

# CHEMISTRY. OLYMPIAD.CH CHEMIE-OLYMPIADE

OLYMPIADES DE CHIMIE OLIMPIADI DELLA CHIMICA

## SwissChO 2023 - Practical Final Exam

SOLUTION KEY





## Synthesis of (*E*,*E*)-Dibenzylideneacetone (20.0 Points)

#### Note for us:

- Prepare vials in advance for them with their name, the experiment, and the weight of the empty vial  $\rightarrow$  we will need this for calculating their yield for the grading!
- Make sure to teach them how to TLC during the week.
- Check on the evening before that the reflux condensers are installed properly and that the water is not leaking.
- For grading we can use IR and melting point analysis to grade purity.
- Give each student:
  - 1. 100 mL of EtOH.
  - 2. A bit more than 50 mL of the  $2.3 \text{ mol L}^{-1}$  NaOH solution.
  - 3. approx. 3 mL of acetone
  - 4. approx. 10 mL of benzaldehyde
  - 5. approx. 10 mL of hexane
  - 6. approx. 10 mL of EtOAc
  - 7. 3 precut TLC plates
  - 8. 3 glass capillaries for TLC
  - 9. the preweighted and labelled vial to submit their product



Figure 1 solution: Correct reaction scheme for task 1.

#### Answers to theoretical questions

1.1	Determine X, Y, and Z in the reaction scheme shown in Fig. 1. See reaction scheme in Fig. 1 solution:	1.5pt
	X = 2	
	Y = 1	
	Z = 2	
	0.5pts per correct coefficient	





1.2	Draw the structure of the expected product.	2.0pt
	-1.0pt if only single aldol condensation (i.e. only one phenyl ring on product). -1.0pt if product shows $(E,Z) / (Z,E) / (Z,Z)$ product.	
1.3	Name the type of reaction you performed in this task. (Double) aldol condensation -0.5pts if "aldol reaction" was written.	1.0pt
1.4	<ul> <li>What are potential driving forces for the elimination of water during the reaction?</li> <li>The elimination of water is entropically favourable.</li> <li>The reaction forms a very large conjugated system.</li> <li>1.0pt per justification</li> </ul>	2.0pt
1.5	<ul> <li>What other methods could you use to favour the elimination of water in this synthesis? Name at least 2.</li> <li>Don't use water as part of the solvent (we add aqueous sodium hydroxide in the first step)</li> <li>Use a Dean-Stark apparatus to remove water during the reaction, if we reflux the mixture</li> <li>Heat the reaction further to make the elimination of water even more favourable</li> <li>Add some sort of drying agent to remove water (mol. sieves, anhydrous sodium sulfate, etc.)</li> <li>1.0pt per correct method. List is not exhaustive, so others are allowed if they do not disturb the reaction (i.e. use molten sodium to remove water).</li> </ul>	2.0pt
1.6	What could be the reason why the reaction (almost) exclusively forms the <i>trans</i> product?	1.0pt

Sterics: There would be quite some unfavourable steric interactions if one or both double bonds were in *cis*-configuration.



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1.7 What is the limiting reagent in the synthesis? Explain your answer.
 Acetone is the limiting reagent. We only add one equivalent of acetone and 2.05 equivalents of benzaldehyde.

0.5pts for correct reagent named. 1.0pt for correct justification.

- **1.8** According to the TLC you obtained immediately after the reaction, has your re- 2.0pt action run to completion? Individual "yes" or "no" answer, which has to be consistent with the TLC plate they handed in. If no TLC plate was handed in, no points for any type of answer.
- **1.9** According to the TLC you obtained after purification, is your dried product pure? 2.0pt Individual "yes" or "no" answer, which has to be consistent with the TLC plate they handed in. If no TLC plate was handed in, no points for any type of answer.
- 1.10 Hand in your product in the labelled vial with your TLCs for analysis.
  5.0pt
  Melting point:
  103 °C: 3.0pts
  Yield:
  If yield is over 20% (1.75 g): 2.0pts
  5.0pts total. 3.0pts for melting point. 2.0pts for yield.





### Love or Hate: Oxalate (18.5 points)

#### Note for us

• Preparatory instructions:

1. Weigh out a sample of oxalic acid for every student (300 mg - 400 mg) and note its mass exactly. DO NOT EXCEED 400 mg! Dissolve the sample in a small amount of water in their 250 mL volumetric flask to make it harder to gauge the amount they got.

2. Give them each 2 glass pipettes.

3. Prepare 2 L of a  $0.025 \text{ mol } \text{L}^{-1}$  NaOH solution and note exactly how much hydroxide was used. For reference: That's 2.00 g for the 2 L. Give every student 130 mL of this solution.

4. Prepare  $2 L \text{ of } a 0.01 \text{ mol } L^{-1} \text{ KMnO}_4$  solution and note exactly how much permanganate was used. For reference: That's 3.16 g for the 2 L. Acidify the solution with 120 mL conc. sulfuric acid (before filling it to the mark, obviously). Do this minutes before the exam to assure that the permanganate is fresh and has not degraded.

5. Give each student a tiny amount (3 mL) of phenolphtalein indicator solution (in EtOH).

#### Answers to theoretical questions

2.1	<b>Note</b> , which deprotonation is responsible for the colour change in the indicator. The second deprotonation is responsible for the change in indicator colour, as we are approaching pH 9. 1.0pt total.	1.0pt
2.2	Observe, that the discolouration of the added permanganate is very slow at first but the reaction rate increases, the more permanganate has already reacted. <b>State</b> , which process is responsible for this phenomenon.	1.5pt

Autocatalytic reduction of  $MnO_4^-$  in the precence of  $Mn^{2+}$  ions.

1.5pts total. 1.0pt for the autocatalysis. 0.5pts for the correct manganese species ( $Mn^{2+}$ ).

**2.3** Write the balanced reaction equations for the half-cell reactions and the full 3.0pt redox reaction involving the permanganate ions. Reduction:  $MnO_4^- + 8 H^+ + 5 e^- = Mn^{2+} + 4 H_2O$ 

Oxidation:  $H_2C_2O_4 = 2CO_2 + 2e^- + 2H^+$ 

Full reaction:  $5 H_2 C_2 O_4 + 2 K M n O_4 + 6 H^+ = 2 M n^{2+} + 10 C O_2 + 8 H_2 O_4 + 2 K^+$ 

Alternative solution for full reaction:  $8 H_2 C_2 O_4 + 2 K MnO_4 = 2 Mn^{2+} + 10 CO_2 + 8 H_2 O + K_2 C_2 O_4 + 2 C_2 O_4^{2-} + 0.5 pts$  per equation for correct species, +0.5 pts per equation for correct coefficients



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A gas is released when the permanganate solution is added. Name the gas and 1.0pt give its molecular formula.
 The released gas is carbon dioxide: CO<sub>2</sub>.

0.5pts for name, 0.5pts for formula

**2.5** From the acid-base titrations, **calculate** the unknown mass of oxalic acid you 6.0pt were given. **Show** your working and obtained values.  $\frac{V_{\text{NaOH}} \cdot c_{\text{NaOH}}}{2} = n_{\text{H}_2\text{C}_2\text{O}_4}$ 

 $m_{tot,\mathsf{H}_2\mathsf{C}_2\mathsf{O}_4} = 10n_{\mathsf{H}_2\mathsf{C}_2\mathsf{O}_4} \cdot M_{\mathsf{H}_2\mathsf{C}_2\mathsf{O}_4}$ 

2.0pts total. 1.0pt for the calculations. 1.0pt if they used at least 3 titrations.

**A.1** From the permanganometric titrations, **calculate** the unknown mass of oxalic 6.0pt acid you were given. **Show** your working and obtained values.  $V_{MnO_4^-} \cdot [MnO_4^-] \cdot \frac{2}{5} = n_{H_2C_2O_4}$ 

 $m_{tot,\mathsf{H}_2\mathsf{C}_2\mathsf{O}_4} = 10n_{\mathsf{H}_2\mathsf{C}_2\mathsf{O}_4} \cdot M_{\mathsf{H}_2\mathsf{C}_2\mathsf{O}_4}$ 

2.0pts total. 1.0pt for the calculations. 1.0pt if they used at least 3 titrations. 4.0pts for accuracy of results.



PS3-1 English (Official)

## **Qualitative Inorganic Analysis**

#### **Preparatory instructions:**

- 1. Give them each the salt mixture in a vial.
- 2. Prepare a test tube rack with all reagents and give them 20 test tubes each.
- 3. Give them each 15 plastic pipettes.

#### Answers to theoretical questions

3.1	<ul> <li>What are your observations on the colours inside your salt mixture? Which of your salts has which colour?</li> <li>CuSO<sub>4</sub>: blue</li> <li>FeCl<sub>3</sub>: dark green/yellowish</li> <li>NH<sub>4</sub>OAc: colourless/white</li> <li>0.5pts per correct colour observation. 1.0pts per correct assignment of colour to salt.</li> </ul>	3.0pt
3.2	What are your observations from the solubility tests you performed? Which of your salts are soluble in water or dilute acid/base and which aren't? CuSO <sub>4</sub> : soluble in water FeCl <sub>3</sub> : soluble in water NH <sub>4</sub> OAc: soluble in water 1.5pts total. 0.5pts for each correct statement.	1.5pt

3.3 What is the composition of your salt mixture? Write down how you were able to identify/verify their presence and write down the balanced reaction equations for their detection.
12pts total. 1.0pt for each correct ion. No points if oxidation state is wrong.
1.0pt for each correct reaction; only 0.5pts if the reaction is not balanced correctly.
If multiple detection reactions are given, only count one.





#### **Cation reactions**

### $\mathrm{Cu}^{\mathrm{2+}}$

1) Addition of ammonia to an aqueous  $Cu^{2+}$  solution gives a deep blue coloured solution, thanks to the hexaammine copper(II) complex:  $Cu^{2+} (aq) + 6 NH_3 = [Cu(NH_3)_6]^{2+} (aq)$ 

2) Copper(II) ions give a reddish-brown precipitate if potassium hexacyanoferrate is added to the solution:  $2 Cu^{2+} (aq) + K_4[Fe(CN)_6] (aq) = Cu_2[Fe(CN)_6] \downarrow + 4 K^+ (aq)$ 

### Fe<sup>3+</sup>

Addition of potassium thiocyanate to an aqueous solution of  $Fe^{3+}$  gives a blood-red solution:  $Fe^{3+}(aq) + 3 KSCN(aq) = Fe(SCN)_3(aq) + 3 K^+(aq)$ 

### $NH_4^+$

Addition of potassium hydroxide solution to a solid ammonium salt will result in the formation of ammonia, which can be identified by its characteristic odour:  $NH_4X(s) + KOH(aq) = NH_3 \uparrow + H_2O + KX(aq)$ 





#### Anion reactions

#### $\mathsf{CI}^-$

Addition of silver nitrate to an aqueous solution of chloride ions results in the formation of a white precipitate. This precipitate is insoluble in dil. HNO<sub>3</sub>, but soluble in dil. NH<sub>3</sub>: AgNO<sub>3</sub> (aq) + Cl<sup>-</sup> (aq) = AgCl \downarrow + NO<sub>3</sub><sup>-</sup>

 $AgCl (s) + NH_3 (aq) = [Ag(NH_3)_2]Cl (aq) \text{ (only required if they mention solubility in dil. NH_3)}$ 

## $\mathrm{SO_4}^{2-}$

Addition of barium chloride solution to an aqueous solution of sulfate ions results in the formation of a white precipitate:  $SO_4^{2-}(aq) + BaCl_2(aq) = BaSO_4 \downarrow + 2 Cl^-(aq)$ 

#### $AcO^{-}$

Addition of acid to an aqueous solution of acetate ions results in the formation of acetic acid, which can be identified by its characteristic odour:  $AcO^{-}(aq) + H^{+}(aq) = HOAc$