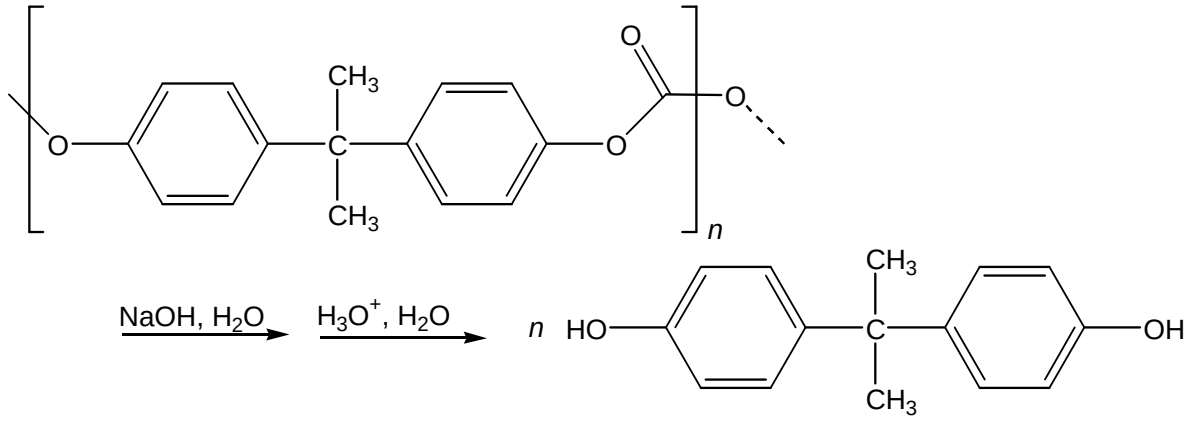
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

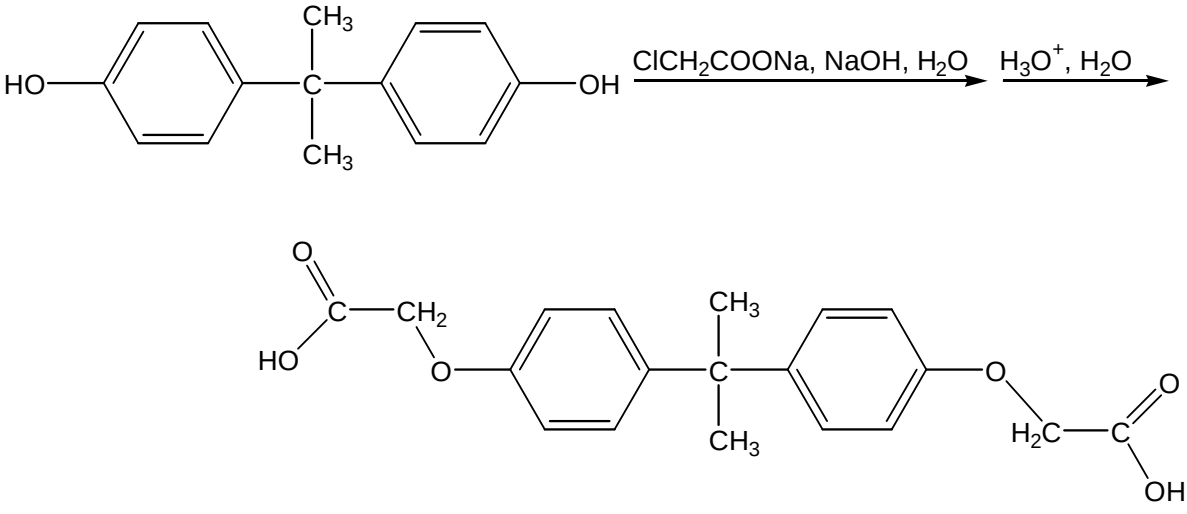
Two-Step Organic Synthesis of 2,2-Bis(*p*-phenyleneoxyaceticacid)propane (Bisphenol A bis(carboxymethyl)ether)

Introduction

In the first step the sodium salt of bisphenol A results as an intermediate from the alkaline hydrolysis of a polycarbonate. By adding an acid this salt is converted into the free 2,2-bis(4-hydroxyphenyl)propane (bisphenol A).



In the second step bisphenol A reacts with sodium chloroacetate to form the phenolic ether, bisphenol A bis(carboxymethyl)ether.



- In each step the product has to be isolated.
  (Drying and weighing will be done by the organizer.)
- For the product of step 2 three melting point tubes have to be filled.
  (Filling of the melting point tubes in step 1 will be done by the organizer.)
  (The melting points will be determined by the organizer.)
- When the organizer receives your labelled beaker A of step 1 you will get 2.00 g of bisphenol A as starting material for the second step.
- Answer the additional questions on the answer sheet **P1**.
- Do not remove the Ceran plate from the magnetic stirrer.

Procedures

Step 1: Preparation of bisphenol A by alkaline hydrolysis of a polycarbonate

Preparation:

- Put the pre-weighed 2.54 g of polycarbonate (No. **1**), 4.0 g of sodium hydroxide (No. **5**) and 3 cm^3 of demineralized water into a 100 cm^3 Erlenmeyer flask with ground-glass joint.
- Close the flask with a plastic plug and swirl it gently so that the solution does not contact the ground-glass joint. For aeration open the plastic plug occasionally. Strong heating can be observed, as the sodium hydroxide partially dissolves.
- Remove the plastic plug after swirling for about 4 minutes, add a magnetic stirring bar and put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Finally, add 20 cm^3 of ethanol (No. **2**) through the condenser while stirring the reaction mixture.
- Heat the reaction mixture under reflux for 60 minutes. In the beginning adjust the thermostat of the heating plate to maximum. When the mixture starts boiling reduce the heat carefully, so that the mixture is kept under gentle reflux.
- A white precipitate is formed on heating.

During this waiting period you are highly advised to start working on the analytical chemistry experiment.

Isolation:

- Stop heating after one hour, allow the reaction mixture to cool down to ambient temperature, remove the condenser, add 25 cm^3 of demineralized water and transfer the reaction mixture into a 400 cm^3 beaker. Rinse the Erlenmeyer flask with 25 cm^3 of demineralized water and add this to the contents of the beaker.
- Finally, fill up to 150 cm^3 with demineralized water.
- If the reaction mixture is not clear, the mixture has to be filtered over fibre glass into an Erlenmeyer flask.
- Add slowly 15 cm^3 of hydrochloric acid (No. **3**) stirring the mixture simultaneously with a glass rod. A rather oily or sometimes crystalline precipitate is formed.
- Ask your instructor for some seed crystals of bisphenol A (No. **27**) in order to accelerate the crystallization.
- Stir the reaction mixture thoroughly with the glass rod. For a quantitative crystallisation continue stirring from time to time till the supernatant aqueous solution is nearly clear.
- Collect the crude product by vacuum filtration, wash it twice with 10 cm^3 portions of demineralized water and transfer it quantitatively into the tared and labelled beaker A.
- For drying and weighing deliver your labelled beaker A into the instructor room.
- Afterwards you will get a small jar filled with 2.00 g of bisphenol A (No. 28), your starting material of the second step.
- On delivery of your product and on receipt of the starting material you have to sign. Even if you do not have any bisphenol A, please bring the empty beaker A to the instructors' room in order to get the starting material for step 2.

Step 2: Reaction of Bisphenol A with Chloroacetic Acid forming 2,2-Bis(p-phenyleneoxyacetic acid)propane (Bisphenol A bis(carboxymethyl)ether)

Preparation:

- Pour all the bisphenol A (No. **28**) you have received from the organizer when you had finished step 1 into a 100 cm^3 Erlenmeyer flask with ground-glass joint.
- Add 10 cm^3 of an aqueous sodium-hydroxide solution (No. **6**), 1 cm^3 of demineralized water and a magnetic stirring bar.

- Put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Heat the reaction mixture with gentle stirring until a clear solution is formed.
- Remove the heating plate and the condenser and add 5.0 g of the sodium salt of chloroacetic acid (No. **4**) to the reaction mixture.
- After reconnecting the flask with the reflux condenser, heat the mixture to reflux with vigorous stirring for 30 min.
- Initially a clear solution is formed on heating. In some cases a colorless solid precipitates. If the complete mixture becomes solid in the course of the reaction, heating must be stopped.
- After that, 50 cm^3 of ethanol (No. **2**) are added carefully through the condenser (beware of sudden boiling!). The mixture is stirred and heated under reflux for 5 minutes. A colourless solid precipitates, or the crystallisation which has already started is completed.

Isolation:

- After leaving it to cool down for 5 minutes, transfer the reaction mixture with another 50 cm^3 of ethanol (No. **2**) quantitatively to a beaker. The reaction mixture should be stirred vigorously.
- The magnetic stirring bar is removed and the reaction mixture is filtered through a suction filter. Solids which separate in the filtrate are rejected. Rinse the beaker with 10 cm^3 of ethanol (No. **2**). The precipitate is washed twice with 10 cm^3 portions of ethanol (No. **2**). (The filtrate must be disposed of in the organic solvent waste!)
- Transfer the precipitate quantitatively into a beaker, add a stirring bar and dissolve it in 150 cm^3 of demineralized water. The mixture must be stirred vigorously. Larger lumps of the solid must be crushed with the spatula.
- If the solution is not clear, it has to be filtered over a folded filter paper into an Erlenmeyer flask.
- The slow addition of 5 cm^3 of hydrochloric acid (No. **3**) to the stirred reaction mixture results in the formation of a white precipitate.
- Collect the crude product by vacuum filtration, wash it twice with 10 cm^3 portions of demineralized water and transfer it quantitatively into the tared and labelled beaker B.

- Take a small sample of the product with a micro spatula, crush it and dry it on a shard. Fill three melting point tubes with the homogenized, dried sample. For a close-packed and 5 mm high filling use the 75 cm glass tube and the measure.
- Put all three melting point tubes into the test tube B, which is labelled with your student code, and give it together with your labelled beaker B with the product to the instructor. On delivery you have to sign.

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SOLUTION

1.1 You started with 2.54 g of polycarbonate. Determine the theoretical yield of bisphenol A in g.

M_1(polycarbonate) = $M_1(C_{16}H_{14}O_3)_nH_2 \approx M_1(C_{16}H_{14}O_3)$ = 254.30 g mol^{-1}

m_1 = 2.54 g

M_2 ($C_{15}H_{16}O_2$) = 228.31 g/mol

$m_2 = m_1 \times M_1^{-1} \times M_2$

Theoretical yield of bisphenol A: 2.28 g

1.2 Determine your theoretical yield of bisphenol A bis(carboxymethyl)ether in g based on 2.00 g bisphenol A.

M_2 ($C_{15}H_{16}O_2$) = 228.31 g/mol

m_2 = 2.00 g

M_3 ($C_{19}H_{20}O_6$) = 344.39 g/mol

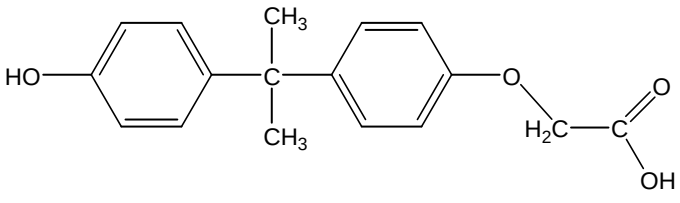
$m_3 = m_2 \times M_2^{-1} \times M_3$

Theoretical yield of bisphenol A bis(carboxymethyl)ether: 3.02 g

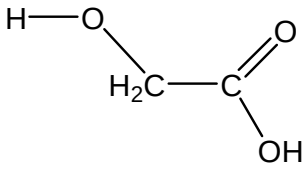
1.3

Unwanted by-products are possible in the second step. Write down the structural formulas of two most probable unwanted by-products.

1. Bisphenol A reacts only once with sodium chloroacetate (monosubstitution):



2. Alkaline hydrolysis of sodium chloroacetate:



PROBLEM 2 (Practical)

Qualitative and Quantitative Analysis of a Superconductor

Introduction

Superconductors based on lanthanum cuprate (La_2CuO_4) have the general composition of $La_xM_{(2-x)}CuO_4$ (M = Ca, Sr, Ba).

This problem consists of two parts:

- the qualitative determination of the alkaline earth metal(s)
- the quantitative determination of lanthanum and copper.

Read the burette as accurately as possible. Report your results on the answer sheets.
Answer the additional questions and write the results with adequate accuracy.
The qualitative and quantitative parts of this experiment may be done in any order.

Procedures

2.1 *Qualitative determination of the alkaline earth metal(s)*

(If the hood is occupied start with the titration 2.2)

In this experiment you have to use the superconductor as a solid ($La_xM_{(2-x)}CuO_4$; No. **14**).
At the beginning, lanthanum has to be separated as an insoluble residue.
All steps must be carried out in the hood!
Dissolve the complete sample in a beaker in about 5 cm^3 of perchloric acid (No. **22**) by heating the mixture. Add 5 cm^3 of demineralized water afterwards.
Cool down the solution until it is lukewarm.

Add about 5 cm^3 of demineralized water and then ammonia solution (No. **17**), until the reaction mixture shows a basic reaction. Lanthanum precipitates as hydroxide and copper forms an intense blue-coloured tetraammine complex. The precipitate is filtered off and washed with a small amount of demineralized water.

An excess of ammonium-carbonate solution (No. **18**) is added to the filtrate and the mixture is being boiled for some minutes. The alkaline earth metal(s) will precipitate as carbonate(s). The precipitate is filtered off and washed a few times with a small amount of demineralized water.

Then, the precipitate is dissolved in acetic acid (No. **16**). Add sodium acetate (No. **9**) and an excess of potassium-dichromate solution (No. **23**). In the presence of barium, yellow $BaCrO_4$ precipitates. After boiling the mixture for one minute barium chromate is filtered off and washed with demineralized water.

(If there is no barium chromate precipitation, proceed in a way as if there were precipitation.)

Ammonia solution (No. **17**) is added to the clear filtrate until it is basic. Add an excess of ammonium-carbonate solution (No. **18**) and boil the mixture for some minutes. In the presence of strontium and/or calcium, white carbonate(s) precipitate(s).

The precipitate is filtered off and washed a few times with demineralized water.

Then it is dissolved in a mixture of about 2 cm^3 of demineralized water and a few drops of hydrochloric acid (No. **3**). This solution is devided between two test tubes:

- Saturated calcium-sulfate solution (No. **21**) is added to one of the test tubes. In the presence of strontium a small amount of white strontium sulfate precipitates. To accelerate the precipitation, you can grind the inner surface of the test tube with a glass rod for a few minutes.
- Ammonium-sulfate solution (No. **20**) is added to the second test tube. In the presence of strontium and/or calcium, white sulfate(s) precipitate(s). The precipitate is filtered off and washed with a very small amount of demineralized water.

  1 cm^3 of ammonium-oxalate solution (No. **19**) is added to the filtrate. In the presence of calcium, white calcium oxalate precipitates after a few minutes.

<u>Preparation of the superconductor parent solution</u>

There is a superconductor solution ($La_xM_{(2-x)}CuO_4$ in perchloric acid; No. 13) in a volumetric flask.

Fill it up with demineralized water to a volume of 250.0 cm^3. From now on this solution is called “parent solution”.

2.2 *Quantitative determination of the total content of lanthanum and copper*

Transfer 25.00 cm^3 of the parent solution into an Erlenmeyer flask. Add about 5-6 piled spatula of sodium acetate (CH_3COONa; No. **8**) and 2 micro spatula of xylenol orange indicator (No. **15**) to this solution and make up with demineralized water to a volume of

about 75 cm^3. The *pH*-value has to be about ***pH* 6** before the determination, otherwise add more sodium acetate.

Titrate the solution with Na_2-EDTA solution (No. **7**). The color of the solution changes from light violet to intensely light-green. (In between, the color changes a few times.)

Repeat this procedure as many times as necessary.

2.3 *Quantitative determination of the copper content*

Transfer 25.00 cm^3 of your parent solution (No. **13**) into the 100 cm^3 volumetric flask and fill up with demineralized water to a volume of 100.0 cm^3. For each titration, transfer 25.00 cm^3 of this solution into an Erlenmeyer flask and add sodium hydroxide solution (No. **6**), until the solution shows an alkaline reaction. During this procedure, a blue precipitate forms. Add sulfuric acid (No. **12**) until the blue precipitate dissolves. The solution has to be acidic (**pH 1-2**) and will contain a small amount of a white precipitate.

Add 10 cm^3 of sodium-iodide solution (No. **9**), and swirl the Erlenmeyer flask for about 1 minute. Titrate the solution with sodium-thiosulfate solution (No. **10**). Add some starch solution (No. **11**) as an indicator just before the end of the titration. At the end, the solution has to be colourless for at least 60 seconds.

Repeat this procedure as many times as necessary.

SOLUTION

2.1 Which alkaline earth metal(s) can be found in the superconductor? Mark only one box!

Ca	☐	Sr	☐	Ba	☒
Ca and Sr	☐	Ca and Ba	☐	Sr and Ba	☐
Ca and Sr and Ba	☐				

Complete the following reaction equations:

$Ca^{2+} + C_2O_4^{2-} \rightleftharpoons CaC_2O_4$

$Sr^{2+} + CO_3^{2-} \rightleftharpoons SrCO_3$

$2\ Ba^{2+} + Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ BaCrO_4 + 2\ H^+$

2.2 Quantitative determination of the total content of lanthanum and copper.

Appropriate consumption of 0.1000 mol dm^{-3} EDTA solution: $V = 11.60\ cm^3$

(accoding to 100 cm^3 of superconductor solution)

2.3 Quantitative determination of the copper content.

Appropriate consumption of 0.01000 mol dm^{-3} $Na_2S_2O_3$ solution: $V = 10.50\ cm^3$
(according to 100 cm^3 of superconductor solution)
Complete the following reaction equations:

$2\ Cu^{2+} + 4\ I^- \rightleftharpoons I_2 + 2\ CuI$

$I_2 + 2\ S_2O_3^{2-} \rightleftharpoons 2\ I^- + S_4O_6^{2-}$

2.4 Mass (in mg) of copper in your parent solution,
mass (in mg) of lanthanum in your parent solution.

[M(Cu) = 63.55 g mol^{-1}; M(La) = 138.91 g mol^{-1}]

Amount of copper:
10,50 $cm^3 \times 0.01$ mol $dm^{-3} \times 4 \times 10 \times 63.55$ g mol^{-1} = 266.9 mg

Amount of lanthanum:
[11.60 – (10.50 / 10 $\times$ 4)] $cm^3 \times 0.1$ mol $dm^{-3} \times 10 \times 138.91$ g mol^{-1} = 1028 mg

Mass Cu: m(Cu) = 266.9 mg
Mass La: m(La) = 1028 mg

2.5 Assume a fictive consumption of 39.90 cm^3 of 0.1000 mol dm^{-3} EDTA solution and 35.00 cm^3 of 0.01000 mol dm^{-3} $Na_2S_2O_3$ solution. Calculate the coefficient x in the formula $La_xM_{(2-x)}CuO_4$ (M = Ca and/or Sr and/or Ba) and give the exact formula of the superconductor

Consumption for lanthanum = [39.90 – (35.00/10 × 4)] cm^3 = 25.90 cm^3

Consumption for copper = (39.90 – 25.90) cm^3 = 14.00 cm^3

n(La) : n(Cu) = 25.90 : 14.00 = 1.85 : 1

coefficient x: 1.85 formula: $La_{1.85}Ba_{0.15}CuO_4$