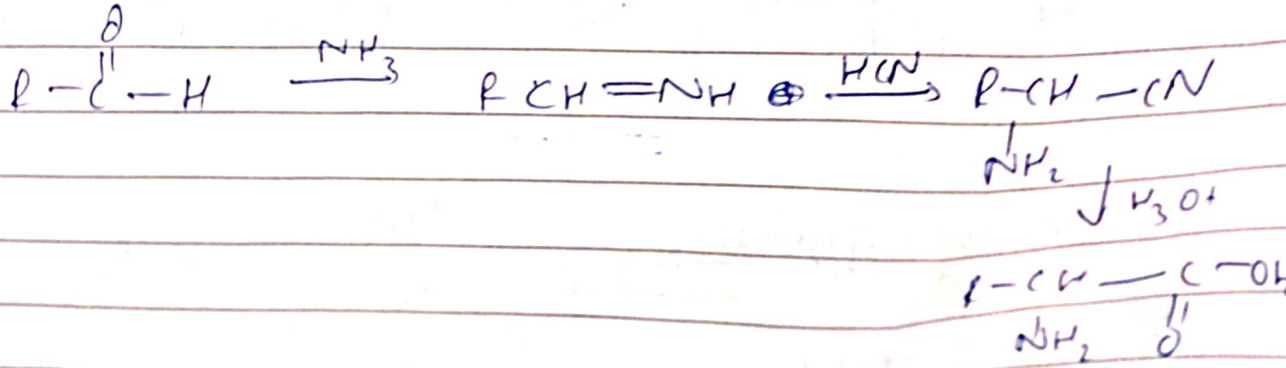


Strecker synthesis



Mech: $NH_4Cl + KCN \longrightarrow NH_4CN + KCl$

$NH_4CN \rightleftharpoons NH_3 + HCN$



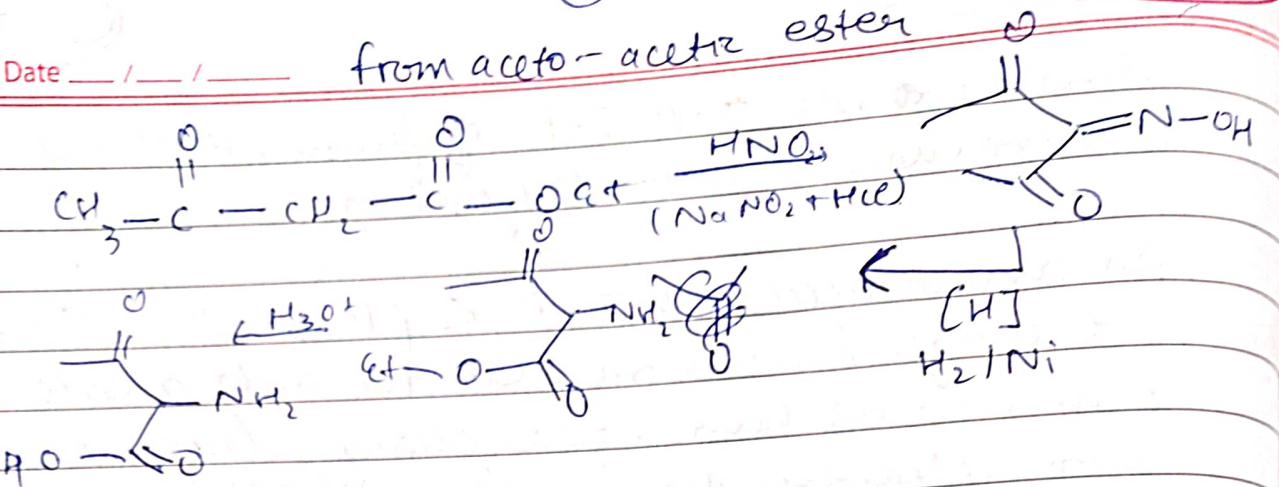
(6) (7)

Saathi

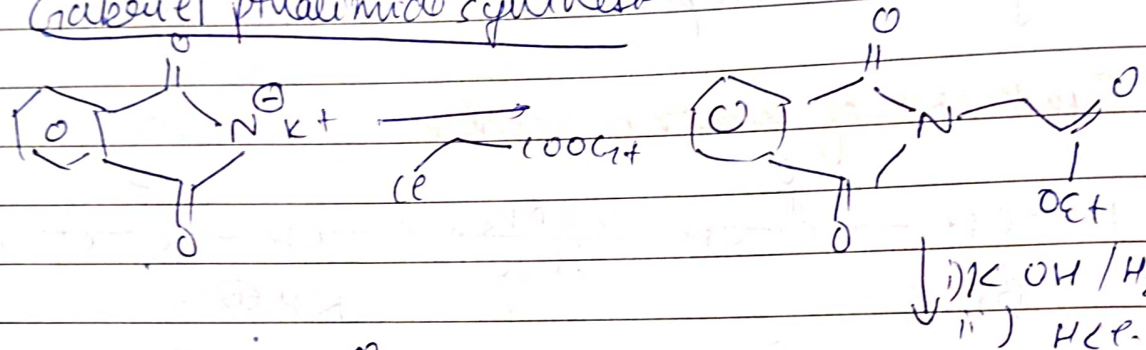
Date ___/___/_____

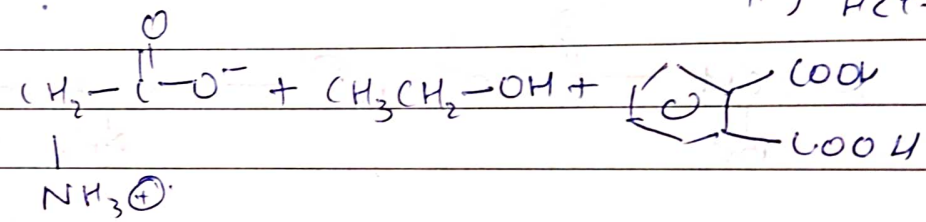
from aceto-acetic ester

(2)

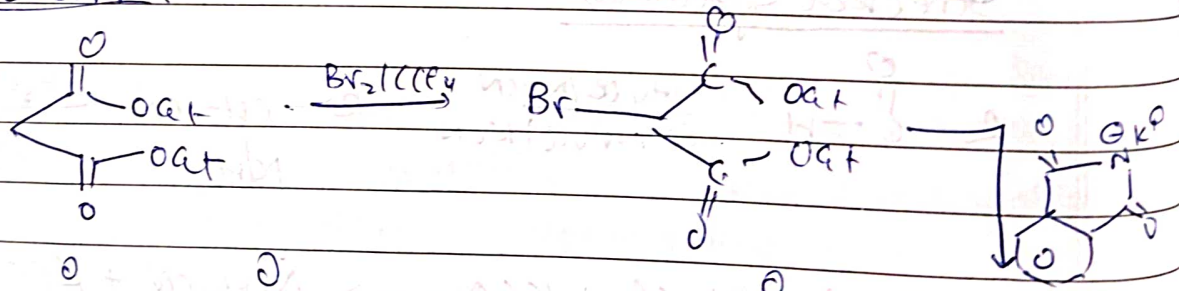


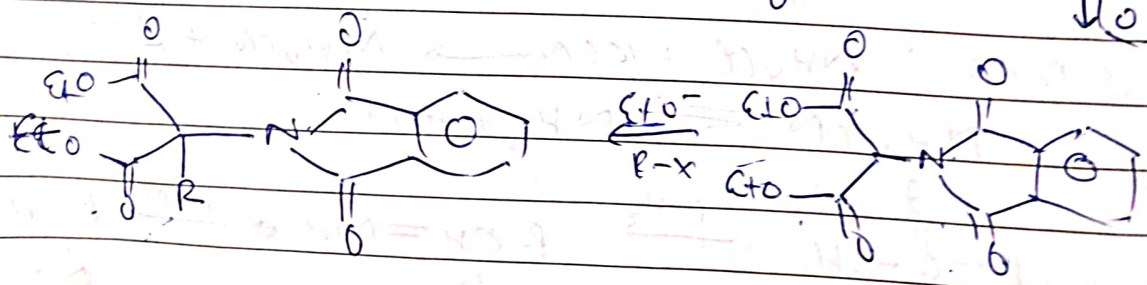
Gabriel phthalimide synthesis



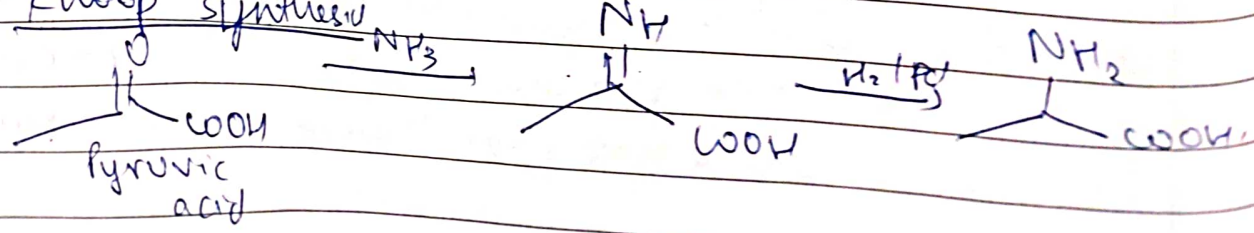


Sorenson





Knoop synthesis



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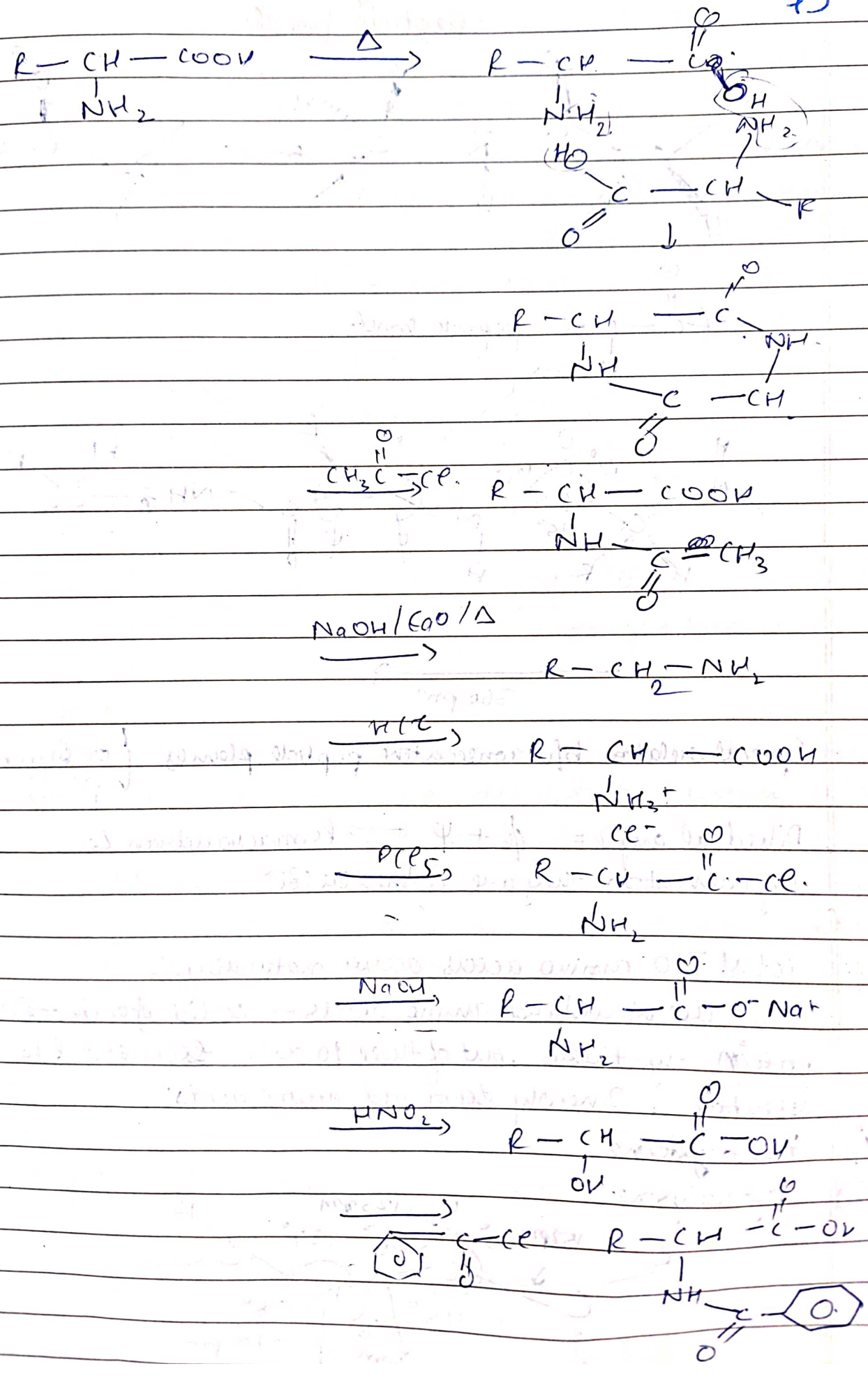
(8) Isoelectric point of glycine

Date __/__/__ Chemical rxn

IP pH = 6

Saathiya



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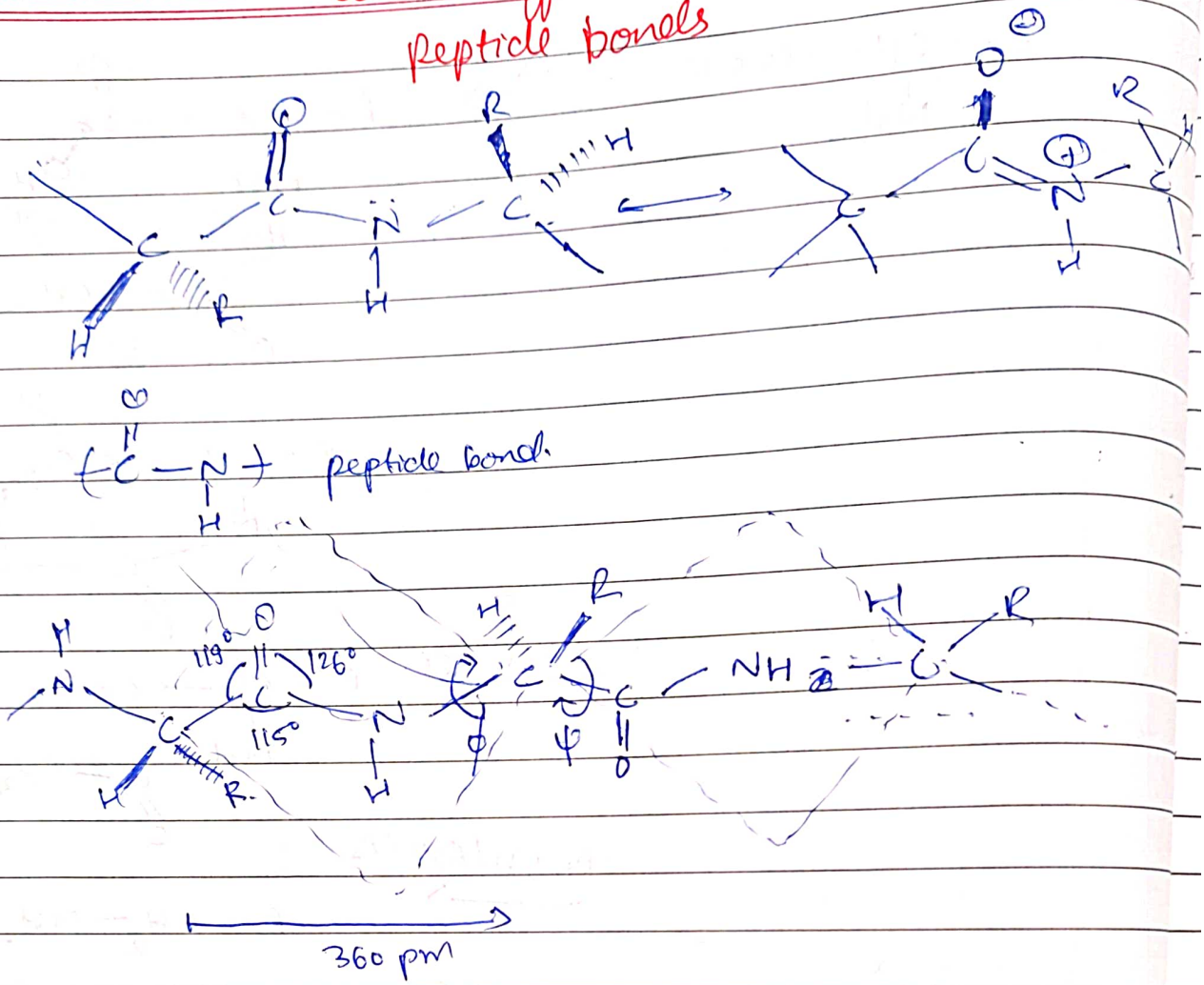
Resonance effect in Peptide bonds

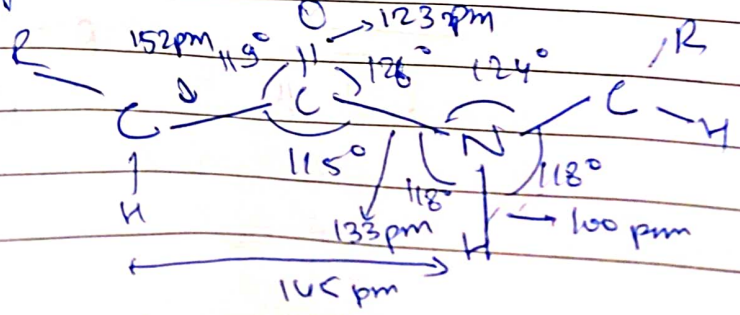


Spacial relation b/w consecutive peptide planes (or Ramachandran plot)

Dihedral angle = $\phi + \psi$ → Ramachandran Gs
By convention, they are defined as 180°

Total 700 amino acids occur naturally
20 are standard amino acids – coded for in DNA for protein synthesis, out of these 10 are essential & 10 non-essential. 2 newly discovered amino acids:

1) Selenocysteine
2) Pyrrolysine



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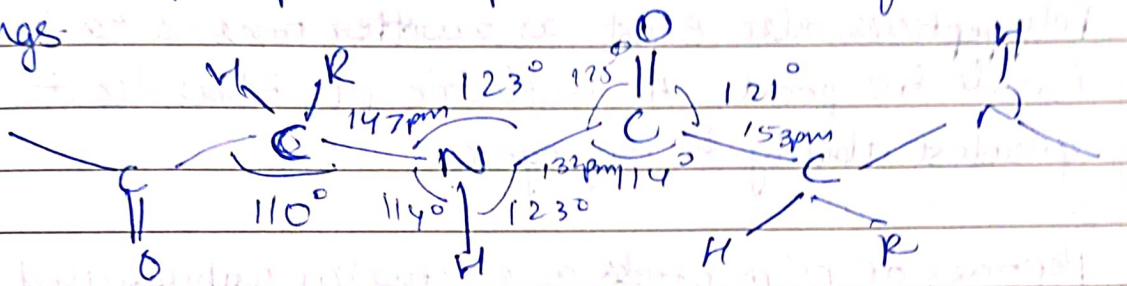
Protein is hydrolysed by heating with 6N HCl for 24 hours at 100°C – 110°C. So all peptide and amide bonds break and a mixture of α-amino acids is obtained. These are separated by ion-exchange column chromatography. One commonly used adsorbent in packing columns is cation exchange resin which is a polymer of styrene and divinyl benzene with $SO_3^-Na^+$ group incorporated on some of the benzene rings.



Partial hydrolysis of protein : using dil acids, endopeptidase or some chemical reagent like cyanogen bromide.

Peptides

By convention, peptide structures are written with N-terminal units (free $-NH_2$ group) on the left and C-terminal unit on the right. In heteropolypeptide, the α-amino acid on extreme left end is called N-terminal amino acid, & on extreme right is called C-terminal acid. Random synthesis of a di-peptide from 2 different α-amino acids can theoretically yield 4 diff dipeptides.

ZMP

No. of possible polypeptides from n-different amino acids is n^m, where m is the total no. of amino acids in the polypeptide (eg dipeptide, $m=2$)

Q Write all dipeptides from Ala (Alanine) & Gly (Glycine)

4: Ala-Ala, Ala-Gly, Gly-Ala, Gly-Gly.

Saathi

Date ___/___/_____

→ Relatively shorter polypeptides containing upto 10 residues are called oligopeptides & longer ones are called polypeptides.

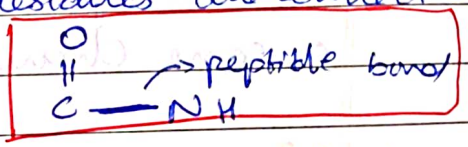
→ Poly peptides are amphoteric

→ Smallest protein contains 100 amino acids & 20 amino acids occur in nature, so total no. of proteins = 20^{100}.

→ 1 letter or 3 letter codes are used to represent polypeptides

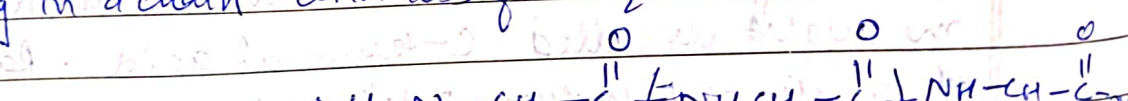
→ Polypeptides also exist as zwitter ions & each has a unique isoelectric point. At isoelectric pt, it has least solubility & greatest ability to aggregate.

Peptides or polypeptides are actually unbranched polymers of α-amino acids containing 2–50 monomeric units. Individual α-amino acids called residues are connected to each other by peptide bonds.

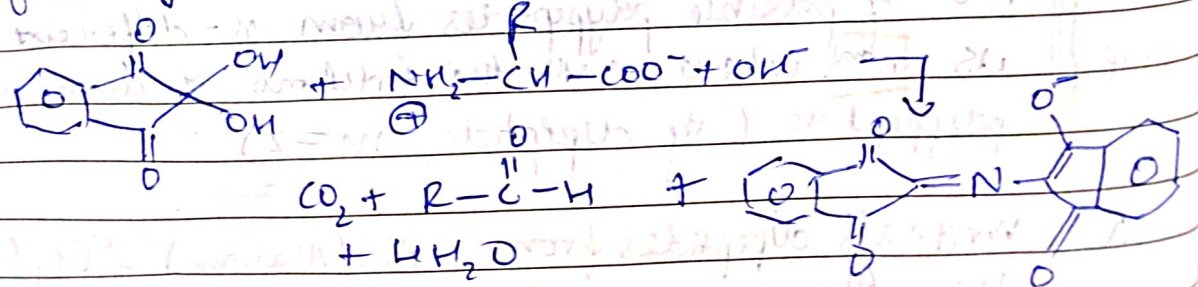


Amide bond in poly-amide of α-aminoacids is called peptide bond

Peptide bonds results from interaction of –COOH group of one α-amino acid with NH_2 of another amino acid resulting in a chain with loss of $1H_2O$.

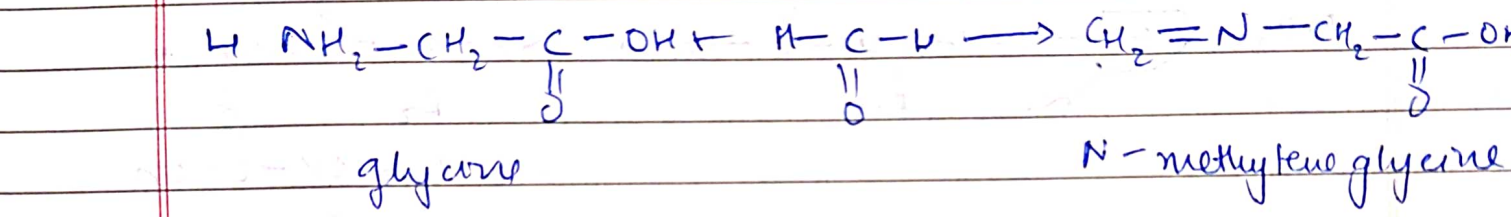


Rx" of ninhydrin with α-Amino acids.



α-Amino acids are colorless compounds but they react with ninhydrin to form a purple compound called Ruhemann's purple. This rxn is useful as a chemical test of α-amino acids

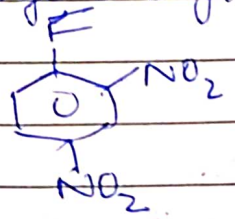
Boling, in which α-amino acid group is 2° gives orange coloured compound
Purple coloured compound gives max light absorption at $\lambda = 570$ nm.



→ To know whether terminal NH_2 is there in a polypeptide chain:

① SANGER'S METHOD.

Sanger's rgt: 1-Fluoro-2,4-dinitrobenzene or F-DNB



It was first used to find which amino acid contained amino end of the polypeptide. Method consists of treating polypeptide with rgt in presence of $NaHCO_3$ soln at room temp to form 2,4 dinitrophenyl derivative of polypeptide

Substituted polypeptide is hydrolysed to the compound A-A & the N= terminal residue, labelled by 2,4-DNP gp is seperated & identified

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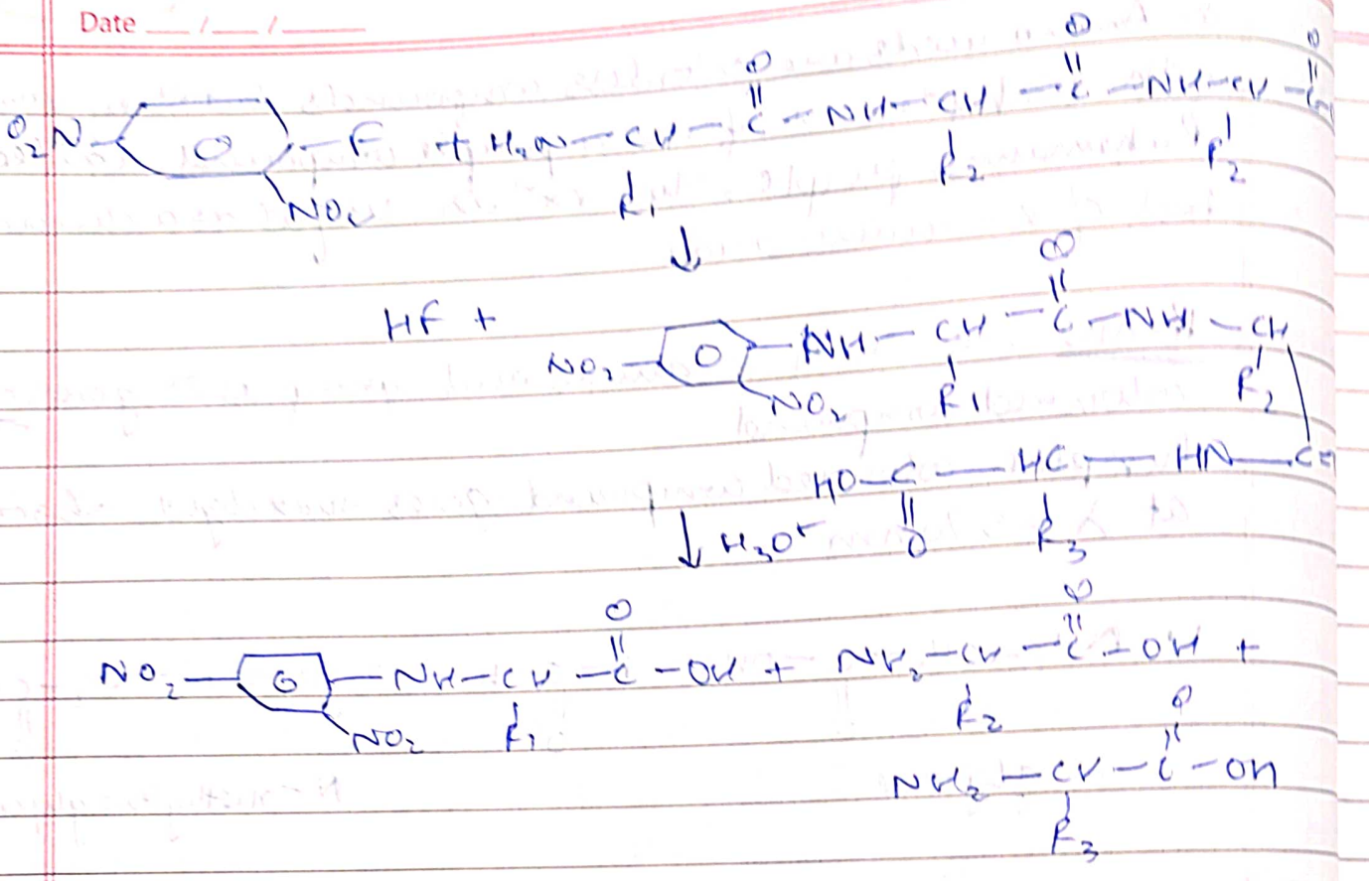
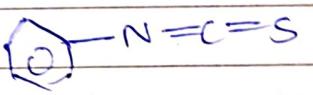


(2) Edman's method

Rgt:



Phenyl isothiocyanide

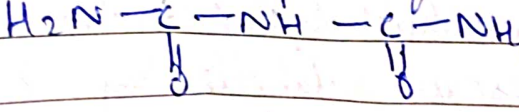
: Test for proteins

1) Ninhydrin test : (Colour rxn of proteins)

Protein when boiled with dil ninhydrin sol^{n}, a purple colour is formed / or with pyridine + ninhydrin, deep blue → violet color

2) Biuret test (color rxn)

Biuret is the compound formed by heating urea



When biuret is heated with dil $CuSO_4$ sol^{n} in alkaline med a purple colour is obtained

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This is the basics of Biuret test of proteins containing atleast 2 peptide bonds.

When a protein is treated with aq NaOH sol^n & few drops of $CuSO_4$ sol^n (dil) ; a violet color is developed.

(3) Xanthoproteic test

Protein + conc HNO_3 ⟶ Yellow color $\xrightarrow{NH_4OH}$ Orange color.

↓

Xanthoproteic acid

Test is +ve only when protein molecule contains an amino acid residue having benzene ring like phenyl alanine, hyrosine, tryptophan.

(4) Millon Test

Millon regt is a sol^n of mercuric nitrate in nitric acid & nitrous acid. or in nitric acid.

Protein + Millon reagent ⟶ Red coloured ppt

Initially white, then heated ⟶ red color

(5) Hopkin's - cole test.

When a mixture containing protein & glyoxalic acid is treated with conc HNO_3, a violet ring is formed at the junction of 2 layers

Amino acid tryptophan present in protein is responsible for this test

If protein does not have tryptophan ⟶ -ve test

(6) Nitroprusside test

Ninhydron + amino acid ⟶ violet color

(7) Molisch test (similar to furfural test)

Protein + α-napthol alcohol + conc HNO_3 → violet ring

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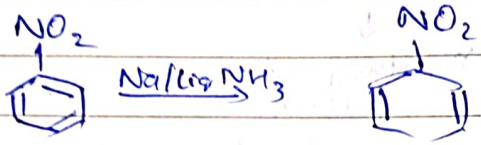
Nitrating agent for aromatic compounds:
N_2O_5, $C_2H_5ONO_2$, $NO_2CF_3SO_3$

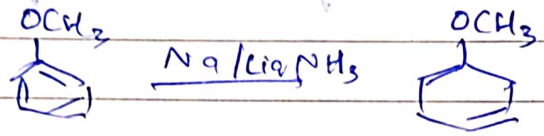
Cine substitution: In aromatic substn, new group takes adjacent to initial group

Birch reduction of aromatic compounds:

1) With EWG:



2) With EDG



POC

Detection of elements:
We need to detect C, H, O, N, S, & X.
No direct test for Oxygen,
For N, S, X, sodium fusion test is necessary.

→ **LASSAIGNE'S TEST (Sod. fusion test)**
To detect nitrogen, sulphur & halogens in organic comp it is necessary to convert them to ionisable inorganic substances so that ionic tests of inorganic analysis may be applied. To do this, compound is fused with metallic Sod (Lassaigne's test).
This produces Sodium cyanide, sulphide, halide. which can be detected easily.

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• If N, S both present then $Na + C + N + S \longrightarrow NaSCN$ thiocyanate

$Fe^{3+} + SCN^- \longrightarrow [Fe(SCN)]^{2+}$: Blood red

If fusion on excess sodium, then normal

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→ Test for nitrogen.

Cyanide ion & hence nitrogen in it (necessarily connected to carbon) may be detected by Prussian Blue Test

→1) $FeSO_4 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + Na_2SO_4$

Ferrous iron (II) ions are produced by ctr & are dissolved & removed using dil H_2SO_4.

→2) $3Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3 \longrightarrow \underbrace{Fe_4[Fe(CN)_6]_3}_{\text{Prussian blue}} + 6Na_2SO_4$

Prussian blue color confirms nitrogen.

→ Test for sulphur

Sulphur in the form of sulphide detected by:

1) To filtered fused sol^n, add dil CH_3COOH → $(CH_3COO)_2Pb$ → black indicates sulphur

2) To the solution, 2-3 drops of freshly prepared sol^n of disodium pentacyanonitrosyl ferrate: $Na_2[Fe(CN)_5NO]$ is added → $Na_4[Fe(CN)_5NOS]$ (purple)

(S^{2-} confirmed)

Na_2S fully added

Purple indicates sulphur, color fades on standing

→ Test for halogen (If N & S absent)

Fusion $\xrightarrow{\text{dil } HNO_3}$ $\xrightarrow{Ex\ AgNO_3}$ ppt indicates halogen.

ppt $\xrightarrow{Ag\,NH_3}$ ppt 2 : white & sol^b : Cl

: pale yellow & difficultly sol^b : Br

: yellow, insoluble : I.

Confirm Br, I

Fusion $\xrightarrow{\text{dil } H_2SO_4}$ $\xrightarrow[\text{vigorous shaking}]{Cl_2 \text{ water}}$

Purple then fades : I

Brown / red : Br

Colourless : none.

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→ Test for halogen, (N/S present)

for the previous test, N, S interfere by forming sulphide cyanide or sulphide. If N,S present, interfering ions must be removed by heating with conc HNO_3

Fusion $\xrightarrow{\text{Conc } HNO_3,\ \text{evap}}$ half orginal vol to expel HCN or H_2S. It decomposes NaCN or Na_2S

or

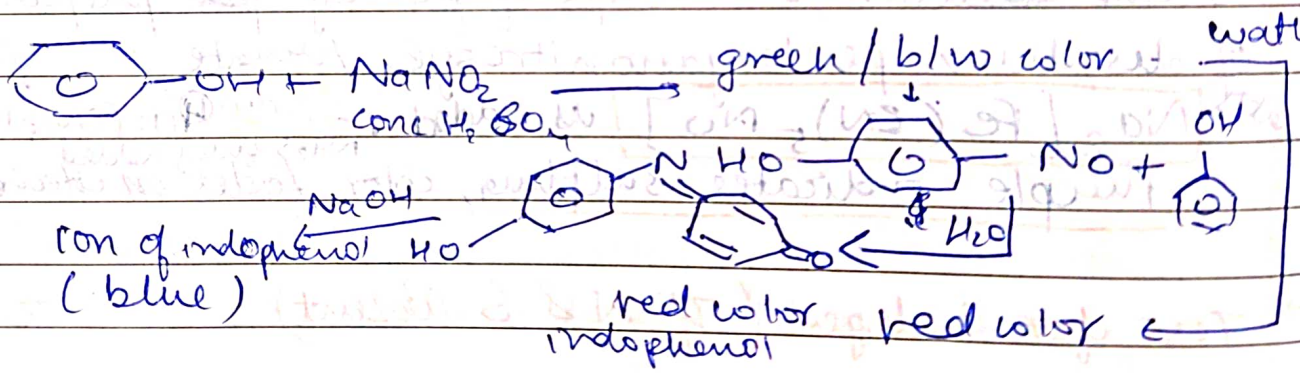
Fusion $\xrightarrow[Ni(NO_3)_2]{1-2 \text{ drops of}}$ filter $Ni(CN)_2$ or NiS. + filtrate

filtrate $\xrightarrow{2M\ HNO_3}$ perform previous test

Other important test.

for phenolic —OH:

Liebermann's test



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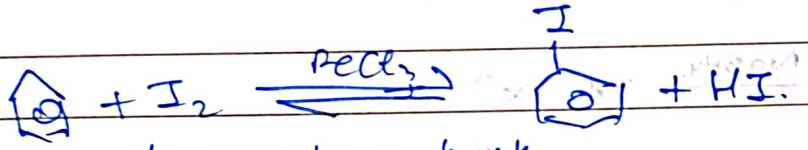
NOTE: SN_1 : Stereoselective : selective : only one product forms

SN_2 : stereospecific : specific : 2 prods formed in which one dominates.

Q Why can't aryl iodides be prepared directly by ewis acids, why is an oxidizing agent required also.

Ans Iodination is reversible:



HI sends reaction back

Or agent like HIO_4 is used, converting HI to I_2, moving rx^n forward

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→ Quantitative analysis of organic compounds:

A) Nitrogen

→ Dumas method

Nitrogen containing compound is heated with CuO in atmosphere of CO_2, yield free N_2, CO_2 H_2O.

$$C_xH_yN_z + (2x+y/2)\,CuO \longrightarrow x\,CO_2 + y/2\,H_2O + z/2\,N_2 + (2x+y/2)\,Cu$$

Traces of nitrogen oxides are reduced to N_2 by copper gauze

→ Kjeldahl's method:

Compound with N is heated in conc H_2SO_4. N gets converted into ammonium sulphate. The resulting acid mixture is then heated with excess of sodium hydroxide.

Measured by double titration.

$$C_xH_yN_z + H_2SO_4 \text{ (conc)} \longrightarrow (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 \xrightarrow{2NaOH} 2NH_3 + Na_2SO_4 + 2H_2O$$

NH_3 is measured by absorbing it in standard H_2SO_4 sol^n, with known conc.

The unreacted H_2SO_4 after absorption is titrated with std NaOH to find amt of H_2SO_4 reacted & hence NH_3 produced and hence amt of N in compound.

NOT APPLICABLE IN:

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- Nitro group: $-N\overset{O}{\rightarrow}O$
- Azo groups $-N=N-$
- nitrogen in rings: 

as nitrogen in these are too strongly bound to be converted to ammonium sulphate

B) **Halogens**

→ Carius method.

$$R-X + AgNO_3 \xrightarrow{HNO_3} AgX\downarrow + CO_2 + H_2O$$

C) **Sulphur**

$$R-SH \text{ or } R-S-R \xrightarrow[\text{or conc } HNO_3 \text{ (fuming)}]{Na_2O_2} H_2SO_4 \xrightarrow{BaCl_2} BaSO_4\downarrow$$

D) **Phosphorus**

$$R-P \xrightarrow{HNO_3} H_3PO_4 \xrightarrow{(NH_4)MoO_4} (NH_4)_3PO_4 \cdot 12MoO_3$$

or ppted as $MgNH_4PO_4$ and on heating becomes $Mg_2P_2O_7$

E) **Oxygen**

$$\text{Compound} \xrightarrow{\Delta} O_2 + \text{other gases}$$

$$2C + O_2 \xrightarrow{1373K} 2CO$$

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

Titration for measuring