

XVIII Baltic Chemistry Olympiad



Practical Problems-

- Organic Synthesis

Code:

16-18 April 2010
Tartu, Estonia

Instructions

- **Safety rules** – follow them as in the Preparatory problems described, no eating or drinking is allowed in the lab. You should wear safety glasses, gloves and lab coats.
- **Violating safety rules** – you get one warning, offend again: you are out.
- **Total time** – 2.5 hours for second task.
- Write your **student code** on first sheet.
- **Answers** – only in the appropriate places of the sheets, nothing else will be marked. Relevant calculations have to be shown.
- **Results.** The number of significant figures in numerical answers must conform to the rules of evaluation of experimental error. Mistakes will result in penalty points even if your experimental technique is flawless.
- **Questions** concerning safety, apparatus, chemicals, organization, toilet break: **ask your lab assistant.**
- **You must stop your work immediately after the stop signal has been given. A delay of 5 minutes will result in zero points for the current task.**
- Do not leave the room until permitted by the supervisors.
- This examination has **6** pages.
- The official English version of this examination is available on request only for clarification.

Synthesis of hydrobenzoin

Sodium borohydride was discovered in 1943 by H. I. Schlesinger and H. C. Brown. Brown devoted his entire scientific career to this reagent and received a Nobel price for his work. This reagent is nowadays one of the most useful and cheapest reducing agent in organic synthesis.

In present experiment you have to carry out the reduction of benzil which is a typical sodium borohydride reduction.

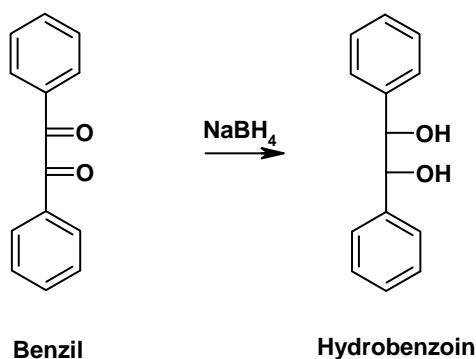
Chemicals

benzil (exact mass)	in small glass vial labeled Bzl
sodium borohydride (exact mass)	in Eppendorf tube labeled NaBH₄
ethanol	in graduated test tube labeled EtOH
ethyl acetate	in test tube labeled EtOAc
hexane	in test tube labeled Hex

Apparatuses and glassware

round bottomed flask (50 mL)
Liebig condenser (as air condenser)
glass filter funnel
plastic funnel
ice bath
vacuum filtration equipment (one for two persons)
magnetic stirrer
magnetic stirring bar
graduated test tube (2)
plastic pipette (3)
Petri dish
Eppendorf tube for TLC sample, labeled **TLC**
TLC plate (silica gel 60; layer thickness: 0.25 mm, on aluminium support)
glass capillary
tweezers
wide-mouth bottle with cap (developing chamber)
UV-lamp

Procedures



Synthesis

In 50 mL round bottomed flask, mix **0.5 g** of benzil in **5 ml** of 95% ethanol by stirring. Then add **0.1 g** sodium borohydride (large excess) with spatula in few portions. The benzil dissolves, reaction mixture warms up slightly. Connect the Liebig condenser and stir the mixture 10 more minutes. Then add **5 ml** of distilled water and heat the mixture to the boiling. Add more distilled water to the mixture up to the point of saturation (ca 10 ml) and set the solution aside to cool to room temperature and thereafter into ice bath.

The product separates in lustrous thin plates. Filtrate the product on glass filter funnel, wash the crystals with few milliliters of distilled water and take to the Petri dish for drying and weighing.

Analysis

Dissolve the sample of product in ethyl acetate and analyze the product by TLC using mixture of hexane and ethyl acetate (1 : 1; ca 6 ml) as eluent. Visualize the plate under UV-lamp. Calculate the R_f values of any spot you detected on TLC plate.

Questions

1. Calculate the yield (%) of product.

Yield of the product:

Calculations:

2. How many isomers does the hydrobenzoin have? Draw the structural formulas of all existing isomers.

Number of hydrobenzoin isomers:

Structural formulas:

3. How many isomers are formed by reduction of 4-*tert*-butyl-cyclohexanon? Draw the structural formulas of these isomers.

Number of 4-*tert*-butyl-cyclohexanol isomers:

Structural formulas:

4. Write the mechanism of carbonyl group reduction with NaBH_4 .

Mechanism of carbonyl group reduction with NaBH_4 :

5. Calculate the number of moles of NaBH_4 theoretically needed for complete reduction of one mole of benzil.

Number of moles of NaBH_4 needed for complete reduction of one mole of benzil:

Calculations:

6. Calculate the R_f values of all detected spots.