

# Synthesis of Indigo and Vat Dyeing

Adapted by Brandon English and others from a micro scale procedure by James R. McKee and Murray Zanger, *J. Chem. Ed.*, 1991, 68, A242-A244

## Introduction

### William Perkin and the Development of the Synthetic Dye Industry

William Henry Perkin considered a career as an artist. He also thought of following in his brother's footsteps to become an architect, as his father wished. Either way, the organic chemicals industry still would have come into existence. Its beginnings probably would have occurred about when they did, shortly after the midpoint of the 19th Century. The time was ripe, after all, thanks to recent advances in theoretical knowledge about organic chemistry.

But Perkin, after he was shown some elegant crystals by a friend at an early age, became exchanted -- almost obsessed -- by chemistry. And so it was Perkin, in fact, who launched the industry.

The oft-told saga of Perkin's remarkable achievement is the first episode in Anthony S. Travis' "The Rainbow Makers: The Origins of the Synthetic Dyestuffs Industry in Western Europe" (Lehigh University Press, 1993). That's because the first products of the synthetic organic chemical industry -- and the brightest achievements of its first half century -- were textile dyes.

Perkin had a solid grounding in organic chemistry (at least what was known about it then) after a couple of years at the Royal College of Chemistry in London. There he had learned laboratory technique under August Wilhelm von Hofmann, an expatriate German who was probably the best teacher of the subject at that time.

During Easter vacation in 1856, Perkin, then barely 18, decided to experiment in the ill-equipped lab at his home. He was trying to synthesize quinine, a medicinal much in demand by his compatriots traveling on empire-building missions to the malaria-infested tropics. He naively thought that he might form the quinine molecule ( $C_{20}H_{24}O_2N_2$ ) by oxidizing two molecules of allyltoluidine ( $C_{10}H_{13}N$ ). Heating a salt of allyltoluidine with potassium bichromate, all he got was a dirty brown sludge. Curious, nevertheless, he repeated the experiment with a simpler base, aniline. This time the precipitate was black. Hoping a few crystals of quinine might lurk in the sludge, he extracted it with ethanol. The resulting solution was an intense purple.

What Perkin had done so far was largely a matter of blind luck. But then his youthful and opportunistic genius came into play. He found that the solution was a good dye. (One story has it that he noticed a purple stain spread over his white shirt when he accidentally spilled a drop of the extract.)

Perkin abandoned his chemical studies, much to Hofmann's displeasure. He didn't really know exactly what he had produced, but he thought he might be able to sell it to England's prosperous textile industry. So he patented his discovery. With the financial backing of this father, a builder, and the able assistance of his older brother, he built near London the first plant ever dedicated to making organic chemicals. He had to find suppliers or learn to prepare for himself the raw materials (such as benzene, nitric acid, nitrobenzene, and aniline) needed for his process. He had to design and fabricate his own process equipment. And he had to market his product to the tradition-bound textile mills, showing dyers how to use it (thus pioneering the concept of technical service).

By the end of 1857, Perkin's plant was operating. Fortunately, purple was a shade much in fashion at the time, so Perkin's aniline purple -- which he called Tyrian purple but which soon became popularly known as mauve -- was a quick commercial success. The rest, as the saying goes, is history.

That history is the subject of Travis' exhaustive and fact-filled account of the European synthetic dye industry for its first 40 years, from mauve to indigo. The success of mauve itself was relatively short-lived. Perkin's dye, in fact, was a rather muddy, washed-out hue, in part because it was ma mixture rather than a single chemical entity.

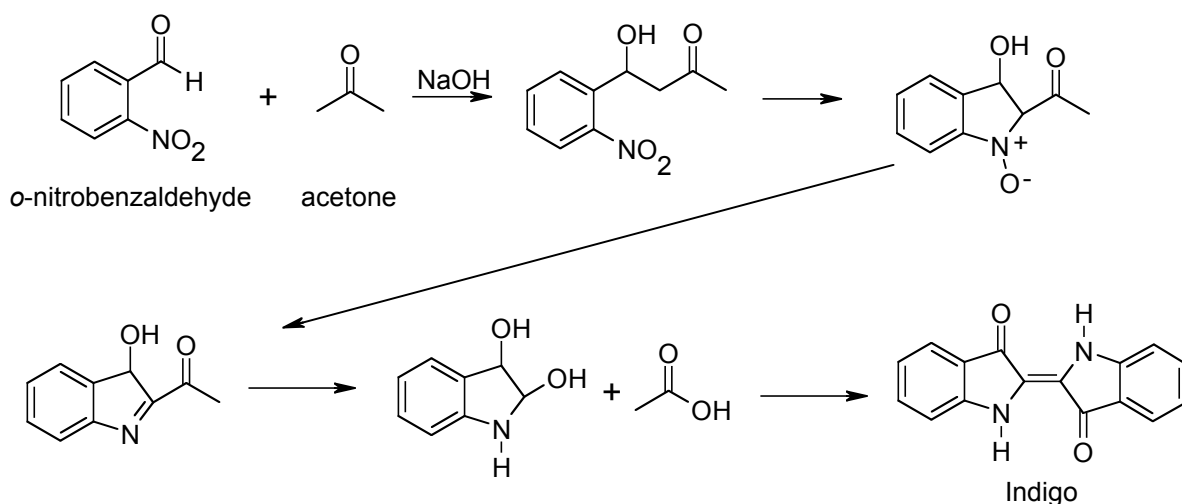
But other chemists in England and France soon followed down Perkin's path, experimenting empirically with aniline to produce more brightly colored dyes such as aniline red (magenta), aniline blue, and aniline violet (synthesized first by Hofmann himself).

German chemists, several of whom gained their initial experience with dyes in England, also turned their attention to synthetic dyes. Aided by rapid growth in understanding the structure of aromatic molecules, their experiments became more based on theory. Their first big achievement, in 1869, was the synthesis of alizarin, a brilliant red dye previously obtained from the roots of the madder plant. Perkin also found how to make alizarin; in fact, his company beat the Germans in producing it on an industrial scale, thereby briefly reviving his fading commercial fortunes.

But the German dye producers, among them the forerunners of such modern chemical behemoths as BASF, Hoechst, and Bayer, were strongly in the ascendancy. Their increasingly astute employment of chemical research culminated with development of an industrial process for synthetic indigo (previously available only as a natural product) by BASF in 1897. Intensely competitive, these German companies soon dominated the market. As for Perkin, he sold off his company in 1874 (it eventually became part of ICI) and devoted the rest of his life to chemical research, discovering the Perkin reaction for making unsaturated acids and studying the magnetic rotary power of organic compounds.

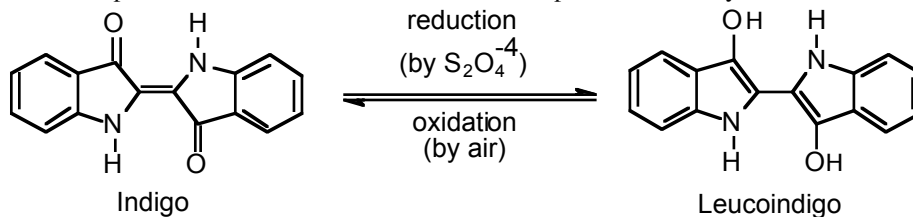
Indigo is a blue dye that has been used to dye cloth for thousands of years. Its first use was by ancient Egyptians to dye mummy cloths. Today, it is used mainly in the dyeing of blue jeans. Indigo was first artificially synthesized in 1880 by J. F. W. Adolph von Baeyer who won the Nobel Prize in 1905 for his work with organic dyes. Although Baeyer's synthesis method does not work well for producing the large amounts of indigo that would be needed for industrial applications, it does work well for micro scale production and will be used in this experiment.

In this experiment indigo will be produced using the Baeyer-Drewson reaction. This involves reacting *o*-nitrobenzaldehyde with acetone under highly basic conditions. The series of reactions below outlines the steps that the reactants go through in forming the final product.



Indigo, like most commercial dyes, is water insoluble. This means that the dye will not wash out of clothing in the washing machine. Unfortunately, however, it also means that indigo cannot be introduced into fabrics by simply immersing them in an aqueous solution of the dye. In order to introduce indigo into fabric a process called vat dyeing must be utilized.

Vat dyeing involves reducing the dye to a leuco derivative which is soluble in a dilute alkali solution. The fabric is immersed in this solution which allows the leuco compound to adhere to the fabric by hydrogen bonding. The fabric is then exposed to air which oxidizes the leuco compound into the dye.



In this experiment, indigo, after being synthesized and isolated, is reduced with sodium hydrosulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) under basic conditions to form leucoindigo. Fabric is then soaked in this leucoindigo solution and air dried. During air drying the leucoindigo is oxidized back to indigo which is strongly imbedded into the cloth fibers.

**Prelab Exercise** (Must be finished and handed in prior to starting experiment.)

1) Explain why substituting *p*-nitrobenzaldehyde for *o*-nitrobenzaldehyde in this experiment would not produce a stable heterocyclic product.

2) During the indigo synthesis, why must the ethanol used to wash the filtered indigo be cold? Why should the cap not be placed on the 20-mL vial used for the reaction?

### CAUTION!

**The chemicals you will be working with are potentially hazardous!** *O*-nitrobenzaldehyde is a confirmed mutagen, which means it can alter the structure of DNA, therefore gloves must be worn throughout the entire experiment. Indigo is only a mild irritant, so it poses very little health risk. It will, however, stain skin, clothing, some lab apparatus, and almost anything it contacts. Lastly, the leucoindigo solution produced gives off a highly undesirable odor so, as a courtesy to others, it should be kept in the fume hood during the experiment.

### Synthesis of Indigo

To a capless 20mL vial (*Note: the cap should NOT be placed on the vial at any time during this experiment.*) add: a 1-cm stir bar, 5mL acetone, 5mL distilled H<sub>2</sub>O, and 0.50g *o*-nitrobenzaldehyde. Begin stirring. Add 2.5mL 1M NaOH drop wise over a period of 5 minutes. Next, let the mixture stir for 5 minutes to allow it to return to room temperature. Using a Hirsch funnel, vacuum filter the contents of the vial as quickly as possible. (Indigo forms very fine crystals that may clog the filter like mud if it is poured through too slowly. A Buchner funnel may work better for slow pourers. Also, do not allow the filtrate to become dry while filtering or the system will clog.) Next, rinse the vial with 10mL H<sub>2</sub>O and add this to the filter before the product becomes dry. Before this liquid passes through the filter completely, wash the filtrate with 5mL cold 95% ethanol. Remove the product from the filter, allow it to air dry, and then weigh the dry product. Indigo's melting point is above the range of laboratory thermometers so do not attempt to find the melting point of the product.

### Vat Dyeing

Dissolve 3 NaOH pellets in 10mL H<sub>2</sub>O and add this solution to a 50-mL filter flask with an operating 1" stir bar. To this add the indigo produced by the synthesis above. Stir and heat this mixture to boiling in a shallow sand bath. While waiting for the mixture to boil, stir 3g sodium hydrosulfite (sodium dithionite Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, found in the lab refrigerator) into 27 mL H<sub>2</sub>O to make an approximately 10% solution. When the indigo solution reaches boiling add 2mL of the sodium hydrosulfite solution to the boiling solution drop wise. Continue adding sodium hydrosulfite solution drop wise until the blue color has completely left the solution yielding leucoindigo, a clear yellow liquid. While it is still hot, add the leucoindigo solution to 75 mL H<sub>2</sub>O in a 125-mL filter flask which also contains a fabric test strip from the Advanced shelf. Do not be concerned if a blue precipitate forms on the surface of this solution, the final washes will eliminate this problem. Close the flask with a stopper and a slit Pasteur pipette bulb over the side arm. The amount of reducing agent required and the odor produced are significantly less than with open dye-bath containers. Heat the flask to almost boiling; the slit safely equalizes the pressure and minimizes exposure of the leucoindigo to air. Cool, remove the fabric strip from the solution and hang it to dry. Once dried, wash the fabric strip with cold H<sub>2</sub>O to remove any excess dye clumps and dry again.

### Cleaning Up

Dispose of the dye solution and acetone rinses of glassware in the appropriate waste container. Place filter papers and remaining solids in the waste bin.

### Final Report

Calculate the percent yield of synthesized indigo, answer the below questions (include in the Discussion section of your final report), and attach the dried fabric test strip to the final report.

- 1) Offer an explanation as to why indigo is more colorful than leucoindigo that involves the types of conjugation in the two molecules.
- 2) The main component in cotton fibers is the cellulose polymer pictured below. Explain why indigo adheres to the cotton fabric so effectively, based on intermolecular forces.

