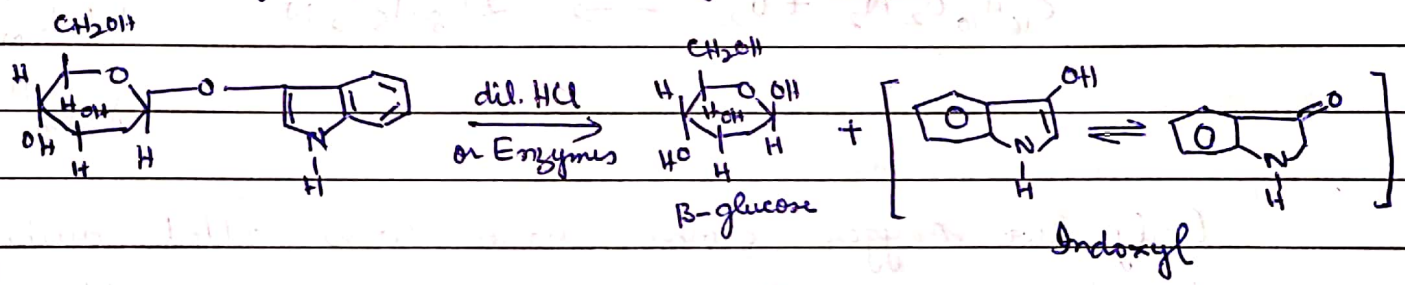
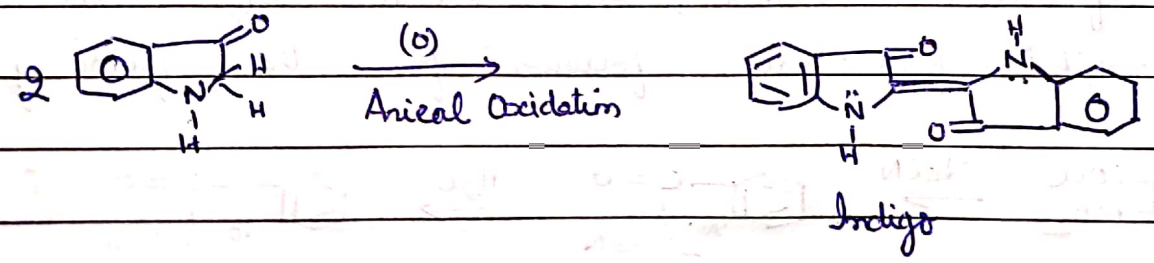
Indigoid dyes

Indigo It is the oldest vat dye known. India is the birth place of indigo, its offical name being indigotin. Egyptian mummy clothes, 5000 years old, were dyed with it. It occurs as the glucoside indican, in the tropical Indian plants of the indigofera group (e.g., Indigofera tinctoria) and the European plant isatis tinctoria. The natural indigo is a mixture of several related dyes. The chief component indigotin is loosely designated as indigo.

Preparation of indigo from natural sources

The appropriate plants, cut shortly before flowering, are treated with water at 25-30°C in wooden tanks. The enzymes present in the leaves of the plant hydrolyse the glucoside indican into indoxyl and glucose. The liquid extract is then agitated in the presence of lime in open vats when indoxyl is oxidised to indigotin consisting of insoluble blue flakes. The crude indigotin thus obtained is boiled with water, filtered and dried to get the natural dye indigo.





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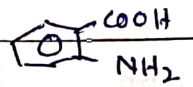
Structure of Indigotin / Indigo

The structure of indigo has been deduced as follows :

1. Elemental analyses and molecular weight determination have shown that the molecular formula of indigo is $C_{16}H_{10}O_2N_2$

2. Its destructive distillation yields aniline, suggesting the presence of at least one benzene ring in it.

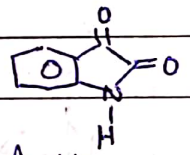
3. Fusion of indigo at low temperatures produces anthranilic acid and / or aniline, confirming the presence of the benzene ring.

$$C_{16}H_{10}O_2N_2 \xrightarrow{NaOH,\ fuse}$$ 

Anthranilic acid

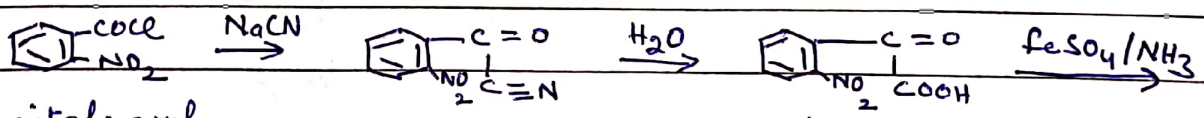
This, also, suggests that indigo contains one ortho substituted benzene ring, in which one position is attached to a carbon atom while the other is linked to nitrogen atom.

4. Oxidation of indigo with HNO_3 yields two molecules of isatin $C_8H_5O_2N$

$$C_{16}H_{10}O_2N_2 + O_2 \longrightarrow 2C_8H_5O_2N$$ 

Isatin

Only two oxygen atoms have been added during this transformation. Further, the structure of isatin as 2,3-diketo-hydroindole follows from the following synthesis,



O-nitrobenzoyl chloride

O-nitrobenzoyl formic acid

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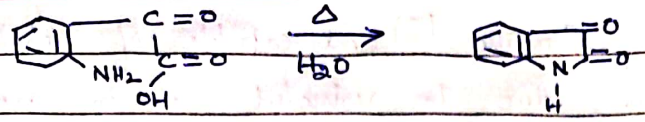
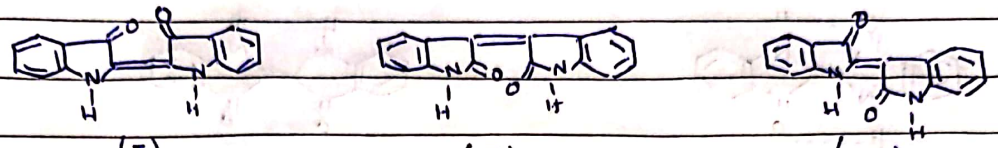


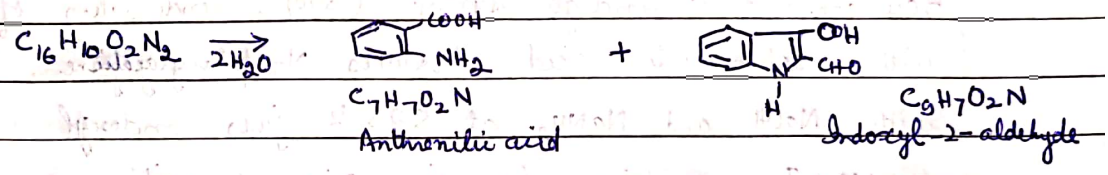
o-aminobenzoyl formic acid — Isatin

5. On the basis of the structure of isatin, the following three structures (I, II and III) are possible for indigotin.



(I) (II) (III)

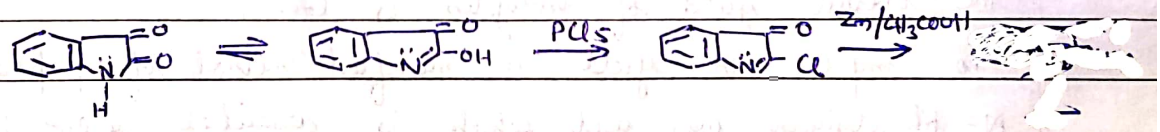
6. Treatment with dilute alkali yields anthranilic acid and indoxyl-2-aldehyde

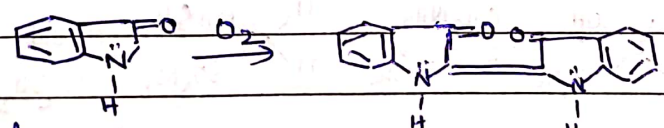


$C_{16}H_{10}O_2N_2 \xrightarrow{2H_2O}$ $C_7H_7O_2N$ Anthranilic acid + $C_9H_7O_2N$ Indoxyl-2-aldehyde

Formation of indoxyl-2-aldehyde suggests that the two identical units in indigotin are connected through position-2 of indoxyl moiety with position-3 carries an oxygen containing functional group. These arguments suggest that most probable structure of indigotin is I

The formation of these two products can be explained only by the structure (I). The following synthesis also supports the structure (I) for indigotin.

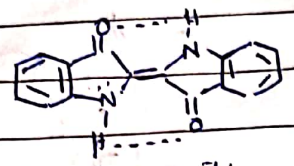




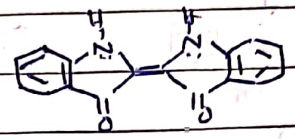
Indoxyl — Indigotin

Fine structure The structure (I) is capable of exhibiting geometrical isomerism, due to restricted rotation around carbon-carbon double bond joining the two indole units.

X-Ray analysis has shown that indigotin possess the trans-configuration, the stabler of the two forms



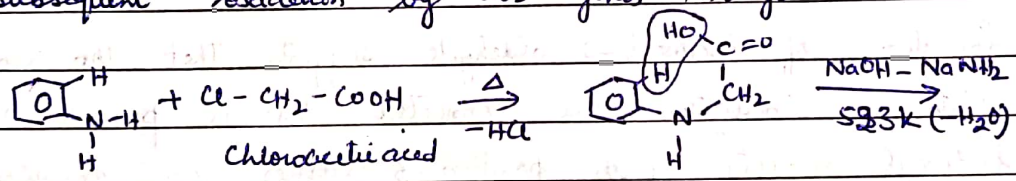
trans-indigotin
(stablized by H-bonding)



cis-form

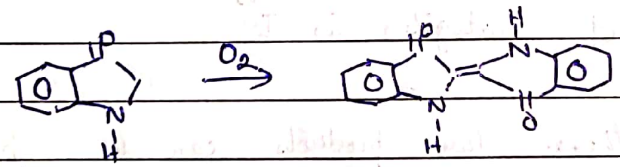
This structure has been confirmed by the following syntheses:

1. Heumann's first indigo synthesis (1890). Condensation of aniline with chloroacetic acid produces N-phenylglycine. This fusion with NaOH and $NaNH_2$ at 523 K gives indoxyl which upon subsequent oxidation by air gives indigotin



Aniline

N-phenylglycine

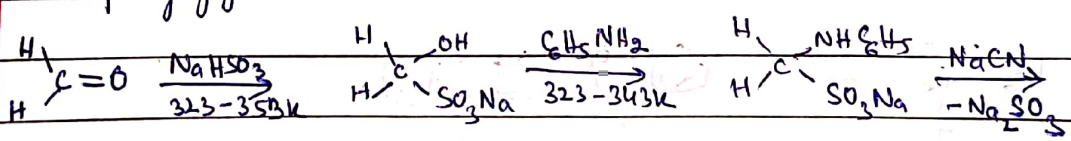


Indoxyl

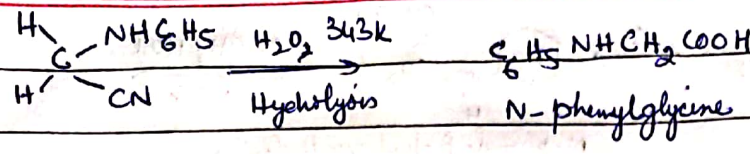
Indigotin

The overall yield of indigotin is low.

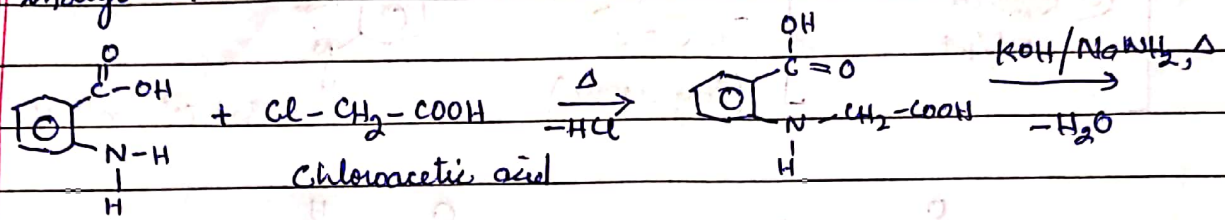
To improve the yield, a modified method of preparation of N-phenylglycine was used which is described below:



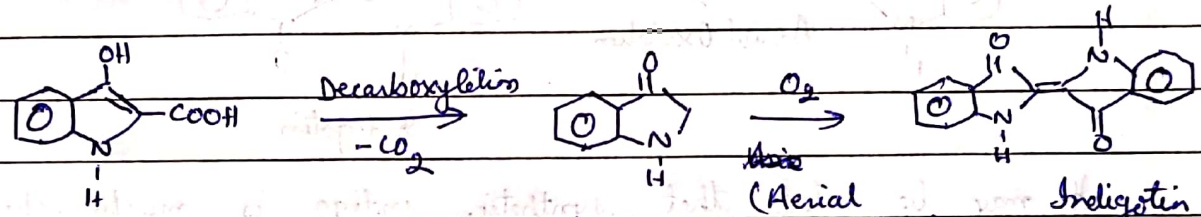
formaldehyde



2. Heumann's Second Indigo synthesis (1896) This involves the condensation of anthranilic acid with chloroacetic acid to form N-phenylglycine-o-carboxylic acid. This when fused with KOH/NaNH2 produces indoxylic acid which subsequently undergoes dicarboxylation to form Indoxyl. Aerial oxidation of indoxyl finally gives indigotin.



Anthranilic acid



Indoxylic acid (unstable)

Indoxyl

3. From aniline and ethylene oxide (1943) Aniline on treatment with ethylene oxide forms N-phenyl β-hydroxyethylamine (I) and this upon fusion with a mixture of NaOH/KOH at 473K gives the corresponding sodium/potassium alkoxide (II). When this sodium/potassium salt is heated with sodamide and a mixture of sodium/potassium hydroxides at 473K, the N-sodio/potassium derivative (III) is produced. This is then dehydrogenated on heating rapidly to 573K, and on rapid cooling to 508K, ring closure occurs to form sodium/potassium salt of indoxyl (IV). This upon treatment with water and oxidation by air gives indigotin.

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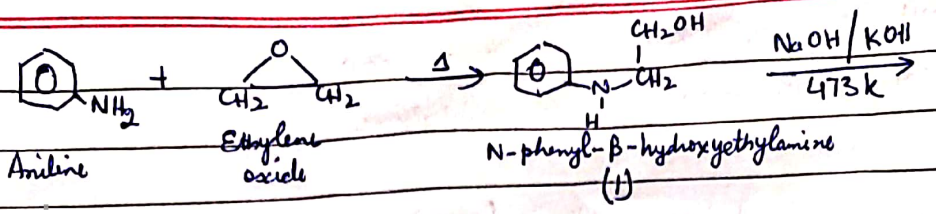
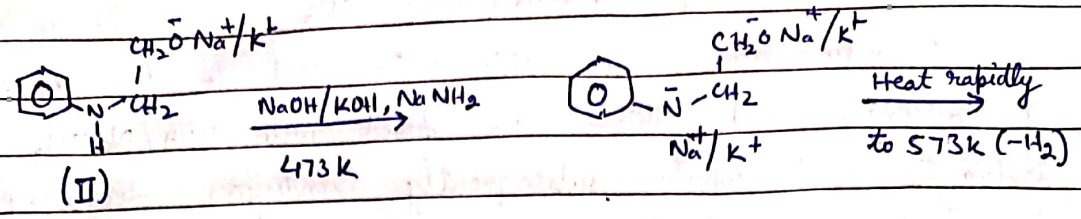
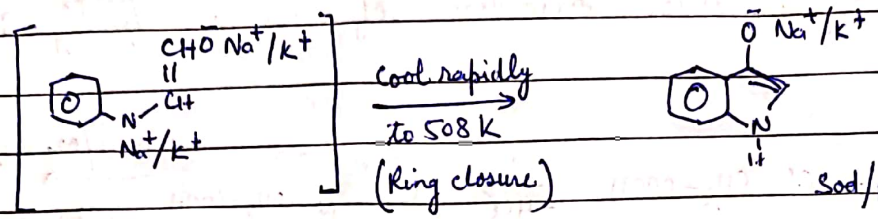
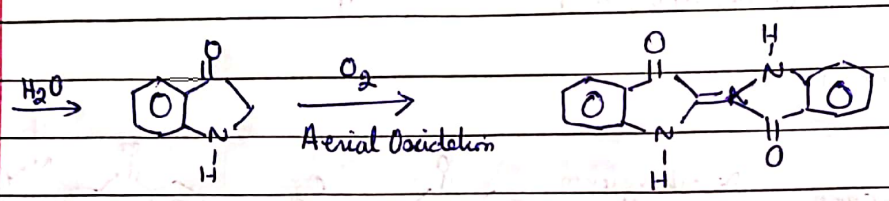




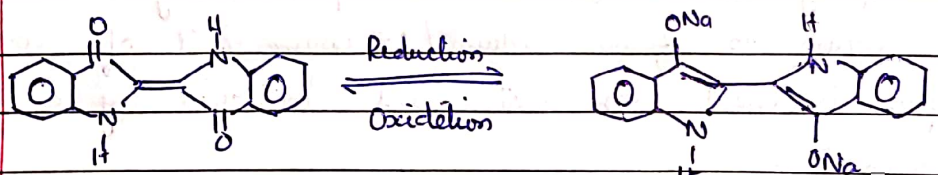




It may be noted that synthetic indigo is much cheaper than natural indigo. In fact, synthetic indigo has virtually wiped out the indigo plantation so popular at one time in India.

Properties : 1. Indigotin is a dark blue powder, with coppered lustre, m.p. 663 K. It is insoluble in water and most-organic solvents.

2. When a paste of indigotin is agitated with alkaline sodium hyposulphite in large vats, the insoluble indigotin is reduced to the soluble leuco compound, called <u>indigotin white</u>.



Indigotin blue

Indigotin white
(leuco compound soluble in H_2O)

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The cloth to be dyed is soaked in this alkaline solution and then exposed to air, when the original blue colour is regenerated on the cloth.

Uses 1. Indigotin is extensively used for dyeing cotton. The quality of colour is excellent and is stable to light, washing etc.

2. It is also used in printing inks.

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