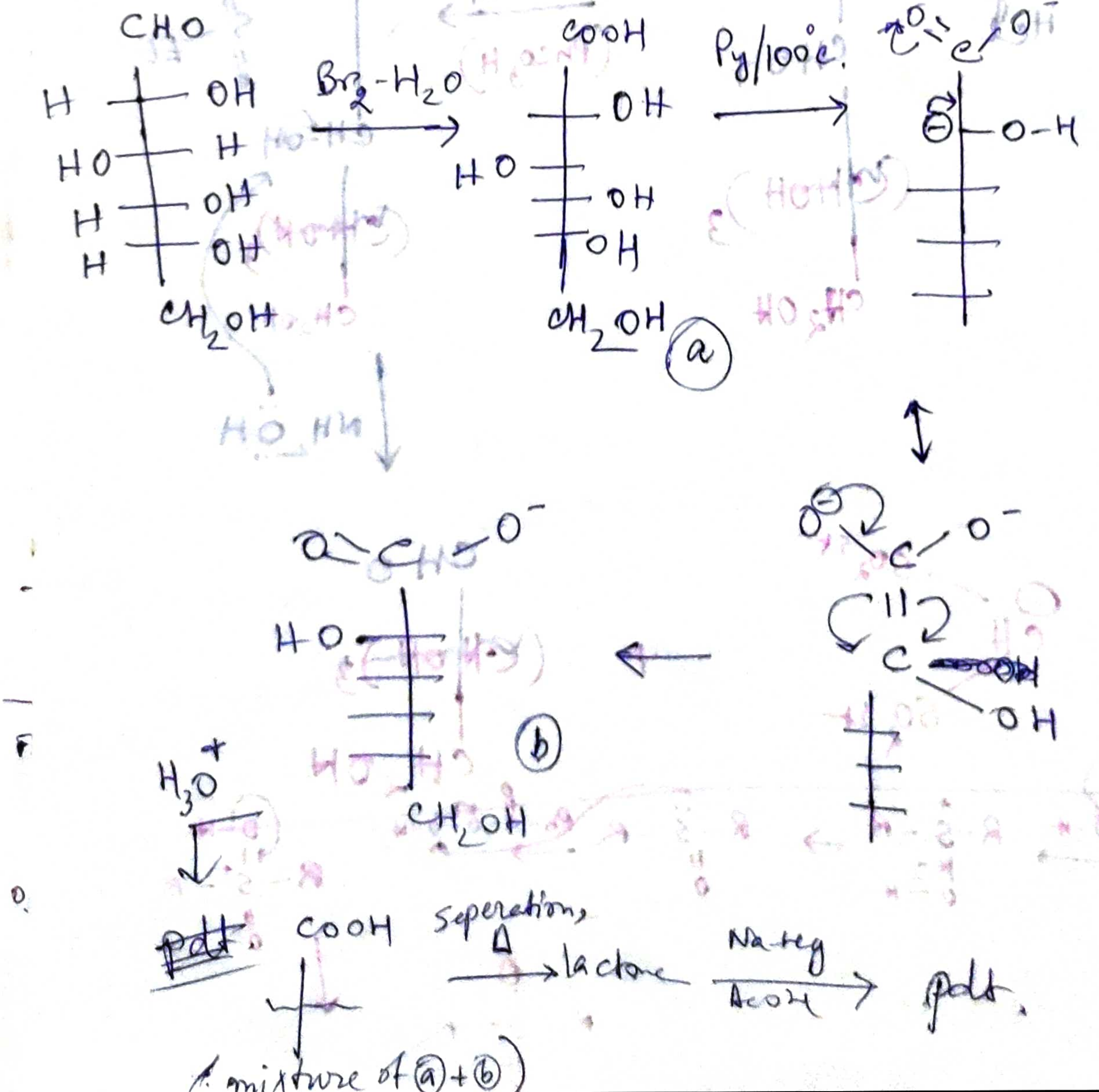
Epimerisation:—

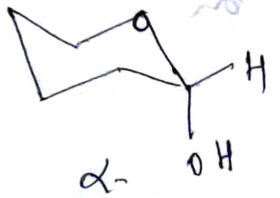
When 2 stereoisomers, containing several fixed assymetric C-atoms differ only in the configuration, one of these stereocentres they are said to be epimers. Both D-glucose and D-mannose have 4-assymetric C-atoms. But they differ in configuration only at C_2. They have the same configuration at ~~C_2~~, C_3, C_4, C_5. So, D-glucose and D-mannose are C_2 epimer to each other.

- D-glucose ⟶ D-mannose

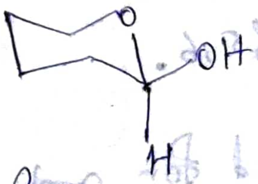


Anomer :-

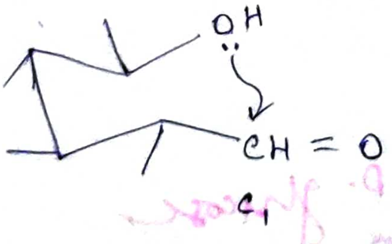
Anomer comes from the Greek word 'ano' means 'upper'. Anomers differ in configuration at the upper most chiral centre preset in the many chiral centres, in the molecule of monosacharide. Thus anomers are two molecules that differs only at C_1 or anomers are stereoisomers of a cyclic monosacharide that differ in the position of OH gr. at the hemiacetal C.



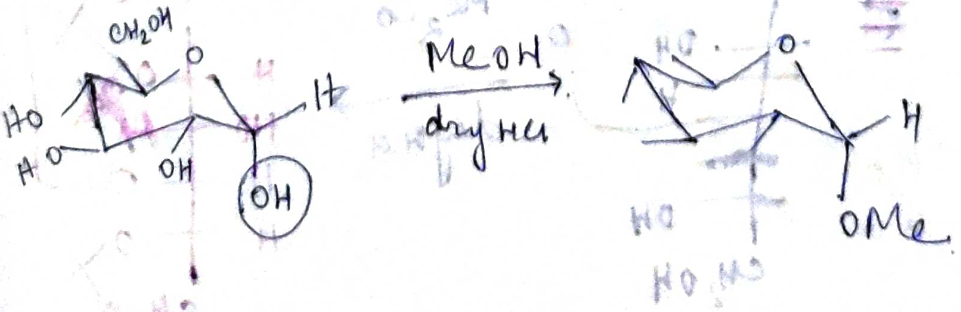
α-



β-g



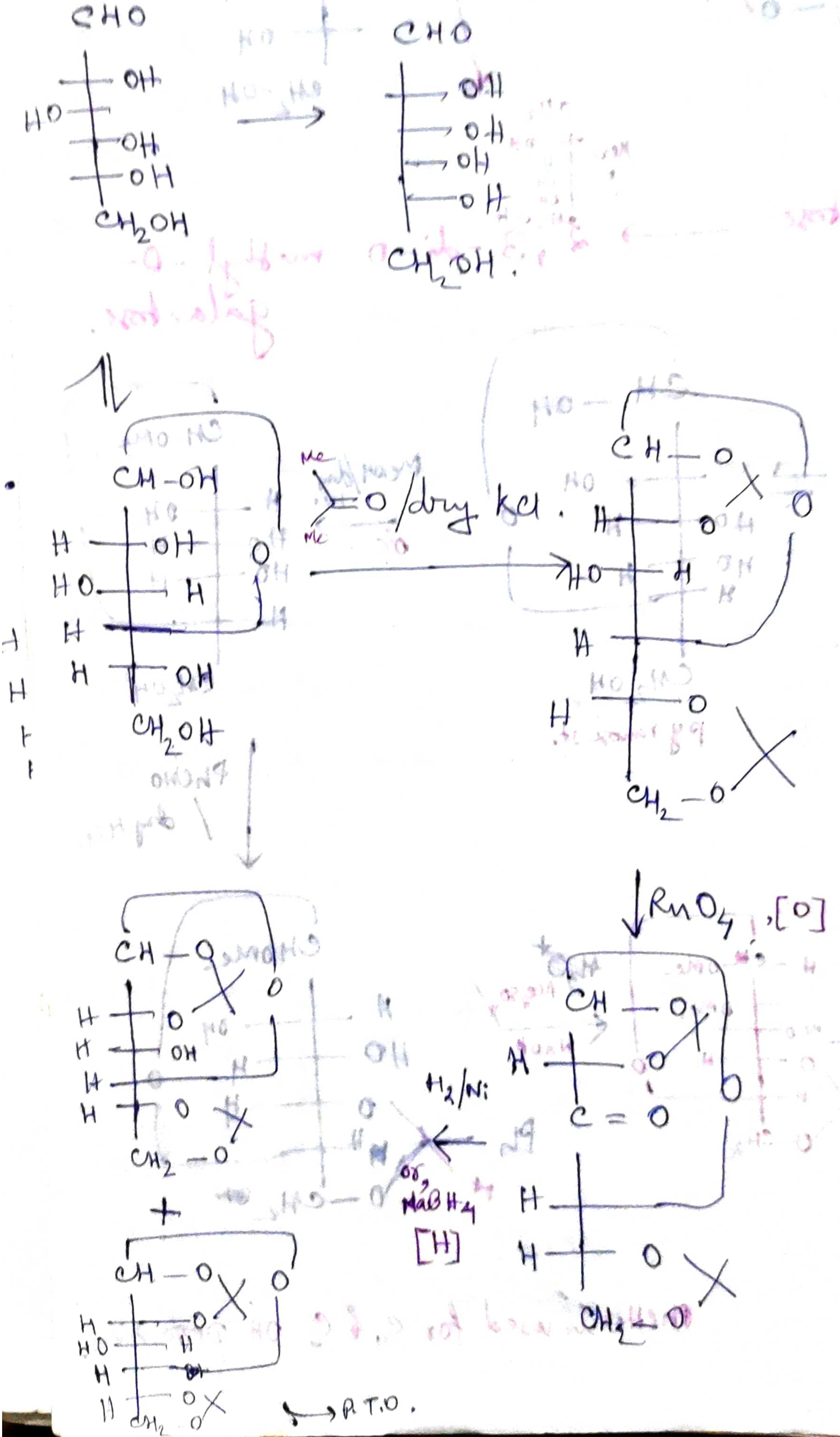
Hemiacetal :



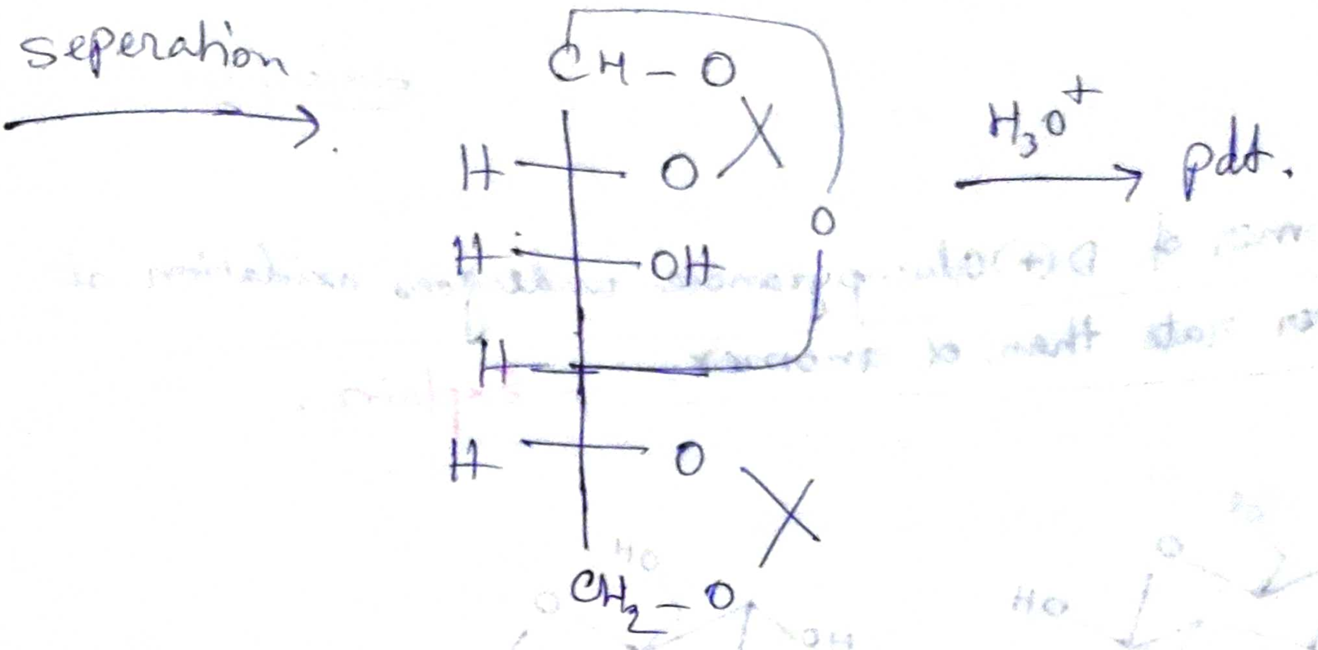
acetal

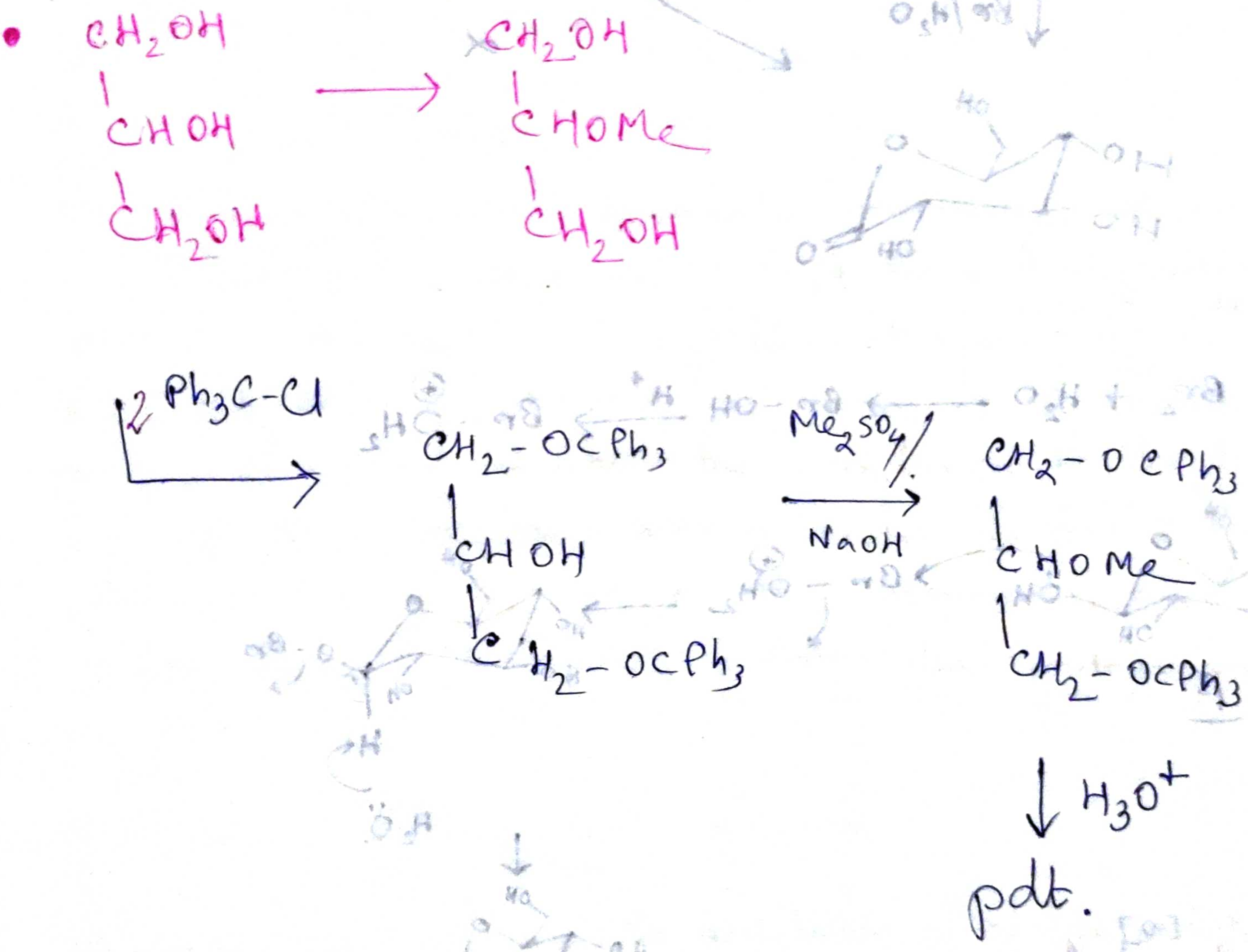
or, α-D-(+) methyl glycoside.

- D-glucose → D-allose.



→ P.T.O.

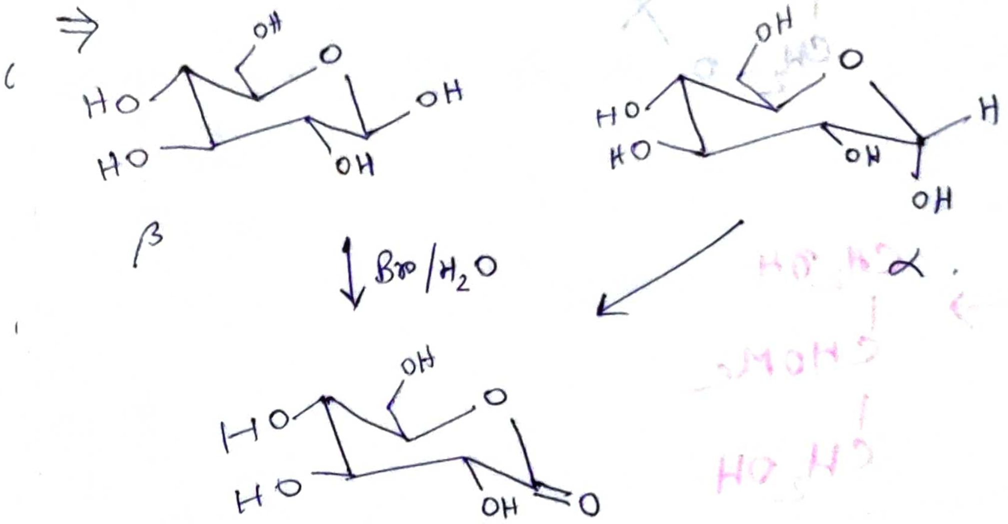

seperation
CH – O
H
O
H
OH
O
H
H
O
CH2 – O
H3O+
pdt.


CH2OH
CHOH
CH2OH
CH2OH
CHOMe
CH2OH
2 Ph3C-Cl
CH2 - OCPh3
CHOH
CH2 - OCPh3
Me2SO4/
NaOH
CH2 - OCPh3
CHOMe
CH2 - OCPh3
H3O+
pdt.

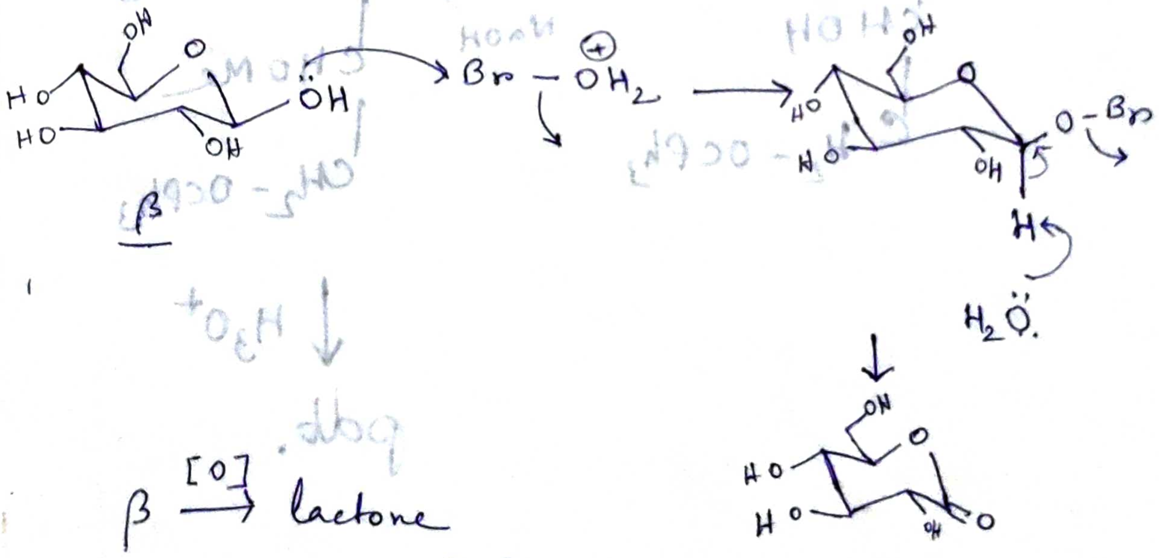
* *

Q. β-anomer of D(+)Glucopyranose undergoes oxidation at a faster rate than α-anomer. — Explain.

⇒

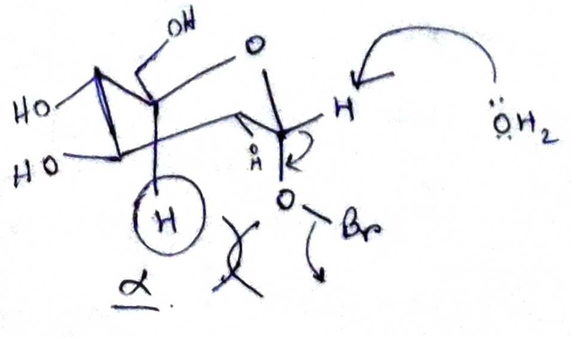


$Br_2 + H_2O \longrightarrow Br-OH \xrightarrow{H^+} Br-\overset{\oplus}{O}H_2$



$\beta \xrightarrow{[O]}$ lactone

$[\alpha] \rightleftharpoons \beta \xrightarrow{[O]}$ lactone.



$\not\longrightarrow$ no rxn.

In β-form, C-H and O-Br bonds are antiperiplanar which is stereochemical requirement of E_2 elimination. Again T.S. is less crowding. Hence oxidation occurs at a faster rate. Again In case of α-form, TS is very much crowding due to syndiaxial interraction. Actually this type of T.S. is not developed. α-form first converts to β-form & then gets oxidized to form lactone. Since β-form is oxidized directly, rate of oxd^n of this form is greater than α-form.

■ Acetylation with $(Ac_2O)_2$ and pyridine :-

Free sugar exists as an anomeric mixture, thus glucose in a bottle is a mixture of α & β form. Acytylation of glucose with Ac_2O and pyridine at room temp ~~produces~~ result fully acetytated compounds as a mixture of 2 anomers. ~~corr~~ Under this condition, the acetylation of the free hydroxyl group at the anomeric centre is faster than the competing process of the hemiacetal and mutarotation. (Acetylation is faster than mutarotation).

■ Acetylation with (Ac_2O) and CH_3COONa :-

CH_3COONa is a weak base. So, acetylation of glucose with (Ac_2O) and CH_3COONa can not be carried out at room temp. Actually acetylation is carried out at approximately 100°C, and fully acetylated pdts of this rxn are usually # β-acetate. As for example: in case of ~~pent~~ glucose penta-O-acetyl β-(D) glucopyranose is the major pdt. The selectivity may be rationalized by the fact that at elevated temp., the mutarotation which leads to α/β eq^m; is faster than actual acetylation rxn. Since, the β-hydroxyl is more nucleophilic than axial α-counter part, the β-component reacts in preference the overall results is selective formation of β-penta acetate.

▨ Acetylation with (Ac_2O) and Lewis acid :- ($ZnCl_2$)

Acetylation can also be catalysed by the addition of Lewis acid such as $ZnCl_2$ to the mixture. In presence of Lewis acid an eqn^{m} is established bet/. α & β anomer. And in this case, thermodynamically more stable α-pdt is obtained as a predominant pdt.

(8.) What do you mean invent sugar ?

As we know sucrose is disacharide of D-glucose & D-fructose. Thus, on hydrolysis, sucrose will form a mixture of these 2 monosacharides in equal amount. Again, sucrose is dextrorotatory with a specific rotation of +66.5° while its constituent monosacharide are of opposite optical rotation → D glucose is dextro rotatory (+52.6°) but D-fructose is laevorotatory (-92°). Since D-fructose has high specific rotation in comparison to D-glucose, net optical rotation of the resulting mixture as obtained on hydrolysis of sucrose would become laevo with a magnitude of (-) 39.4°. Thus, the hydrolytic mixture has an optical rotation opposite in direction to that of sucrose. Hence, hydrolysis of sucrose is known as the inversion of cane-sugar and the hydrolytic mixture is said to be the inverse sugar.