: Carbohydrate:

Carbohydrates are the most abundant organic constituents of plants. They not only serve as important source of chemical energy for living organism but also in plants & in some animals they serve as important constituents of supporting tissue

Carbohydrates are defined as polyhydroxy aldehyde & ketones or substance that hydrolyse to yield polyhydroxy aldehyde & ketones. Most of them have general formula $C_x(H_2O)_y$ [hydrate of carbon].

e.g Glucose $C_6(H_2O)_6$; Sucrose $C_{12}(H_2O)_{11}$.

But; acetic acid $C_2(H_2O)_2$ are not carbohydrate.

ii) formaldehyde $C_1(H_2O)_1$

Also some carbohydrate Rhamnose $C_6H_{12}O_5$ is a carbohydrate which does not fit in definition.

Other examples; 2-deoxyribose $C_5H_{10}O_4$.

Classification of Carbohydrate

=> i) Monosaccharides: A carbohydrate which cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone. About 20 monosaccharides are known in nature.

example: Glucose; fructose; Ribose etc.

ii) Oligosaccharides: Carbohydrates that yield 2-10 unit of monosaccharide units on hydrolysis are called Oligosaccharides. It can be di, tri... tetrasaccharides. etc depending upon the number of monosaccharides they provide upon hydrolysis. 1 mole of Maltose $\xrightarrow{H_2O}$ 2 mole of glucose

Maltose ⇓ Disaccharide; glucose: Monosaccharide

1 mole of Sucrose $\xrightarrow{H_3O^+}$ 1 mole Glucose + 1 mole Fructose
Disaccharide (Monosaccharide)

1 mole of Lactose $\xrightarrow{H_3O^+}$ 1 mole Glucose + 1 mole Galactose
Disaccharide (Monosaccharide)

: Polysaccharide:
Carbohydrates which yield a large number of monosaccharide units (>10) on hydrolysis are called polysaccharides. Some common examples are i) Starch ii) glycogen iii) Cellulose.

1 mole of starch or 1 mole of Cellulose (Polysaccharides) $\xrightarrow{H_3O^+}$ many moles of Glucose. (Monosaccharide)

Classification of Monosaccharide:

=> Aldose Polyhydroxy aldehyde.

$$\begin{array}{l} CH=O \\ | \\ (CHOH)_n \\ | \\ CH_2OH \end{array}$$

n=1, Aldotriose n=3 Aldopentose
n=2 Aldotetrose n=4 " hexose.

glucose is example of Aldohexose.

=> Ketose Polyhydroxy ketone.

$$\begin{array}{l} CH_2OH \\ | \\ C=O \\ | \\ (CHOH)_n \\ | \\ CH_2OH \end{array}$$

n=0 ketotriose n=2 ketopentose
n=1 ketotetrose n=3 ketohexose.

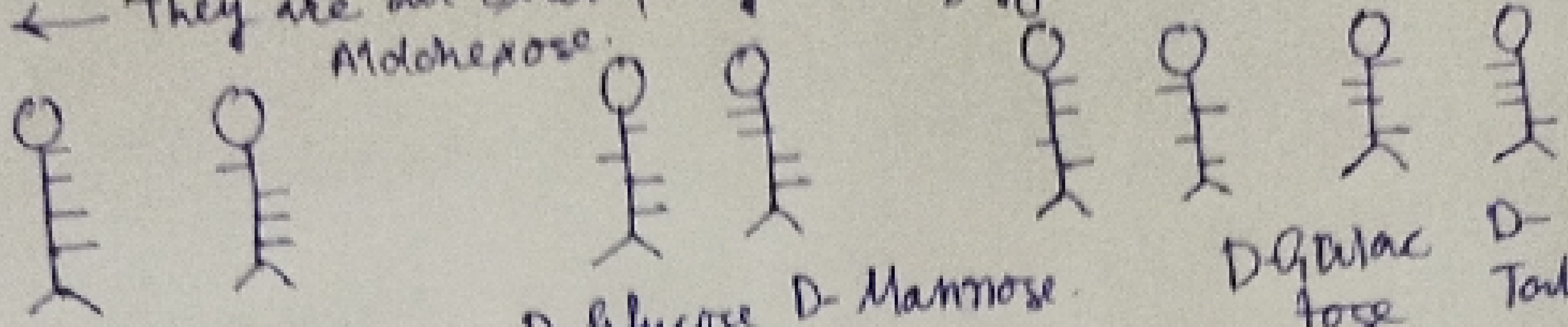
Fructose is example of ketohexose.

=> Mono/Oligosaccharides are sweet in taste whereas Polysaccharids are tasteless.

=> $C_3(H_2O)_3$ => Lactic Acid is not considered as carbohydrate. ; The aldose & ketose can exist in D & L structure.

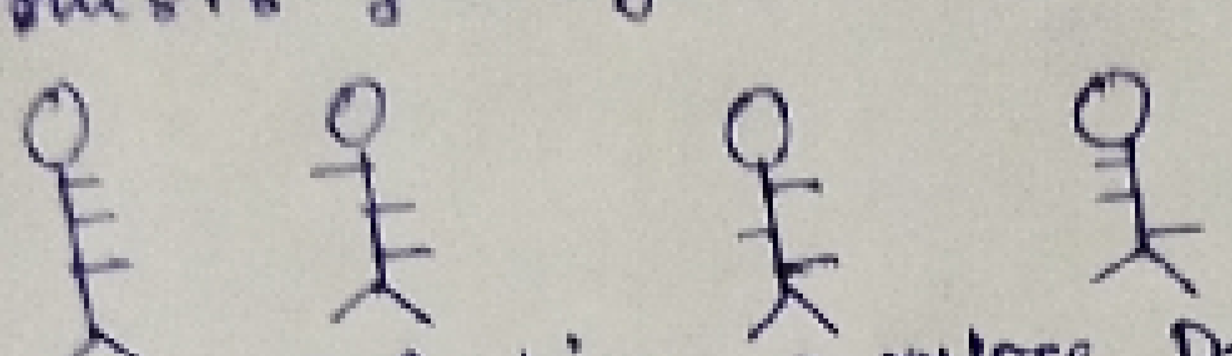
: Structure of Aldose: / D-family.

← They are all example of Aldohexose —— D-Gulose D-Idose →

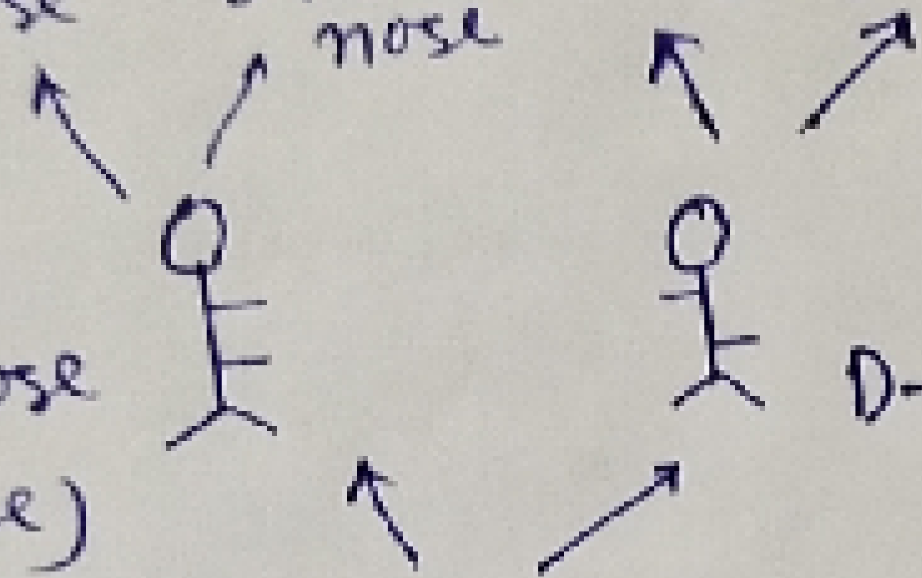


D-Allose D-Altrose D-Glucose D-Mannose D-Galactose D-Talose.

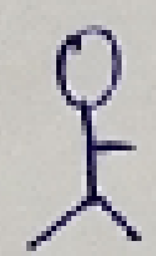
[All altruists gladly making gums in gallon tanks]



D-ribose D-Arabinose D-xylose D-Lyxose (Aldopentose)



D-Erythrose (Aldotetrose) D-Threose. (Aldotetrose)



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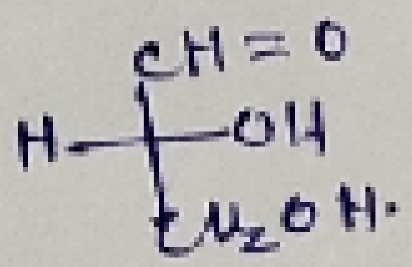


D-glyceraldehyde (Aldotriose)

⇒ There are
a) {1 Aldotriose (D-family) / 1 Aldotriose (L-family)} ENT w.r.t each other

b) {2 Aldotetrose (D-family) / 2. Aldotetrose (L-family)} 2 pair of ENT possible.

c) 4. Aldopentose (D-family) / 4. Aldopentose (L-family) 4 pair of ENT possible.

d) 8- Aldohexose (D-family) / 8- Aldohexose (L-family) 8 pair of ENT possible.

D/L nomenclature does not have any correlation with sign of rotation.

∴ Points to be remembered:

⇒ Molecular formula of Aldotetrose $C_4(H_2O)_4$.

& aldohexose $C_6(H_2O)_6$.

⇒ Molecular formula of tetrose tetrasaccharide is $4\,C_4(H_2O)_4 - 3H_2O \Rightarrow C_{16}(H_2O)_{13} \Rightarrow C_{16}H_{26}O_{13}$

⇒ Molecular formula of starch $[C_6(H_2O)_6 - H_2O]_n$

& Sucrose/Maltose $\Rightarrow 2 \times C_6H_{12}O_6 - H_2O \Rightarrow C_{12}H_{22}O_{11}$

⇒ Molecular formula of polymer of Aldopentose

e.g. Polypentoside, $[C_5(H_2O)_5 - H_2O]_n$ $[C_5(H_2O)_4]_n$

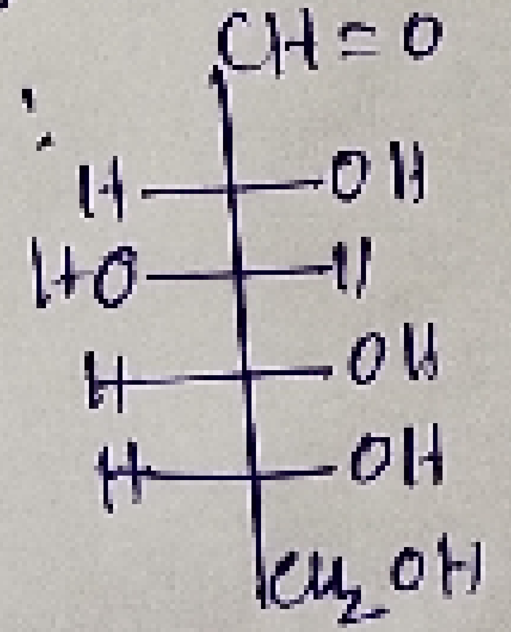
⇒ No. of chiral centres present in Aldohexose = 4.

$CH=O$
$(CHOH)_4$
CH_2OH

So Number of stereoisomers $= 2^n = 2^4 = 16$ (All are optically active)

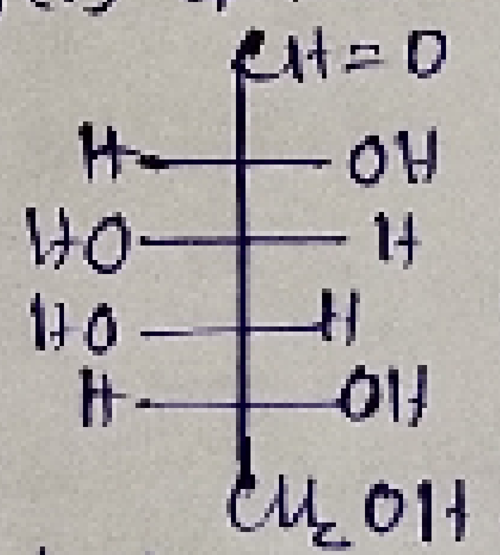
8 (D-family) & 8 (L-family).

e.g. D(+) Glucose:



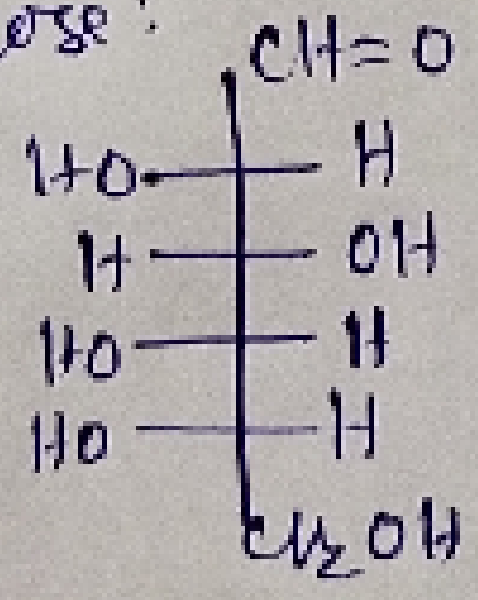
X_1

(D)(+) Galactose



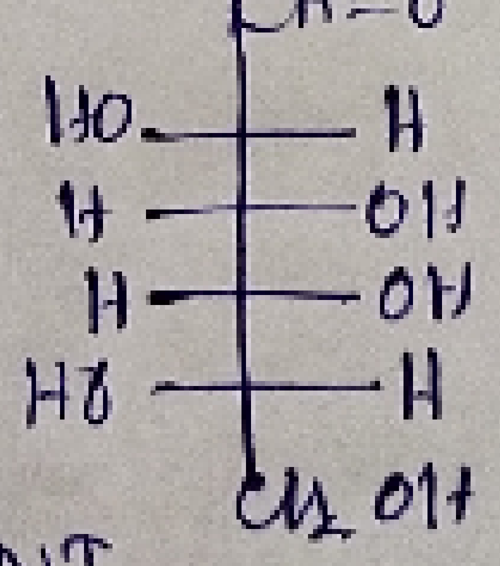
X_3

L(−) Glucose:



X_2

L(−) Galactose

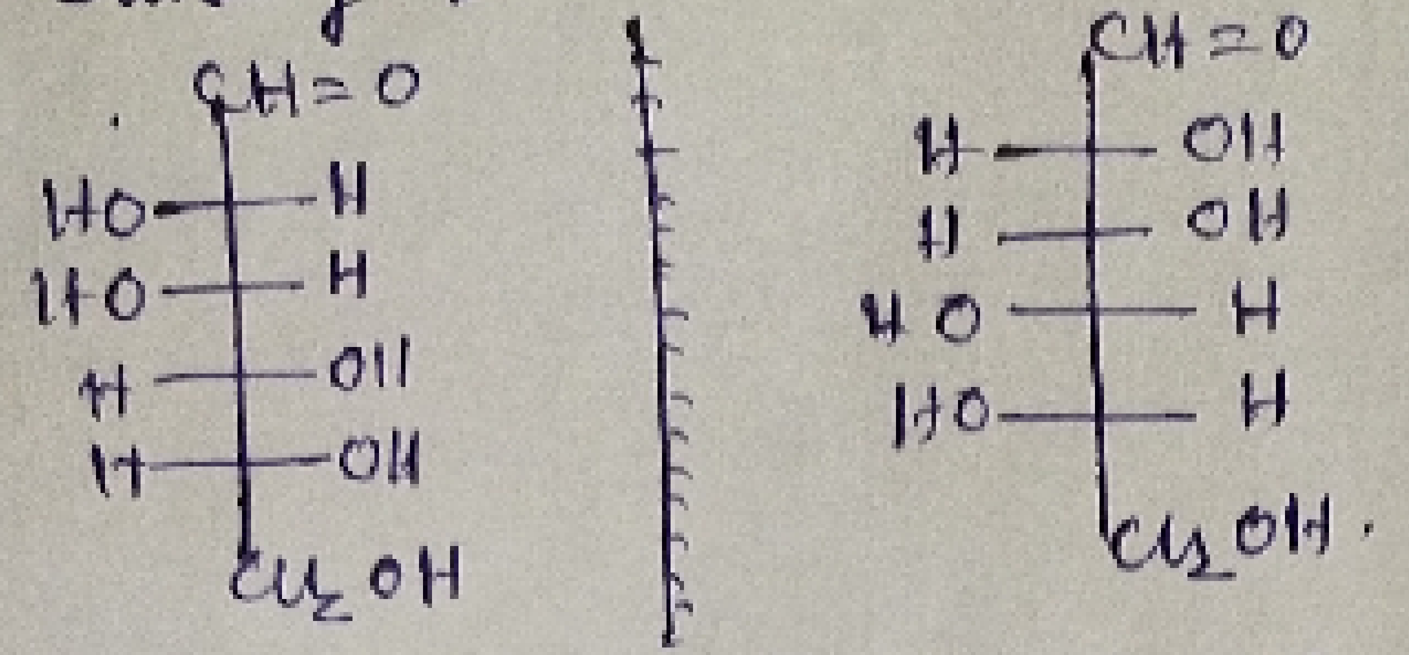


X_4

X_1 & X_2 are related as ENT.

X_3 & X_4 are related as ENT.

Structure of D(+) Mannose: & L(-) Mannose

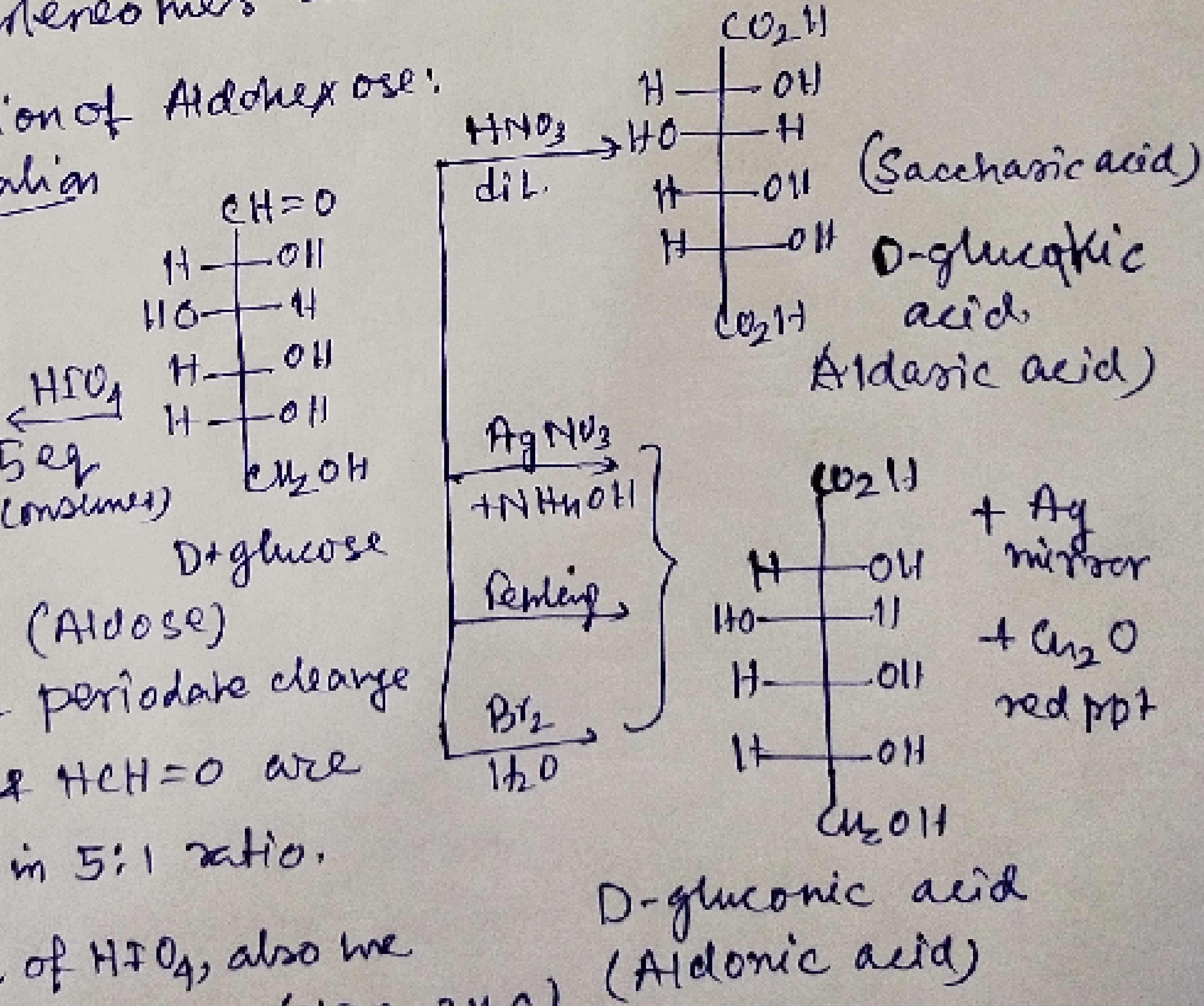


D(+) glucose & D(+) Mannose are related as C-2 epimer; D(+) glucose & D(+) galactose are related as C-4 epimer.

: Defn of Epimer: For multichiral centre of a carbohydrate, if there is change of absolute configuration in one of the chiral centre, then structures are related as epimer. All epimers are related as diastereomers but vice versa is not true.

⇒ Reaction of Aldohexose:

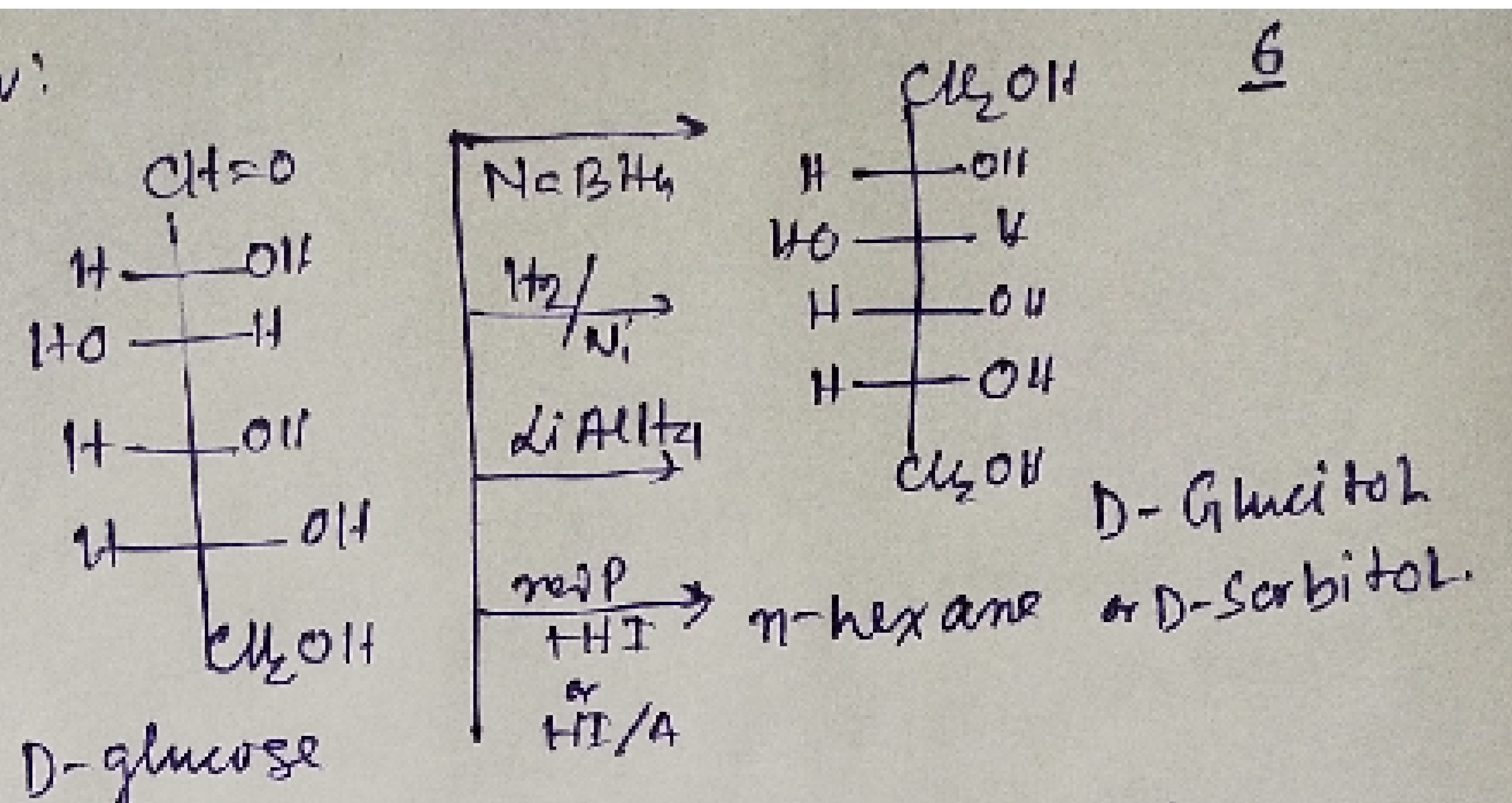
I: Oxidation



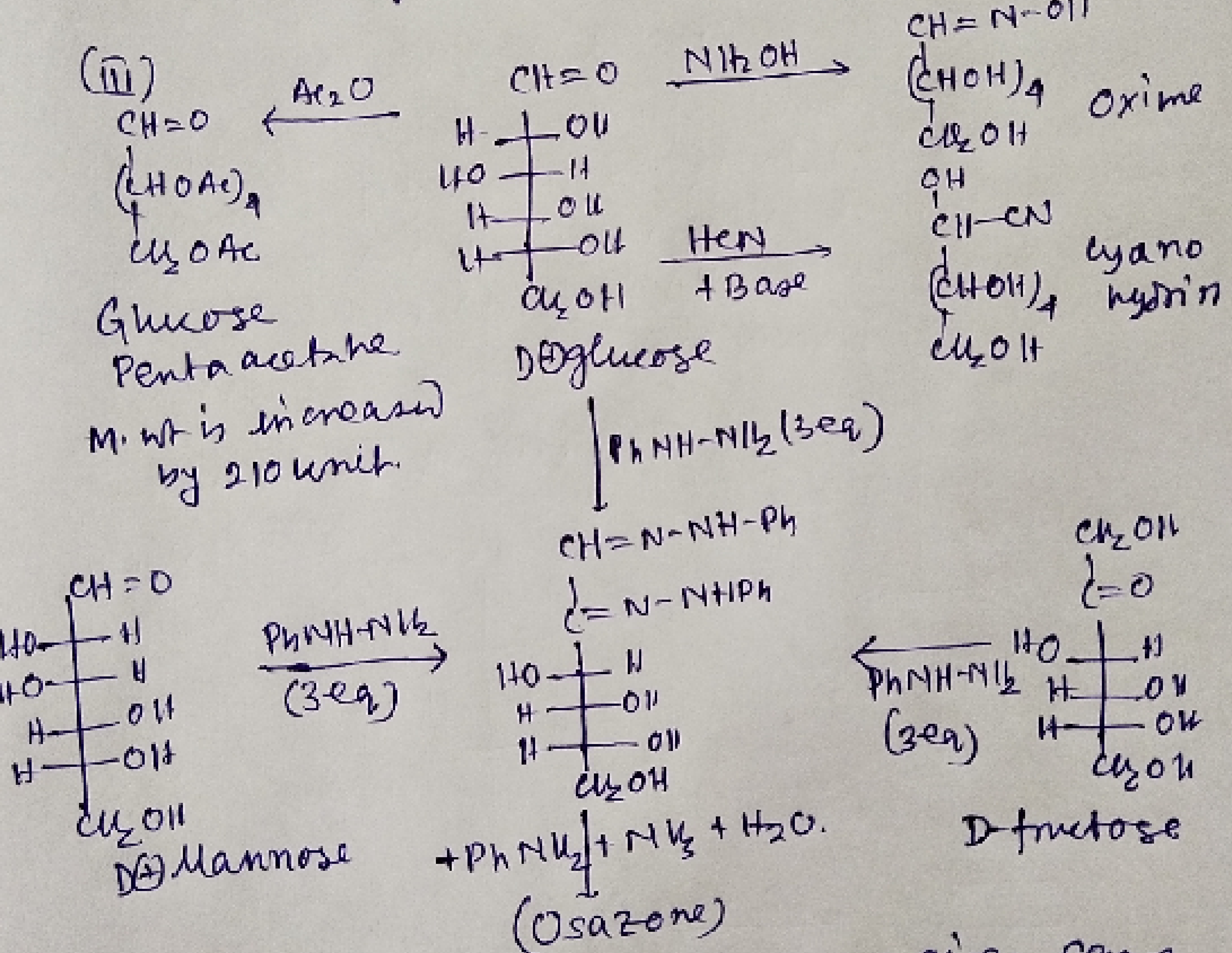
The oxidised product is formed by periodate cleavage HCO_2H & $HCH=O$ are formed in 5:1 ratio.

Instead of HIO_4, also we can use H_5IO_6 ($HIO_4 \cdot 2H_2O$)

II. Reduction:

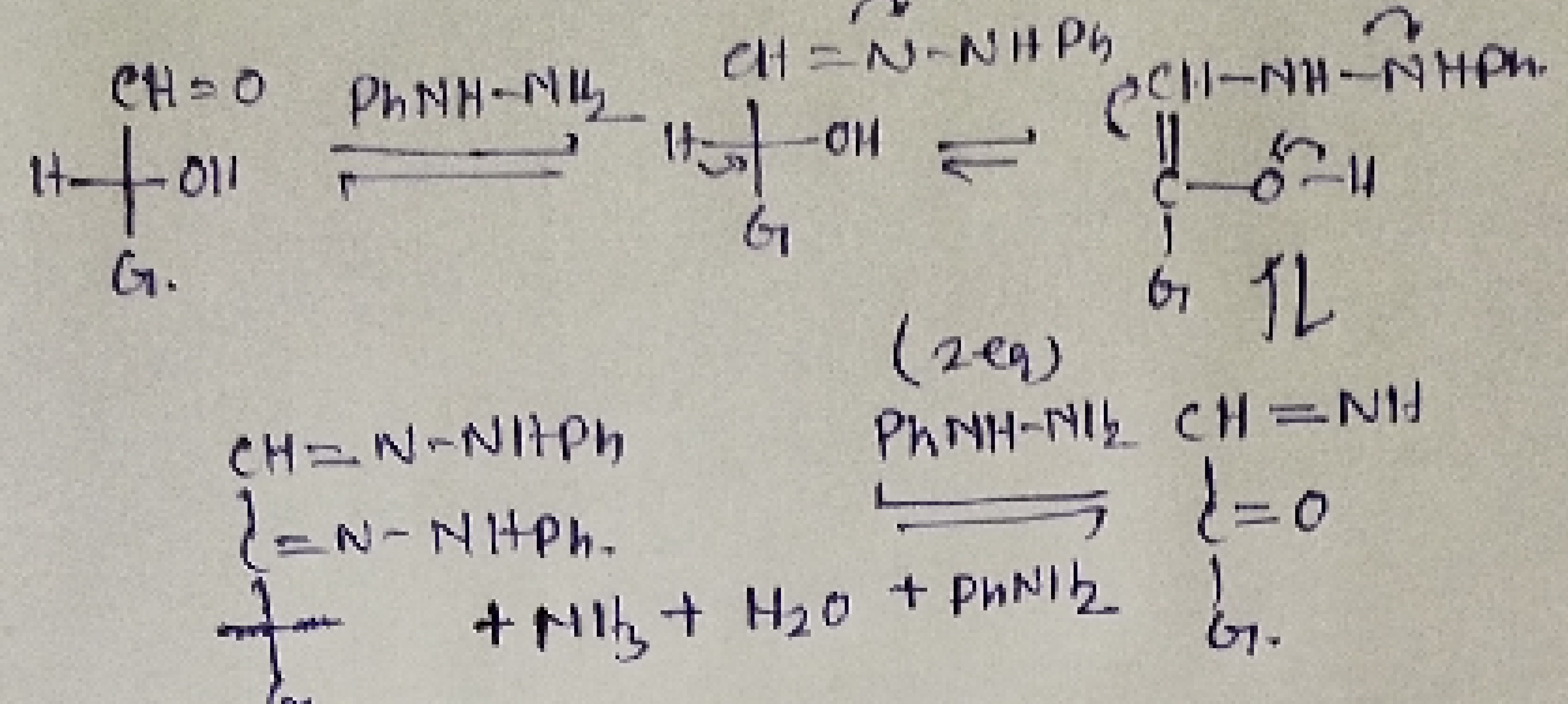


(III)



C-2 epimer D(+)glucose & D(+) Mannose gives same osazone. Also D(-) fructose & D(+) glucose gives same osazone. For same osazone, the configuration of last 3 chiral centre are identical.
Osazone is coloured crystalline product.

Mechanism for Osazone formation:



$\Rightarrow$: Points to be remembered:

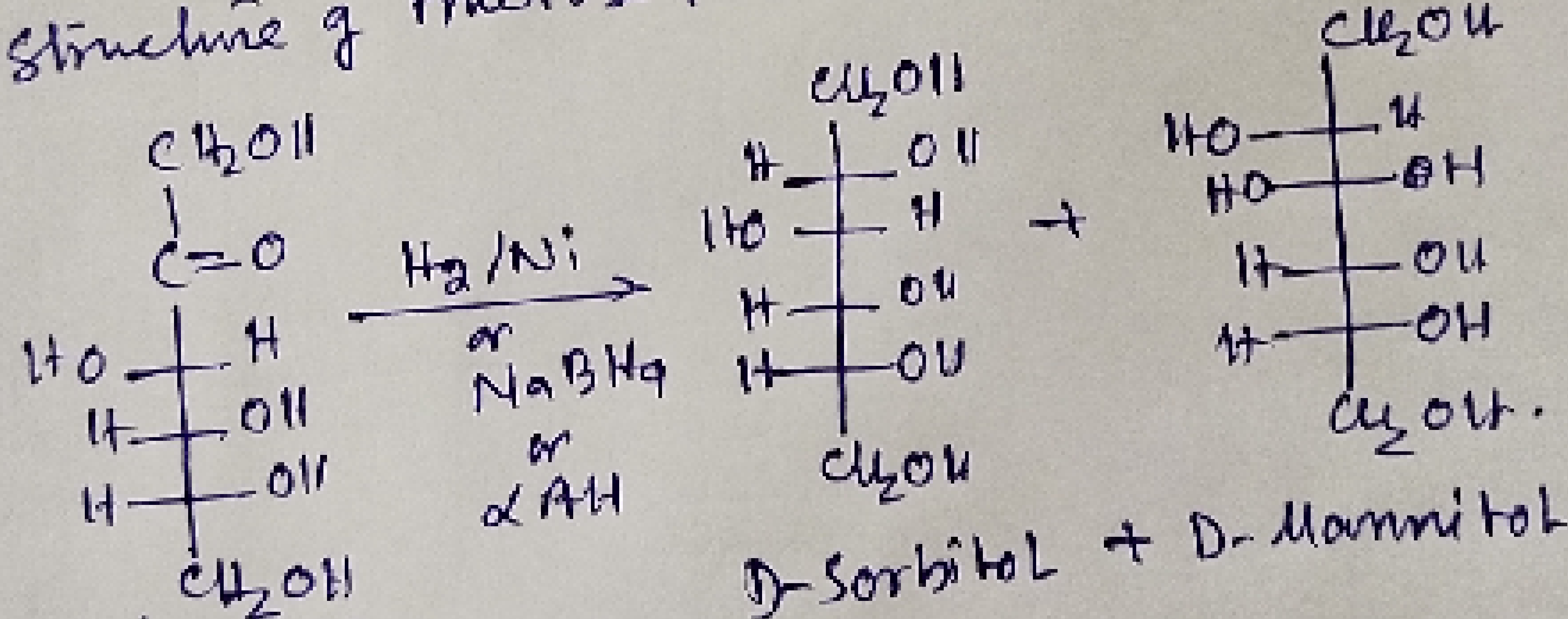
$\Rightarrow$ glucose does not give +ve Schiff's test

$\Rightarrow$ glucose does not give +ve test with $NaHSO_3$.

$\Rightarrow$ glucose does not give +ve test with 2,4.D.N.P

$\Rightarrow$ glucose give +ve Benedict test & reddish brown ppt is obtained.

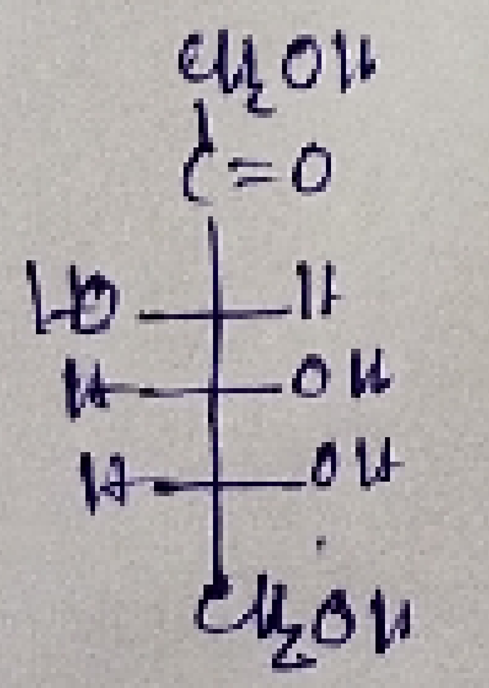
: Structure of fructose & its reaction



D fructose

D-Sorbitol + D-Mannitol.

(D-) fructose



$\xrightarrow{Br_2 + H_2O}$ no reaction; so Br_2 water can be used to distinguish D-glucose & D-fructose

Tollens → Ag mirror

Fehling → Cu_2O ↓ reddish brown ppt.

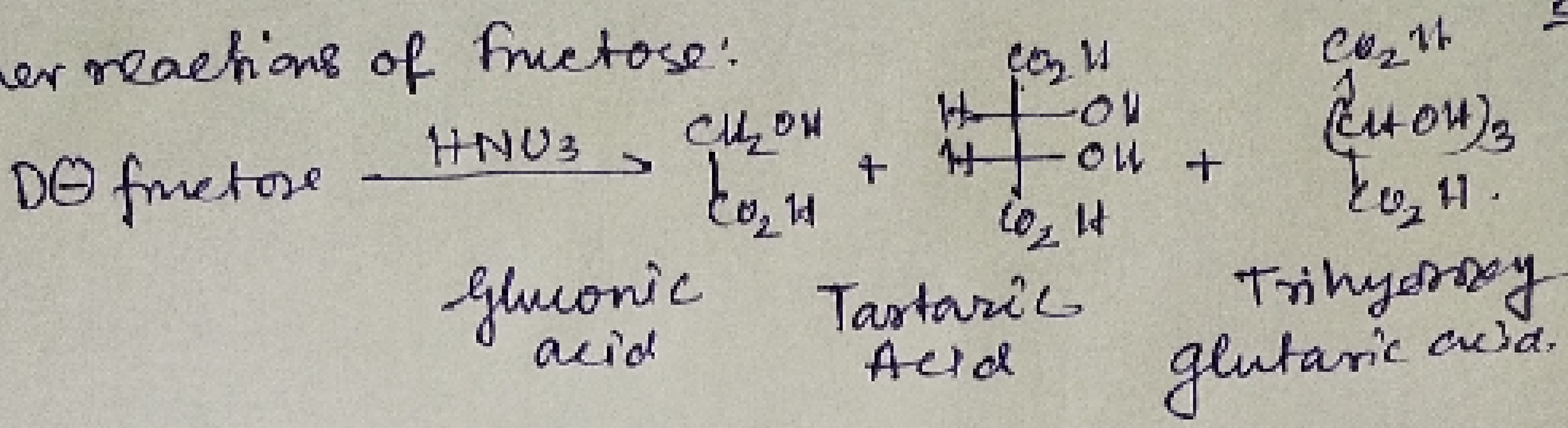
Benedict → Cu_2O ↓

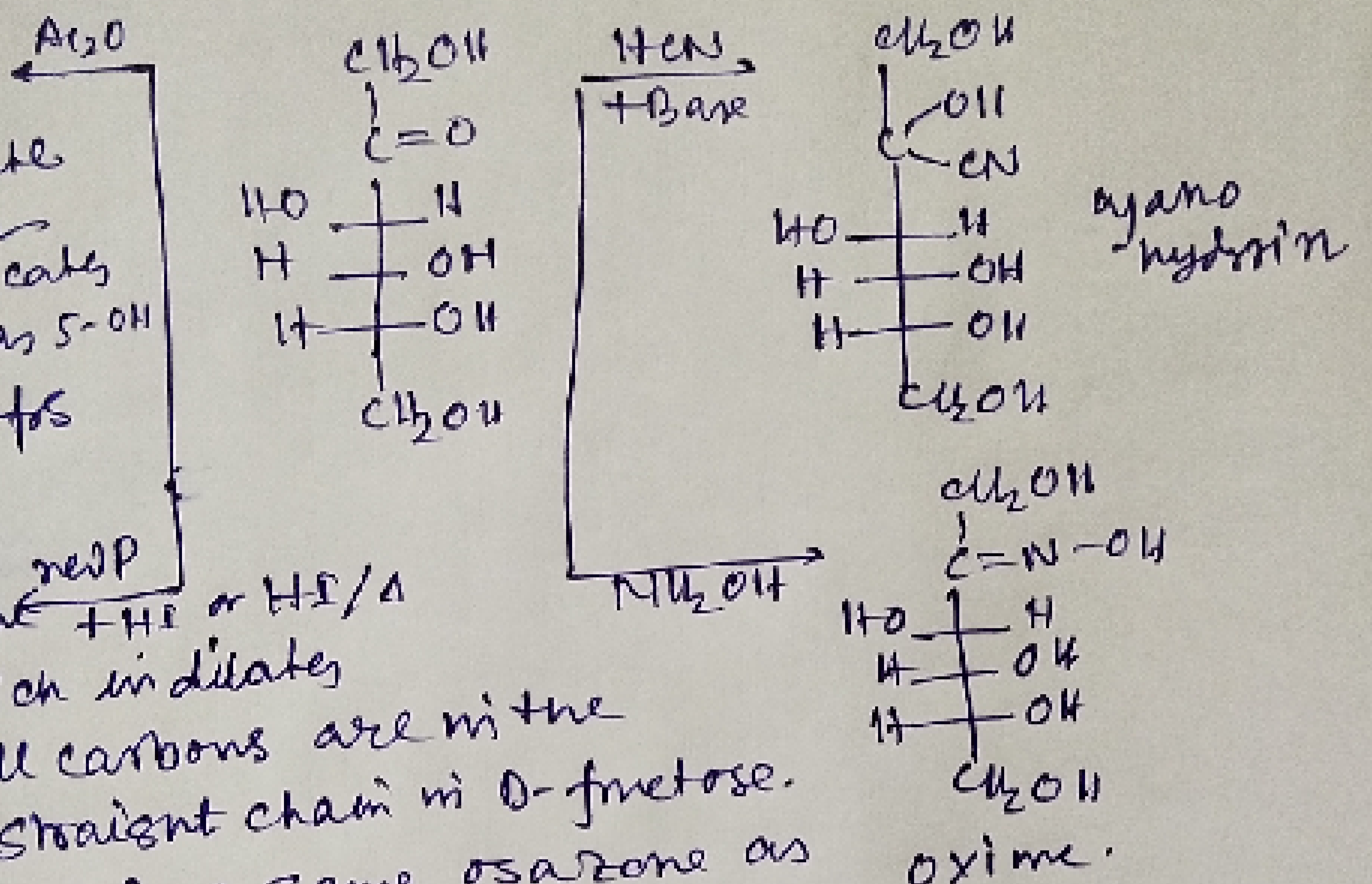
Same as that of D+ glucose

HIO_4 → CO_2 ↑ + 2eq. $HCH=O$ + 3-eq HCO_2H.

↳ can be used to distinguish D⊕ Glucose & D⊖ fructose

: Other reactions of fructose:





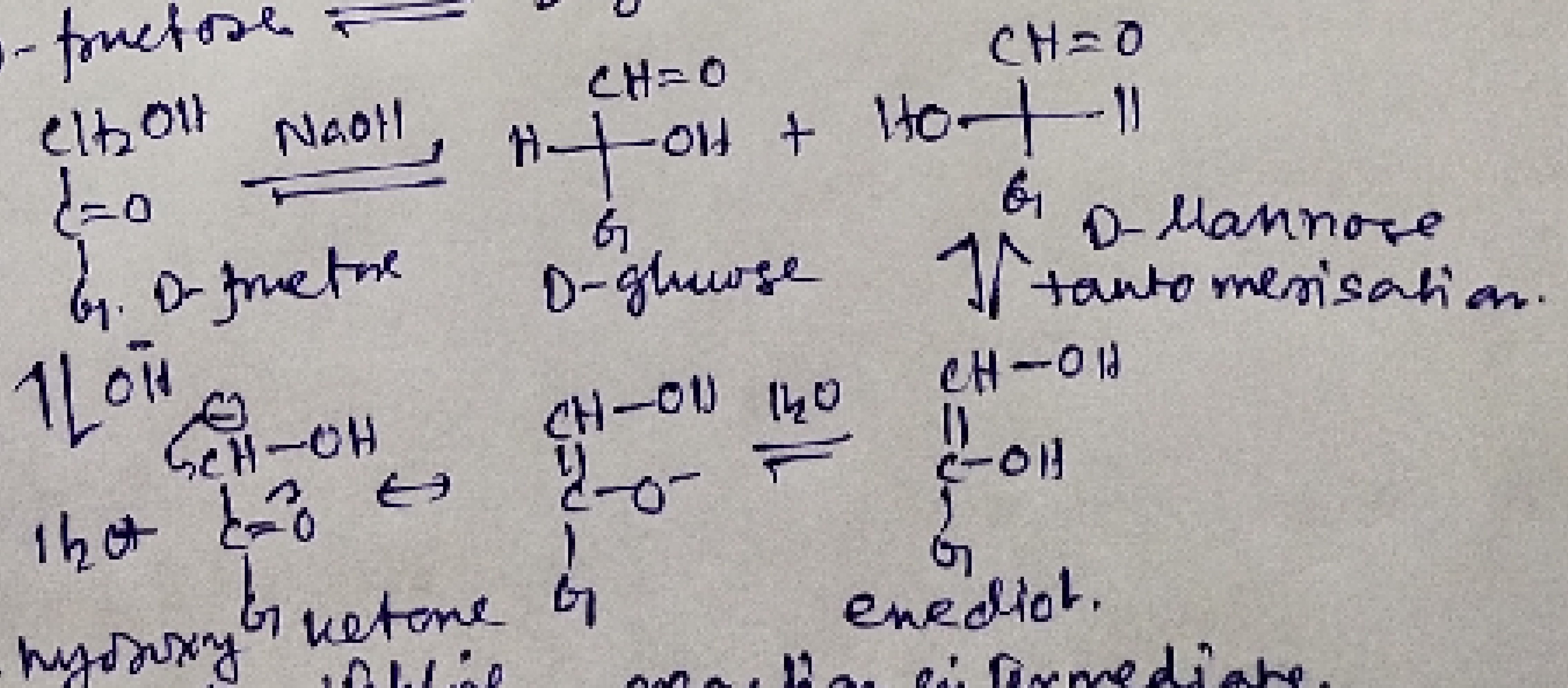
Penta acetate which indicates it has 5-OH groups

n-hexane + HI or HI/Δ which indicates all carbons are in the straight chain in D-fructose.

Also it forms same osazone as that of D(+) Glucose.

Lobry-de Bruyn-Van Eken stein transformation.
Lobry-de Bruyn-Van Ekenstein transformation
This reaction involves base catalysed transformation of an aldose into the ketose isomer & vice versa. Here tautomeric enediol is formed as reaction intermediate.

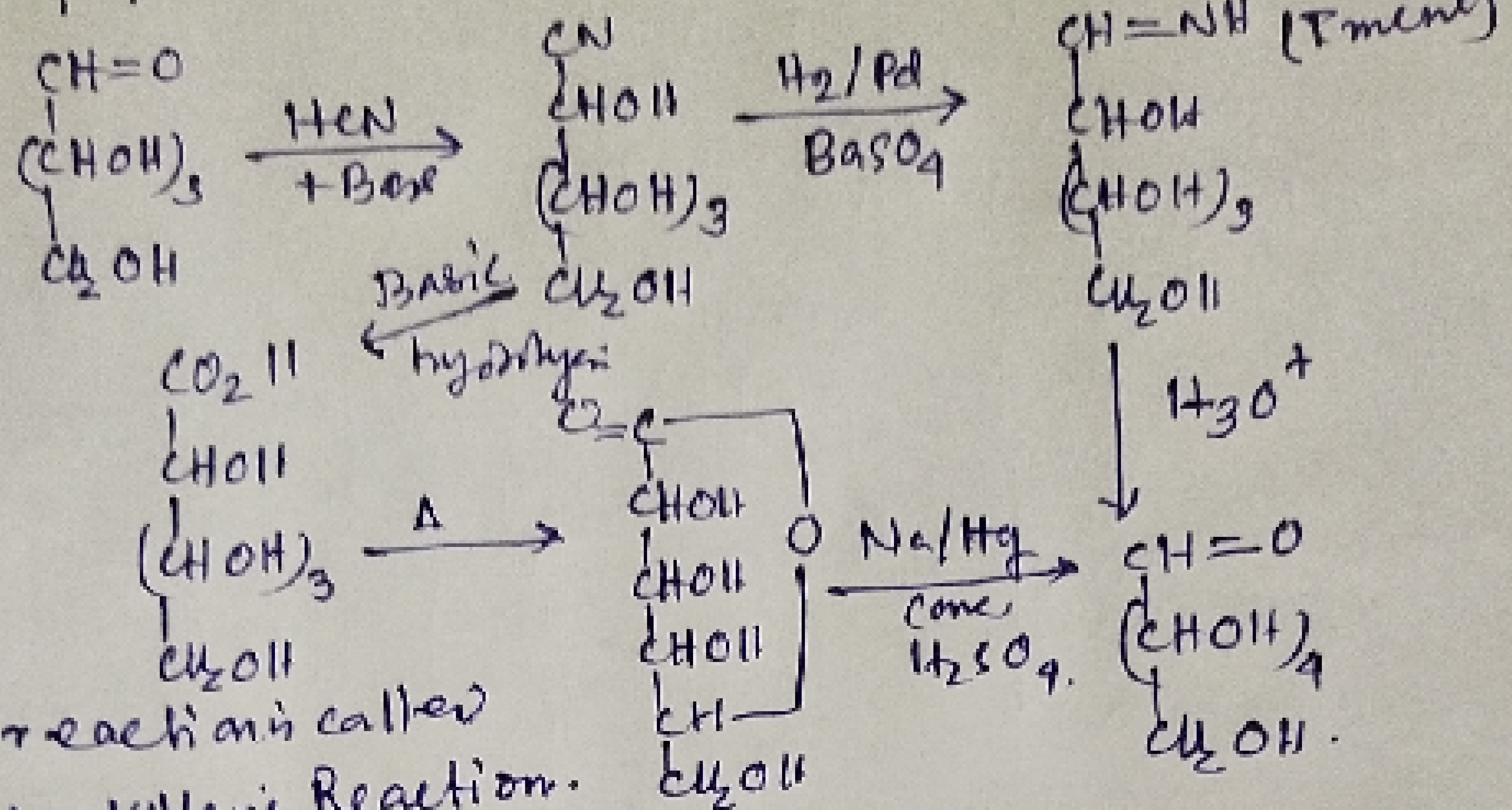
D-fructose $\overset{NaOH}{\rightleftharpoons}$ D-glucose + D-Mannose



So α-hydroxy ketone gives the Tollens / Fehling test.

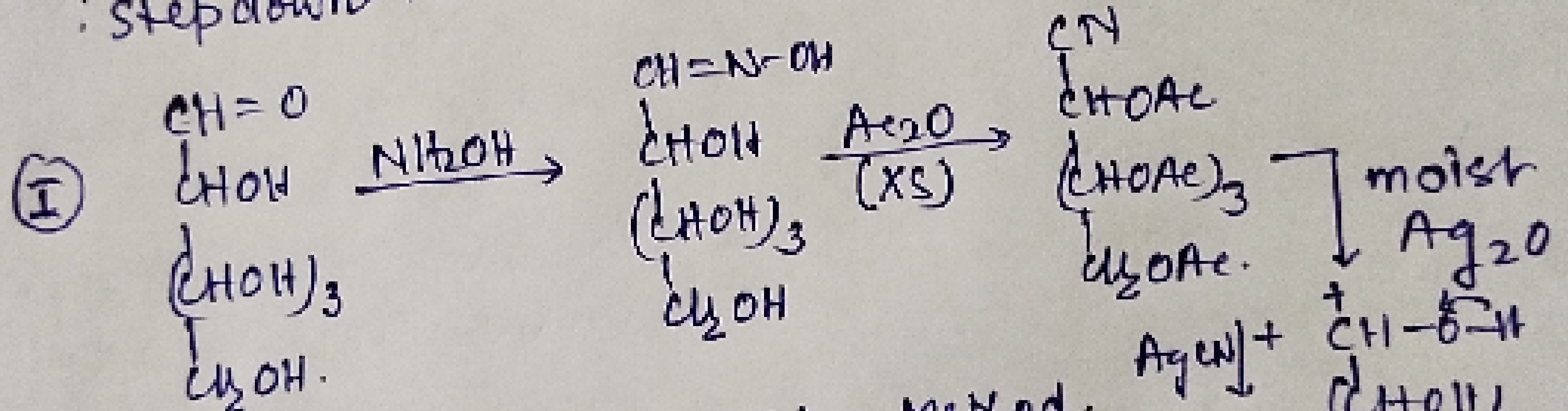
: Interconversion:

: Stepup reaction: Aldopentose → Aldohexose.

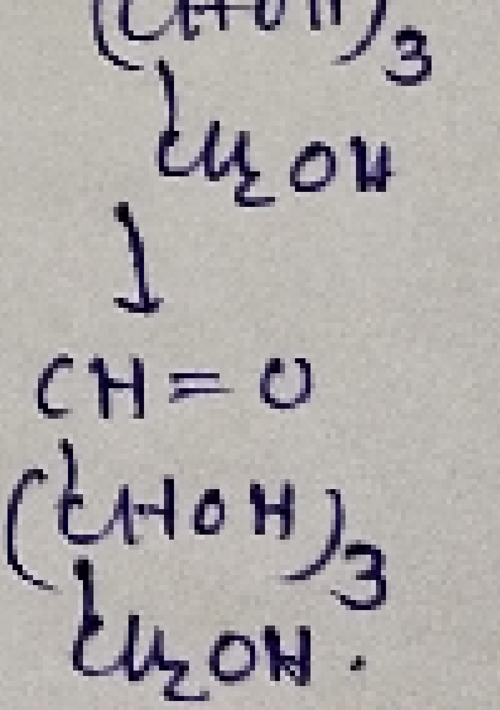


This reaction is called Fischer Killani Reaction.

: Stepdown reaction: Aldohexose → Aldopentose.

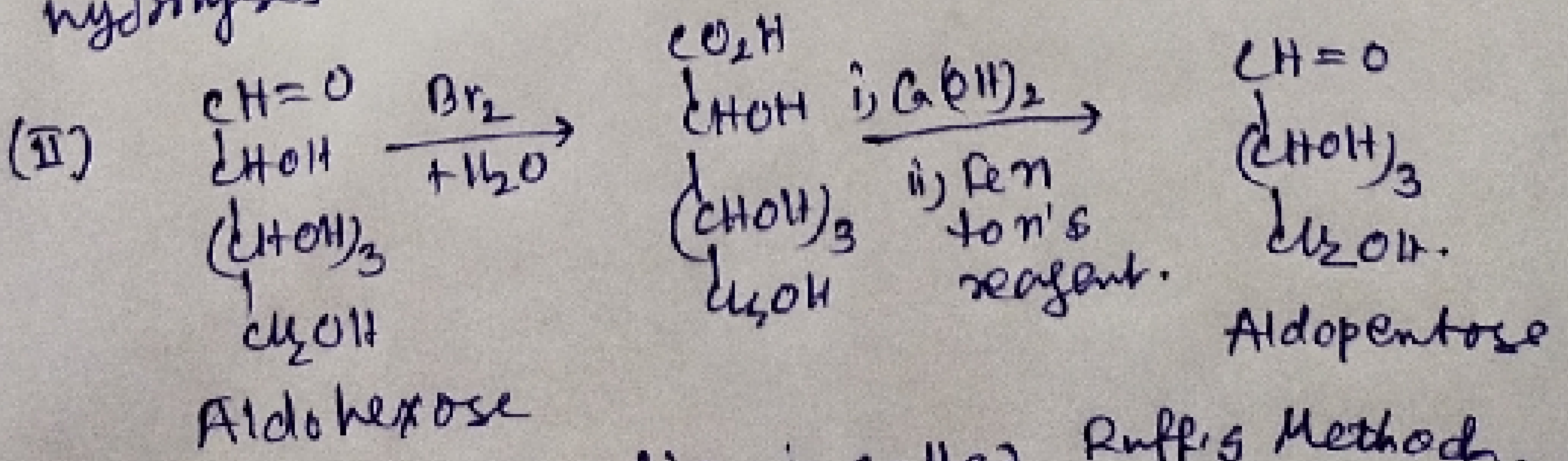


This reaction is called Wohl's Method.



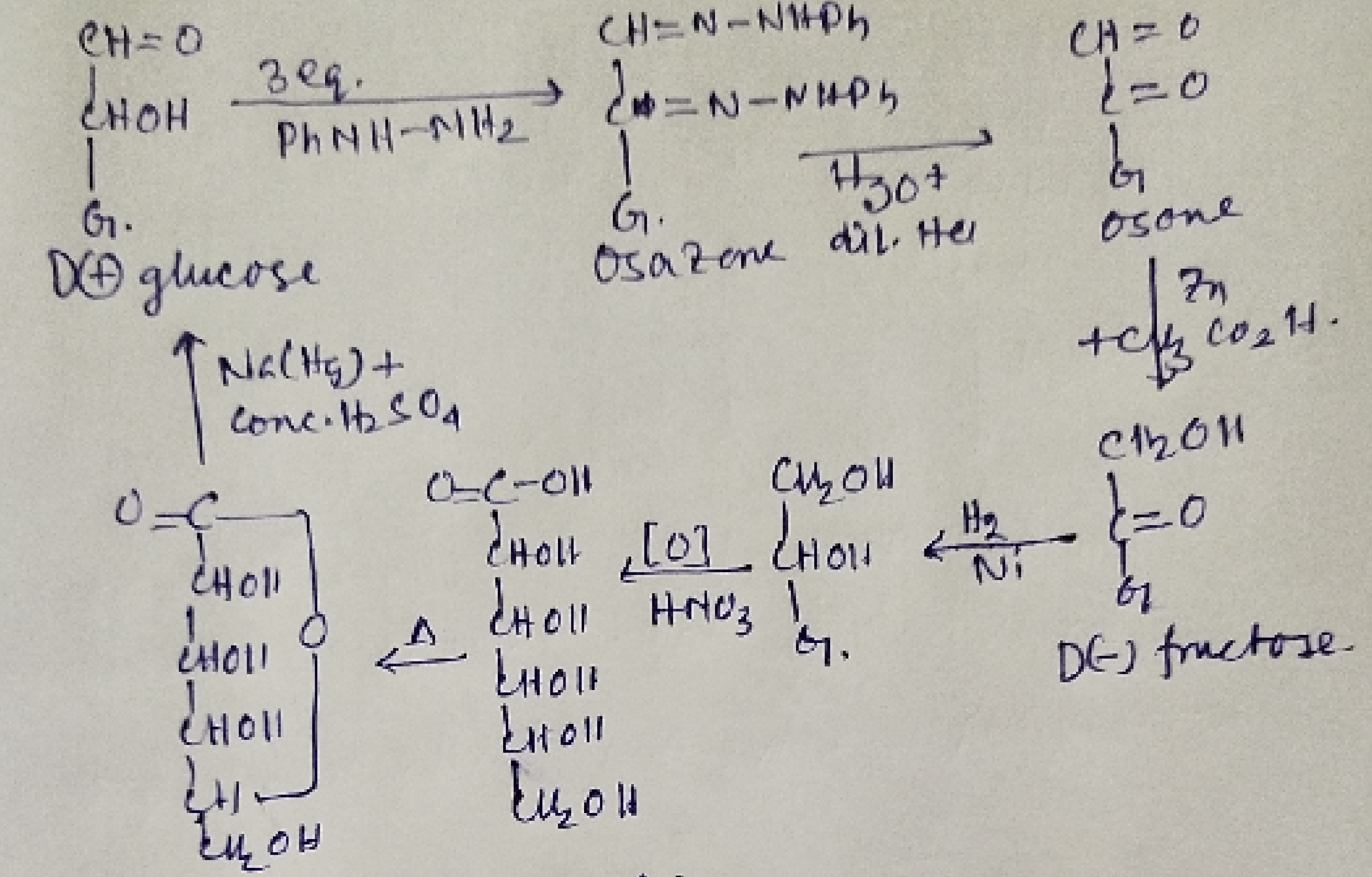
⇒ This reaction is called Wohl's Method, it acts as

⇒ Ac_2O has dual purpose, it acts as acylating reagent & also acts as dehydrating reagent. moist Ag_2O hydrolyses $-OAc$ to $-OH$ & removes $-CN$ grp.



The above reaction is called Ruff's Method.

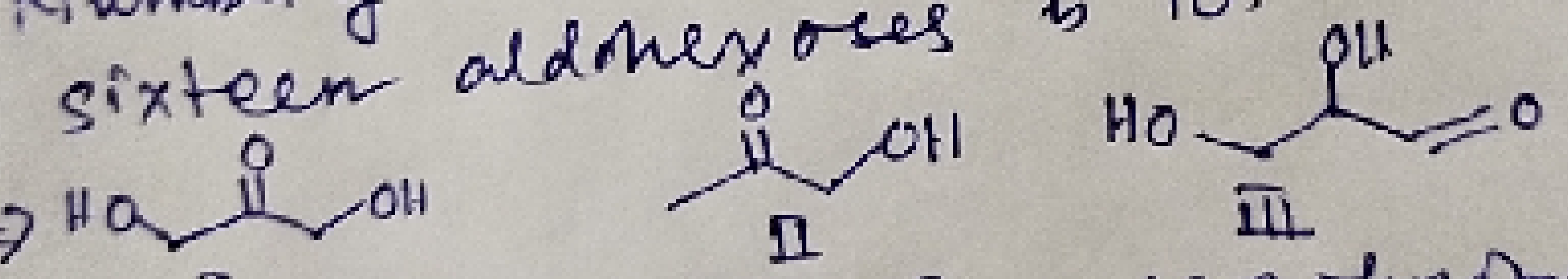
Conversion of an Aldose into ketose & vice versa.



: Points to be remembered:

⇒ Two plant polysaccharides consisting of D-glucose units are starch & Cellulose (Natural polymer).

⇒ Number of aldaric acids obtained from sixteen aldohexoses is 10.



I, III are considered as carbohydrate but II is ~~cons~~ not considered as carbohydrate.

⇒ fructose $\xrightarrow[\text{iii) red P + HI}]{\text{i) HCN/Base} \quad \text{ii) } H_3O^+}$ 2-methyl hexane

⇒ glucose $\xrightarrow[\text{iii) red P + HI}]{\text{i) HCN/Base} \quad \text{ii) } H_3O^+}$ n-heptane.

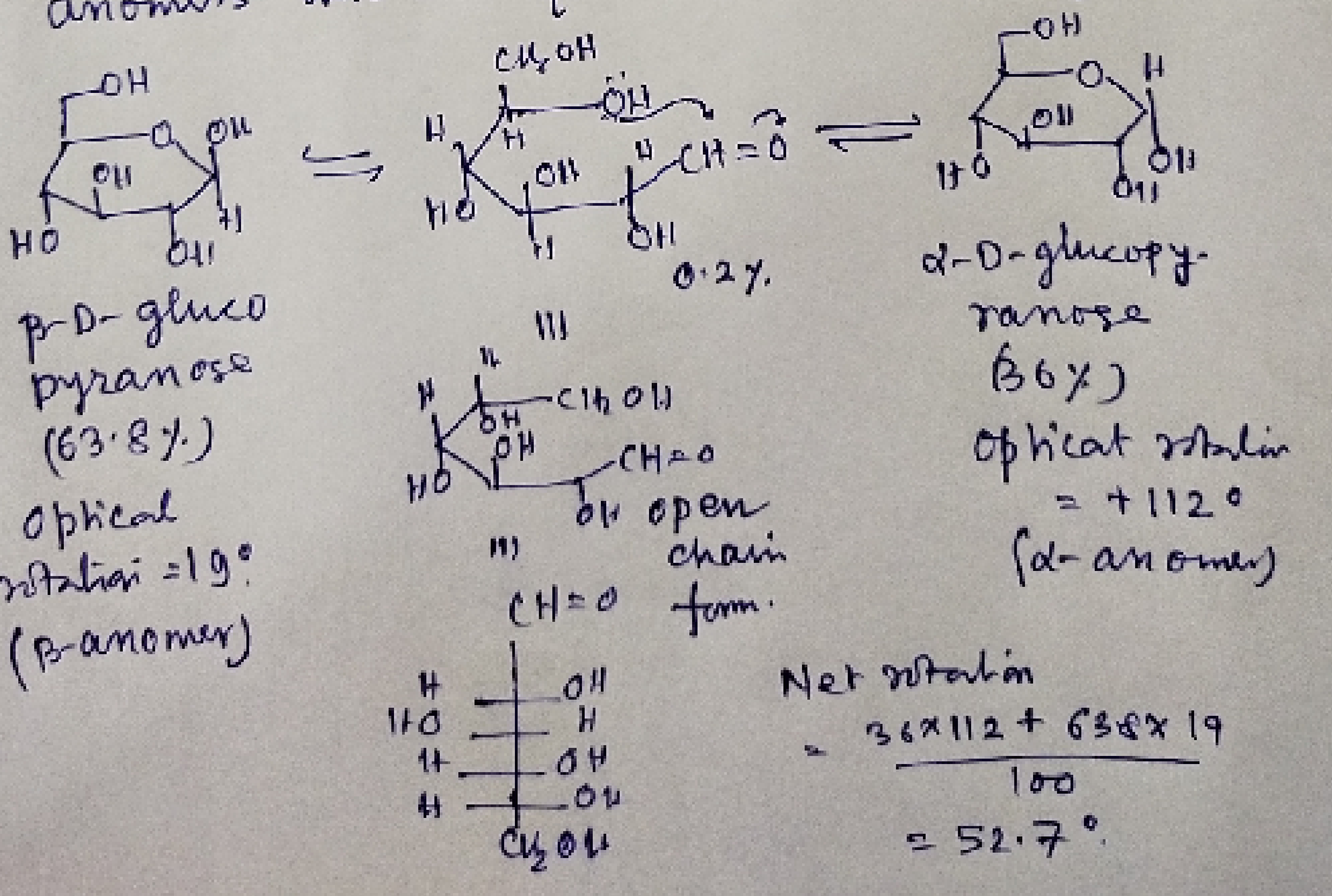
⇒ D-Xylose on treatment with dil. HNO_3 & $NaBH_4$ gives optically inactive product but D-Lyxose with same reagent gives optically active product.

Cyclic structure

: Experimental data : ⇒ D-glucose does not reacts with 2,4, D.N.P, $NaHSO_3$, NH_3 & schiff's reagent though it has, $-CH=O$ group which suggests it may have such structure where free aldehyde group is absent.

⇒ Also glucose pentaacetate does not react with NH_2OH. indicating the absence of free $-CH=O$ group.

⇒ When pure D-glucose (α-form) is dissolved in water its specific rotation is found to be +112°, however the specific rotation of solution decreases ultimately reaches +52.5°. When β-D-glucose is dissolved in water it has a specific rotation 19°. The specific rotation of this solution increases with time to become 52.5°. This change of optical rotation with time is called mutarotation. Mutarotation is catalysed by both acids & base. It is caused by conversion of α & β-glucopyranose into an equilibrium mixtures of both anomers.



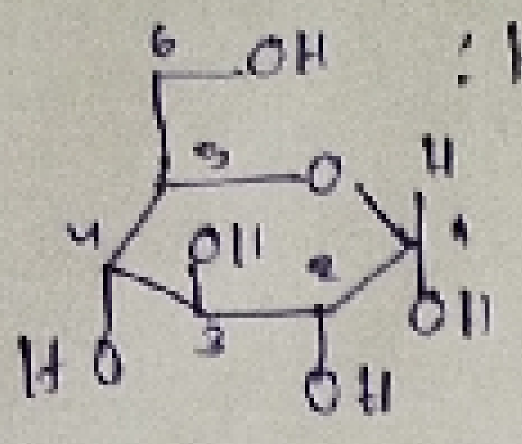
Net rotation

$$= \frac{36 \times 112 + 63.8 \times 19}{100}$$

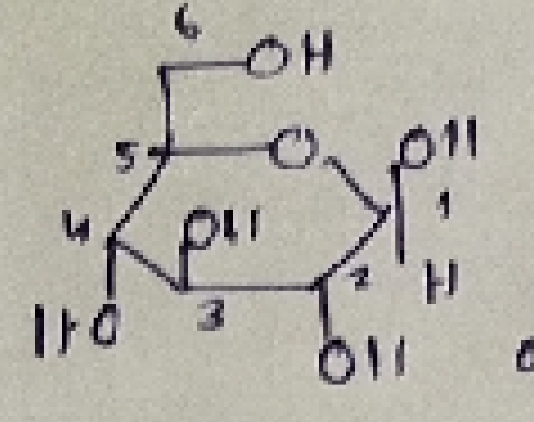
$= 52.7°$

Other presentation of α & β-glucopyranose :

: Haworth structure :

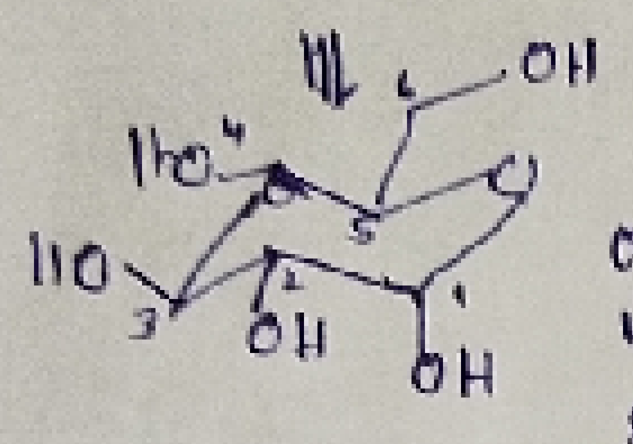


α form of D-glucopyranose ⇌

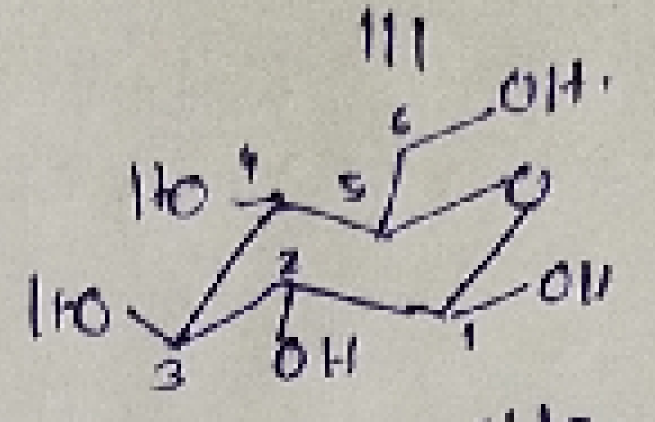


β form of D-gluco pyranose

: Chair form :

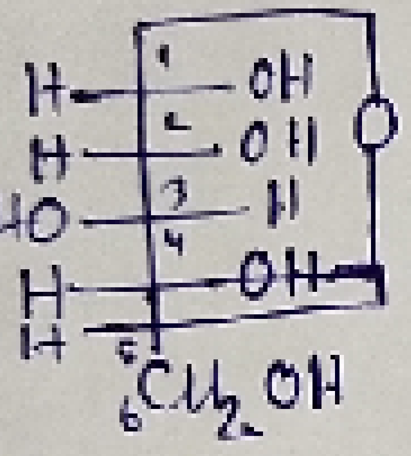


one –OH grp is in axial site. So it is less stable.

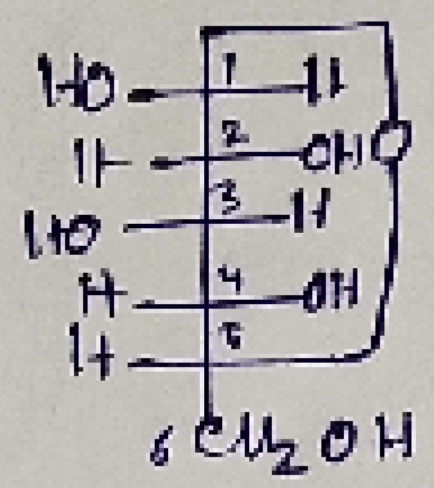


all are in equatorial site. So it is more stable.

Stability <



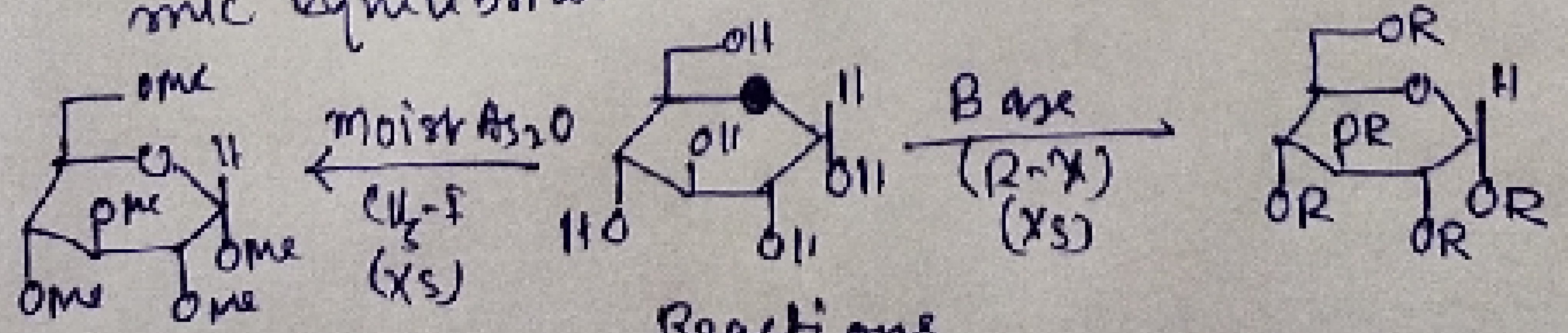
α-D-glucopyranose



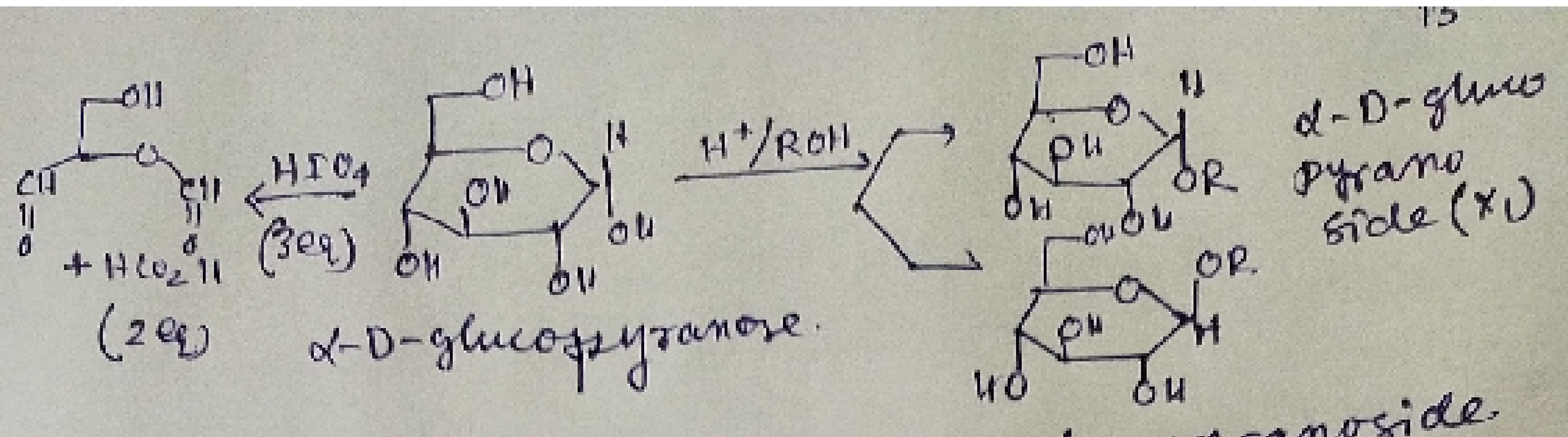
β-D-glucopyranose

The two cyclic hemiacetal forms of Glucose differ only in the configuration of hydroxyl group at C_1, called anomeric carbon (the aldehyde carbon before cyclisation. Such isomers i.e α form & β-form are called anomers. The six membered cyclic structure of Glucose is called Pyranose structure.

Glucose has cyclic hemiacetal. Thus it gives the Tollens/ Fehling test & is called reducing sugar. All reducing sugar show mutarotation & dynamic equilibrium between anomers take place.



Reactions of α-D-glucopyranose



HIO_4 (3eq), $+ HCO_2H$ (2eq)

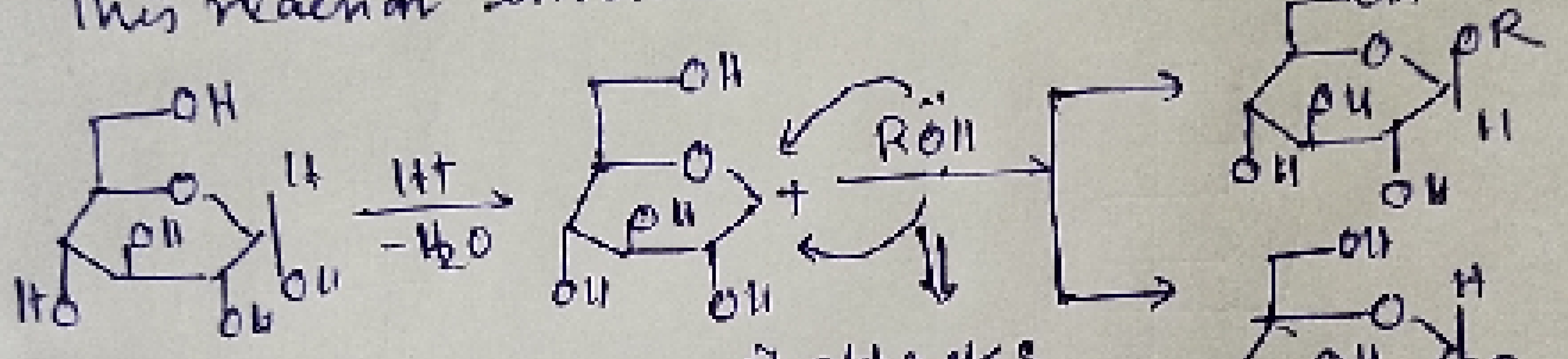
α-D-glucopyranose

H^+/ROH

α-D-glucopyranoside (X_1)

β-D-glucopyranoside (X_2)

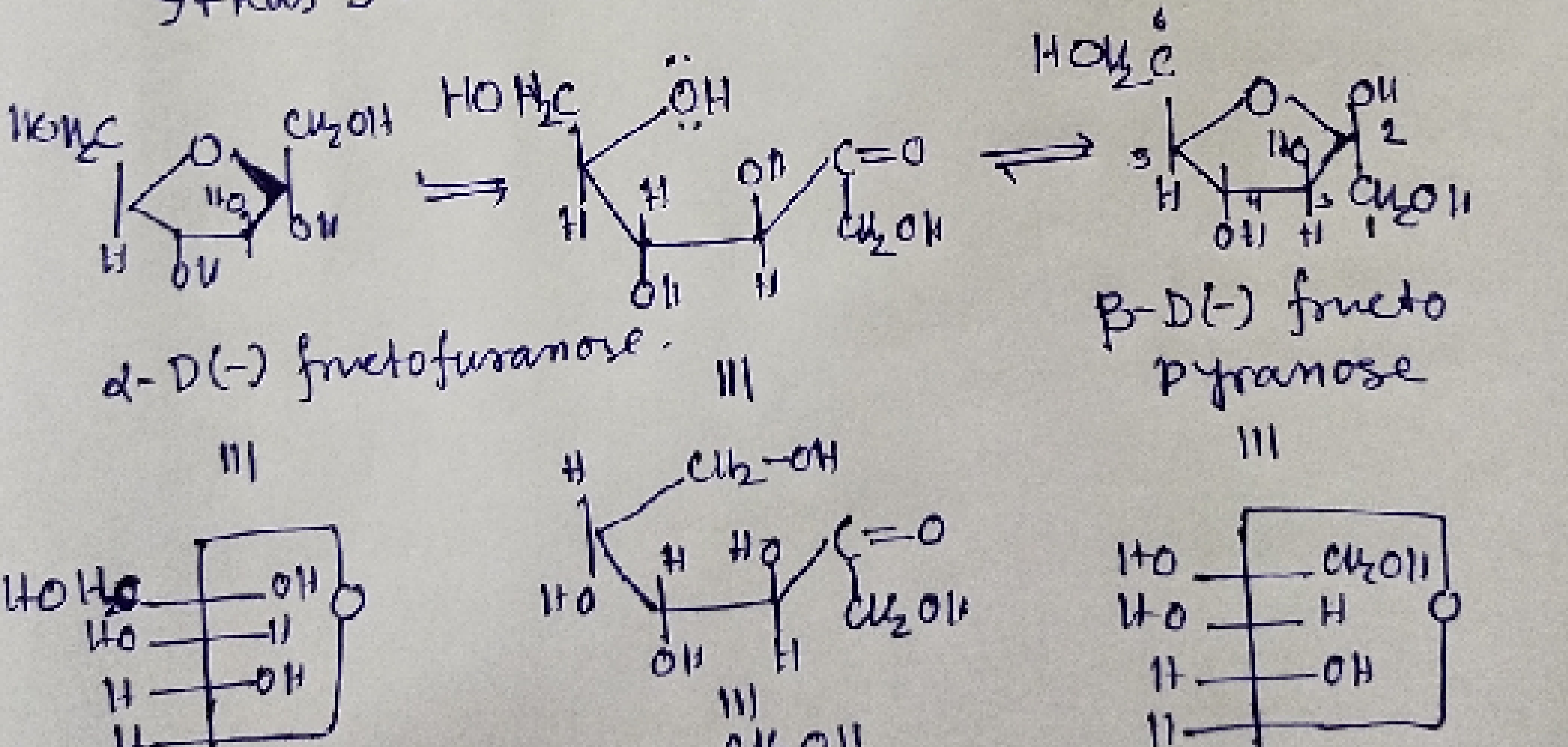
X_1, X_2 are example of acetals.
They are nonreducing sugar.
This reaction involves carbocation intermediate.



it attacks both side of vacant p-orbital of C^+.

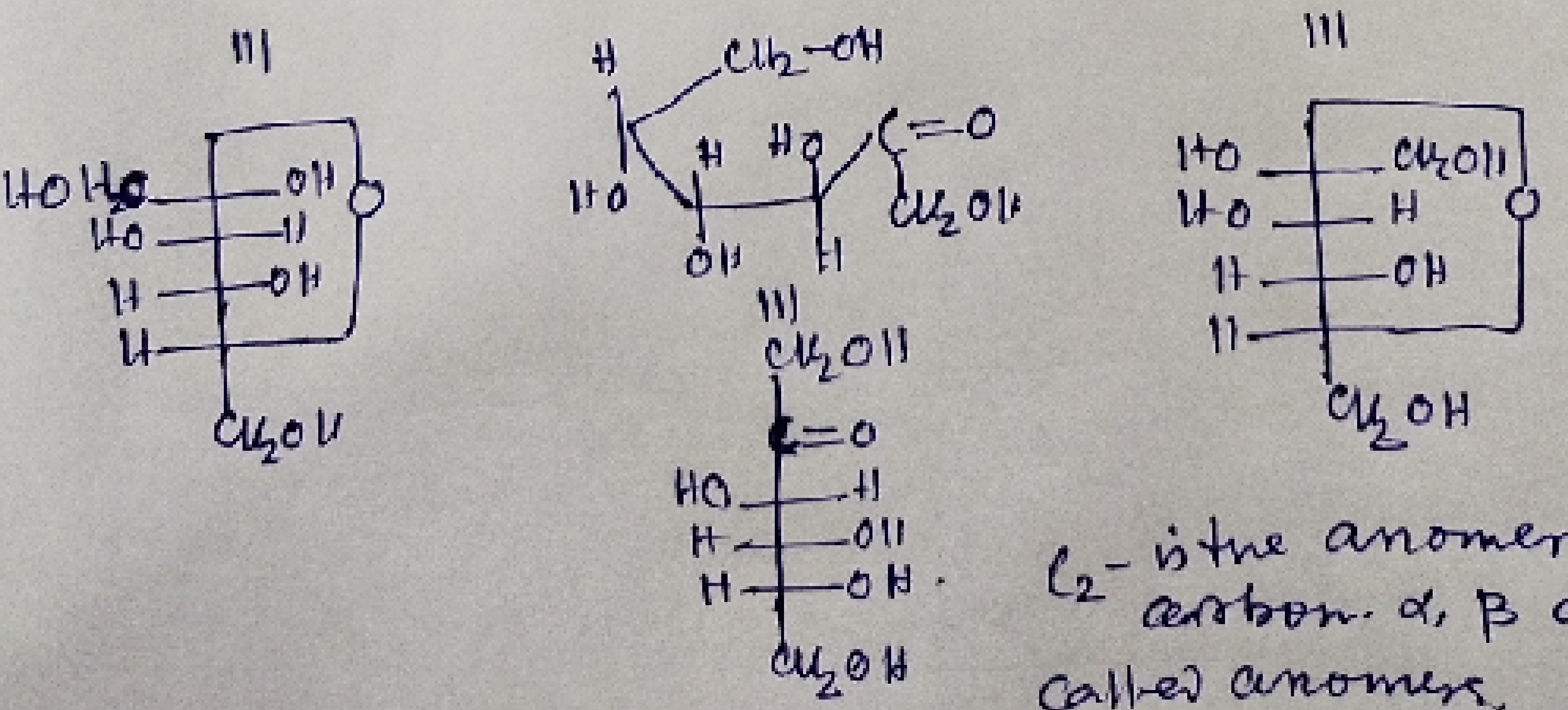
Cyclic structure of fructose

It has 5 membered ring called furanose structure.



α-D(-) fructofuranose

β-D(-) fructopyranose

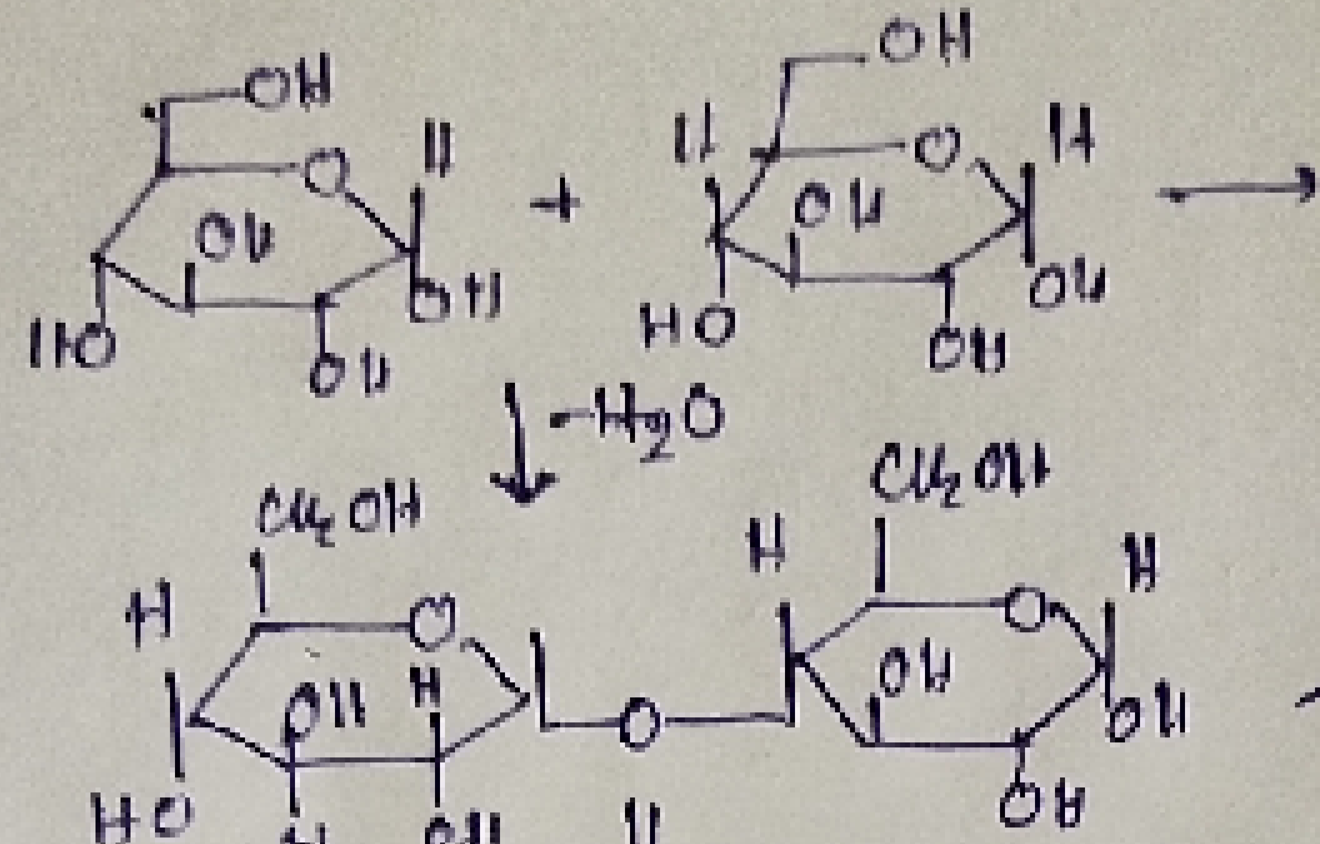


C_2 is the anomeric carbon. α, β are called anomers.

Structure of Disaccharide.

1. Maltose ⇒ Reducing sugar; water soluble

⇒ on hydrolysis it gives 2 mole α-D-glucopyranose.



⇒ C_1 of glucose unit is linked to C_4 of another glucose unit.

⇒ Pyranose str. exists.

⇒ Osazone formed.

structure of Maltose.

m.f $C_{12}H_{22}O_{11}$

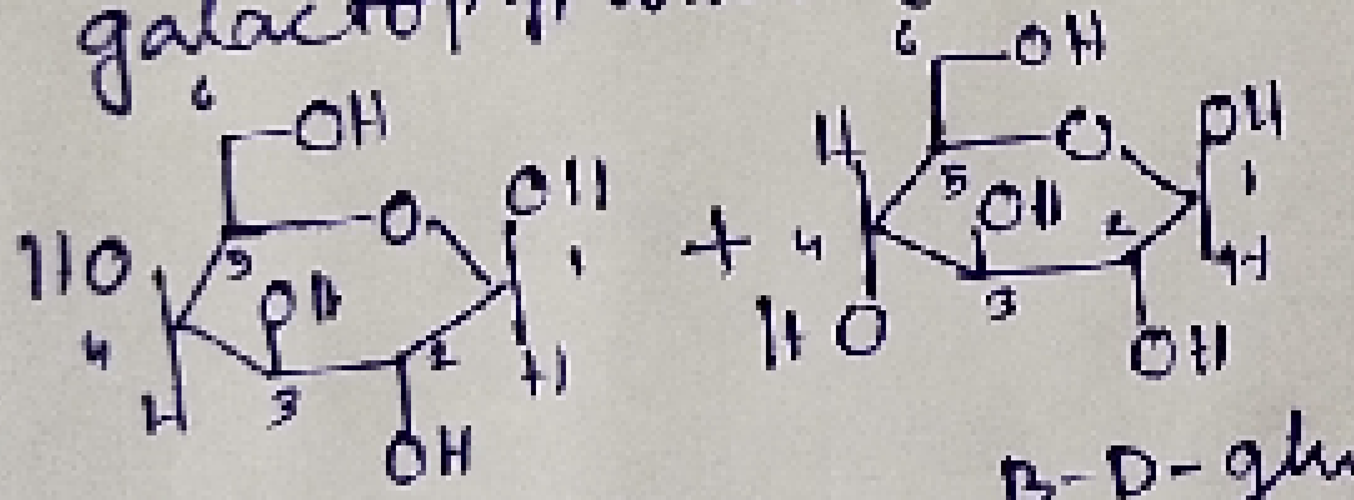
⇒ Shows mutarotation.

(Maltose) glycosidic linkage

Maltose $\xrightarrow{H_3O^+}$ α-D-glucopyranose + α-D-glucopyranose

2. Lactose ⇒ Reducing sugar; water soluble.

⇒ On hydrolysis it gives β-D-glucopyranose & β-D galactopyranose (1 mole each)



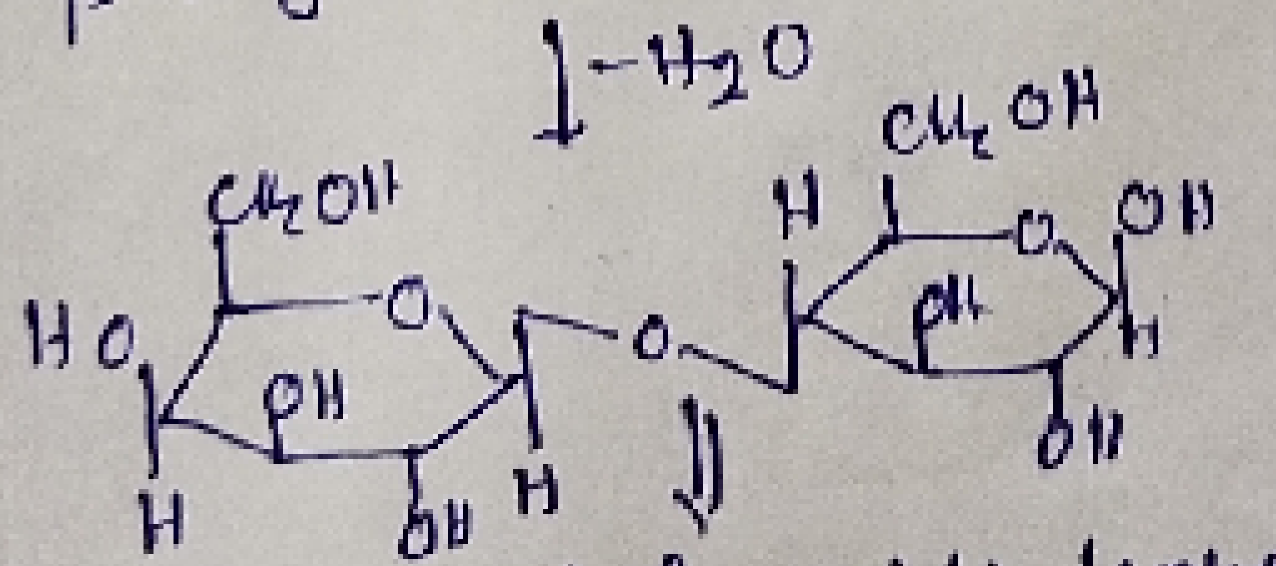
β-D-galactose β-D-glucose.

⇒ C_1 of galactose unit is linked to C_4 of an glucose unit

⇒ Pyranose str exits but β-form of both combines.

⇒ Osazone formed.

⇒ Shows Mutarotation



(glycosidic linkage)

Lactose.

m.f $C_{12}H_{22}O_{11}$

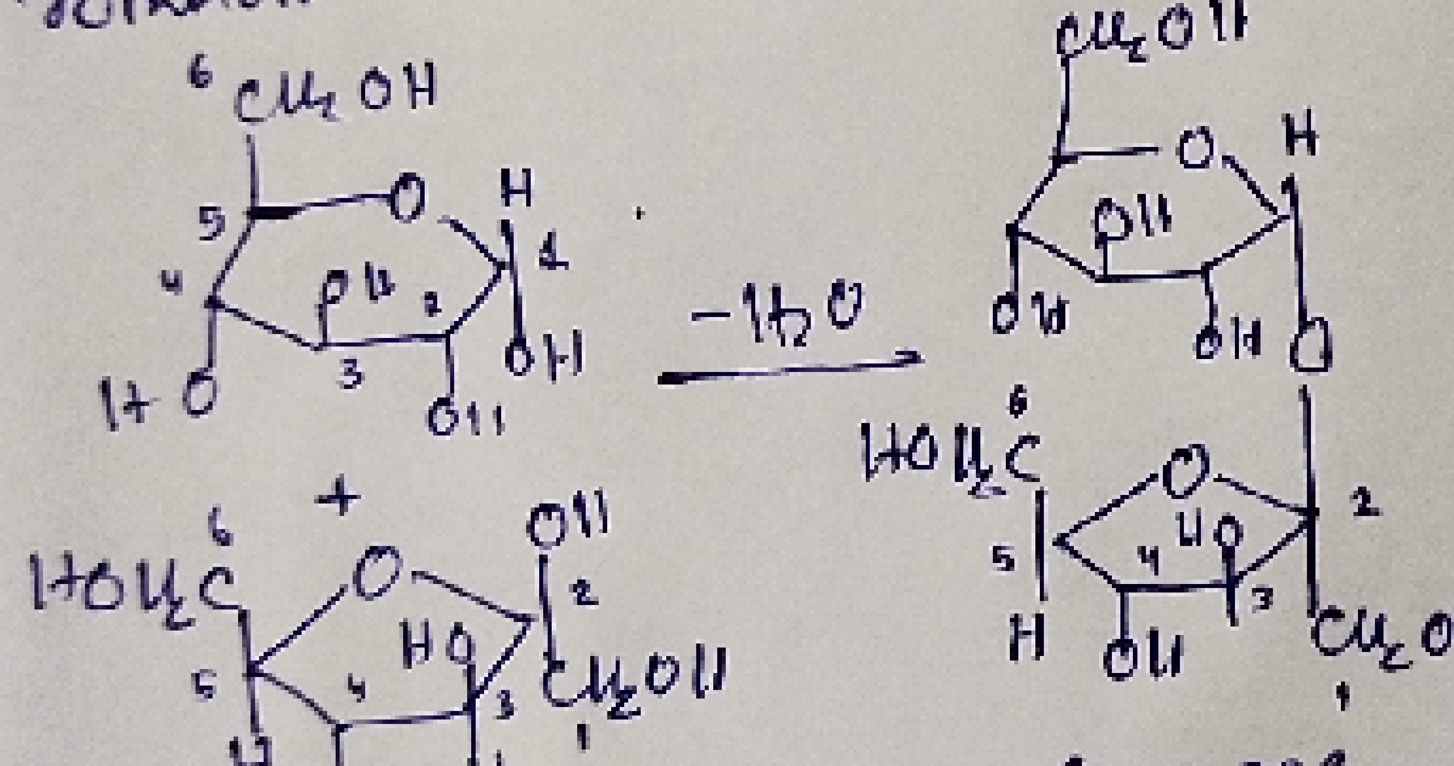
Lactose $\xrightarrow{H_3O^+}$ β-D glucopyranose + β-D-galactopyranose.

Reducing unit is present in glucopyranose unit

3. Sucrose: ⇒ It is non reducing sugar; white crystalline, sweet water soluble substance.

⇒ It has no hemiacetal linkage, it does not reduce Tollens, Fehling & Benedict solution.

⇒ When it undergoes hydrolysis it gives a mixture of D(+) glucopyranose & D(−) fructofuranose whose optical rotation is respectively $+52°$ & $-92°$. So dextrorotatory Sucrose on hydrolysis becomes Laevo-rotatory as the magnitude of −ve sign is more. The equilibrium mixture of D(+) glucopyranose & D(−) fructofuranose is called invert sugar. & inversion of solution takes place from reactant side to pdt side.



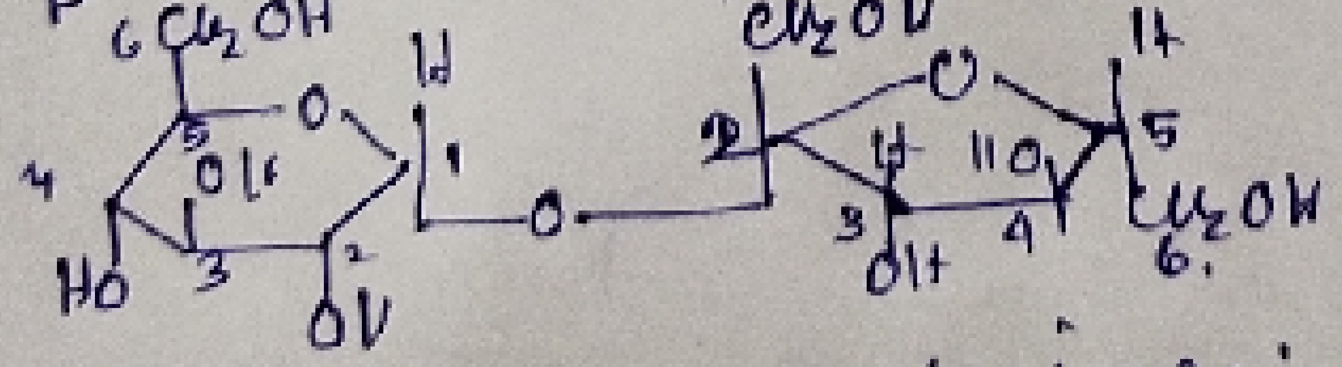
Sucrose.

[α-D-glucopyranose + β-D-fructofuranose.

⇒ No. of chiral centre = 9.

⇒ Glycosidic linkage is formed between C_1 of α-glucose & C_2 of β-fructose.

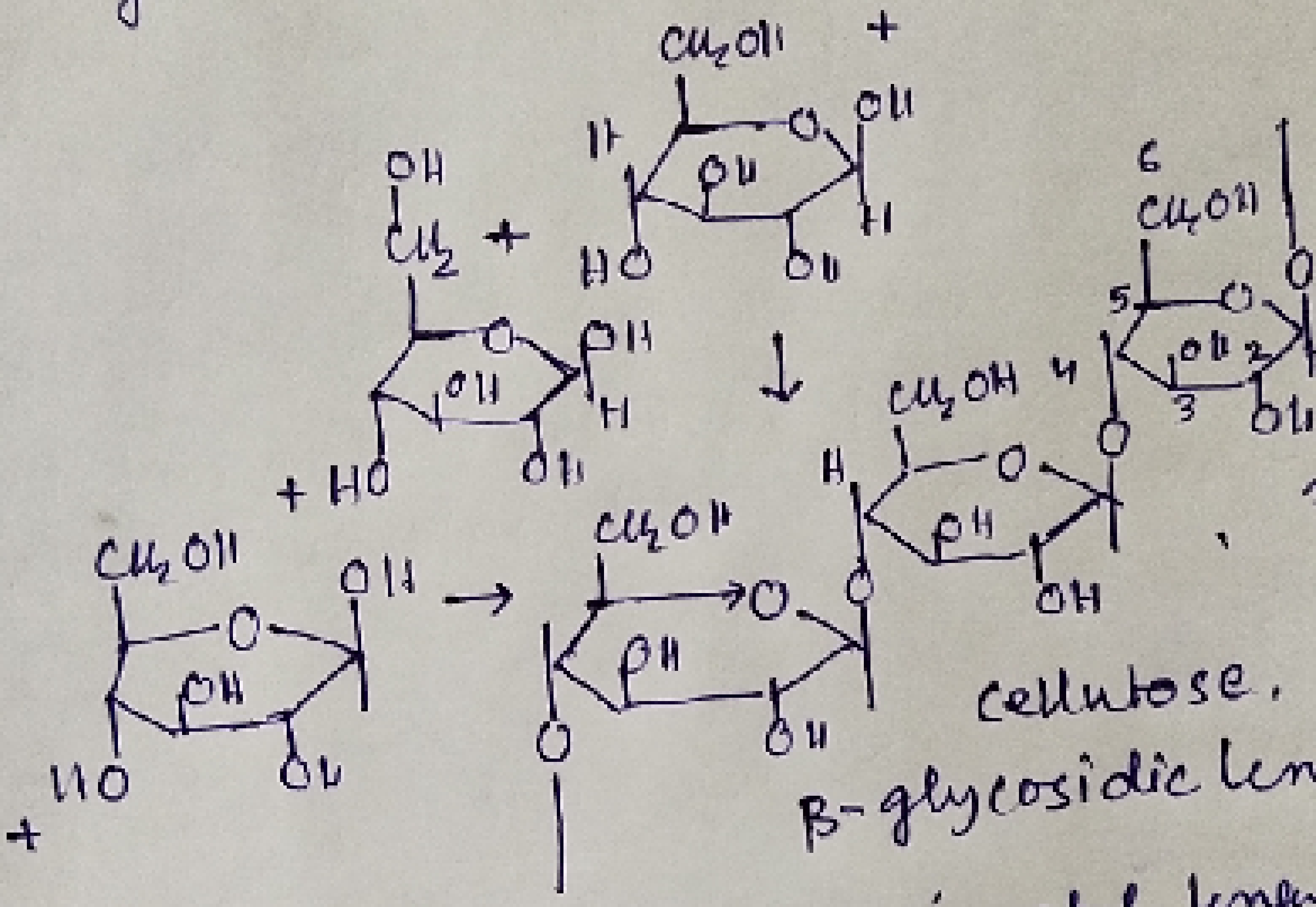
Another presentation of sucrose.



⇒ Defn of glycosidic linkage: The linkage between two monosaccharide units through oxygen atom is called glycosidic linkage. Glycosidic linkage is less strong than peptide linkage.

: Polysaccharide:

: Cellulose: Cellulose occurs exclusively in plant & most abundant organic substance in plant kingdom. It is a straight chain polysaccharide composed only of β-D-glucopyranose which are joined by glycosidic linkage between C_1 of one unit & C_4 of the next unit.



m.f $(C_6H_{10}O_5)_n$

cellulose.

β-glycosidic linkage.

⇒ Nonreducing sugar; no hemiacetal linkage present

⇒ Natural polymer. 3 free -OH groups are present in each β-D-glucopyranose unit at C_2, C_3 & C_6 of each β-D-glucopyranose unit.

⇒ So it can form triacetate; Cellulose triacetate (after extensive acylation of cellulose) formed is example of nonreducing; semisynthetic polymer.

⇒ Commercial name of Cellulose triacetate is "Rayon".

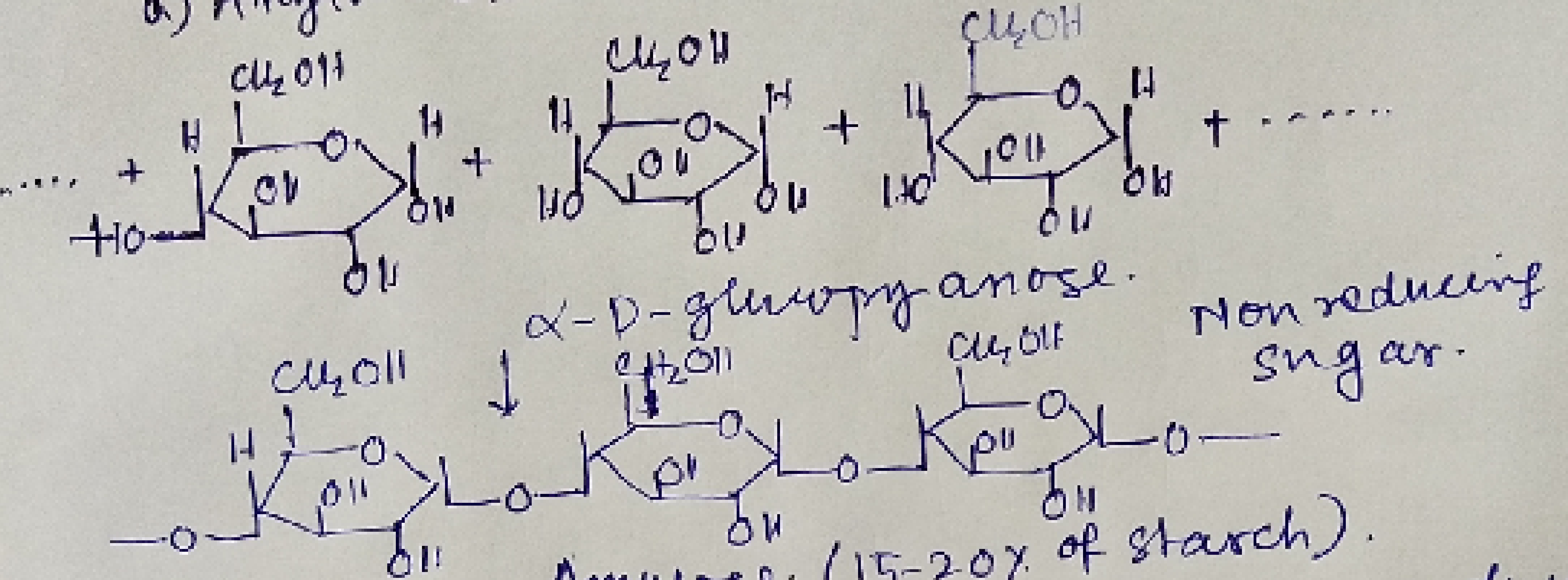
⇒ Cellulose has extensive intra & inter molecular H bonding. So it is soluble in water

⇒ It is unbranched polymer of glucose. it connects cells to form tissues.

: Starch:

Starch is the most important dietary source for human being. It is found in cereals, roots, some vegetables. It is the main storage polysaccharide of plants. It is a polymer of α-D-glucopyranose. It has two components a) Amylose b) Amylopectin

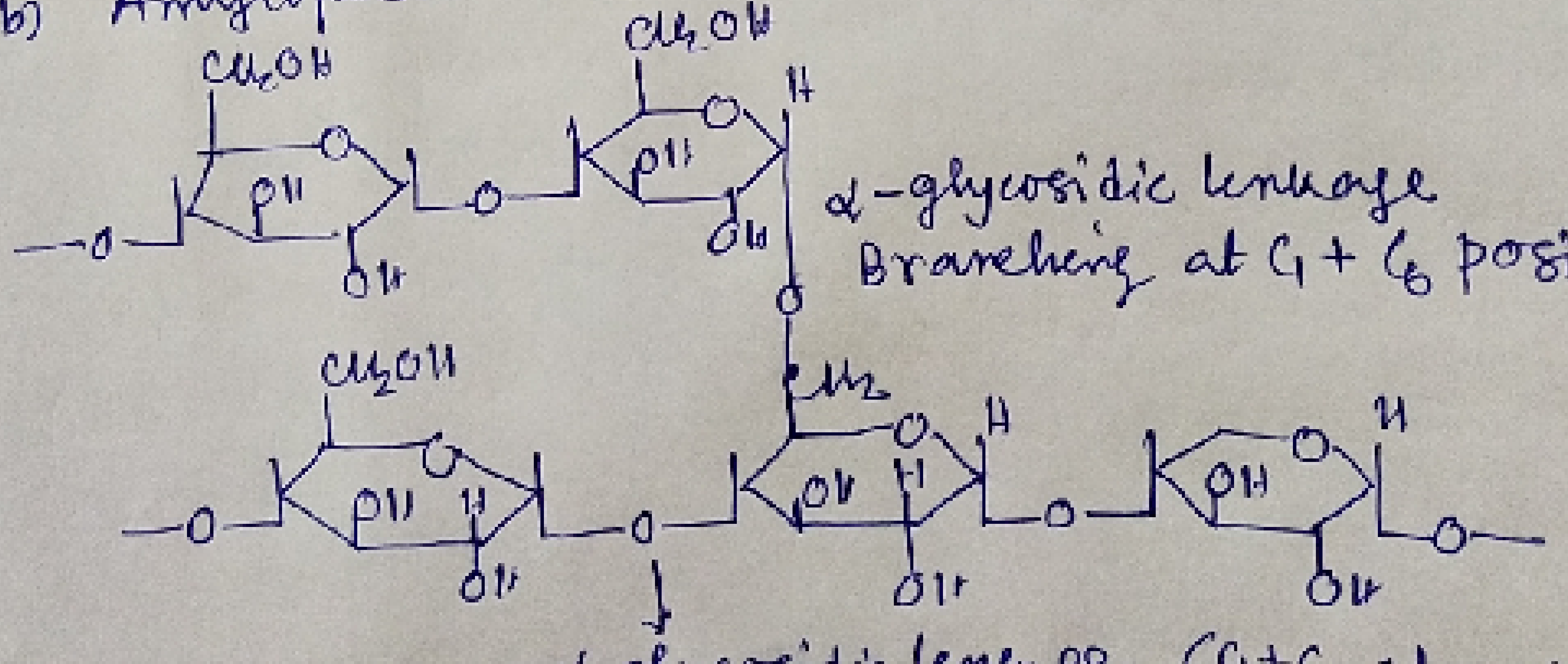
a) Amylose structure



Amylose. (15-20% of starch).

=> water soluble;
=> long unbranched chain 200-1000 unit of α-D-glucopyranose.
=> held by C_1-C_4 glycosidic linkage

b) Amylopectin structure



=> water insoluble
= 80-85% of starch consists of Amylopectin.
=> chain is formed by $C_1 + C_4$ & branching $C_1 + C_6$.
=> starch water (sparingly soluble / insoluble)