Practical

55TH INTERNATIONAL CHEMISTRY OLYMPIAD SWITZERLAND 2023

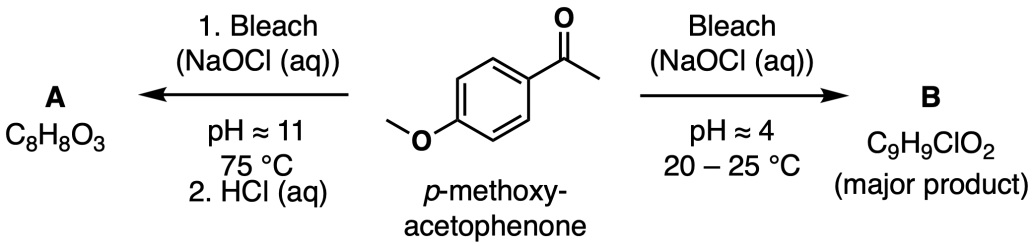
Q1-1

English (Official)

Bleach, a Chameleonic Reagent

16% of total													
Question	Yield **A**	TLC **A**	Deductions **A**	Yield **B**	TLC **B**	Deductions **B**	1.1	1.2	1.3	1.4	1.5	1.6	**Total**
Points	25	3	-6	25	3	-25	4	2	2	2	2	2	**70**
Score													

Experimental Procedure



Legend for translation: Bleach, p-methoxyacetophenone, major product

Preparation of Product A

1. **Turn on** the magnetic stirrer hotplate and **set** the control knob between $100\ °C$ and $150\ °C$ in order to reach the desired water bath temperature of $70-80\ °C$. While stirring, **control** the temperature of the water bath with a thermometer clamped to the stand.

2. While the water bath is heating up, **take** a small sample (small spatula tip) of *p*-methoxyacetophenone from the vial labeled "**SM-A**", **transfer** it to the vial labeled "**TLC-SM**" and **set** it **aside** for thin layer chromatography (TLC) analysis (to be carried out after the preparation of product B).

3. To a $50\ mL$ round-bottom flask, **add** a stir bar (olive-shaped), *p*-methoxyacetophenone ($500\ mg$, entire content of the vial labeled "**SM-A**", a weighing paper may be used for the transfer), NaOH (aq) ($6.7\ mL$, entire content of the vial labeled "**NaOH (aq)**"), and bleach ($7.5\ mL$, entire content of the vial labeled "**Bleach-A**").

4. **Clamp** the flask to the stand and **lower** it into the water bath by adjusting the position of the clamp. **Make sure** the reaction mixture is stirring rapidly (ca. $750\ rpm$).

5. **Attach** a Vigreux column to the flask (Figure 1). To the top of the Vigreux column, **attach** the bent hose adapter which is connected via tubing to a gas bubbler (filled with a trap solution of NaOH in EtOH/H_2O). **Secure** the joint with a clip.

6. **Let** the reaction **run** at $70 - 80$ °C for 60 minutes.

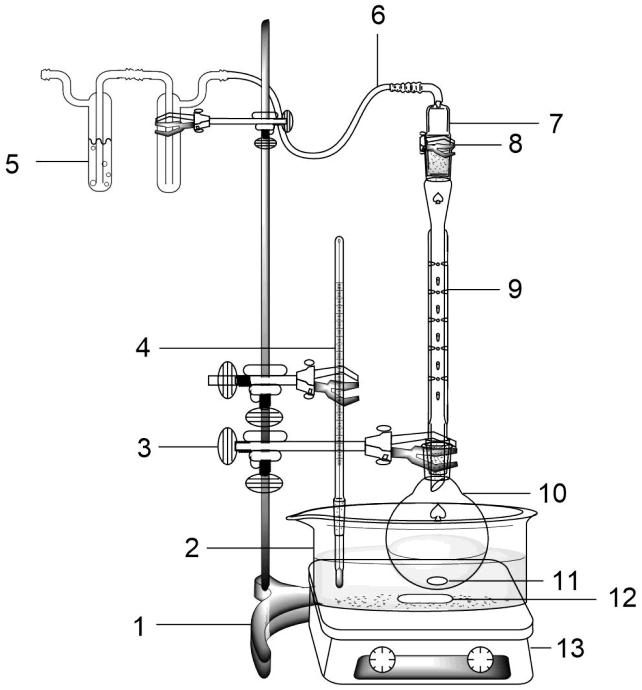


Figure 1: 1 = Laboratory stand, 2 = water bath, 3 = clamp holder with clamp, 4 = thermometer, 5 = gas bubbler, 6 = tubing, 7 = hose adapter with inner ground glass joint, 8 = joint clip, 9 = Vigreux column, 10 = round-bottom flask, 11 and 12 = magnetic stir bar, 13 = magnetic stirrer with hotplate

7. **Turn** off the heating, **raise** the flask above the water bath by adjusting the position of the clamps~~,~~ ~~carefully~~. ~~**remove**~~ **Raise** the technical assistance card for the removal of the water bath ~~and~~ by an assistant. ~~**allow**~~**Allow** the mixture to cool down while stirring and proceeding with the next steps.

8. **Disconnect** the gas bubbler from the Vigreux column by removing the bent hose adapter. **Remove** the Vigreux column (it will be reused in the preparation of product B).

9. **Ask** a lab assistant for crushed ice and **cool** the reaction flask in an ice-water bath while stirring (ca. 5 minutes).

10. With the flask still in the ice-water bath, slowly **add** $NaHSO_3$ solution (aq, 40%) (ca. 5 mL from the vial "~~**$NaHSO_3$**~~ **NaHSO3 (aq)**"; 1 mL corresponds to ½ Pasteur pipette, see Figure 2) with a Pasteur pipette. **Keep** stirring. A white precipitate (product A) will form.

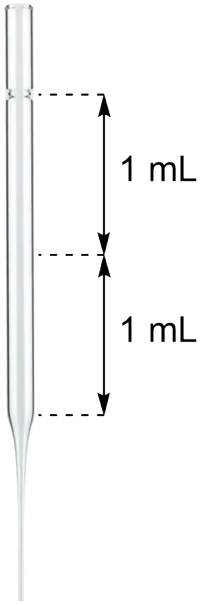


Figure 2: Pasteur pipette with approximate volume indications (scale 1:2)

11. **Adjust** the pH to 1–2 by adding 2 M HCl (aq) (ca. $6-8$ mL, from the screw cap glass bottle labeled "**2 M HCl (aq)**") with a Pasteur pipette. **Check** the pH of the reaction mixture, using pH indicator strips (for reference color pattern see Figure 3). To do so, **withdraw** a small aliquot of the reaction mixture with a fresh Pasteur pipette and **drip** a drop onto a pH indicator strip, **do not dip** the strips into the reaction mixture. **Continue** adding HCl until pH ≈ 1–2, then **stop**.

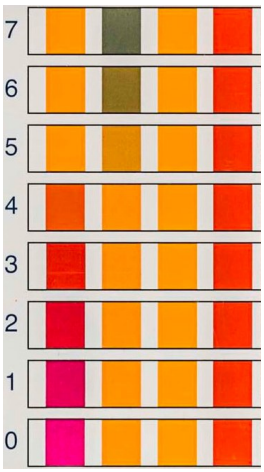


Figure 3: Color scale for pH determination by visual comparison with the reaction zones on the indicator strips. All four reaction zones on the pH paper strip have to match the color scale at the given pH value. The pH values are the numbers indicated on the left. You may ask your lab assistant to see the commercial product with the color scale printed on it.

12. **Ask** a lab assistant for a magnetic stir bar remover, **turn off** the stirrer and **remove** the stir bar from the flask. **Clean** the stir bar by rinsing it first with water (→ "~~Aqueous~~**Waste (aq)**~~Waste~~"), then with acetone (→ "~~**Organic**~~ **Waste (org)**") and **dry** it with a paper towel. It will be reused later.

13. **Set up** a vacuum filtration apparatus: **Clamp** the suction flask to the laboratory stand and **make sure** the conical rubber gasket is sitting on the rubber protection sleeve (Figure 4).

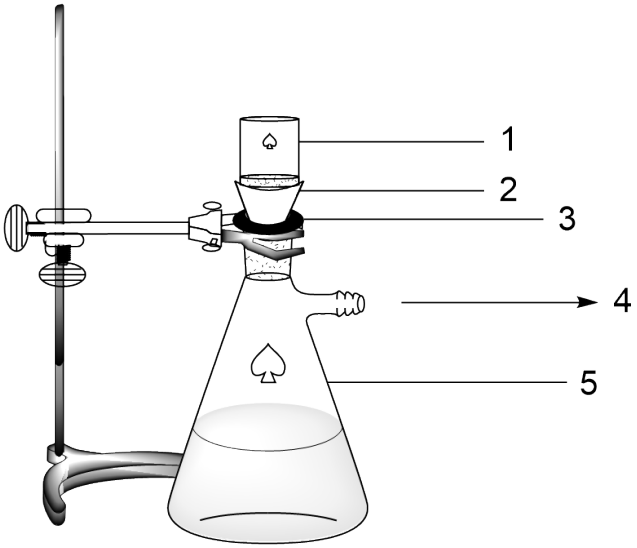


Figure 4: 1 = Glass filter crucible, 2 = conical rubber gasket, 3 = rubber protection sleeve, 4 = towards vacuum, 5 = suction flask

14. **Place** the glass filter crucible onto the conical rubber gasket. **Make sure** it fits tightly.

15. **Apply** vacuum and **pour** the suspension of the solid to be filtered into the glass filter crucible. Depending on the amount of liquid, this needs to be done portionwise.

16. **Wash** the solid thoroughly with water (2 x $10\ \mathrm{mL}$; a measuring cylinder may be used).

17. **Let** air suck through the precipitate to remove most of the water (no more than $10\ \mathrm{minutes}$), then **turn off** the vacuum and **disconnect** the vacuum source.

18. **Set aside** a small sample (1 small spatula tip) of product A in the glass vial labeled "**TLC-A**" for thin layer chromatography (TLC) analysis (to be carried out later).

19. **Transfer** the product from the glass filter crucible to the vial labeled "**Product A + [student code]**" with a spatula.

20. **Cap** the vial labeled "**Product A + [student code]**". At the end of the exam, it will be picked up by your lab assistant.

21. **Dispose of** the filtrate (suction flask) in the "~~**Aqueous**~~ **Waste (aq)**" bottle.

Preparation of product B

1. **Take** a fresh $50\ \mathrm{mL}$ round-bottom flask, add a magnetic stir bar (olive-shaped) and **clamp** the flask to the stand.

2. **Add** *p*-methoxyacetophenone ($500\ \mathrm{mg}$, entire content of the vial "**SM-B**", a weighing paper may be used for the transfer) and glacial acetic acid ($4\ \mathrm{mL}$, entire content of the vial "**AcOH**") to the flask.

3. While stirring, **add** bleach ($4.0\ \mathrm{mL}$, entire content of the vial "**Bleach-B**") **dropwise** over a period of $1-2\ \mathrm{minutes}$, using a Pasteur pipette.

4. **Attach** a Vigreux column to the flask.

5. Rapidly **stir** the reaction ($750\ \mathrm{rpm}$) at room temperature for $45\ \mathrm{minutes}$.

6. **Remove** the Vigreux column and dropwise **add** aqueous sodium bisulfite solution ($40\ \%$) (ca. $3\ \mathrm{mL}$, remaining content of the vial "~~**$NaHSO_3$**~~ **NaHSO3 (aq)**") to the mixture over a period of $1\ \mathrm{minute}$, using a Pasteur pipette. Note that the mixture warms up during the addition.

7. **Ask** a lab assistant for a magnetic stir bar remover, **turn off** the stirrer and **remove** the stir bar from the flask.

8. **Clamp** a $50\ \mathrm{mL}$ separatory funnel to the stand. **Add** $10\ \mathrm{mL}$ of water (a measuring cylinder may be used).

9. **Pour** the reaction mixture from the round-bottom flask via a glass funnel into the separatory funnel.

10. **Add** toluene (ca. $10\ \mathrm{mL}$, from the screw cap bottle "**Toluene**"; a measuring cylinder may be used), then **remove** the funnel.

11. **Seal** the separatory funnel with a stopper and **shake** it vigorously for a while. **Make sure** to interrupt shaking and to vent the funnel from time to time, with its spout pointing away from yourself and others.

12. **Stop** shaking, **vent** the funnel one more time, then **clamp** it to the stand. **Remove** the stopper and **let** the layers separate.

13. **Drain** the lower (aqueous) layer into the used reaction flask (round-bottom flask). **Pour** the top (organic) layer containing product B into a $50\ \mathrm{mL}$ Erlenmeyer flask.

14. **Extract** the aqueous phase two more times with toluene by repeating steps 9 to 13 twice. **Collect** the organic extracts in the same Erlenmeyer flask.

15. **Rinse** the glass funnel with acetone ($\rightarrow$ "~~**Organic**~~ **Waste (org)**") and **let** it dry.

16. **Add** sodium sulfate (entire content of the vial "~~Na_2SO_4~~ **Na2SO4**") to the Erlenmeyer flask with the combined organic extracts. **Add** a stir bar (rod-shaped) and **stir** the suspension for $3\ \mathrm{minutes}$ on the magnetic stirrer, then **turn off** the stirrer.

17. **Let** the glass funnel sit on a clamp and **have** its spout **protrude** into the volumetric flask labeled "**Product B + [student code]**". **Place** a filter paper into the glass funnel and **wet** it with a small amount of toluene using a Pasteur pipette.

18. **Filter** the contents of the Erlenmeyer flask into the volumetric flask "**Product B + [student code]**" (the solution does not reach the mark). **Rinse** the Erlenmeyer flask with toluene (ca. $5\ \mathrm{mL}$), using the same Pasteur pipette, and **pour** the solvent into the filter.

19. With a Pasteur pipette, **transfer** 4 drops of your "**product B**" solution into the vial "**TLC-B**".

20. **Stopper** the volumetric flask. At the end of the exam, it will be picked up by your lab assistant.

21. **Dispose of** the aqueous phase collected in the reaction flask ($\rightarrow$ "~~**Aqueous**~~ **Waste (aq)**").

Thin Layer Chromatography (TLC) Analysis

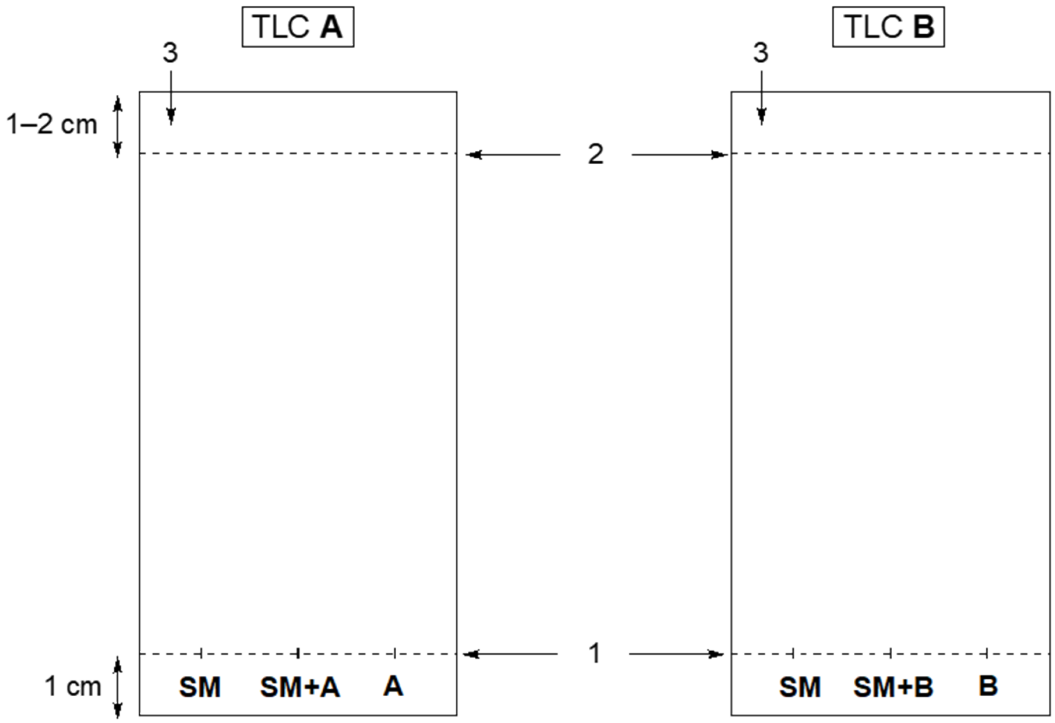


Figure 5: **SM** = starting material = *p*-methoxyacetophenone, **A** = product A, **SM+A** = co-spot of starting material and product A, **B** = product B, **SM+B** = co-spot of starting material and product B.
1 = starting line, 2 = front line, 3 = position to write down your student code.

1. **Prepare** the elution chamber: **Load** it to a level of ca. $0.5\ \mathrm{cm}$ with the eluent (mixture hexane/EtOAc in a 80:20 ratio, screw cap bottle "**Eluent**") and **cover** it with the lid. If necessary, you can get extra eluent from your lab assistant without penalty.

2. **Prepare** your samples: Using a Pasteur pipette, **add** ca. $0.5\ \mathrm{mL}$ of eluent to each of the vials "**TLC-SM**", "**TLC-A**", and "**TLC-B**" to dissolve/dilute the respective samples. **Cap** the vial "**TLC-A**" and **shake** it (ca. $0.5\ \mathrm{minute}$) for faster dissolution.

3. **Prepare** a TLC plate (stationary phase: SiO_2 on aluminium) for the analysis of product A (Figure 5, left): With pencil and ruler, gently **draw** the starting line ca. $1\ \mathrm{cm}$ above the bottom of the plate and **mark** the positions to spot 3 samples. **Label** them "**SM**" = starting material = *p*-methoxyacetophenone, "**A**" = product A, and "**SM+A**" = co-spot of SM and product A (both compounds are deposited on the same point of the TLC plate). On the top left of the plate, **write down** your **Student Code**.

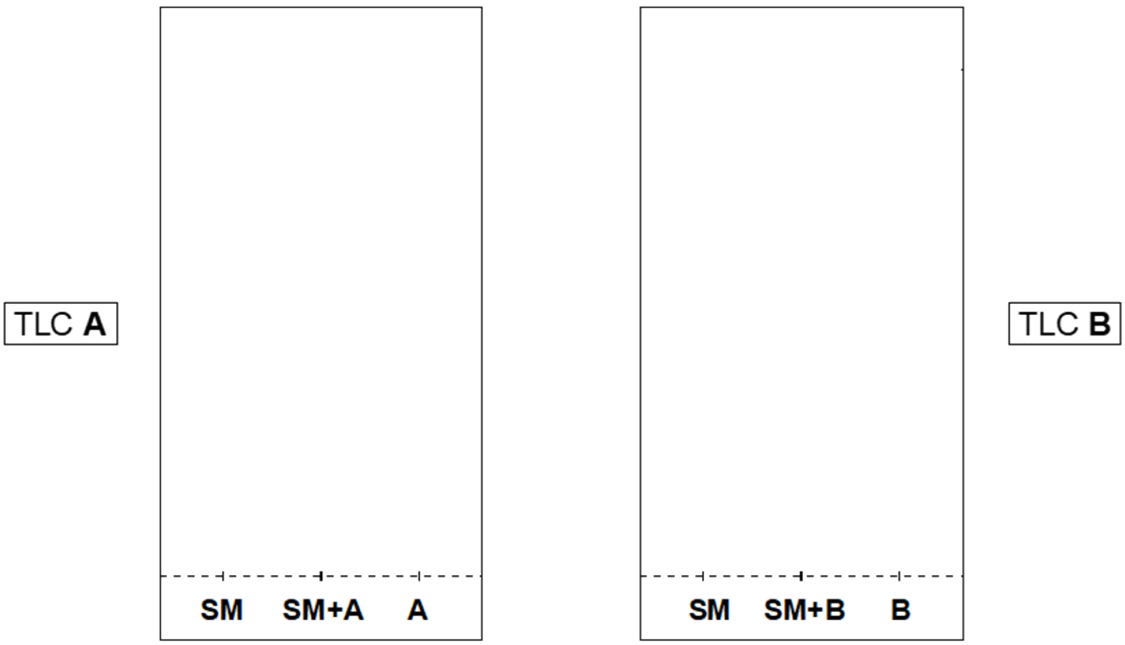
4. Similarly **prepare** another TLC plate for the analysis of product B (Figure 5, right).

5. Using capillary spotters, **spot** the two TLC plates on the starting line according to the labeling just done (Figure 5). **Use** a different capillary for each sample. **Wait** until the solvents have evaporated and the spots are dry.

6. **Develop** the TLC plates (either simultaneously or one after the other): Using tweezers, **insert** the TLC plate(s) into the elution chamber and **cover** it with the lid. **Let** the eluent **reach** a level of $1-2$ cm below the top of each plate. **Remove** the lid and, using tweezers, **remove** the plate(s) from the chamber. **Mark** the eluent front gently with a pencil and **let** the plate(s) air-dry.

7. **Visualize** the dry TLC plates under the UV lamp kept on a common bench. With a pencil, gently **circle all** visible spots.

8. **Complete** the templates **on the answer sheet** by sketching in the spots observed under the UV light. **Use** these sketches to answer the TLC-related questions on the answer sheet.



9. Carefully **place** your dry TLC plates into the zip lock bag with your student code. **Avoid** that the plates scratch each other.

10. **Have** the following items **ready** to be picked up by your lab assistant:

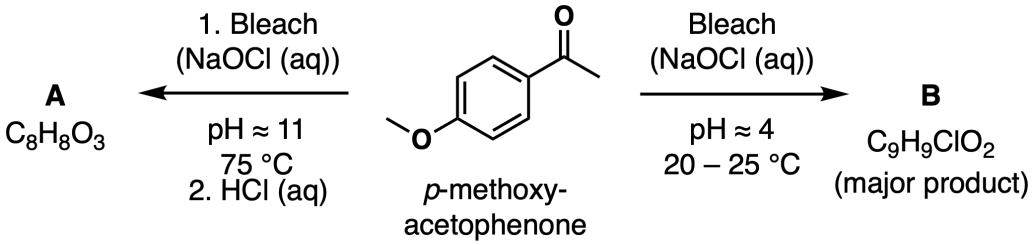
    - The **glass vial and the volumetric flask with your products**. They are labeled with your student code and the designation of the respective product ("**Product A + [student code]**" and "**Product B + [student code]**").

- A **zipped bag** labeled with your student code and **containing the two TLC plates** (TLC analysis of products **A** and **B**).

Analytics - Reserved for administration (not to be filled by the participant)

Yield.A	25pt
TLC.A	3pt
Ded.A	-6pt
Yield.B	25pt
TLC.B	3pt
Ded.B	-25pt

Questions



Legend for translation: Bleach, p-methoxyacetophenone, major product

Answer each of the following questions by ticking the appropriate checkbox (1 correct answer per question; ambiguous answers will be marked as incorrect).

1.1 Answer questions a – d based on the above **sketch** of your TLC plates (stationary phase: SiO_2 on aluminium; eluent: hexane/EtOAc in a 80:20 ratio). No points will be attributed if the sketch is not done. 4pt

a. Which of the two products is more polar, **A** or **B**? **Choose** the correct answer.

b. Which of the following two compounds is more polar, product **A** or the starting material (**SM**)? **Choose** the correct answer.

c. Does your product **A** contain some remaining starting material? **Choose** the correct answer.

d. Does your product **B** contain some remaining starting material? **Choose** the correct answer.

1.2 **Identify** the structure of product **A** (empirical formula $C_8H_8O_3$). The possible answers can be found of the **answer sheet**. 2pt

1.3 As apparent from the empirical formula of product **A** ($C_8H_8O_3$), a C_1 (= one carbon atom containing) fragment is cleaved off the starting molecule ($C_9H_{10}O_2$) in the course of the formation of **A**. After the reaction, the C_1 fragment ends up containing chlorine. **Identify** its structure. The possible answers can be found on the **answer sheet**. 2pt

1.4 The formation of product **A** is a redox reaction. 2pt

a. In this reaction, which atom type (element) is affected by an increase in oxidation number? **Choose** the correct answer on the answer sheet.

b. In this reaction, which atom type (element) is affected by a decrease in oxidation number? **Choose** the correct answer on the answer sheet.

1.5 **Identify** the structure of product **B** (empirical formula $C_9H_9ClO_2$). The possible answers can be found on the **answer sheet**. 2pt

1.6 At some point in the synthesis of product **B**, $NaHSO_3$ (aq) is added to the reaction mixture. While serving its purpose, hydrogensulfite (HSO_3^-) undergoes a chemical reaction. **Identify** the resulting sulfur-containing species. **Note** that this question is **not** aimed at the protonation state of the resulting S-containing species (acid-base equilibria are ignored here). The possible answers can be found on the **answer sheet**. 2pt