

Title: Preparation of 4-nitrophenol

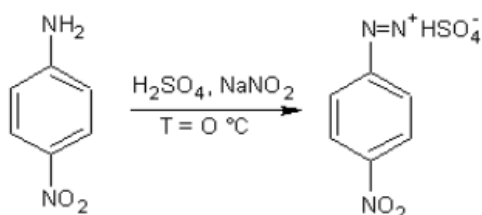
Work instructions

Task:

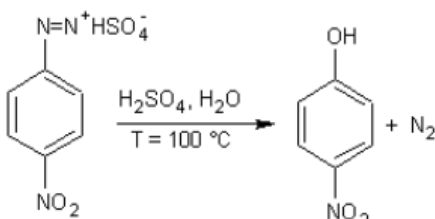
1. Make a diazotisation of 4-nitroaniline, divide the obtained solution of 4-nitrobenzenediazonium sulfate into two parts (4 ml and the rest). Keep both solutions in an ice bath.
2. With 4 ml of the sample, carry out the demonstration of the diazonium salts by an azo copulation reaction with phenol, 2-naphthol and H-acid. Discuss the effect of structure on the colour of the compound.
3. The major fraction of the diazonium salt was converted by the Griess reaction to 4-nitrophenol.
4. After crystallisation, measure the melting point and calculate the percentage yield of the reaction.

Theory

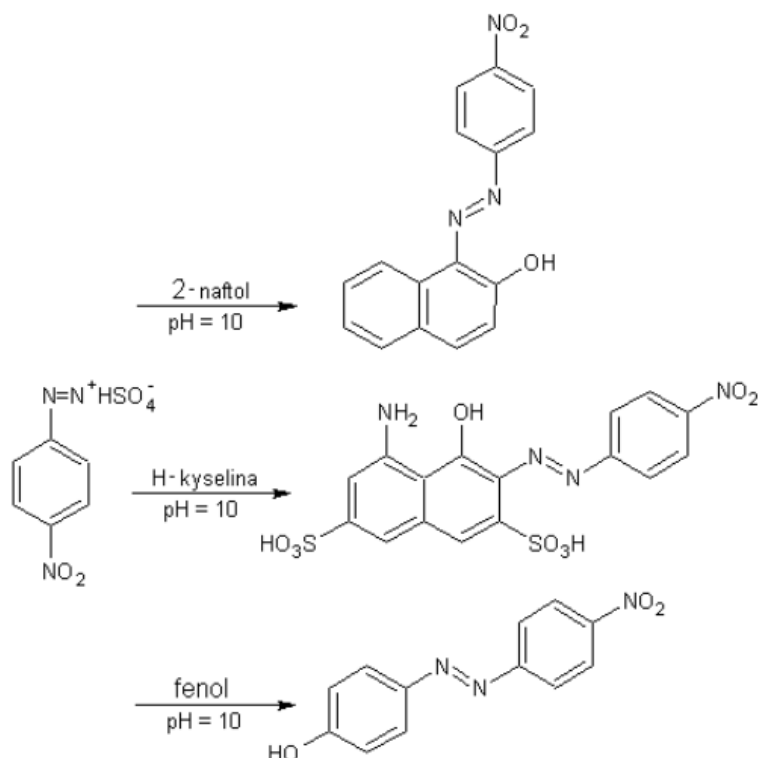
Diazotisation is the reaction of primary aromatic amines with nitrous acid to form a diazonium salt. The reaction proceeds according to the Eq:



The Griess reaction is the decomposition of a diazonium salt by hydrolysis according to Eq:



Evidence of diazonium salt by azo copulation reactions proceeds according to Eqn:



Equipment: heating mantle, Liebig condenser, ring stand, clamps, holder, burner, tripod, wire gauze, beakers (100, 250 ml), graduated cylinder (10, 100 ml), glass rod, ice bath, scales, thermometer, pipette, pipetting balloon, test tubes, Erlenmeyer flask (250 ml), boiling chips, filter paper

Chemicals: 4-nitroaniline, sulfuric acid, sodium nitrite, phenol, 2-naphthol, H-acid, sodium hydroxide

Procedures:

1. All work is carried out with safety goggles!

Diazotisation

1. Pour 20 ml of water into a 200 ml beaker and carefully (SHIELD!) add 14 ml of conc. sulfuric acid, stirring constantly. To the hot solution add 7 g of finely crushed 4-nitroaniline.
2. Cool the resulting solution in an ice bath to 5°C, add 25 g of ice and add a solution of 3.9 g of sodium nitrite in 18 ml of water at (0-5°C) while stirring and cooling. The diazonium salt formed makes a clear solution.
3. Remove 4 ml for the proof reaction, hydrolyse the rest.

Proof of diazonium salt

1. Divide the collected 4 ml sample into 3 tubes. Keep the temperature at 0°C.
2. Drop a sample of the diazonium salt successively into a solution of phenol, naphthol and H-acid (0.1 g in 3 ml of 5% NaOH). Do the same by drop reaction on filter paper.

Hydrolysis of diazonium salt

1. Pour 15 ml of water and 15 ml of concentrated sulfuric acid into a 250 ml flask with a reflux Liebig condenser and heat the solution to boil. Add the diazonium salt solution to the boiling solution, one at a time, using the condenser, so that the mixture continues to boil.
2. Rinse the residue of the diazonium salt from the beaker and the cooler with 15 ml of water. Heat the mixture to boiling for 10 minutes, then pour into a 250 ml Erlenmeyer flask, cool with water and then in an ice bath.
3. The eluted product is aspirated and recrystallised from hydrochloric acid diluted 1:1. Dry, calculate the yield and measure the melting point.

Management of chemical substances

Chemicals	Form	H-statements	P-statements
4-Nitroaniline	Solid	H301, H301 + H311 + H331, H311, H331, H373	P261, P273, P280, P301 + P310, P311
H ₂ SO ₄	Liquid, 98%	H290, H314	P260, P280, P303 + P361 + P353, P304 + P340 + P310, P305 + P351 + P338
NaNO ₂	Solid	H272, H301, H319, H400	P210, P220, P221, P301 + P330 + P331 + P310, P305 + P351 + P338, P370 + P378
Phenol	Solid, 99%	H301, H301 + H311 + H331, H311, H314, H315, H319, H331, H341, H373, H411	P260, P280, P301 + P330 + P331 + P310, P303 + P361 + P353, P304 + P340 + P310, P305 + P351 + P338
2-Naphthol	Solid, 99%	H302, H332, H400	P273
H-acid	Solid	---	---

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Chemicals	Form	H-statements	P-statements
NaOH	Solid	H290, H314, H315, H319	P260, P280, P303 + P361 + P353, P304 + P340 + P310, P305 + P351 + P338
4-Nitrophenol (product)	Solid	H301, H312 + H332, H373	P261, P301 + P310 + P330, P302 + P352 + P312, P304 + P340 + P312

Sources of risk and assessment of risk severity

There is no risk if all the principles for working with chemicals are followed and personal protective equipment (gloves, goggles, lab coat) is used.

Waste management method

These substances and their packaging must be disposed of as hazardous waste. Dispose of waste substances in a labelled container. Do not return unconsumed residues in storage bottles. Dispose of broken glass in a labelled container.

This combustible material may be incinerated in a chemical waste incinerator equipped with an afterburner and gas scrubber. Take leftover quantities and unusable solutions to a certified company for disposal. Dispose of contaminated packaging as unconsumed product.

Risk reduction measures

Wear a protective shield or goggles. Wear protective gloves. Gloves must be inspected before use. Use proper glove removal technique without touching the outer surface of the gloves to prevent skin contact with this product. Do not eat, drink or smoke while working. Wash your hands with soap and water or treat them with a protective cream when you have finished working or when you stop working. In case of an accident or if you feel unwell, inform the teacher immediately. Avoid further leakage or spillage unless there is a risk involved. Do not allow it to reach the sewer. Avoid discharging into the environment.

Worksheet

Chemical calculations and evaluation

Proof of the diazonium salt by the azocoupling reaction

Substance	Result	
	Test tube reaction	Drop reaction–filter paper
Phenol		
2-Naphtol		
H-acid		

1. Discuss the effect of structure on the colour of a compound.
2. Convert the major fraction of the diazonium salt by the Griess reaction to 4-nitrophenol. After crystallisation, measure the melting point and calculate the percent yield of the reaction.

Yield	Substance	Value
Theoretical yield		
Practical yield		
Refractive index	4-nitrophenol	

Conclusion

Evaluate your work.