

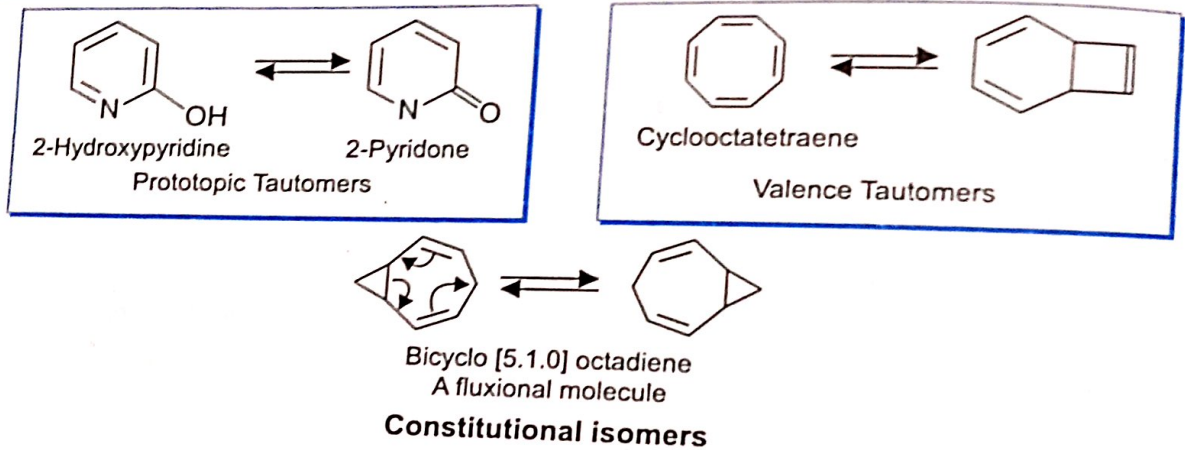
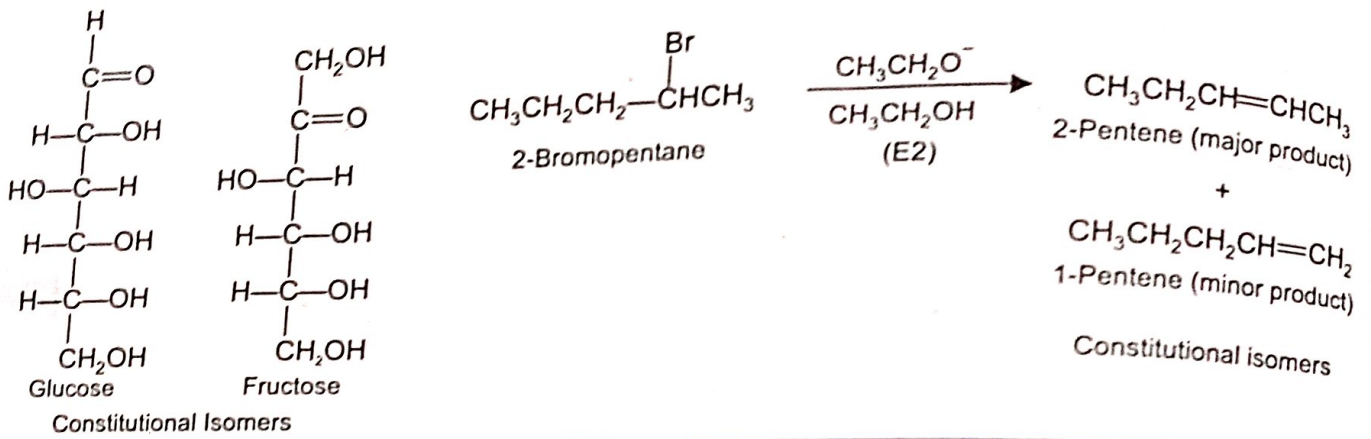
SCHEME 1.1

(A) Constitutional Isomers

Constitutional isomers differ in the connectivity of atoms including bond multiplicity; disregarding configuration and conformation. The equivalent older term structural isomers is obsolete and redundant. All isomers are structural isomers and structure includes constitution, configuration and conformation.

Glucose and fructose (scheme 1.1a) are constitutional isomers, glucose is an aldehyde while fructose is a ketone. E2-elimination is regioselective since more of one constitutional isomer is formed.

- Some other examples of constitutional isomers include:
- **Tautomers.** Isomers of different energies which are interconvertible via a low energy barrier, the isomerization involves atom or group migration.
 - **Proton tautomers (Prototropy).** Enol-keto isomerization is an example of prototropy (i.e., a change in the position of a proton) and the interconversion of the tautomers, 2-hydroxypyridine and pyridone is an example (scheme 1.1a) of prototropy i.e., change in the position of a proton and involves proton tautomers.
 - **Valence isomers.** These isomers or degenerate species that are interconvertible by reorganization of some of the bonding electrons. The interconversion is accompanied by atom movement and not atom migration. Valence isomers are not tautomers. Valence isomers can be separately identified and in case these have the same structure (degenerate species) the individual atoms can be separately identified. The interconversion of cyclooctatetraene and its bicyclic isomer is an example of valence isomers (scheme 1.1a)



SCHEME 1.1a

- **Fluxional molecules.** Molecules which undergo rapid degenerate rearrangement i.e., a rearrangement into indistinguishable molecules e.g., via bond reorganization (scheme 1.1a).
- **Allylic isomers.** These isomers result due to a rearrangement involving the allyl (propenyl group) and is recognized separately. These rearrangements may occur via the intermediate formation of a delocalized ion or a radical. The loss of X at one end and its return to the opposite end of the allyl system (scheme 1.1b) leads to the over-all rearrangement. The allylic isomers arise due to a 1, 3-rearrangement.