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• both carbonyl and alcoholic moieties present together, in a plethora of compound.

Note: As 'aldoses' are represented duly by 'glucose', and 'ketoses' by 'fructose', the various chemical reactions (*i.e.*, their *chemistry*) shall be specifically studied pertaining to their references.

The **'chemistry of monosaccharides'** will be discussed with particular reference to the following typical reactions and supplemented duly by appropriate examples whenever necessary; together with plausible explanations to understand the mechanism(s) of reactions:

- Oxidation,
- Reduction,
- Acetylation,
- Formation of Glucosides,
- Phenylhydrazine Reaction,
- Epimerization and
- Reaction with alkali.

4.1. Oxidation

Monosaccharides undergo 'oxidation' to yield a good number of products of reaction which solely depends upon the exact nature of the oxidizing agent being employed. Following are an array of oxidizing agents together with their respective products of reaction duly obtained from 'glucose' and 'fructose':

4.1.1. Bromine Water

It is usually regarded to be a 'mild oxidizing agent', which critically oxidizes the aldose (viz., Glucose) to an *alcohol* known as alditol (or sorbitol) through *three* sequential steps as indicated below:

Explanations: The above course of reactions are explained as under:

Step-I: The Oxidation of aldose (Glucose) with Br_2 -water helps in the conversion of the terminal aldehyde function into the corresponding carboxylic acid function thereby producing aldonic acid (gluconic acid).



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4.5.1. Fischer's Mechanism

Fisher mechanism judiciously suggest that the *osazone formation either* from aldoses or ketoses actually takes place in *three* stages in a sequential profile:

Stage-I: Conversion of Aldose/Ketose to Corresponding Phenylhydrazone:

It takes up the very first molecule of phenylhydrazine with the elimination of one mole of water.

Stage-II: Conversion of Glucose/Fructose Phenylhydrazone to Corresponding Glucosone/ Fructosone: In this case, the *second molecule of phenylhydrazine* specifically oxidizes:

• the C-2 hydroxyl (-OH) moiety in 'glucose' to a carbonyl group, or

• the C-1 hydroxyl (-OH) moiety in 'fructose' to a carbonyl group.

Besides, phenylhydrazine gets reduced to one mole each of aniline and ammonia.

Stage-III: Conversion of Newly Formed Carbonyl Moiety (Stage-II) Glucosone/ Fructosone to Corresponding Glucosazone/Fructosazone : In the final stage, the third molecule of phenylhydrazine reacts duly to produce Glucosazone/Fructosazone.

These reactions are provided as given under:

(a) Phenylhydrazine Reaction with Glucose:



(b) Phenylhydrazine Reaction with Fructose:



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Note: It may be explicitly noticed that in D (+) glucose (I) and D (+)-mannose (II) the critical difference being the orientation of H and OH at C-2 only.

Obviously, one may easily lay hand on a quite convenient practical means to identify 'a pair of epimers' by the careful preparation of 'osazones' only. Since, in the critical formation of osazones' the prevailing asymmetry at C-2 atom of the glucose (aldose) is lost completely; and, therefore, the 'epimers' viz., glucose and mannose invariably produce identical osazones.

4.7. Reaction with Alkali [or Lobry de Bruyn-van Ekenstein Rearrangment]

It may be observed commonly that **sugars** on being warmed with concentrated alkali (NaOH) solutions first changes into yellow-brown-and turn into a resinous product finally; however, the probable mechanism still remains a mystery. Importantly, the *sugars* on being treated with *amines* or *dilute alkalis* undergo spectacular rearrangment to produce rather a mixture comprising **more than one sugar entities**.

Example: Glucose when reacted with *dilute alkali (e.g., 0.2 M NaOH)* gets duly converted into a mixture of *three* monosaccharides *viz.,* glucose, mannose, and fructose.

The above typical reaction is named after its discoverer as Lobry de Bruyn-van Ekenstein rearrangment.



Later on, Wohl (1900) duly postulated that a common 'enediol' *intermediate* is obtained in the course of the actual transformation *via* the 1, 2-enolisation of three monosaccharides, namely: **D** (+)-Glucose, **D** (+)-Mannose, and **D** (-)-Fructose, as given under:

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Important Inferences: These essentially comprise:

- (i) From the above reactions it is quite evident that the compounds [III] and [VI] are D-(-)-Ribose and D-(-)-Lyxose respectively.
- (ii) In the same vein, compounds [IV] and [V] represent D-(-)-Arabinose and D-(+)-Xylose respectively.
- (iii) However, the *oxidation* of the 'aldopentoses' give rise to the formation of [IV] and [VI] *i.e.*, Arabinose and Lyxose; whereas, [III] and [V] designate duly Ribose and Xylose.
- (iv) Therefore, one may affirmatively confirm that: [III] = Ribose; [IV] = Arabinose; [V] = Xylose; and [VI] = Lyxose as adequately supported by the *two* factual statements submitted above.