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Review Article

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Indigo – Development of Chemical Synthesis Procedures

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Abstract

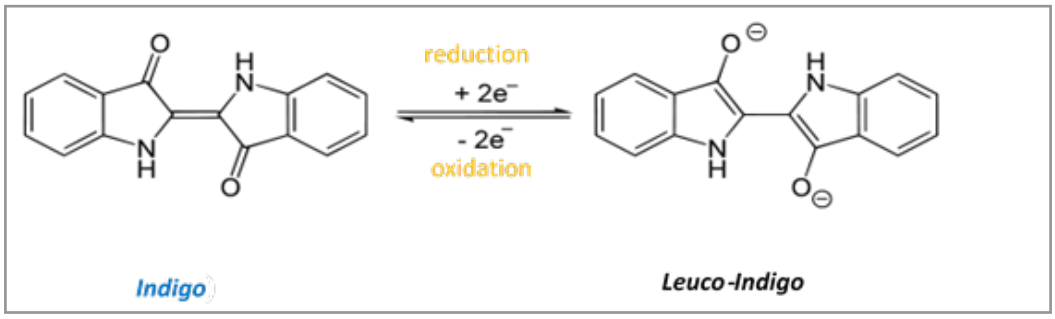
The dye Indigo, since the end of the 19th century produced synthetically through various chemical reactions, is widely known as the blue color used for coloring blue jeans trousers. Originally, in Europe the color was produced from dyer´s woad (the "European Indigo" Isatis tinctoria) and later also from the imported "Indian Indigo" Indigofera tinctoria. As the obtaining of the color from the plants was very time intensive, it was one of the expensive dyes and was used for special purposes. One very popular usage started, when in the last quarter of the 19th century, Levi Strauss invented the jeans fabric for very hardwearing clothes – using the blue Indigo color for their coloration. From the usage of the blue dye from Genua, the word "Jeans" was derived from "Bleu de Gênes". The cotton used for the sturdy trousers came from the place "Nimes" in the South of France from which the designation "Denim" comes from. With the possibility for producing Indigo on an industrial scale via chemical synthesis procedures, its usage increased very fast. In the presentation, a historic overview of the traditional blue coloring with the dyer´s woad Isatis tinctoria and the Indian Indigo Indigofera tinctoria will be given as well as the development of the chemical synthesis starting with the history of the determination of the chemical structure of the Indigo molecule and the first steps to reproduce Indigo from its parts. In the following, an overview of different approaches for chemical synthesis will be described. Important researchers and companies in this synthesis process will be presented, chemical reaction equations will give explanations for the development of finally the best synthesis way at the beginning of the 20th century.

Keywords: Indigo, Chemical Synthesis, Jeans, Dye

Introduction

The dye Indigo is widely known as the blue color used for coloring blue jeans trousers. In Europe, the color was originally produced from the dyer´s woad plant Isatis tinctoria – also known as the "European Indigo". Later, also the imported plant Indigofera tinctoria (the "Indian Indigo") was used.

As a water-insoluble pigment, before usage as coloring dye, Indigo has to be transformed into the water-soluble substance Leuco-Indigo via reduction. Through oxidation (e.g. in air), the blue Indigo is than formed.



Equation 1: Chemical structure formulas for Indigo and Leuco-Indigo [1].

In the last quarter of the 19th century, Levi Strauss used the blue Indigo for the coloration of his invented jeans fabric for very hardwearing clothes. Two brand names have been created at that time. “Jeans” which comes from the usage of blue dye from Genua (in French “Bleu de Gênes”) and “Denim” as the cotton used for the sturdy trousers came from the place “Nimes” in the South of France.

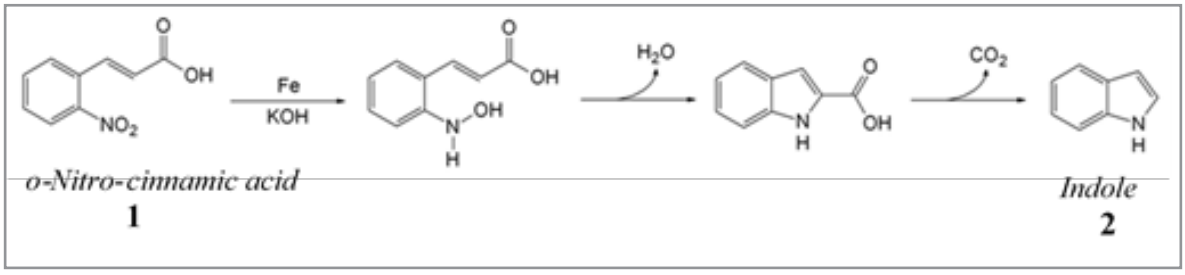
The Indigo color became very popular and nowadays it is still the most common coloring chemical for blue jeans trousers. As the obtaining of the color from the plants was very time intensive, a way to produce Indigo synthetically was needed.

The paper will give an overview of the history of the chemical synthesis of Indigo.

Chemical Synthesis of Indigo

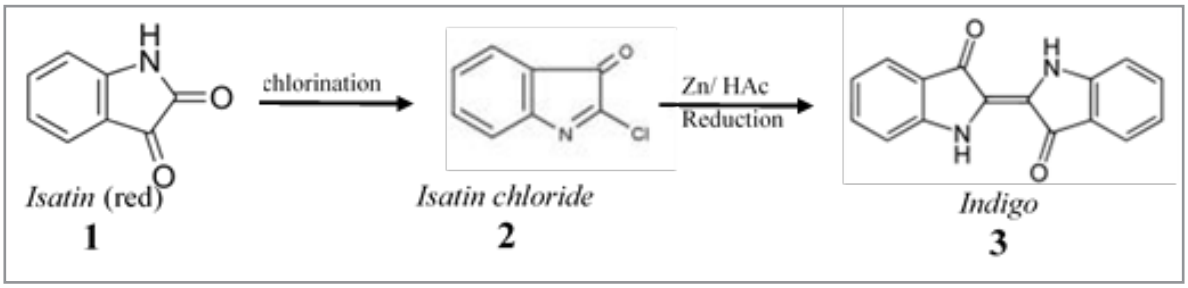
After various decomposition experiments of natural Indigo and chemical analyzes of the structure of the fragments and the Indigo itself, the work to synthesize synthetic Indigo started in the 2nd half of the 19th century. One of the pioneers in this field was A. von Baeyer (German chemist; 1835-1917). For his works in dye chemistry he received the Nobel prize in 1905.

Together with A. Emmerling (German chemist; 1842-1906), A. von Baeyer described 1869 a way to synthesize Indole, one found fragment in earlier decomposition experiments. Their synthesis started with o-Nitro-cinnamic acid 1. Under alkaline conditions, ring-formation and decarboxylation, Indole 2 is obtained.



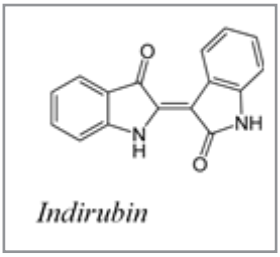
Equation 2: Reaction of o-Nitro-cinnamic acid to Indole

A. von Baeyer continued his research with Indigo and in 1870, he was able to transform Isatin 1 (which he obtained from the oxidative decomposition of the natural Indigo) over the intermediate product Isatin chloride 2 back to Indigo 3.



Equation 3: Producing Indigo from Isatin

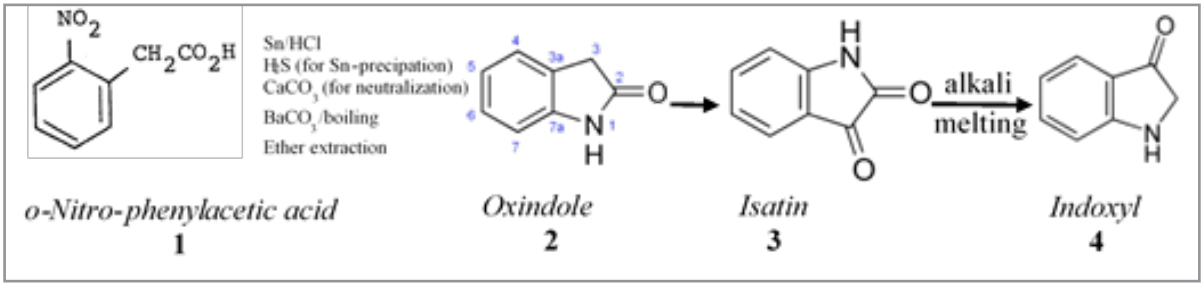
As the red Indirubin A is a side-product in this process - reducing the yield of Indigo - Baeyer continued his experiments trying to achieve a more selective process and a higher yield on Indigo [2].



Baeyer-Emmerling Synthesis

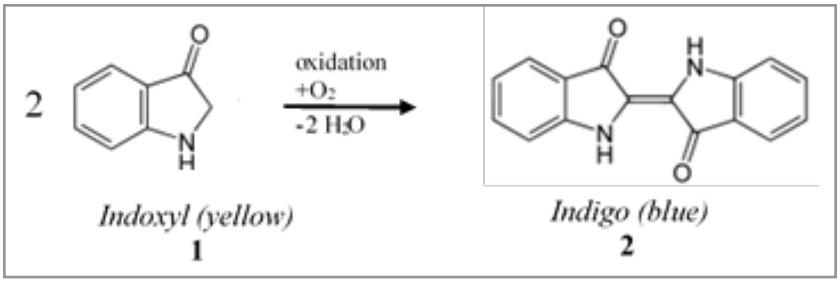
In 1878, A. Baeyer and A. Emmerling were the first to describe a process for a full synthesis of Indigo.

Starting with o-Nitro-phenylacetic acid 1, Oxindole 2 (an isomere of Indoxyl) is produced via a series of chemical worksteps. After oxidation Isatin 3 and further on in alkali melting Indoxyl 4 is obtained.



Equation 4: Producing Indigo from o-Nitro-phenylacetic acid

In the last step, by combining two Indoxyl 1 molecules under oxidative conditions Indigo 2 is obtained.

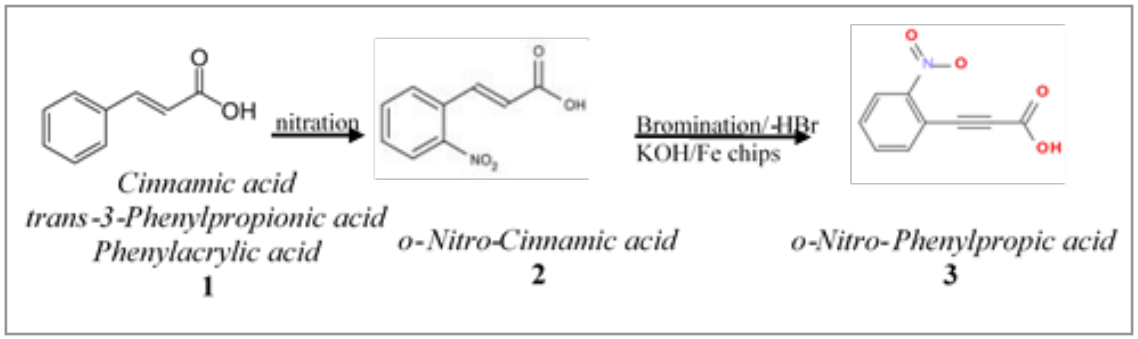


Equation 5: Two Indoxyl molecules react to Indigo

Due to side reactions, this synthesis was not suitable for high yields of Indigo [3].

Baeyer Synthesis

Baeyer continued his research for the full synthesis of Indigo and patented an improved synthesis way in March 1880 (DE 11857 A) which he then sold to BASF (Badische Anilin und Soda Fabrik). Starting with Cinnamic acid 1, o-Nitro-Phenylpropic acid 3 with a C-C triple bond is obtained via the intermediate product o-Nitro-Cinnamic acid 2.



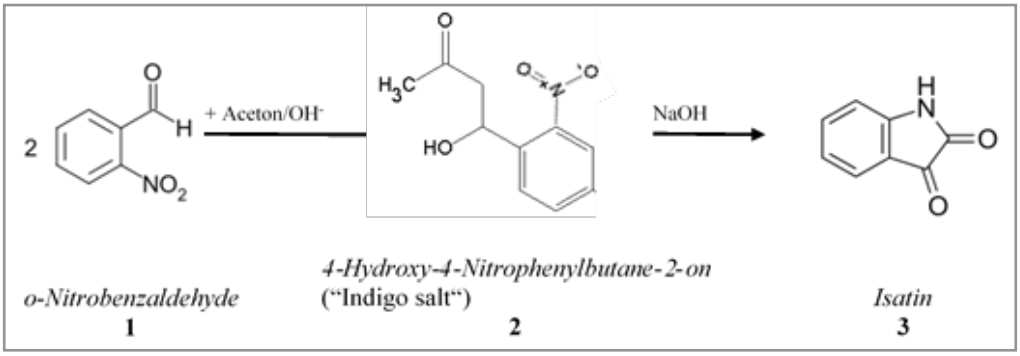
Equation 6: Synthesis of o-Nitro-Phenyl-Propionic acid from Cinnamic aci

Through alkaline reduction and Glucose Indoxyl and subsequently Indigo is directly produced on the textile fiber [4].

Nevertheless, the small production plant "Little Indigo" which started its work in 1881, had soon got to be closed again due to lack of economic success.

Baeyer-Drewsen Synthesis

In 1882, A. Baeyer and V.B. Drewsen (Danish chemist; 1858-1930), described another synthesis way to produce Indigo (BASF patent DE 19768 A). Hereby, two molecules of o-Nitro-benzaldehyde 1 (derived from Toluene) react in an aldol condensation with Acetone under alkaline conditions to 4-Hydroxy-4-Nitro-phenylbutane-2-on 2 ("Salt of Indigo") and further on in a cyclisation reaction to Isatin 3, which leads to Indoxyl (see equation 4) and after a coupling of two molecules to Indigo (see reaction equation 5) [5].

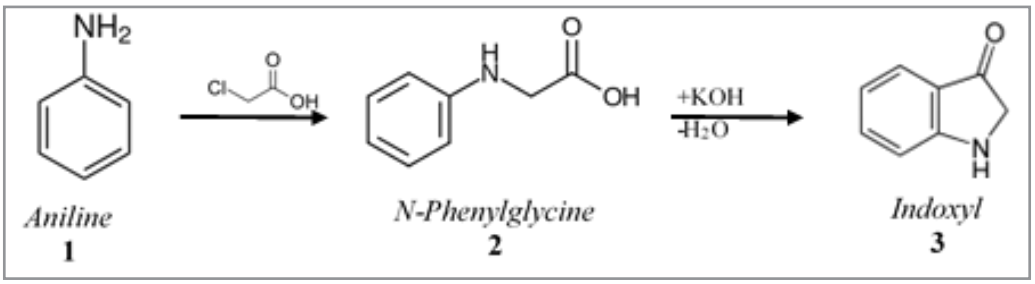


Equation 7: Synthesis of Isatin from o-Nitrobenzaldehyde

However, as this synthesis was quite costly (e.g. needing around 4 times as much Toluene as Indigo could be produced), expensive and time consuming, the research for optimized synthesis ways went on.

1st Heumann Synthesis

In 1890, Karl Heumann (German chemist; 1850-1894) described a way with Aniline 1 as starting molecule. This could – advantageously be obtained cheap and sufficient from the company BASF (Badische Anilin und Soda Fabrik) [5]. Together with Chloroacetic acid N-Phenylglycine 2 is produced, which – by the process of a ring-formation under alkaline conditions - leads to the water-soluble Indoxyl 3 wherefrom Indigo can be formed (see equation 5).



Equation 8: Synthesis of Indoxyl from Aniline

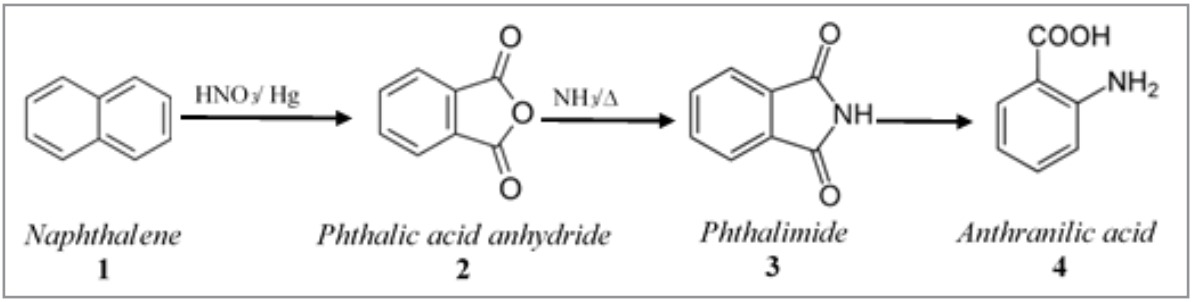
Disadvantageously, due to the high temperatures, N-Phenylglycine partly disintegrates which decreases the yield of Indoxyl and further on the yield of Indigo. Therefore, again, other synthesis ways or modifications had to be searched.

2nd Heumann Synthesis (BASF Synthesis)

1893, Heumann used Anthranilic acid as starting molecule which increased the Indigo yield in comparison to the 1st Heumann synthesis and was so adopted for industrial production from BASF (Heumann had sold the patent for his first production way). So, in 1897, the "2nd Heumann synthesis" or "BASF synthesis" started the first industrial-scale Indigo production with an Indigo-yield of 70-90% [6, 7].

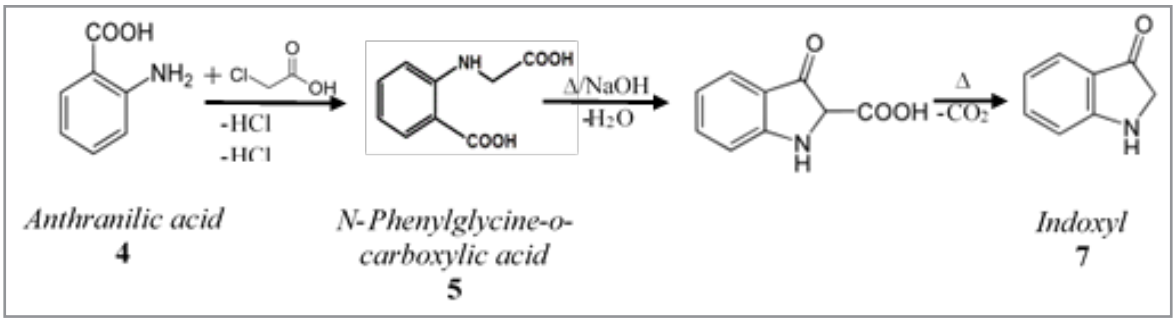
Therefore, in the following years, the industrial Indigo synthesis increased whereas the Indigo production from plants decreased enormously (from around 19,000 tons in 1897 to less than 4,000 tons in 1907 and below 1,000 tons in 1917 [4].

In this optimized synthesis, the starting molecule Naphthalene 1 is oxidatively converted to Phthalic acid anhydride 2, which reacts to Phthalimide 3 and finally to Anthranilic acid 4.



Equation 9: Synthesis of Anthranilic acid from Naphthalene

Similar to the 1st Heumann synthesis, the second step is a reaction with Chloroacetic acid, leading to the formation of N-Phenylglycine-o-Carboxylic acid 5 and under alkaline conditions and heat with a ring formation to 2-Indoxy-Carboxylic acid 6. Further heating produces Indoxyl 7 which leads to Indigo (see equation 5).

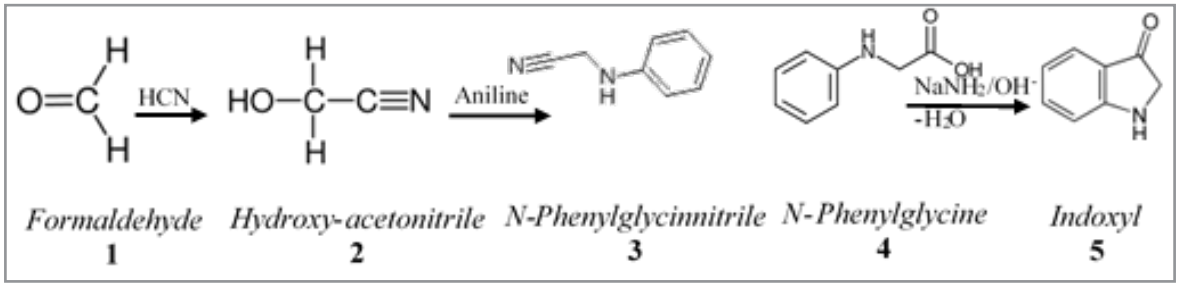


Equation 10: Synthesis of Indoxyl from Anthranilic acid

Heumann-Pfleger-Synthesis (Degussa Synthesis)

Heumann continued his research for an industrial Indigo production, still aiming to optimize the Indigo yield and costs, and in 1901, the "Heumann-Pfleger-synthesis" ("Degussa synthesis") was described. Compared to the 1st Heumann synthesis of 1890, due to lower temperatures, this process gave a higher yield of Indigo, was cheaper (also because of lower temperatures), less elaborate and less error-prone.

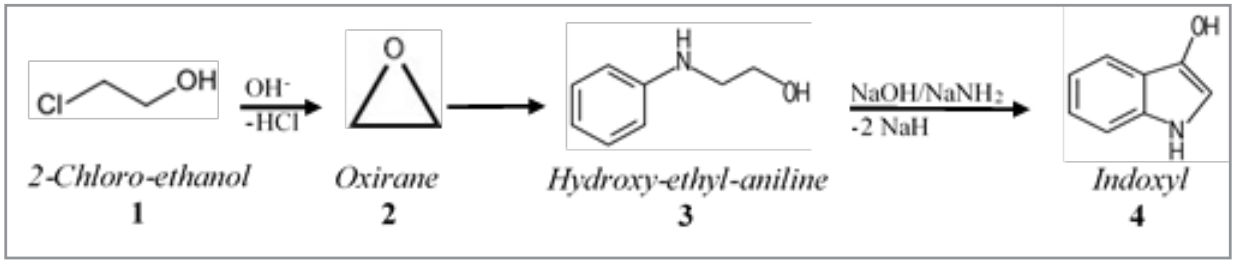
The starting molecule Formaldehyde 1 reacts with Prussic acid to Hydroxy acetonitrile 2 which further forms N-Phenylglycine nitrile 3 in the reaction with Aniline. Under alkaline conditions N-Phenylglycine 4 and after a ring formation Indoxyl 5 is formed from which Indigo can be derived (see equation 5).



Equation 11: Synthesis of Indoxyl from Formaldehyde

Hoechst-BASF-Process

Another optimization brought the "Hoechst-BASF"-process, which was described in 1904 and – after some production changes – also became the industrial production process from 1926 on. The process starts with 2-Chloro-ethanol 1 from which Oxirane 2 is formed under alkaline conditions [7]. Through a reaction with Aniline, Hydroxy-ethyl-aniline 3 and in alkaline conditions Indoxyl 4 is produced from which Indigo can be derived from (see equation 5).



Equation 12: Synthesis of Indoxyl from 2-Chloro-ethanol

Conclusion

Research and a lot of experiments allowed that an industrially important molecule – Indigo – could be analyzed and produced synthetically. This was another big achievement in organic chemistry. Indigo is still a widely used dye.

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