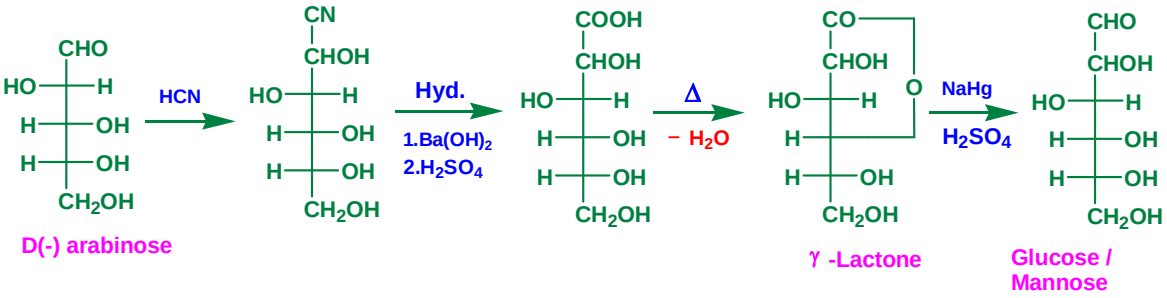
B.Sc Sem (IV) CHB-401 Section –B (Organic Chemistry)

Dear B.Sc IV Sem. N(D) batch students, this is the continuation of my lecture of Organic Chemistry (CHB-401). Please complete the whole syllabus and if you have any doubt or query contact me at 9450200221.

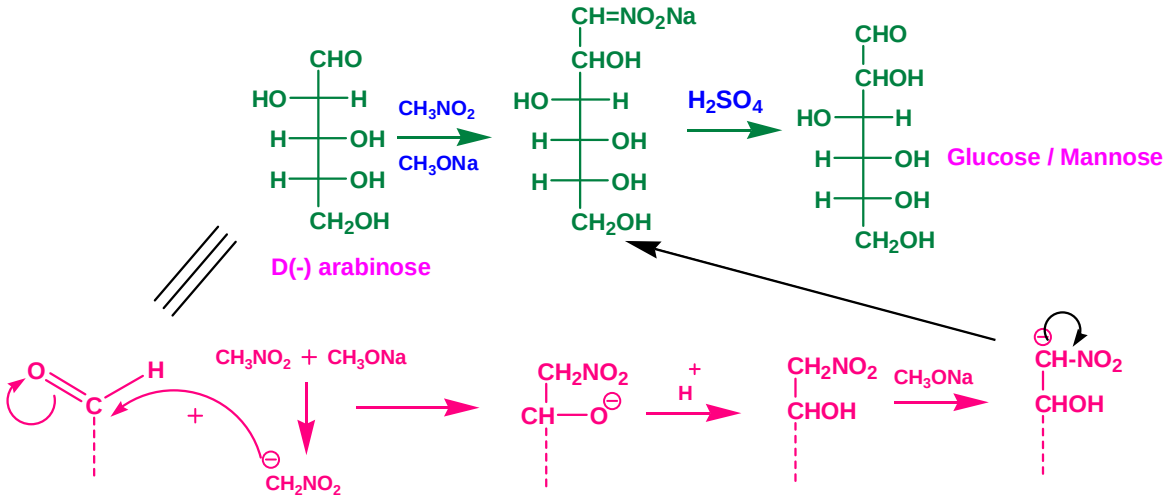
Chapter 3: Carbohydrates

Ascending the Sugar Series: an aldose may be converted into its next higher aldose.

(i) Kiliyani Synthesis

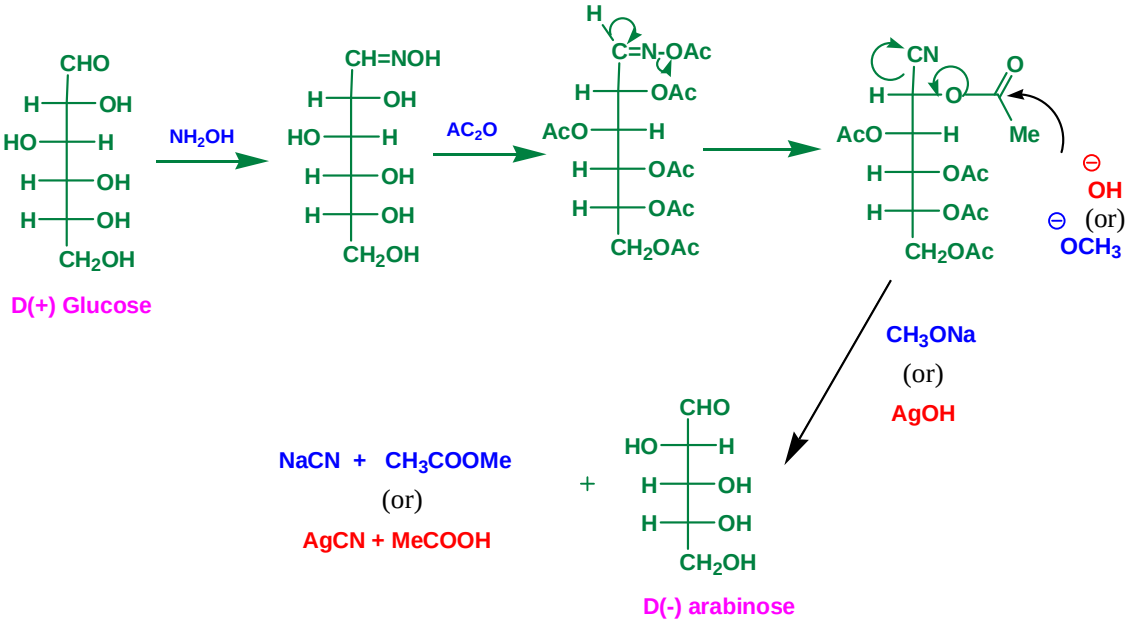


(ii) Sowden method

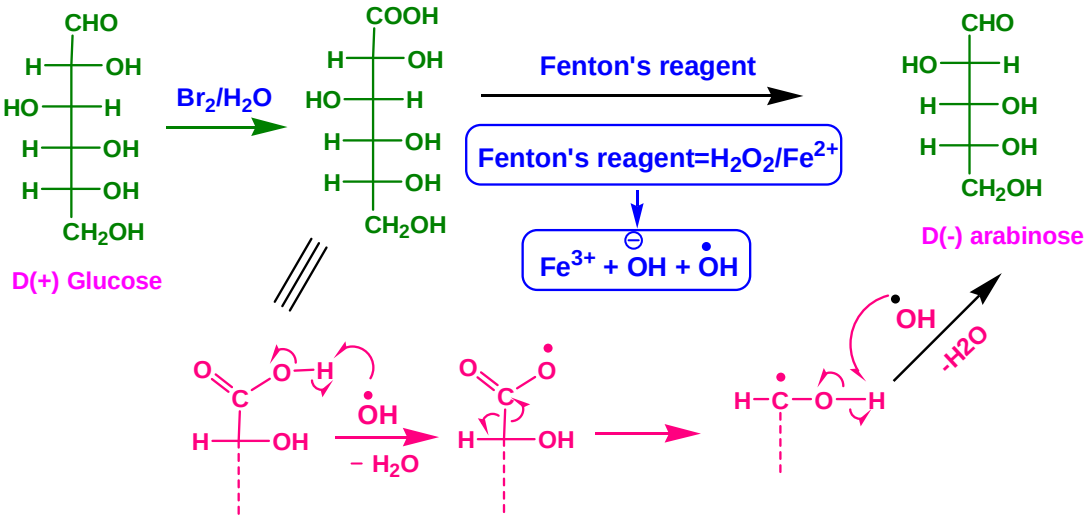


Descending the Sugar Series: an aldose may be converted into its next lower aldose.

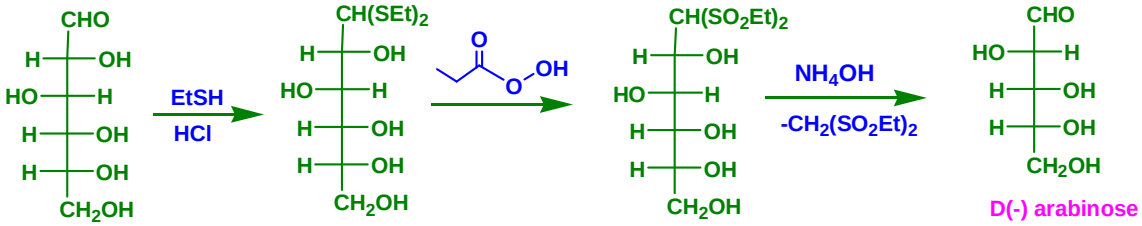
(i) Wohl's method



(ii) Ruff's method



(iii) Macdonald method

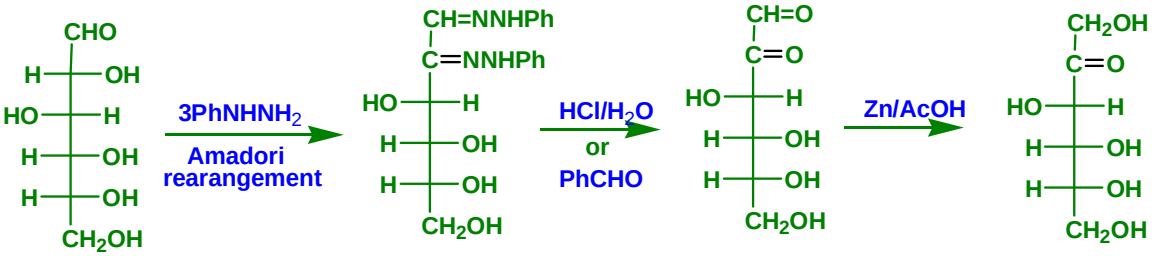


D(+) Glucose

D(-) arabinose

Conversion of Aldose to Ketose:

(i) Through osazone formation



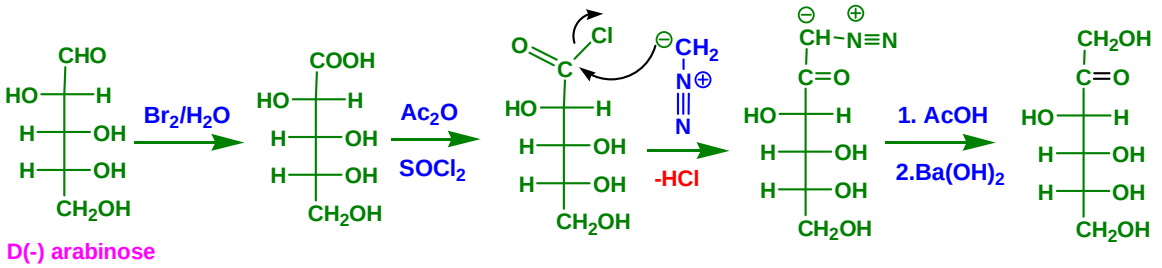
D(+) Glucose

Osazone

Osone

Fructose

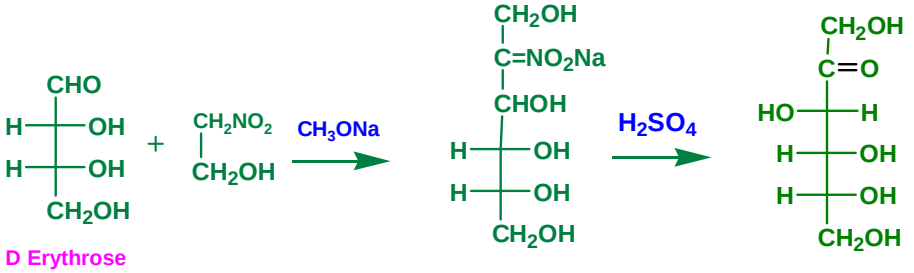
(ii) Wolform method (with one carbon ascending)



D(-) arabinose

Fructose

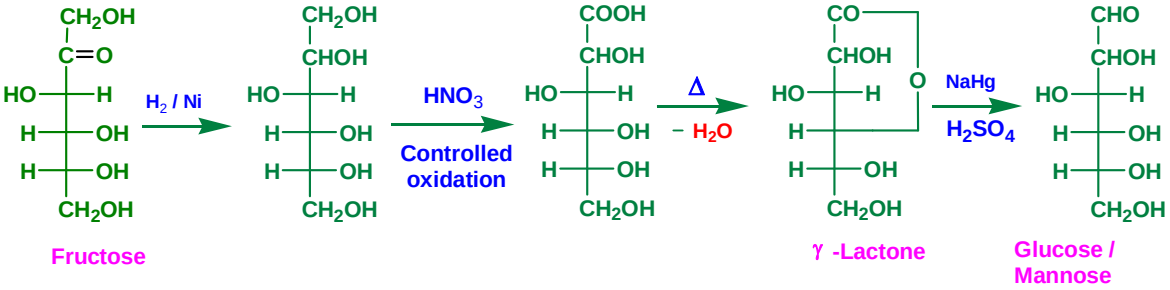
(iii) Sowden method (with two carbon ascending)



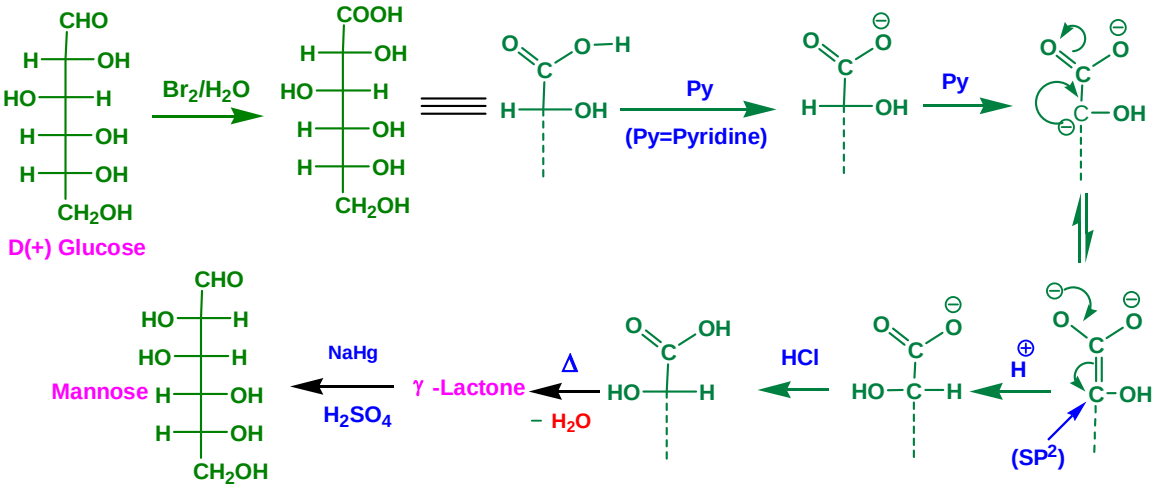
D Erythrose

Fructose

Conversion of Ketose to Aldose:

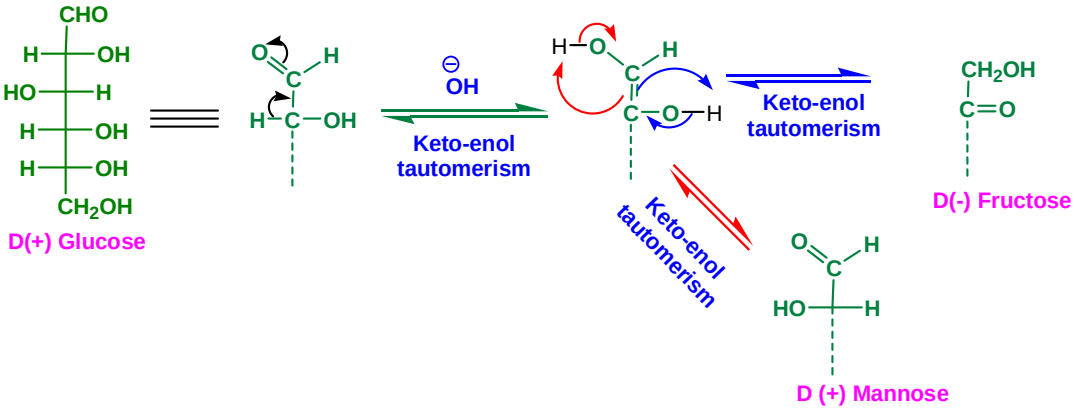


Epimerisation: The change of configuration of one asymmetric carbon atom in a compound containing two or more asymmetric carbon atoms is known as epimerization.



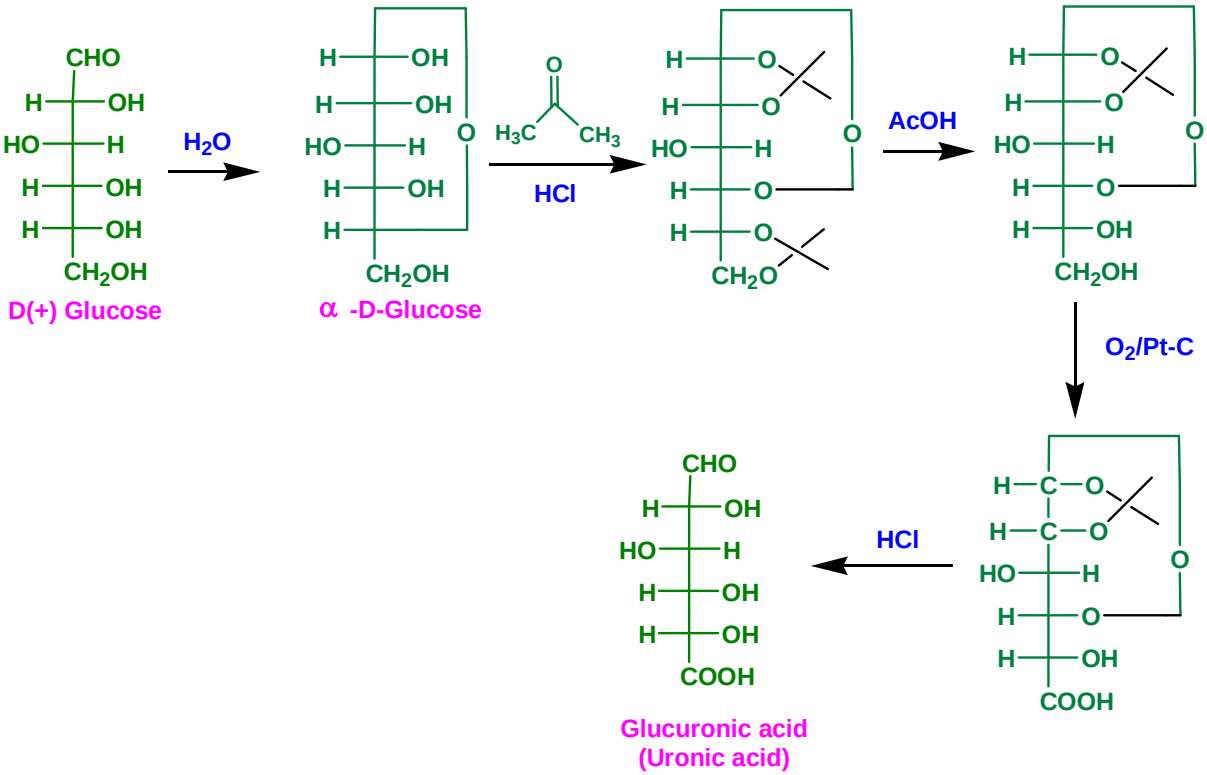
Lobry de Bruyn-Van Ekenstein rearrangement:

A dilute solution of glucose, in the presence of NaOH, is converted into an almost optically inactive solution from which have been isolated glucose, mannose and fructose.



Preparation of Glucuronic acid:

Uronic acids are produced by oxidation of only the terminal-CH_2OH in an aldose.



Chapter 4: Colour and Constitution

When white light falls on a substance, the light may be totally reflected (white colour) or totally absorbed (Black). If a certain proportion of the light is observed and the rest reflected, the substance has the colour of the reflected light.

Dyes

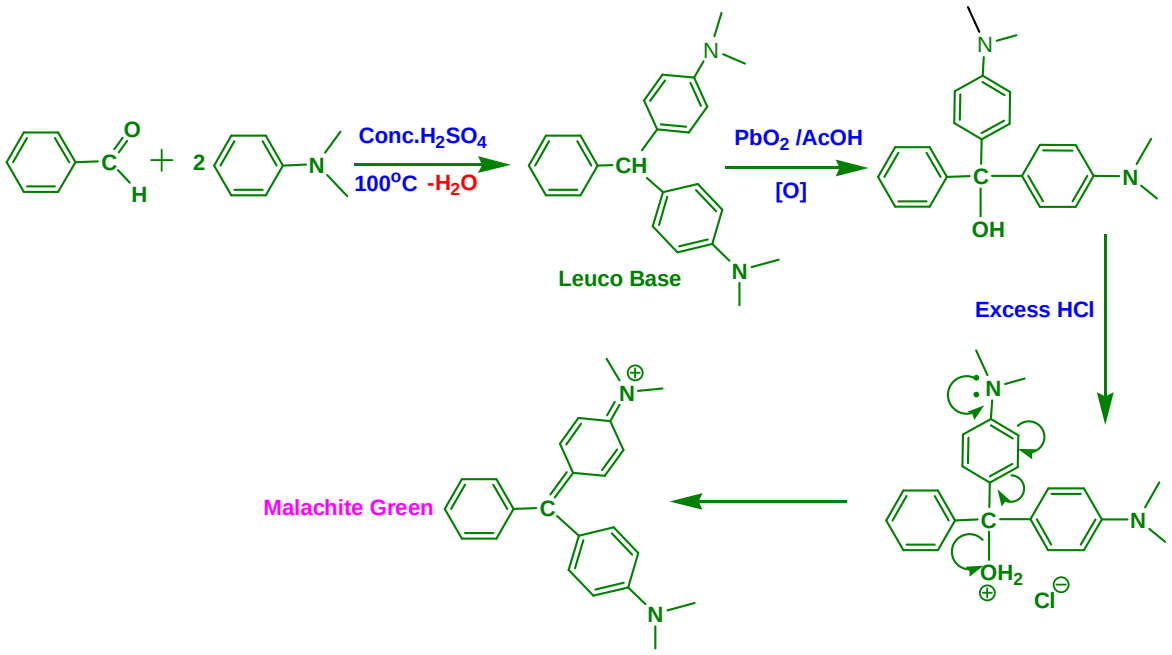
Classification of Dyes: (According to the application)

1. Acid Dyes are the Na salt of sulphonic and carboxylic acid and are applied to wool, silk, polyamide and acrylic fibres.
2. Azoic Dyes are insoluble azo dyes which are prepared in situ and are applied to cellulosic fibres.
3. Mordant Dyes do not dye a fibre directly. They required a mordant. For acidic dye: metal hydroxide, for basic dyes tannin are used.
4. Metal complex dyes are made of dyes and metal complexes.
5. Vat Dyes are used in their reduced form (Leuco compound) and after the application to the fibre are oxidized to the dye. They are used mainly cotton fibres.
6. Silphur Dyes are applied to cellulosic fibres.
7. Disperse Dyes are insoluble dyes which are dispersed by suitable reagents.
8. Reactive dyes are containing a reactive group which combines directly with cellulose fibres.
9. Organic Pigments are water insoluble compounds which are used for colouring paints.

Malachite Green (Triarymethane Dyes)

Malachite green is prepared by condensing two molecules of diethylaniline with benzaldehyde at 100°C in the presence of conc. Sulphuric acid. The Leuco-base produced is oxidized with lead dioxide in a solution of acetic acid containing HCl. Malachite green dyes wool and silk directly and cotton mordanted with tannin.

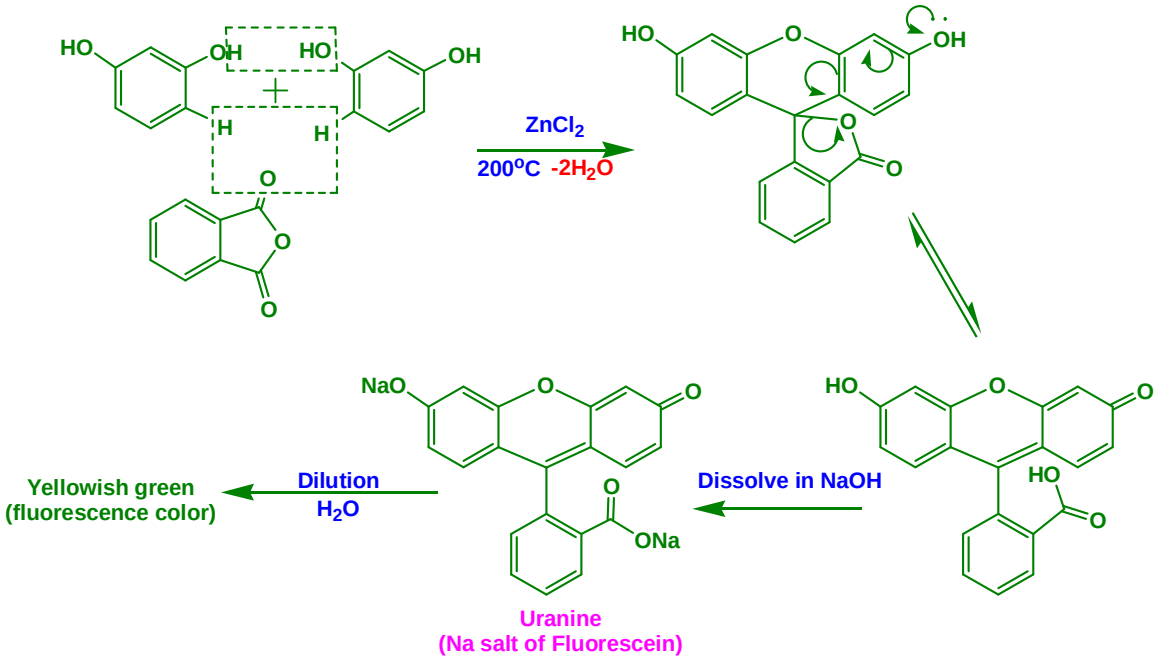
Synthesis:



Fluorescein (Xanthen Dyes)

Fluorescein is a xanthen derivative (dibenzo-1,4-pyran) and is prepared by heating phthalic anhydride with two molecules of resorcinol at 110-120^{o}C. fluorescein dissolves in alkalies to give a reddish-brown solution which on dilution gives a strong yellowish-green fluorescence. Fluorescein dyes wool and silk fibres.

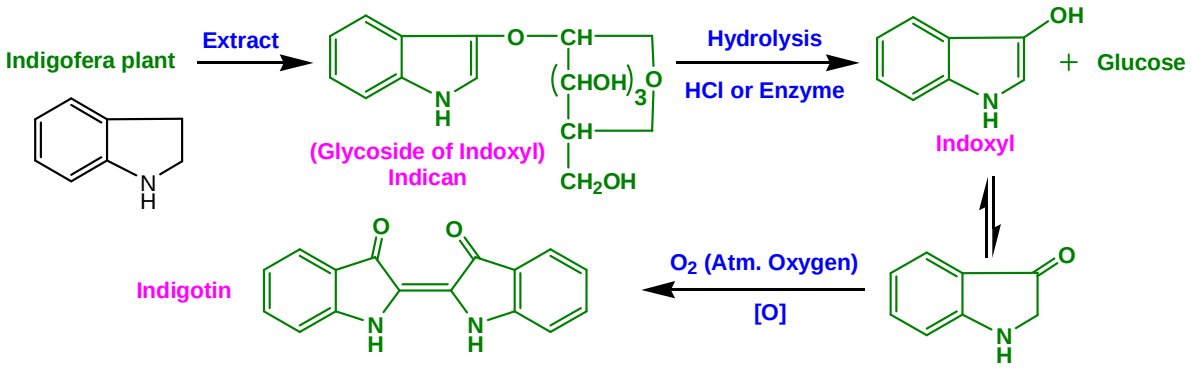
Synthesis:



Indigotin (Vat Dyes)

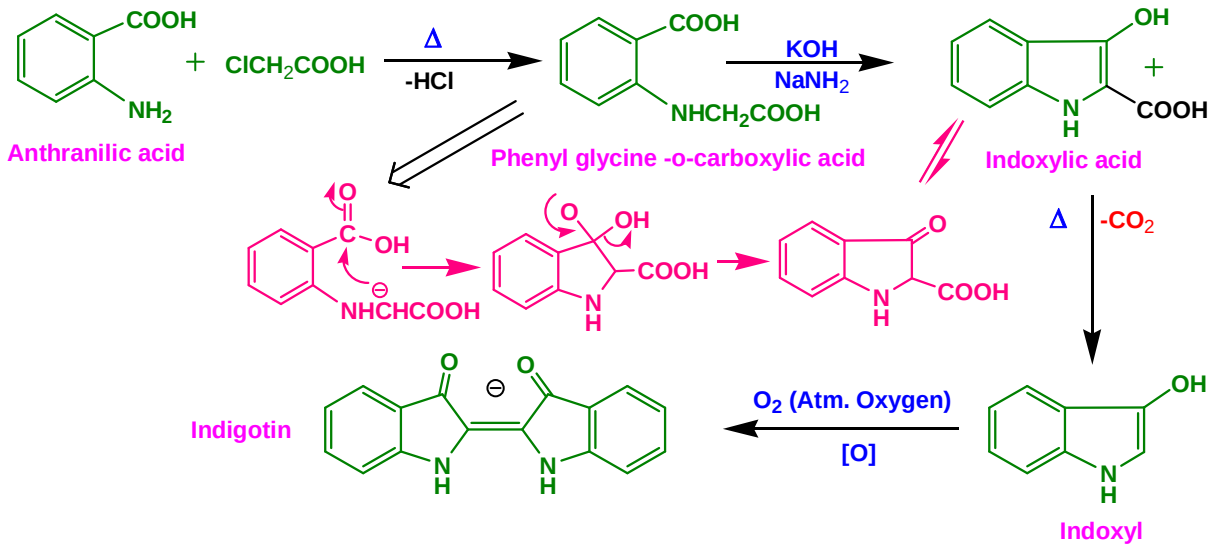
India appears to be the birth place of Indigotin. It is the oldest known dyes (5000 years old and have been found that MUMMY cloths were dyed with indigotin). Indigotin is dark blue powder and insoluble in water.

Isolation from Indigofera plant

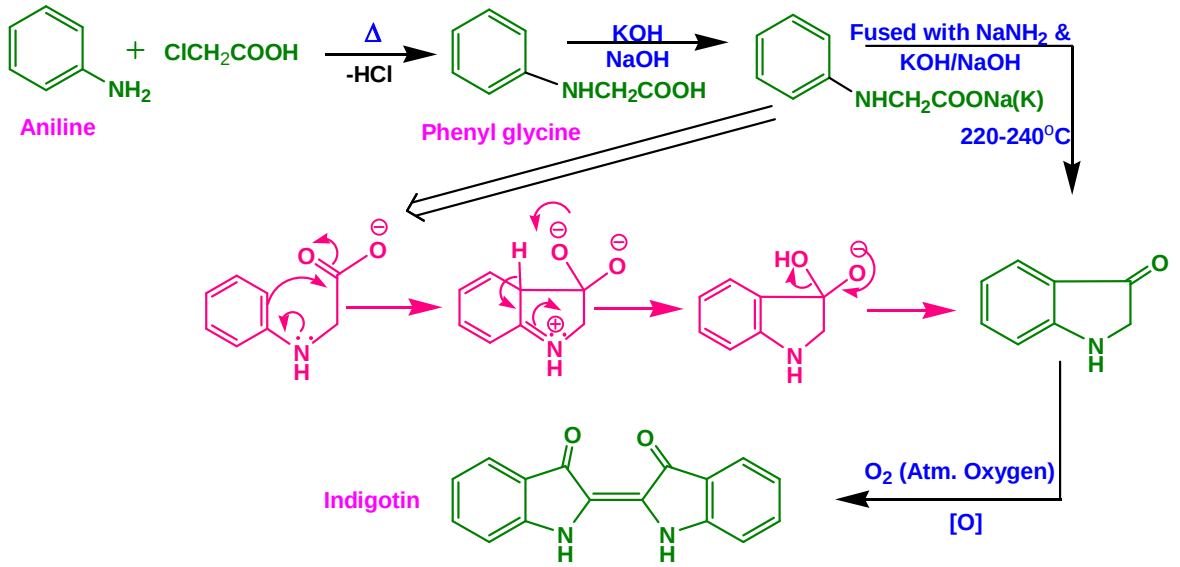


Synthesis:

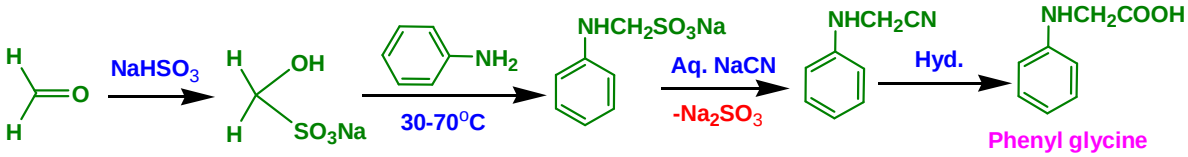
(i) From Anthranilic acid



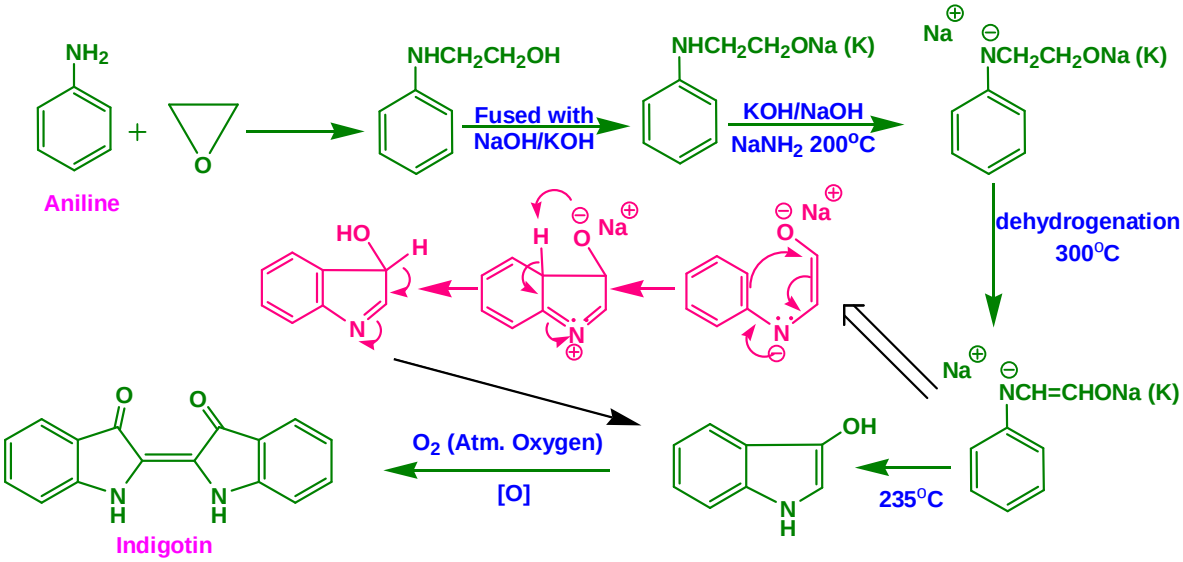
(ii) From Aniline (with chloroacetic acid)



Preparation of Phenyl glycine

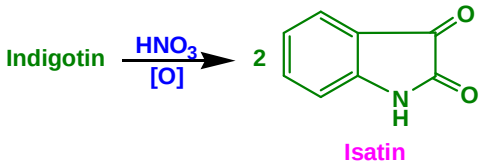


(iii) From Aniline (with ethylene oxide)



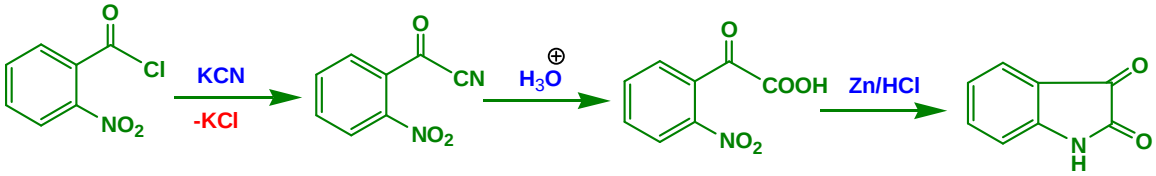
Structure elucidation (Constitution) of Indigotin

- Elemental analysis and molecular weight determination shows that molecular formula of Indigotin is $C_{16}H_{10}O_2N_2$
- Indigotin oxidize with nitric acid produced two molecules of Isatin ($C_8H_5O_2N$).



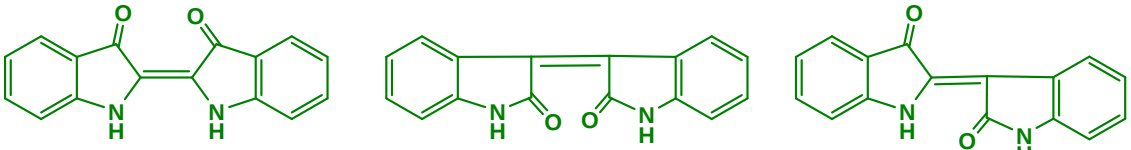
Isatin

- The structure of Isatin has been proven by its synthesis.



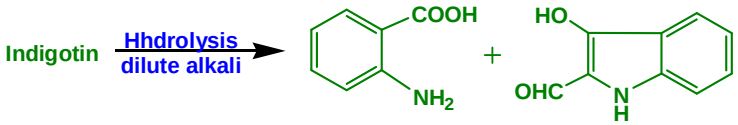
Isatin

- When compared the molecular formula of Indigotin ($C_{16}H_{10}O_2N_2$) and two molecules of Isatin ($2 \times C_8H_5O_2N = C_{16}H_{10}O_4N_2$), only two oxygen atoms being added during oxidation of indigotin.
- There are three possible structures of Indigotin can be given according to the formation of two Isatin molecules



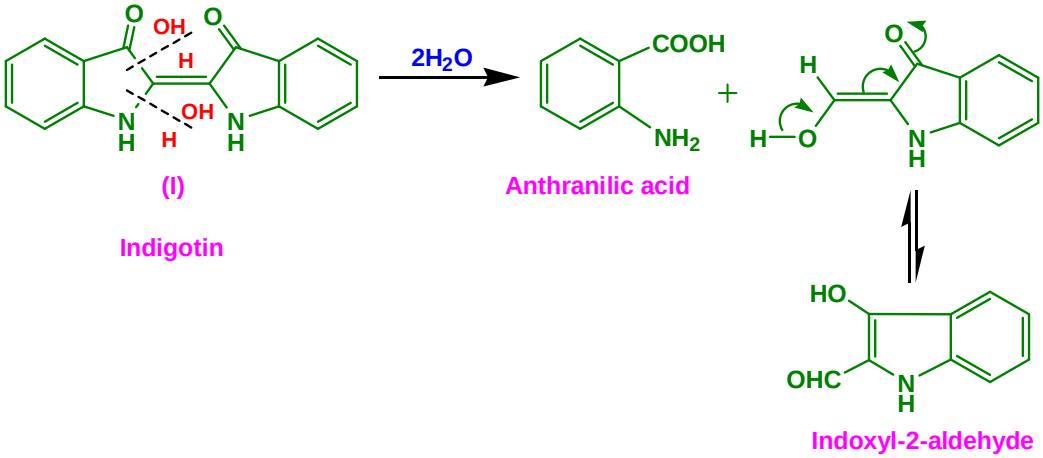
(I) (II) (III)

- When Indigotin under goes hydrolysis with dilute alkali, It produces anthranilic acid and Indoxyl-2-aldehyde.

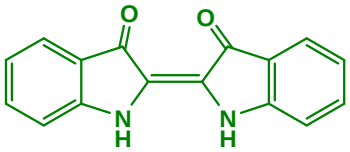


Anthranilic acid Indoxyl-2-aldehyde

Only the Indigotin structure (I) give rise to these two products as shown below:

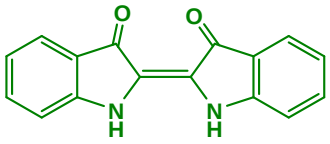


- Therefore, the structure of Indigotin is structure (I)

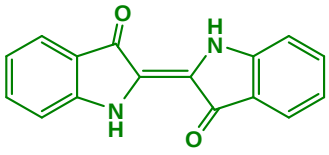


(I)

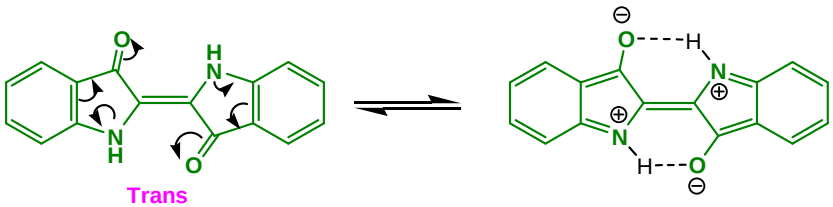
- Since Indigotin has one double bond, there are two geometrical isomers are possible i.e cis and trans. Among cis and trans, the trans isomer is more stable due to intra molecular hydrogen bonds.



Cis

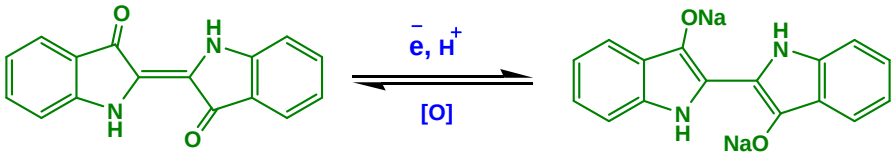


Trans



Trans

Indigotin is insoluble in water, but when its paste is agitated with alkaline sodium hyposulphite in large vats, the insoluble indigotin is reduced to the soluble Leuco-compound Indigotin white. The material to be soaked in this alkaline solution and then exposed to the air, whereupon the original blue dye is regenerated in the cloth.



Water insoluble

Leuco Compound

Water soluble

ALL THE BEST