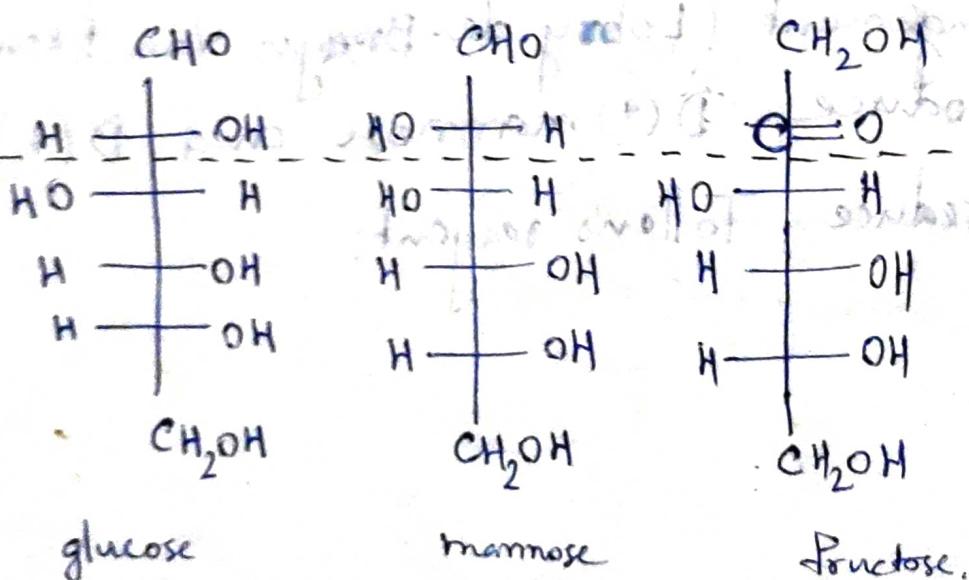
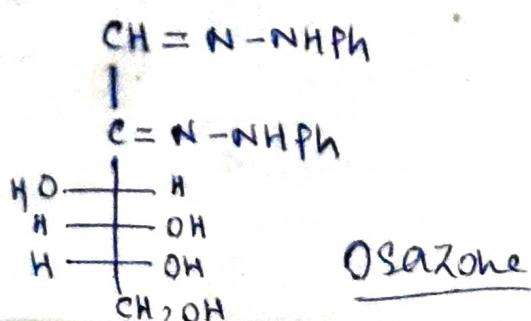
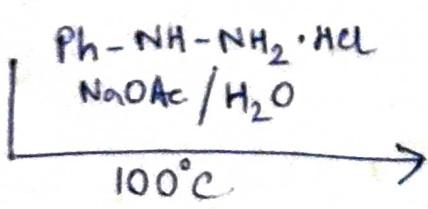


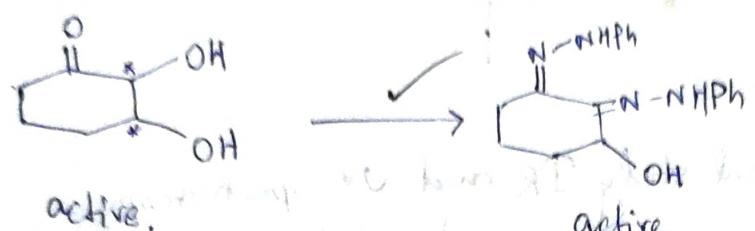
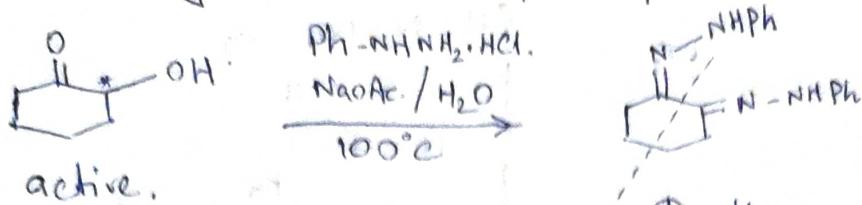
Osazone formation :-



[Configuration 3, 4, 5 & 6 of all compound same.
Osazone formation is limited to carbon 1 & 2.
So, all the compound form same osazone.]

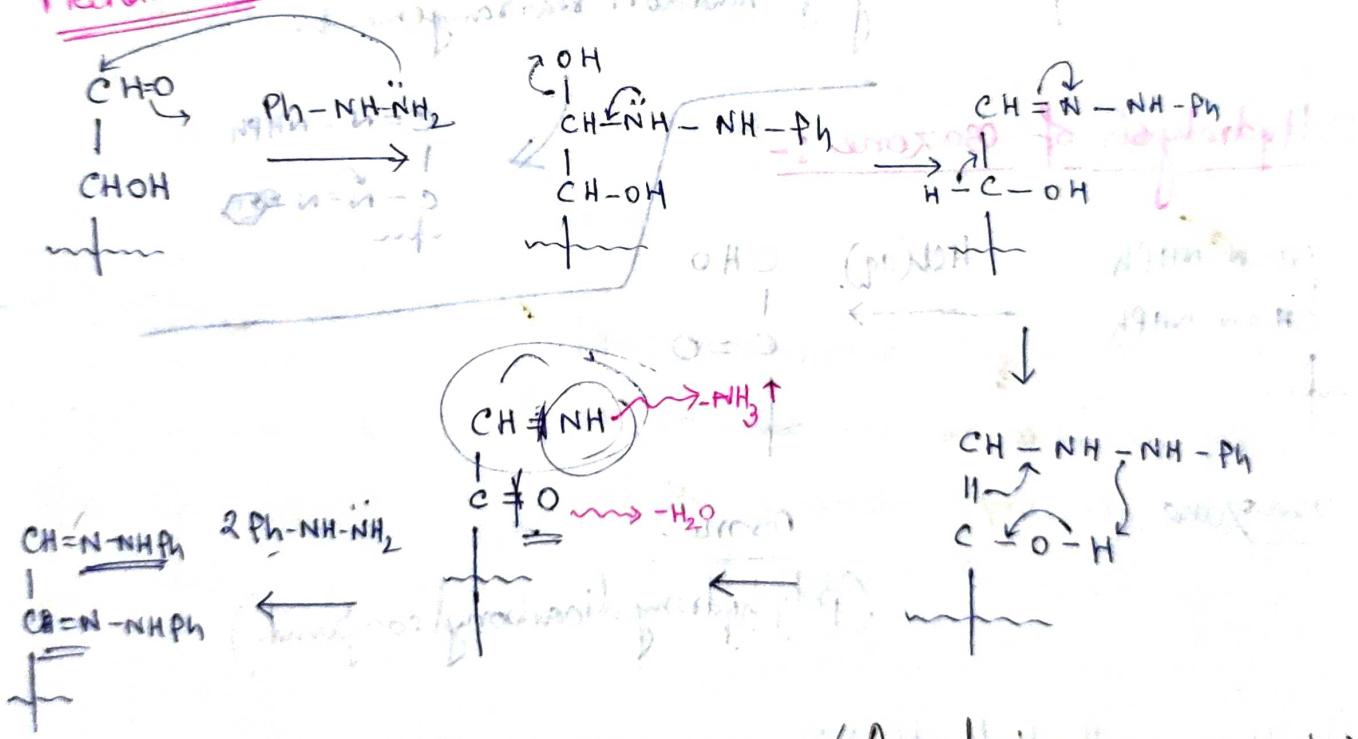


Give an evidence in favour of osazone formation that only first 2 C participate in osazone formation.



[In 3rd OH gr. participate, these inactive osazone is formed. But we get active osazone that has no plane of symmetry.]

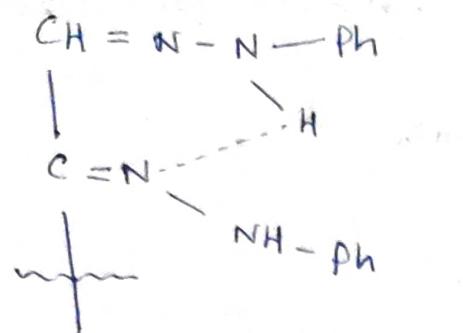
Mechanism:



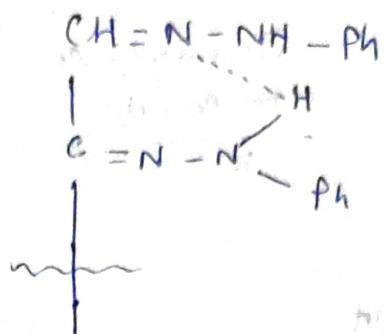
osazone. (Total 3 moles of ph hydrazines are required)

1 equiv. of phenylhydrazine functions as an oxidising agent and reduced to aniline and ammonia. Amadori rearr. is limited to first 2 C, the failure to undergo amadori rearr. can be explained by stabilization of osazone by chilation or intra.

molecular H-bonding.

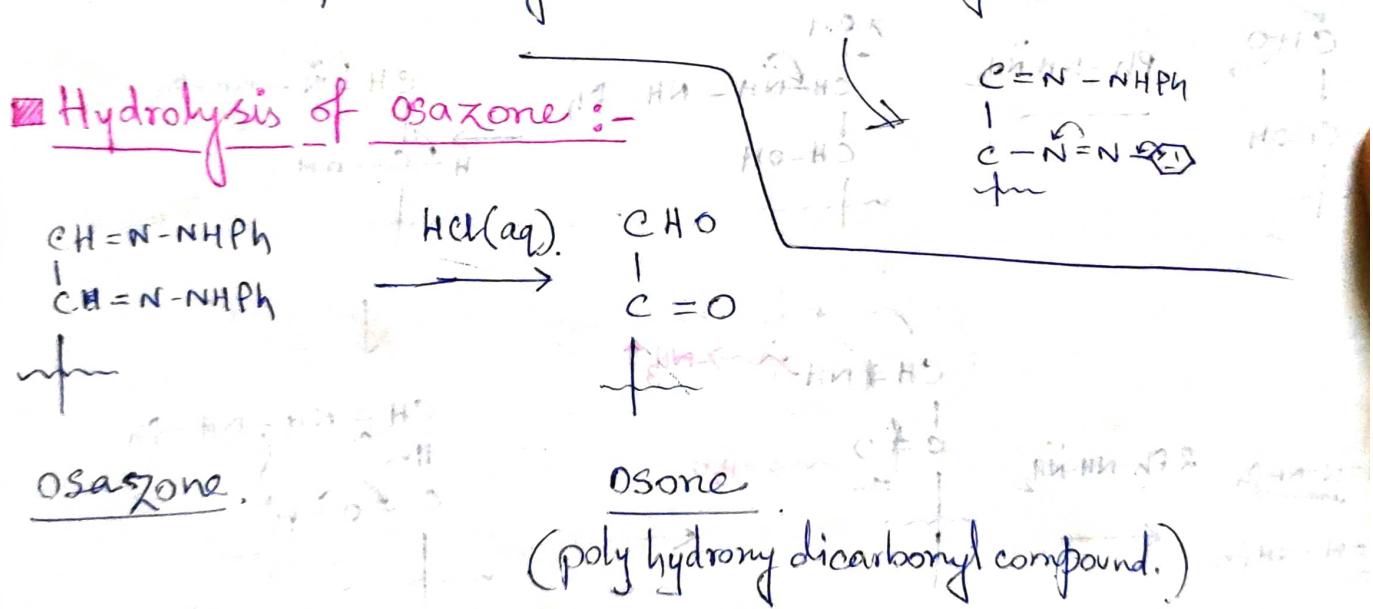


or,



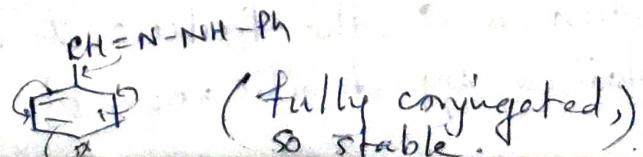
Again from their chemical study IR and UV spectroscopy proves that, there is a $\text{N}=\text{N}$ gr. i.e. phenyl diazo structure at C_2 -carbon, and this is slightly stable because π -bond π -electron of $\text{N}=\text{N}$ interacts with through resonance. So, this structure is stable and prevents further proceeding of Amadori rearrangement.

Hydrolysis of osazone:-



Another method of obtaining osone is to add benzaldehyde to osazone.

In this case Ph-CHO reacts with osazone and benzaldehyde phenylhydrazone is precipitated and osone is formed. Since phenyl hydrazone of benzaldehyde is more stable than osazone due to conjugation.

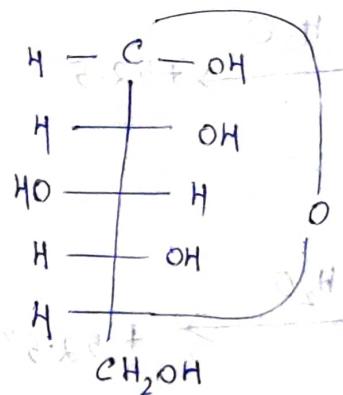
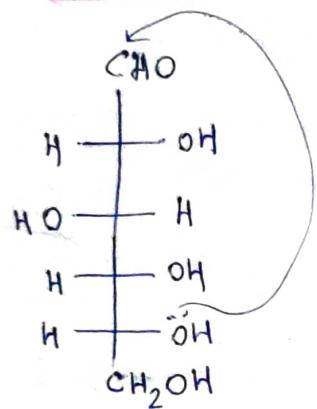


D-ribose and D-glucose are C_2 epimers.

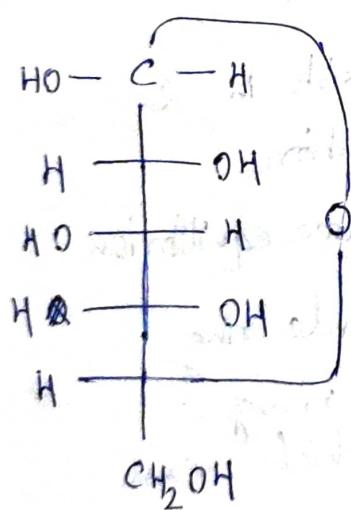
D-glucose and D-mannose are C_2 epimers.

2-aldohexose which produce same osazone has same configuration at C_3 , C_4 , C_5 carbons. But only C_2 are different. Since configuration at C_2 is lost during osazone formation.

Muta-rotation :-



II



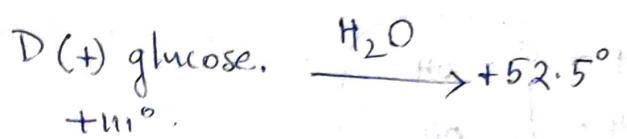
B

When monosaccharide is dissolved in water, the optical rotatory power of the solution gradually changes until it reaches a const. value.

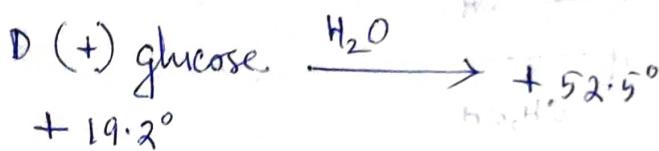
This spontaneous change of sp. rotation due to dissolution of monosaccharide is called muta-rotation.

A freshly prepared D-glucose crystallises from cold saturated aq. soln has a sp. rotation (+) 111° and another soln of D-glucose crystallises from hot conditions is

(+) 19.2°, when two crystals of D-glucose is dissolved in water. Sp. rotation gradually changes to (+) 52.5° and remains const. value. The final stage can be reached rapidly either by heating the soln or by adding some acid or base in catalytic amount. This changes of sp. rotation is called mutarotation.



(146°C mp.)



(mp. 148°C)

These observations shows that D-glucose exists in 2 different forms. Both the forms show sp. rotation 52.5° by dissolving in water. Thus they produce equilibrium mixture in water. Tollen's suggested oxide ring structure. Due to formation of this ring, one new chiral centre is produced which can exist in two configurations. These are α & β form. These 2 structures exists in equilibrium through openchain tautomerization in aq. medium.

Let, α form = $x\%$

β form = $(100-x)\%$

Opt. rot. of α form = $+111^\circ$
Opt. rot. of β form = $+19.2^\circ$

$$\therefore \frac{x \times 111^\circ + 19.2 (100-x)}{100} = 52.5\%$$

Ans: $\alpha = 36\%$

$\beta = 64\%$.

α & β form is called anomer to each other.

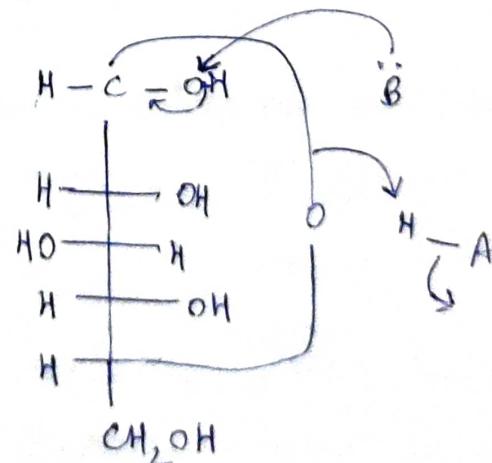
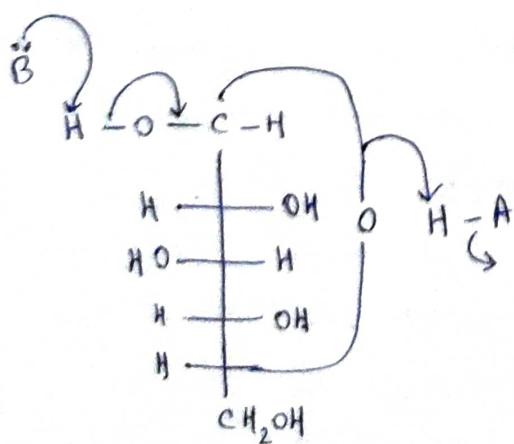
■ Mechanism of Mutarotation :-

Mutarotation is only possible in presence of amphiprotic solvent i.e. solvent which can act as a acid and base property. So mutarotation is a acid-base catalysed rxn.

D-glucose does not show mutarotation in pyridine only.

When mix. of pyridine and p -cresol are taken, it shows mutarotation.

Glucose can show mutarotation because water can acts as acid and base.

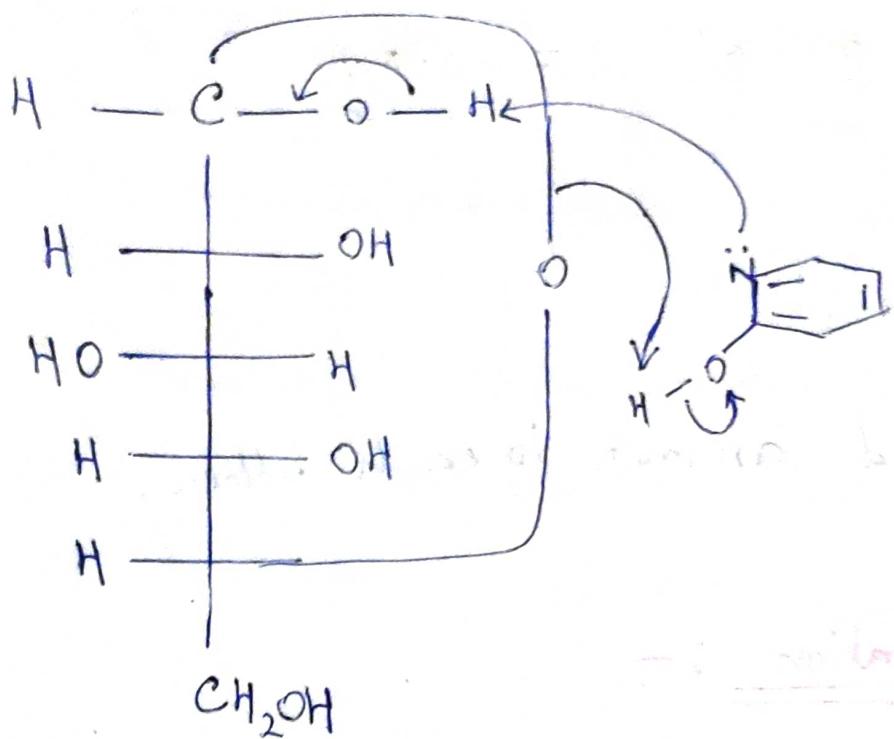


β

α

rate $\propto [\text{sub}][\text{acid}][\text{base}]$

3rd order



$$\text{Rate} \propto [\text{subs.}] [\text{T.S.}]$$

2nd order

O-hydroxy pyridine is more effective than phenyl pyridine mixture.

Since, the rxn in O-hydroxy pyridine is 2nd order. One possible explanation for increasing rate, is that the cyclic T.S. with 2-hydroxy pyridine requires lower E_{act.} than T.S. involving simultaneous attack by phenol and pyridine.