Organic chemistry

Synthesis and purification or organic compounds
Synthesis of organic compounds

LD Chemistry Leaflets

C2.4.1.1

Indigo synthesis

Aims of the experiment

- Synthesis of the organic product indigo
- Explanation of the chromaticity of indigo.
- Folloing the Bayer-Drewsen reaction mechanism.
- Calculation of yield.

Principles

Indigo synthesis was discovered in 1870 by Adolph von Bayer. It made it possible, for the first time, to synthetically produce indigo, one of the oldest and most important natural dyes. Today, dyeing of jeans is still the main use of indigo. With an annual worldwide production of 30,000 tons,indigo is still the most used textile dye.

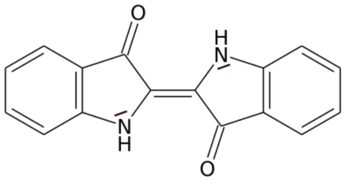

Fig.1: Structure of indigo.

The chromaticity of indigo can be explained by the formation of a conjugated π system with a total of 22 π electrons. In addition, there are 18 electrons from 9 double bonds and 4 electrons from free electron pairs at the nitrogen atoms.

In organic dyes, it is the P orbitals which run perpendicular to the core bond axis that form the conjugated π systems if they lie in a common plane and are adjacent to one another. The electrons distribute across the bonding molecular orbitals and are delocalised over the entire π system.

Through electromagnetic radiation, electrons can be lifted from the bonding molecular orbitals to antibonding molecular orbitals if the energy of the irradiating light quanta corresponds to the energy of the orbital transition. This process is called absorption. The wavelength at which a substance absorbs the most light is determined by the energy difference between the highest occupied and the lowest unoccupied molecular orbital.

The more orbitals involved in a π system, the more the energy states that exist vary and the lower the energetic gap is between the highest occupied and the lowest unoccupied orbital. As the size of the π system increases, the absorption maximum of a dye shifts to the longer-wave spectral range.

The absorbed portion of light is removed from the spectrum of emitted light. Indigo absorbs light in the yellow spectral range. The emitted light appears to us in the complementary colour blue.

Through structural modification of indigo, other colour shades than blue, which is characteristic of indigo, can be generated. The group of substances derived from indigo is called indigoid dyes.

In the experiment presented here, indigo will be produced according to the Bayer-Drewsen reaction from 2-nitrobenzaldehyde. In the evaluation, the reaction mechanism will be elucidated and the yield is calculated. The use of indigo in dyeing is presented in experiment C5.2.4.1.

Fig.2: Set-up of the experiment.

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Risk assessment

When carrying out the experiment, wear goggles, an apron and gloves. Be careful in particular when adding the sodium hydroxide pellets, as they are very corrosive. Keep the bottles of organic solvent away from possible flame sources.

Sodium dithionite	
Signal word: **Hazard**	**Hazard statements:** H251: Can heat up by itself; can ignite. H302: Harmful if swallowed. EUH031: Poisonous gases will develop in contact with acid. **Safety statements:** P370+P378: In case of fire: Use sand to extinguish.

Acetone	
Signal word: **Hazard**	**Hazard statements:** H225: Highly flammable liquid and vapour. H319: Causes serious eye irritation. H336: May cause drowsiness or dizziness. EUH066: Repeated contact can lead to brittle or cracked skin. **Safety statements:** P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking. P233: Keep container tightly closed. P305+P351+P338: IF IN EYES: Rinse carefully with water for several minutes. Remove contact lenses if present and easy to do so. Continue rinsing.

2-nitrobenzaldehyde	
Signal word: **Caution**	**Hazard statements:** H302: Harmful if swallowed. H315: Causes skin irritation. H319: Causes serious eye irritation. H335: May cause respiratory irritation. **Safety statements:** P261: Avoid breathing dust/fume/gas/mist/vapour/aerosol. P305+P351+P338: IF IN EYES: Rinse carefully with water for several minutes. Remove contact lenses if present and easy to do so. Continue rinsing.

Ethanol	
Signal word: **Hazard**	**Hazard statements:** H225: Highly flammable liquid and vapour. **Safety statements:** P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

Equipment and chemicals

1 Erlenmeyer flask, DURAN, 100 ml, squat 664 246
1 Spatula with spoon end, 150 mm 666 967
1 Electronic balance 440-3N, 200 g : 0.01 g 667 7977
1 Graduated pipette 5 ml................................ 665 996
1 Pipetting ball.. 666 003
1 Measuring cylinder, 10 ml, with plastic base . 665 751
1 Büchner funnel, 45 mm diam. 665 161
1 Water jet pump.. 375 56
1 Rubber collar (Guko) 665 060
1 Suction flask 250 ml 664 865
1 Vacuum rubber tubing, 8 mm diam., 1 m 667 186
1 Beaker, DURAN, 100 ml, squat.................... 664 101
1 Glass stirring rod 200 mm x 8 mm diam........ 665 212ET10
1 Round filter type 595 40 mm diam................ 661 030
1 2-nitrobenzaldehyde, 5 g............................. 673 9390
1 Acetone, 1 l 670 0410
1 Soda lye, 1 mol/l, 500 ml 673 8420
1 Ethanol, absolute, 500 ml............................ 671 9711
Additionally required:
Distilled water

Set-up and preparation of the experiment

Synthesis of indigo

In a 100 ml Erlenmeyer flask, 1 g of 2-nitrobenzaldehyde is weighed out. Acetone, 1 N sodium hydroxide and distilled water are prepared. Also, a 5 ml graduated pipette with a pipetting ball is provided and a 10 ml measuring cylinder.

The porcelain Büchner funnel is inserted in to the suction flask with the rubber collar. The suction flask is then connected to the water jet pump through a tube. A type 595 round filter is placed in the Büchner funnel in such a way that all holes of the funnel are covered. A 100 ml beaker is prepared with 50 ml of ethanol.

Dying with indigo

To dye the material, a 150 ml beaker is filled with 100 ml of distilled water and placed on a magnetic stirrer with hotplate. 2 g of sodium dithionite is weighed out onto a watch glass. Sodium hydroxide pellets and ethanol are also needed.

Performing the experiment

Synthesis of indigo

The weighed out 2-nitrobenzaldehyde is dissolved in 3 ml of acetone. Then, 3 ml of distilled water and 1 ml of 1N soda lye are added. The solution changes colour to dark brown in the process. After 5 minutes, the solution is filtered. To do so, the water jet pump is first turned on. The filter is made wet with a bit of ethanol. *Note: Check to see that the filter is situated correctly! All holes of the funnel must be covered by filter paper.*

Only then are the contents of the Erlenmeyer flask poured over the filter in small steps. Contents remaining in the Erlenmeyer flask are flushed out with ethanol and also added to the Büchner funnel. After the liquid in the Erlenmeyer flask is filtered, the residue in the Büchner funnel is washed again with a bit of ethanol. Then the pump is turned off. The residue obtained will still look a bit brown, but can be used for dying.

Observation

1. After adding the sodium hydroxide to 2-nitrobenzaldehyde and acetone, the solution turns dark brown.

2. During nutsch filtering, a blue-brown mixture is obtained.

3. The dried indigo weighs about 1.1 g.

Result of the experiment

Indigo synthesis mechanism

In indigo synthesis 2 molecules of acetone formally react with 2 molecules of 2-nitrobenzaldehyde with splitting of 2 molecules of acetic acid and 2 molecules of water to form indigo.

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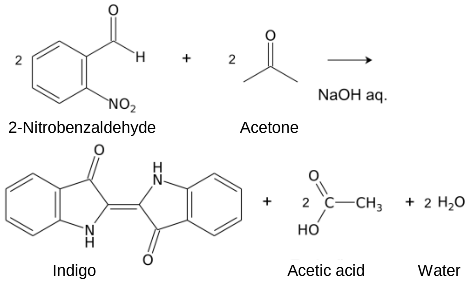

Fig. 3: Overall reaction equation of indigo synthesis.

The first step of the mechanism is an aldol addition. The sodium hydroxide causes an acidic proton to split off. The acetone can then attack the carbonyl group of the 2-nitrobenzaldehyde as a nucleophile. The result of the aldol reaction is an aldol (Fig. 4).

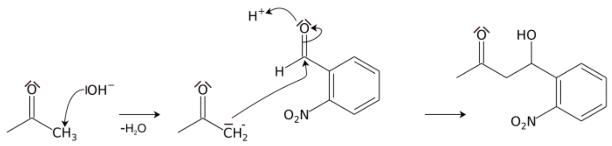

Fig. 4: Step 1 - Aldol addition.

Another acidic proton can be split off. In the second step, the free electron pair at the carbon atom attacks the nitro group nucleophilically in an intramolecular reaction. The splitting of the third acidic proton leads to the formation of a double bond at the nitrogen and enables the splitting of one of the oxygens as water. After the formation of the double bond, a fourth acidic proton can be split off. A double bond is generated next to the hydroxide group. The electron pair of the double bond at the nitrogen travels to the previously formally positively charged nitrogen (Fig. 5).

The third step is a tautomeric conversion of the enol to the keto form (Fig. 6).

In the fourth step, a hydroxide ion nucleophilically attacks one of the carbonyl groups. Acetic acid and water are split off. The instabile orange indolone is produced as an intermediate synthesis product (Fig. 7).

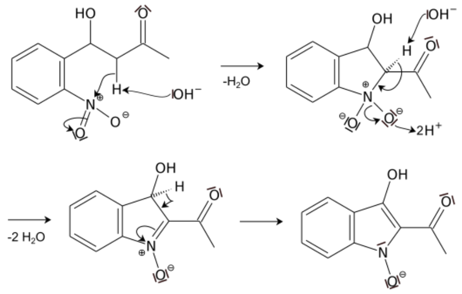

Fig. 5: Step 2 - Intramolecular nucleophilic attack.

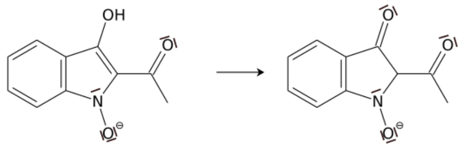

Fig. 6: Step 3 - Keto-enol tautomerisation.

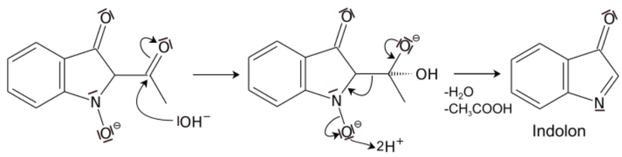

Fig. 7: Step 4 - Splitting off of acetic acid.

This dimerises in aqueous solution to form indigo (Fig. 8).

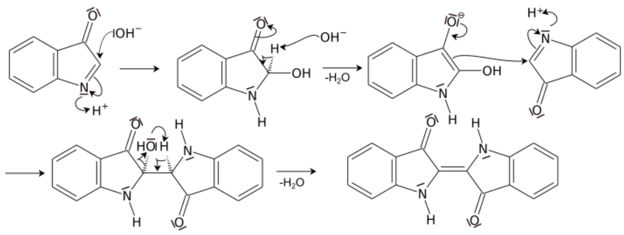

Fig. 8: Step 5 - Dimerisation of indolone to indigo.

The brownish colour after addition of sodium hydroxide is explained as a mixed colour of orange indolone and blue indigo since the dimerisation does not initially proceed to completion.

Determination of Yield

For the calculation of yield the theoretically possible amount of indigo is compared to the actual isolated amount. Limited starting material in this case I 2-Nitrobenzaldehyde. The other substances are present in excess.

2 g Nitrobenzaldehyde (M = 151,12 g/mol) are 13,2 mmol. Looking at the reaction equation (Fig 2), 2 molecules of 2-Nitrobenzaldehyde yield 1 molecule of indigo. The maximal amount is thus 13,2 / 2 mmol = 6,6 mmol Indigo (M = 262,27 g/mol). In the filter, a maximum of 6,6 mmol · 262,27 g/mol = 1,7 g indigo can be present. In the experiment, 1.1 g Indigo were isolated. Thus, the yield is 65%.

Cleaning and disposal

The wash water contains ethanol, therefore, it must be added to the container for organic solvent waste.

The rest of the vat can be added to the container for inorganic solvent waste.