

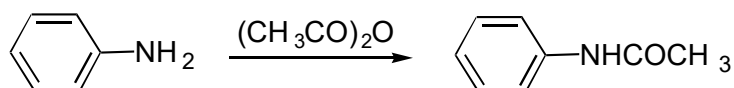
Title: Preparation of 4-nitroacetanilide and 4-nitroaniline

Work instructions

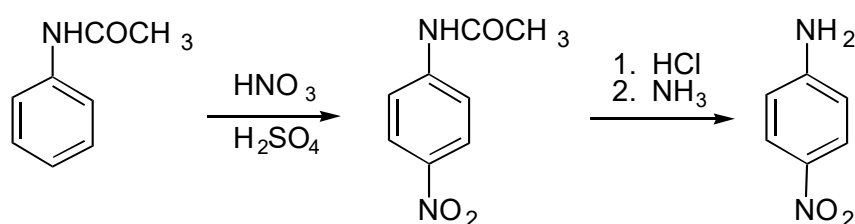
Task: Prepare 4-nitroacetanilide by nitration of acetanilide, which by subsequent acid hydrolysis affords 4-nitroaniline.

Theory

Acetylation of aniline is the addition-elimination reaction of an aromatic amine with acetic anhydride to form N-acetylaniline (acetanilide) according to Eq:



Nitration of acetanilide by a nitration mixture proceeds regioselectively to the para-position by electrophilic aromatic substitution to form 4-nitroacetanilide, which is subsequently hydrolysed to 4-nitroaniline by an addition-elimination reaction with water in an acidic medium according to Eq:



Equipment: Erlenmeyer flask with stopper, graduated cylinder, beaker, Büchner funnel, suction flask, water jet pump, rubber adapter, filter paper, boiling flask, heating mantle, laboratory stand, reflux condenser, cooling water inlet and outlet hoses, glass rod, pH paper, funnel

Chemicals: sulfuric acid (98%), nitric acid (65%), hydrochloric acid (35%), acetic anhydride, aniline, ammonia, activated carbon

Procedures:

1. All work is carried out with safety goggles!

Acetylation of aniline

1. In an Erlenmeyer flask, mix 4.6 g of aniline with 40 ml of water and add 6.6 ml of acetic anhydride to the suspension, stirring vigorously. After all the acetic anhydride has been added, the reaction mixture is shaken for 10 min, the spontaneous precipitation of the crystalline product may be observed during the reaction. Allow the reaction mixture to stand for 30 min to complete the reaction.
2. Aspirate the excluded crystals on a Büchner funnel, squeeze out the mother liquor from the filter cake and wash it with a little cold water. Use 5 g of well-washed crude acetanilide in the next reaction.

Nitration of acetanilide

1. In an Erlenmeyer flask, mix 5 g of wet crude acetanilide (equivalent to approx. 4 g of dry acetanilide) with conc. H_2SO_4 (9 ml). After almost all the acetanilide has dissolved, cool the contents of the flask and carefully add drop by drop the nitration mixture prepared by carefully mixing 2.2 ml of 65% HNO_3 with 2.2 ml conc. H_2SO_4 . Stir the reaction mixture vigorously. Keep the nitration temperature below 35 °C.
2. After the entire volume of nitration mixture has been added, remove the flask from the cooling bath and allow to stand at laboratory temperature for 10 minutes. Then pour the reaction mixture into four times the volume of ice and water. Filter off the excluded 4-nitroacetanilide after mixing and wash with a small amount of water.

Hydrolysis of 4-nitroacetanilide

1. Transfer the wet 4-nitroacetanilide to a boiling flask, add 30 ml of water and 20 ml of conc. HCl , put on a reflux condenser and heat the reaction mixture at boiling point on an air bath for 30 minutes. Pour the resulting solution into a beaker with 30 g of ice. Isolate 4-nitroaniline by alkalizing this mixture with ammonia water. Aspirate the isolated 4-nitroaniline on a Büchner funnel and dry.

Management of chemical substances

Chemicals	Form	H-statements	P-statements
4-Nitroaniline	Solid, crude (product)	H301, H301 + H311 + H331, H311, H331, H373	P261, P273, P280, P301 + P310, P311
H_2SO_4	Liquid, 98%	H290, H314	P260, P280, P303 + P361 + P353, P304 +

Chemicals	Form	H-statements	P-statements
			P340 + P310, P305 + P351 + P338
HNO ₃	Liquid, 65%	H290, H314	P260, P280, P303 + P361 + P353, P304 + P340 + P310, P305 + P351 + P338
HCl	Liquid, 35%	H290, H314	P260, P280, P303 + P361 + P353, P304 + P340 + P310, P305 + P351 + P338
Acetic anhydrid	Liquid, 99%	H226, H302, H314, H332	P280, P305 + P351 + P338, P310
Aniline	Liquid, 97%	H301, H311, H317, H318, H331, H351, H372, H400	P261, P273, P290, P301 + P310, P305 + P351 + P338, P311
Ammonia	Liquid, 30%	H314, H335, H410	P261, P271, P273, P280, P303 + P361 + P353, P305 + P351 + P338

Sources of risk and assessment of risk severity

There is no risk when following all the principles for working with chemicals and using personal protective equipment (gloves, goggles, lab coat).

Waste management method

Dispose of waste materials in a marked container. Do not return unconsumed residues to storage bottles. Dispose of broken glass in a marked container.

Risk reduction measures

Avoid direct exposure, use protective equipment. Do not expose to prolonged or repeated exposure. In the event of an accident or if you feel unwell, inform the teacher immediately. These substances or their containers must be disposed of as hazardous waste. Do not eat, drink, smoke. Wash your hands with warm water and soap or treat them with a reparative cream after work or when interrupting work.

Worksheet

Calculation

- Calculate the volume of aniline corresponding to 4,6g.
 $\rho(\text{C}_6\text{H}_7\text{N}, 20^\circ\text{C}) = \dots\dots\dots \text{g}\cdot\text{cm}^{-3}$
- Calculate the theoretical yield of 4-nitroacetanilide and 4-nitroaniline.
- Calculate the practical yield of 4-nitroacetanilide and 4-nitroaniline in %.

Observation

- Describe the appearance and odor of 4-nitroacetanilide and 4-nitroaniline products.
- Search for the basic physicochemical properties of the products 4-nitroacetanilide and 4-nitroaniline.

Feature	4-nitroacetanilide	4-nitroaniline
Solubility in water		
Solubility in other solvents		
Melting point		

Yield

- Record the mass of the prepared 4-nitroacetanilide.
 $m(\text{C}_8\text{H}_8\text{N}_2\text{O}_3) = \dots\dots\dots \text{g}$
- Record the mass of the prepared 4-nitroaniline.
 $m(\text{C}_6\text{H}_6\text{N}_2\text{O}_2) = \dots\dots\dots \text{g}$

Questions

1. Write the reactions for the preparation of 4-nitroacetanilide and 4-nitroaniline.
2. Write the significance of acetylation of aniline before nitration.
3. Write why nitration of acetanilide is regioselective to the para-position.
4. Explain why it is necessary to keep the temperature below 35 °C during nitration.
5. Write why 4-nitroacetanilide heats up during hydrolysis in an acidic environment.
6. Suggest ways in which you would verify the purity of the final product 4-nitroaniline.
7. Describe the uses of 4-nitroacetanilide and 4-nitroaniline

Conclusion

Briefly summarize the objective of the experiment, the main results and compare them with the expected values.

Name of the project: Digitization of chemistry experiments to improve the quality and support chemistry teaching in secondary schools
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