

## 10th BChO, 2002, Palanga, Lithuania

### Problem 1 – ABC – A pink element

A stream of heated  $\text{Cl}_2$  was passed through 0.300 g of element **A**. On cooling with ice, 1.06 g of pink solid **B** was collected in a receiver flask. Compound **B** was heated in a stream of  $\text{N}_2$ , and then the resulting gases were passed through a KI solution, which darkened in the process. The solution was then triturated with 0.120 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The white compound **C**, obtained by heating compound **B**, was dissolved in a small amount of water. The solution was distilled to dryness, and solid **D** was obtained. The distillate was diluted with water to 150.0  $\text{cm}^3$  (solution of **E**). 20.00  $\text{cm}^3$  of solution of **E** was titrated with 0.100 M NaOH solution. Compound **D** was heated above 400  $^\circ\text{C}$ , and 0.403 g of white solid **F** was obtained. Substance **F** was heated in a stream of  $\text{H}_2$ , and 0.300 g of the initial compound **A** was obtained.

- Write chemical formulas of the compounds **A–F**.
- Write all the equations of the reactions.
- Calculate the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution used for the titration.
- Calculate the volume of NaOH solution used to titrate 20.00  $\text{cm}^3$  of solution **E**.
- Why should compound **B** be heated in a stream of  $\text{N}_2$ ? What can be used instead of nitrogen?

### Problem 2 – THERMO – The first step to fertilizers

The following reaction is of great practical value:  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$

- Determine thermodynamic characteristics for this reaction:  $\Delta H_r^\circ$ ,  $\Delta G_r^\circ$ ,  $\Delta S_r^\circ$  if standard values of enthalpy and Gibbs energy for the reaction of NO formation are  $\Delta H_f^\circ = 91.25 \text{ kJ mol}^{-1}$  and  $\Delta G_f^\circ = 87.58 \text{ kJ mol}^{-1}$ .
- Write the equation for the dependence of  $\Delta G_r^\circ$  on temperature  $T$  assuming that  $\Delta H_r^\circ$  and  $\Delta S_r^\circ$  do not depend on temperature.
- Estimate the temperature at which air (78%  $\text{N}_2$  and 21%  $\text{O}_2$ ) in a closed vessel will contain 0.1% of NO by volume at equilibrium.

NO is a chemically active compound that is readily oxidized by oxygen and halogens. Assume that the reaction of NO with bromine proceeds in 2 steps: **i)**  $\text{NO} + \text{Br}_2 \rightleftharpoons \text{NOBr}_2$  and **ii)**  $\text{NOBr}_2 + \text{NO} \rightarrow 2\text{NOBr}$ , where the final one is the rate-limiting step.

- Write the kinetic equation for the overall reaction of NOBr formation.

### Problem 3 – KINETICS – Logic and kinetics

The enzyme catalyzes the following reaction:  $\text{S} \rightarrow \text{P}$ , where S is the substrate and P is the corresponding product. The reaction rate at different substrate concentrations was measured:

| #                              | 1                   | 2                   | 3                   | 4                   | 5                    |
|--------------------------------|---------------------|---------------------|---------------------|---------------------|----------------------|
| [S], M                         | $1.0 \cdot 10^{-2}$ | $1.0 \cdot 10^{-3}$ | $1.0 \cdot 10^{-4}$ | $7.5 \cdot 10^{-5}$ | $6.25 \cdot 10^{-6}$ |
| $v_0$ , $\mu\text{M min}^{-1}$ | 75.0                | 74.9                | 60.0                | 25.25               | 15.0                 |

- Calculate  $v_{\text{max}}$  and  $K_m$  using only logic and the Michaelis–Menten equation.
- Calculate the  $v_0$  value at substrate concentrations of  $2.5 \cdot 10^{-5}$  and  $5 \cdot 10^{-5}$  M.
- Calculate the  $v_0$  value at a substrate concentration of 0.02 M.

The concentration of the enzyme was increased by a factor of 2.

- d) Determine the value of  $v_0$  if the substrate concentration is  $1 \cdot 10^{-4}$  M.
- e) Calculate the concentration of the product after 3 minutes in the initial concentration of substrate is 0.04 M.

#### Problem 4 – CALC – Professional burette applications

An analytical lab received a sample of some crystalline compound **X** of constant composition for analysis. The laboratory assistant was very experienced in titration, but first of all, he dissolved some part of the sample in water and performed some qualitative trials. He found that the solution of potassium thiocyanate turned red after the addition of some drops of yellow solution **X**. Also, when the solution of sample **X** was mixed with ferrous sulfate and concentrated sulfuric acid was allowed to run slowly down the inside wall of the test tube, a characteristic brown ring appeared at the interface between the two liquids. After that, the lab assistant turned to titration techniques.

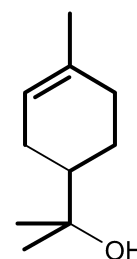
1.00 g of sample **X** was dissolved in 20.00 cm<sup>3</sup> of water and a small excess of TiCl<sub>3</sub> solution was added. Titration of that mixture required 23.00 cm<sup>3</sup> of titrant **A**. Titrant **A** was prepared by dissolving ceric(IV) sulfate in water. During standardization, 28.00 cm<sup>3</sup> of titrant **A** was required to titrate a standard solution prepared by dissolving 0.189 g of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O in water.

As the obtained information was insufficient, the laboratory assistant prepared a solution of titrant **B** (Fischer reagent). He dissolved crystalline iodine in pyridine, then passed SO<sub>2</sub> gas through this solution until the desired mass increase occurred. After that, he diluted the solution with methanol till the desired volume (assume that the solution was prepared using equimolar amounts of iodine and sulfur dioxide). 0.150 g of sample **X** was suspended in 5 cm<sup>3</sup> of methanol and this mixture was rapidly titrated with 8.50 cm<sup>3</sup> of titrant **B** (assume that titrant reacts with analyte in ratio 1 : 1 and cation does not interfere in reaction). During standardization, 3.40 cm<sup>3</sup> of titrant **B** was required to titrate a standard solution prepared by dissolving 0.1 g of KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·4H<sub>2</sub>O in methanol.

- a) What ions does the aqueous solution of sample **X** contain?
- b) Write the equations of standardizations of i) titrant **A** and ii) titrant **B**.
- c) Write the equations for the analysis of sample **X** using two different titrations.
- d) Determine the composition of sample **X**.
- e) What can be the main application of Fischer titration?
- f) Is it possible to titrate aldehydes or ketones using Fischer titration in this way?

#### Problem 5 – MECH, STEREO – Chemistry of essential oils

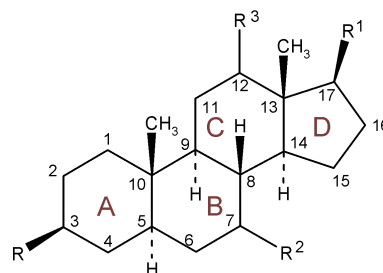
Terpenes are compounds with a carbon skeleton consisting of isoprene (2-methylbuta-1,3-diene) units that are linked in a head-to-tail fashion. They are often found in nature and give a characteristic aroma to many essential oils. Geraniol and nerol are also classified as steroids. These compounds are stereoisomers of a primary alcohol with two double bonds in the molecule. Geraniol is found in geranium oil, and nerol is found in nerol oil and bergamot oil. In the presence of acid, geraniol cyclizes to form α-terpineol, but nerol cyclizes much more rapidly. In the Figure, the carbon skeleton of the precursor alcohols is shown in bold.



- Draw the structural formulas of geraniol and nerol.
- What feature of the structure accounts for the rapid cyclization of nerol?  
 $\alpha$ -Terpineol, when dehydrated, forms terpinolene, which is found in the oil of Monteiro cypress.
- Depict the most probable structure of terpinolene.  
 In the presence of acid, terpinolene isomerizes to form three isomeric monocyclic dienes called terpinenes. Of these,  $\alpha$ -terpinene is the primary product. It is found naturally in marjoram, cardamom, and coriander oil. Only  $\alpha$ -terpinene is capable of a good Diels-Alder reaction. However, when treated with excess hydrogen chloride at low temperatures, all three terpinenes form the same addition product.
- Draw the structural formula of  $\alpha$ -terpinene.
- Draw the structural formula of the Diels-Alder product with maleic anhydride.
- Draw the structural formulas of the two remaining terpinenes.
- Draw the structural formulas of the reaction products of terpinenes with excess hydrogen chloride. Draw all possible stereoisomers of this compound.

### Problem 6 – STEREO, SPECTRA, SYNTH – Spectroscopy on steroids

Steroids are biological regulators in the human body. For example, they control sexual development and fertility. Among the most common steroids, cholesterol is present in almost all human and animal tissues. In steroids, the four cycles are condensed into the tetracyclic structure below. The junctions of the cycles are usually in transposition. The four cycles are labeled A, B, C, and D, and the carbon atoms are numbered according to a steroid-specific scheme. Many steroids have methyl groups at C10 and C13 and oxygen at NW. Bonds to groups above the plane of the steroid molecule are indicated in bold and those below the plane are indicated by dashed lines.



- Alternative wording: Draw the structural formula of the steroid above, indicating the conformations of six-membered cycles.
- Label the chiral atoms in this structure.
- Calculate the number of diastereomers of this molecule.  
 Cholesterol is a steroid in which  $R = OH$ ,  $R^1 = CH(CH_3)CH_2CH_2CH_2CH(CH_3)_2$ ,  $R^2 = R^3 = H$ , and there is a double bond between the 5 and 6 carbon atoms. This steroid is responsible for many circulatory diseases due to the fact that it precipitates in the arteries, causing arteriosclerosis and heart disease.
- Draw the structural formula of cholesterol and identify the configuration of the chiral atoms using (*R,S*)-designations.

Under the action of bacteria in the human digestive tract, cholesterol is converted to coprostanol. Use the following information to determine the structure of coprostanol. When treated with a Cr(VI) reagent, coprostanol forms compound **A** (IR:  $1710\text{ cm}^{-1}$ ; UV:  $\lambda_{\text{max}}(\epsilon) = 281$ ). Reaction of cholesterol with  $H_2$  over Pt gives compound **B**, the stereoisomer of coprostanol. Treatment of **B** with a Cr(VI) reagent gives compound **C**, which has a UV signal very similar to that of compound **A** (UV:  $\lambda_{\text{max}}(\epsilon) = 258$ ) and is, therefore, the stereoisomer of **A**.

Careful addition of Cr(VI) reagent to cholesterol gives **D** (UV:  $\lambda_{\max}(\epsilon) = 286$ ). Catalytic hydrogenation of **D** over Pt also gives **C**.

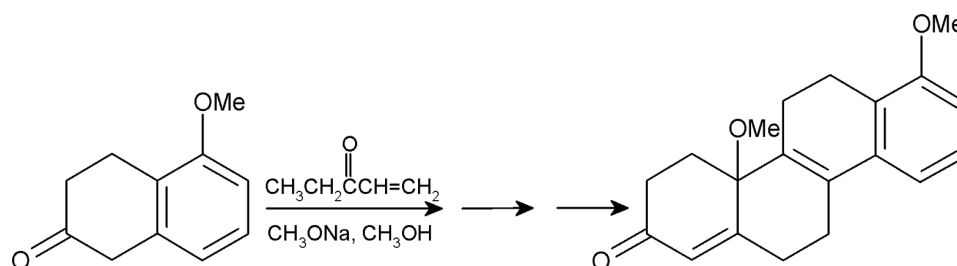
- e)** Draw structural formulas of compounds **A–D**. Label the stereochemistry of the atoms involved in the transformations using suitable steroid skeleton designations.

Cholesterol is the precursor to bile acids in the human body. Bile acids are formed in the liver as part of the fluid going into the duodenum to facilitate emulsification, digestion, and absorption of fats. An example is cholic acid ( $R = OH$ ,  $R^1 = CH(CH_3)CH_2CH_2COOH$ ,  $R^2 = R^3 = OH$ ), in which the articulation of cycles A and B is *cis*. This acid has surface-active properties.

- f)** Draw its conformational formula and a diagram showing the formation of micelles of cholic acid in aqueous solution.

Steroid synthesis in the laboratory is carried out using the Robinson annulation method. This reaction between enolates ketones and  $\alpha,\beta$ -unsaturated compounds is followed by intramolecular aldol condensation.

- g)** Suggest a scheme for the synthesis of the steroid indicated herein from a bicyclic ketone using one or more Robinson annulations and suitable components:



- h)** Write the mechanism of the first step of the synthesis.