

6) Indigoid Dyes :-

a) Indigo

~~ink~~

- ⇒ oldest Vat dye
- ⇒ occurs as the glucoside Indicon.

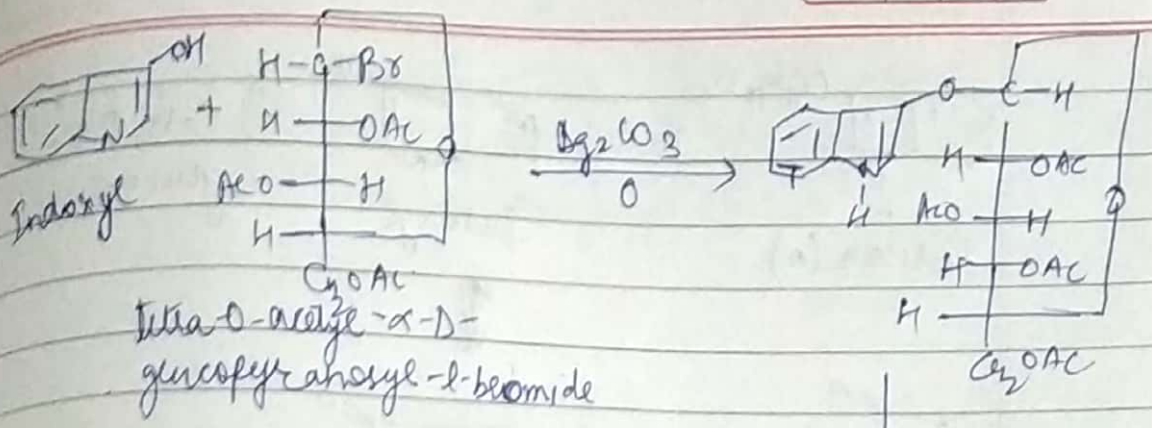
↓

occurs in leaves of Indigo plant of *Indigofera* sp.  
(generally *Indigofera tinctoria* & European *isatis tinctoria*)

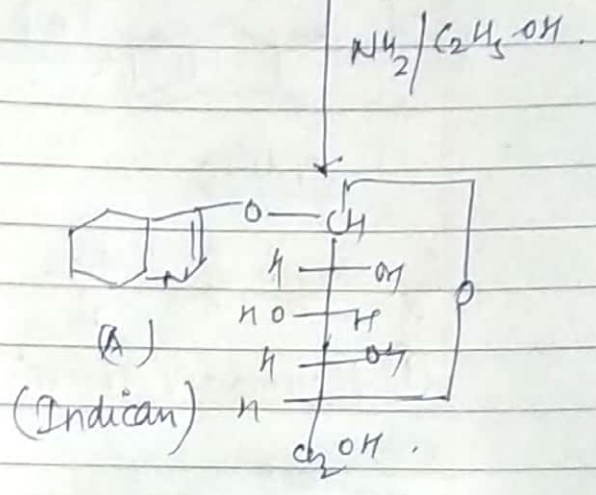
⇒ leaves  $\xrightarrow[\text{(enzyme by hydrolysis)}]{\text{macerated } H_2O}$  glucose + indoxyl  
(Indican)

⇒ then indoxyl  $\xrightarrow{[O], air}$  Indigotin

↓  
boiled  
filtered & dried  
natured Indigo



Structure Establishment



Indican glucoside  $\rightarrow$  MF =  $C_{14}H_{17}NO_5$  It is indoxyl-D-glucoside (since glucose & Indoxyl on hydrolysis)

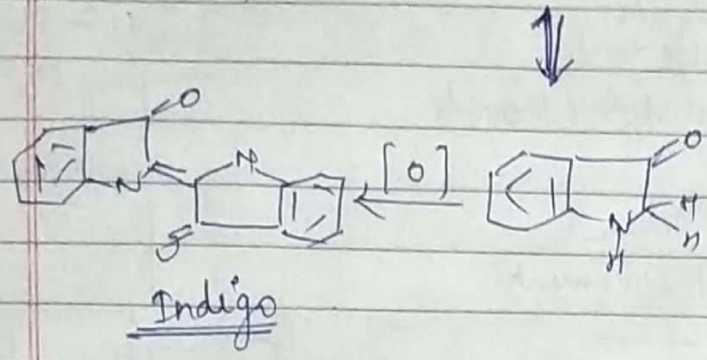
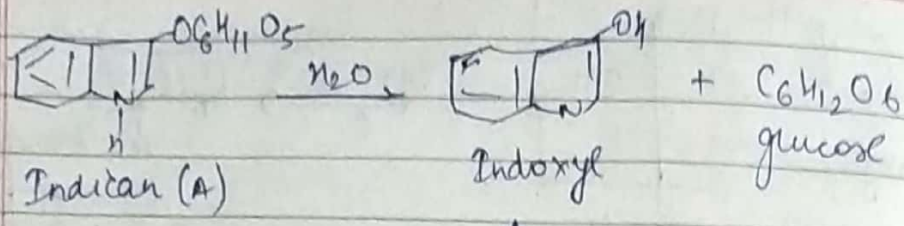
$\rightarrow$  Methylation of Indican ( $CH_3I / Ag_2O$ ) gives tetramethyl Indican, its hydrolysis ( $C_2H_5OH + 17\% HCl$ ) gives Indoxyl & methyl tetra 2,3,4,6-tetra-O-methyl-D-glucoside.

$\Rightarrow$  Above shows glucose present as pyranose

$\Rightarrow$  Hydrolysis of Indican is done by emulsion so link must be  $\beta$

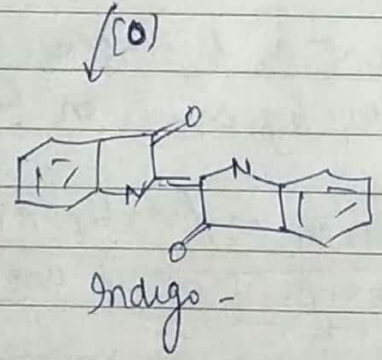
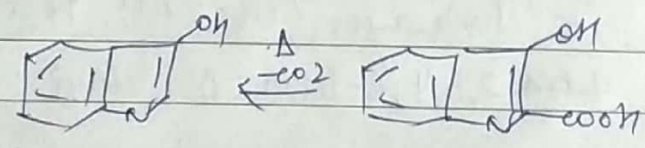
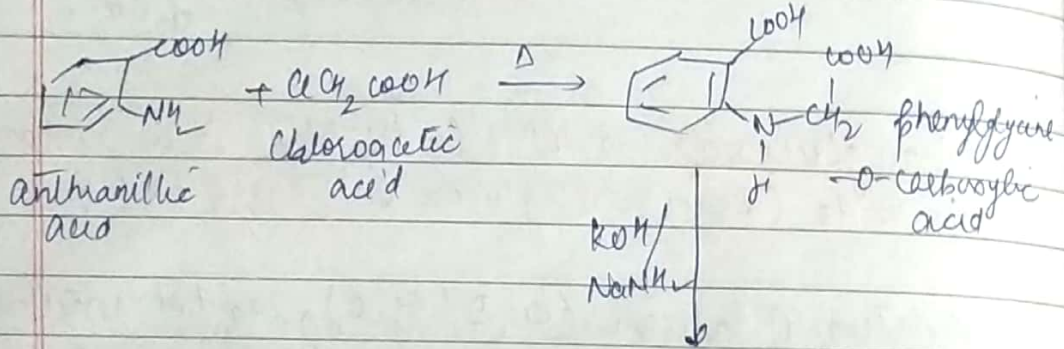
$\Rightarrow$  Thus the structure of Indican is given by (A) i.e. tetra-O-acetyl- $\alpha$ -D-glucopyranosyl-1-bromide and Indoxyl synthesis.

$\rightarrow$  Alterably, various steps involved are given below for naturally synthesis of Indigo.

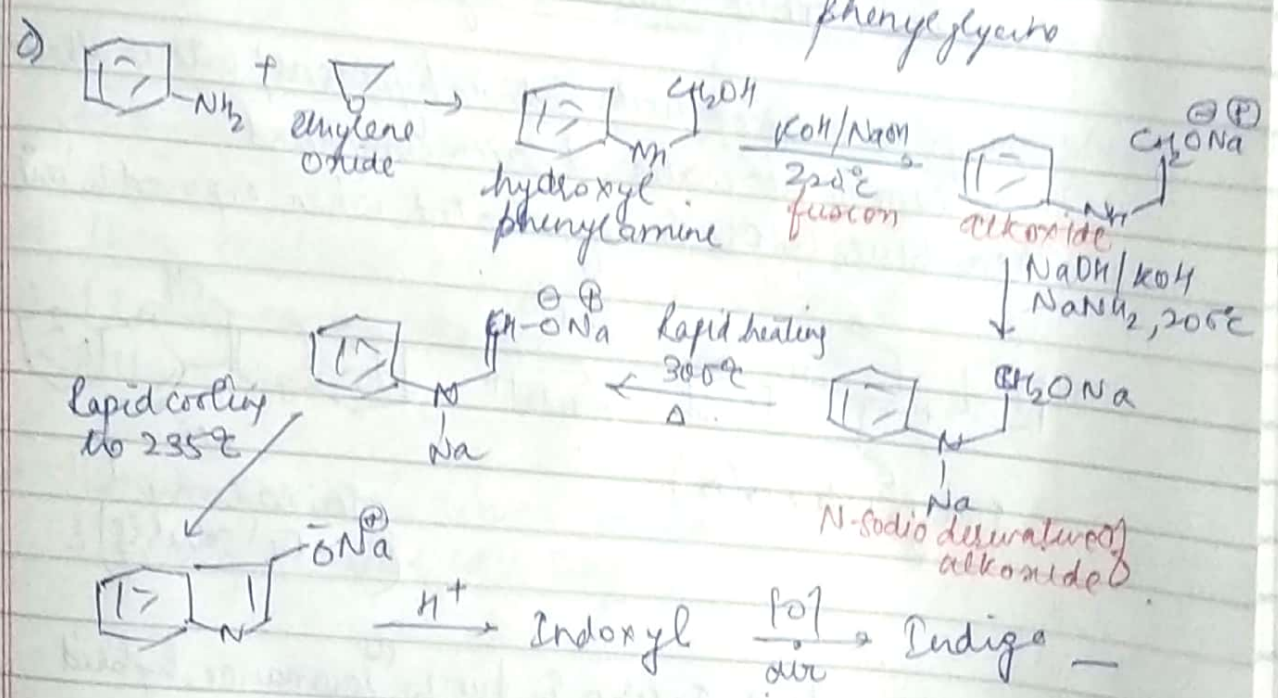
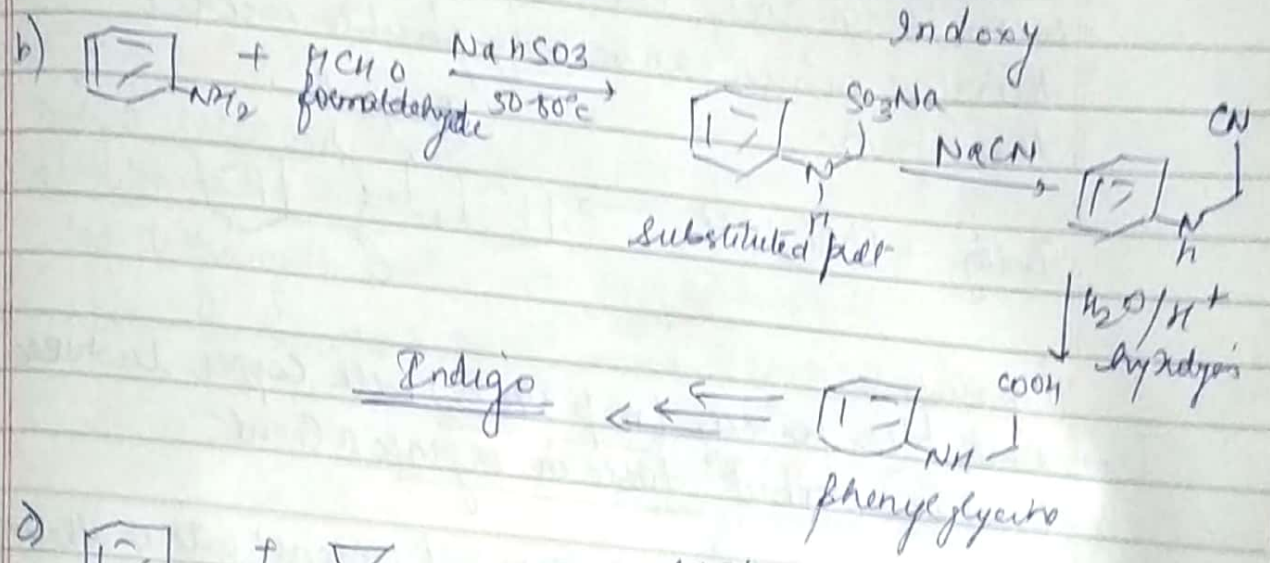
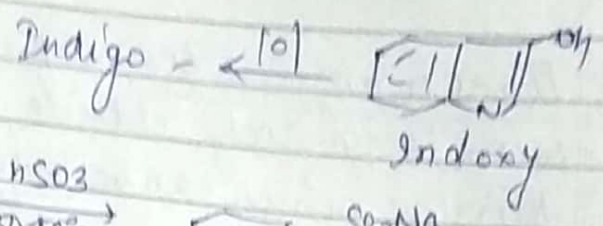
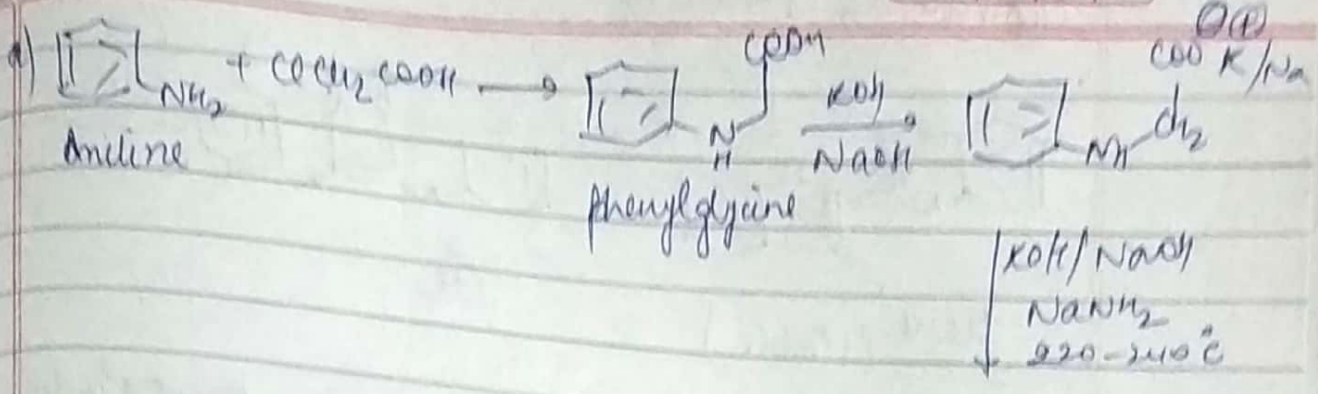


### Synthesis of Indigo

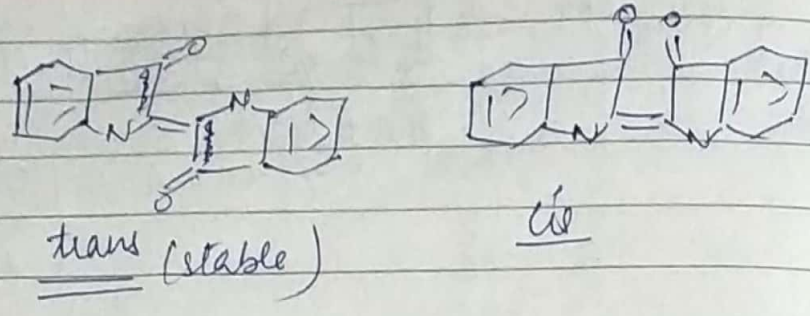
#### ① Heumann's process:-



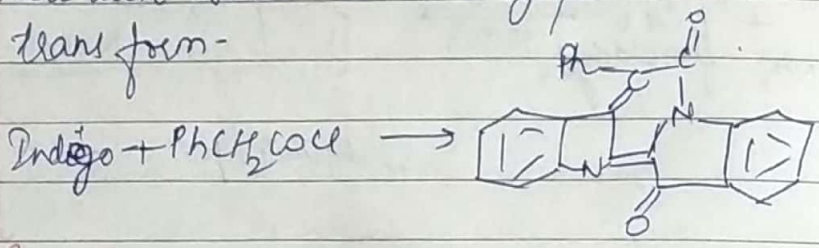
1) 3 steps & aniline is cheaper  
 so we can also do the alternate  $\rightarrow$   
 as shown below -



Geometrical Isomerism :-

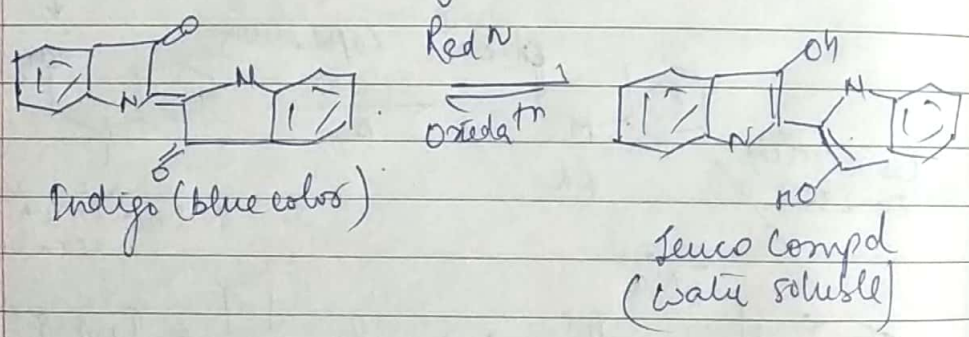


⇒ trans is more stable, confirmed by treatment of Indigo with phenyl acetyl chloride, the prod<sup>n</sup> is cyclic derivative which can be only possible with 1 trans form-

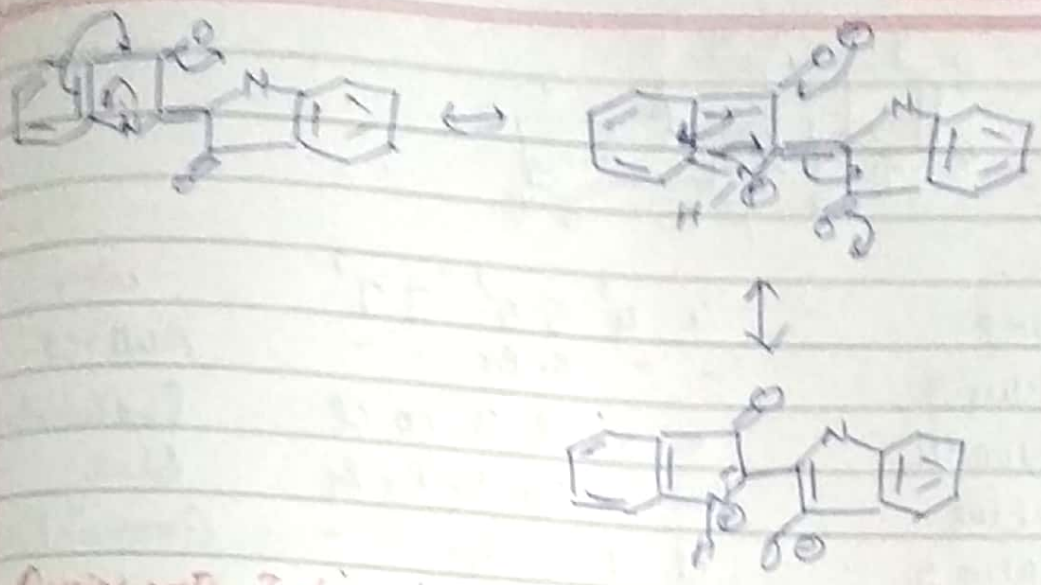


Properties

- ⇒ Dark blue powder (m.p 390°C) with copper lusture
- ⇒ Insol in water but soluble in organic solvent
- ⇒ Indigo is reduced with sodium hydrosulphite in alkaline medium to get water sol leuco compound. Then blue color is regenerated when exposed to air



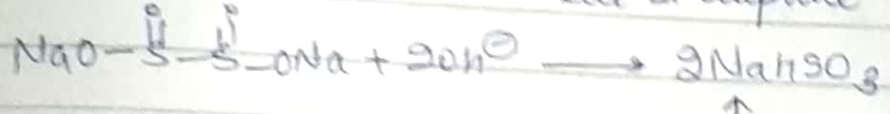
⇒ Deep blue color of Indigo is due to <sup>its</sup> resonance hybrid.



Dyeing with Indigo

Indigo taken in wooden vat & water added, then added sodium dithionate & alkali to it.

Sod. dithionate  $\xrightarrow{OH^-}$  Sod. bisulphide.



↑  
strong red. agent  
converts Indigo to leuco base

This colourless alkaline sol<sup>n</sup> is added to the cellulose fibres for dyeing. Little NaCl is added for exhaustion.

- ⇒ then oxidation is done by oxygen in the air.
- ⇒ Process can be hastened by adding chromic acid or ferric solution.
- ⇒ Then the fibre is rinsed, treated with acid, rinsed again & finally treated with soap.