

14th BChO, 2006, Riga, Latvia

Problem 1 – ABC, EQUIL – Versatile purple

Element **A** can be isolated from its compound **B** that occurs naturally in a mixture with Chile saltpeter. Firstly, compound **B** is treated with aqueous NaSH solution. Then, elemental **A** is extracted from the aqueous solution using xylene, which obtains a violet color. Element **A** also forms a blue-colored compound with a starch solution.

- a) Identify compounds **A** and **B**.
- b) Write the chemical formula of Chile saltpeter.
- c) Write the equation for the treatment of **B** with aqueous NaSH solution.

Element **A** is widely used in medicine. In 1986, after the Chernobyl nuclear power plant disaster, people living near the city of Pripjat were administered medicine containing **A**.

- d) Explain why it is necessary to take medicine containing element **A** during the radioactive nuclear fallout.

Element **A** is also used in electrical engineering. Many vehicles have some electric details containing small quantities of **A** and its tungsten salt.

- e) Write the equation of the reversible reaction taking place in the electric detail during its working cycle.

Upon the reaction of element **A** with wet red phosphorus, a colorless and toxic gas **C** is released. Gaseous compound **C** is a strong acid that protolyzes (dissociates into ions) completely in an aqueous medium.

- f) Write the equation depicting a reaction between element **A** and wet red phosphorus.
- g) 12.79 grams of **C** was dissolved in 1.00 dm³ of water. Calculate the pH value of the aqueous solution of compound **C**.
- h) 1.00 cm³ of the solution described in **g**) was diluted with 10.0 m³ of pure distilled water. Calculate the pH value of the newly obtained solution.

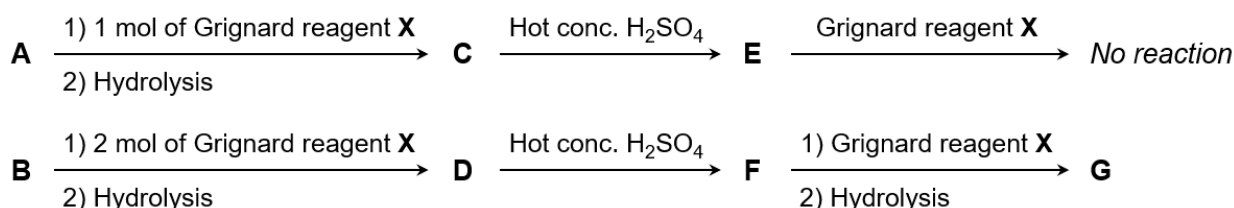
Problem 2 – CRYSTAL – Grand Theft Balls

To keep the gold ration inviolable, the Schah ordered all the gold to be cast into the shape of spheres, 1 cm in diameter. Being very curious and having found out the richness of the master, the first Vizier decided to appropriate the part of treasures. To put his plan into action, he presented a metal box (75×75×75 cm) and Schah put 578813 gold balls into it in the only possible arrangement (arrangement **I**). Every day, Schah shook the box and checked whether it made any noise or not, meaning had anyone taken his treasures or not. The first Vizier replaced the balls (arrangement **II**) and put them in the right arrangement to keep them from thundering so Schah did not find out. So the first Vizier stole a large amount of gold, but it was not enough for him and he replaced the balls once more in such a way that they did not make any sound (arrangement **III**), having made a fool of his master.

- a) Calculate the packing arrangement efficiency of 578813 gold balls in the box. Make a conclusion about the type of arrangement **I**.
- b) Determine the position of atoms in arrangements **I–III**.
- c) Calculate the number of gold balls stolen by the first Vizier at the first and second time.

Problem 3 – SPECTRA, SYNTH – One peak, two downhill pathways

Consider the following schemes:



The ^1H NMR spectra of compounds **A–D** consist of just one singlet (after the addition of a drop of D_2O), the ^{13}C NMR spectra consist of just two lines. The ^1H NMR spectra of compounds **E–G** consist of two singlets (after the addition of a drop of D_2O). Combustion of compounds **A–G** yields only carbon dioxide and water.

- Determine compounds that fit this scheme and write all the reaction equations.
- Arrange compounds **A–D** and **X** in order of decreasing chemical shift of their only signal in the ^1H NMR spectrum.

If the restriction of using 1 mol or 2 mol of the Grignard reagent in the first step of the reaction sequences is removed, one more starting compound fits the first scheme and another starting compound fits the second scheme. Using these compounds leads to the same reaction products **C** and **D**, respectively.

- Determine reaction products **C** and **D**.

Problem 4 – CALC, STRUCT – How to set water on fire

The halogens combine with each other to form interhalogen compounds of four stoichiometries: **XY**, **XY₃**, **XY₅**, and **XY₇**, where **X** is the heavier halogen. In 1813–1814, J. L. Gay-Lussac and H. Davy independently synthesized the first interhalogen compound ICl .

From the rotational spectrum of a gaseous substance, a rotational constant can be determined. This constant can be expressed in hertz Hz (notation B) or in wave numbers (notation $\bar{B}$). The rotational energy of a molecule can be described with the following formula: $E_J = h \cdot B \cdot J(J+1)$.

Rotational constant $B = h/(8\pi I)$, where I represents the moment of inertia $I = \mu R^2$ and μ is reduced mass. For diatomic molecules $\mu = m_1 m_2 / (m_1 + m_2)$, in which case R is the distance between two bonded atoms. The rotational constant of $^{127}\text{I}^{37}\text{Cl}$ is $3.28 \cdot 10^9$ Hz.

- Calculate bond length (in pm) in $^{127}\text{I}^{37}\text{Cl}$ molecule.

Volatile molecular liquid ClF_3 is one of the most reactive chemical compounds known. It spontaneously ignites asbestos, wood, and other building materials. This substance was used in incendiary bomb attacks in World War II. ClF_3 reacts explosively with water and with most organic substances. Big amounts of this substance are used in nuclear fuel processing to produce UF_6 (g): $\text{U(s)} + 3\text{ClF}_3(\text{g}) \rightleftharpoons \text{UF}_6(\text{g}) + 3\text{ClF}(\text{g})$.

- Write the Lewis structure for ClF_3 .
- Sketch drawing that shows ClF_3 molecular structure. Approximately predict bond angles and show them in your drawing.

In a closed evacuated container with excess solid uranium, some amount of ClF_3 was injected. The initial concentration of this gaseous substance in the container was 0.0453 M.

When equilibrium in the container at 87 °C was established, the total pressure in the container was 1.69 atm.

d) Calculate the partial pressure of each gaseous substance in equilibrium.

Another interhalogen ClF reacts with AsF₅: $\text{AsF}_5 + 2\text{ClF} \rightarrow [\text{Cl}_2\text{F}]^+[\text{AsF}_6]^-$.

e) Suggest the best Lewis structure for cation $[\text{Cl}_2\text{F}]^+$.

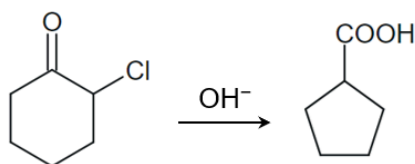
f) Choose the role of AsF₅ in this reaction: **i)** Lewis base or **ii)** Lewis acid.

Four interhalogen compounds between iodine and fluorine are known.

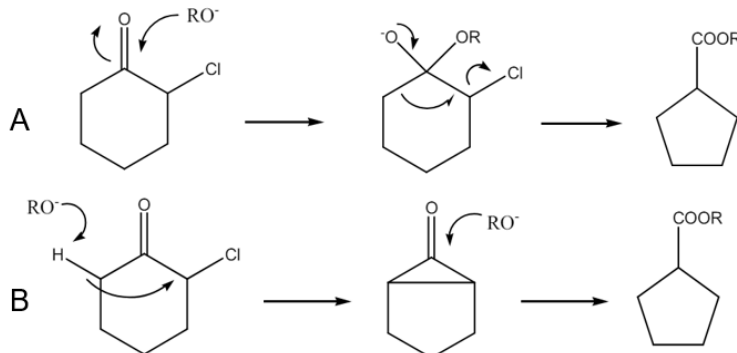
g) Which of these molecules is/are nonpolar: **i)** IF, **ii)** IF₃, **iii)** IF₅, **iv)** IF₇.

Problem 5 – MECH, SYNTH – Organic juggling

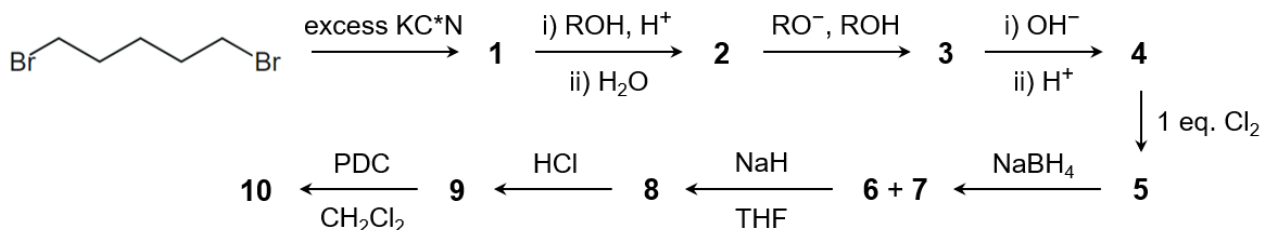
Molecular rearrangements are very important in organic chemistry not only as a versatile synthetic method but also being mechanistically very interesting. In the course of such reactions, functional groups usually undergo changes and atoms' connectivity order is altered. One of the most famous reactions of this kind is a Favorskii rearrangement, discovered more than a hundred years ago. A typical example of this reaction is shown below:



Favorskii rearrangement could also work with other nucleophiles such as alkoxide or cyanide ions. Two alternative mechanisms, A and B, have been proposed for this reaction:



In order to establish the real mechanism, a substrate with a radioactive carbon ¹⁴C label was synthesized according to the scheme:



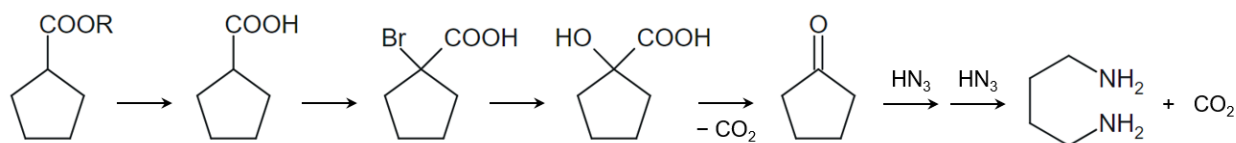
a) Draw the structural formulas of compounds **1–10** and denote ¹⁴C atom with “*.”

b) After the reduction of **5**, two isomeric compounds, **6** and **7**, were obtained. Only one of them, compound **7**, reacts further to give a compound **8**. Show stereochemical formulas of **6** and **7** and write the reaction mechanism with NaH.

The reaction of **10** with NaOMe affords Favorskii rearrangement product **11**.

- c) Show the place of the radioactive label and its relative intensity (radioactivity) in compound **11** according to mechanisms **A** and **B**.

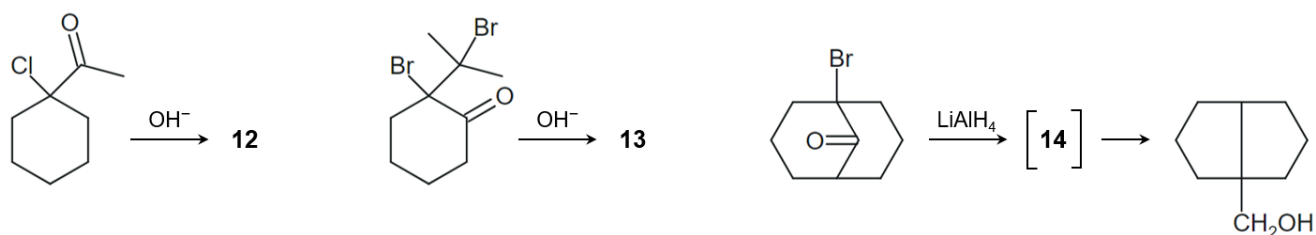
The product **11** was further degraded as shown below:



- d) It was shown that the total radioactivity of all degradation's gaseous products is 25% less than that of a starting ester. Which mechanism explains this fact?

There are a number of reactions that proceed via the Favorskii-type mechanism.

- e) Draw the structure of compounds **12–14** and the reasonable mechanisms of its formation. The compound **13** has a strong vibrational band at 1670 cm^{-1} .



- f) What are the possible by-products when α -haloketones react under Favorskii reaction conditions?

Problem 6 – EQUIL, THERMO – Killer lake

Nyos is a low-activity volcanic lake. It is grievously known as a killer lake after a disaster happened in 1896 when the release of CO_2 gas from the lake's depths caused the death of 1746 people. According to one of the hypotheses, cold tropical rain cooled the "surface layer" (50 meters), which fell 130 meters down, displaced "deep water" and disturbed the equilibrium. As a result, the lake "has exploded" like a bottle of champagne.

	CO_2 (g)	H_2CO_3 (aq)	H_2O (l)
ΔH_f°	-393.5	-699.0	-285.8
ΔS_f°	213.8	190.0	70.1

Assume that the lake looks like a cylinder with a bottom surface area of 1.20 km^2 and a height (depth) of 120 meters. The bottom of the lake is composed of FeCO_3 , which is in equilibrium with CO_2 via dissolution. It is also known that the "surface-layer" water (50 meters) does not mix with the deeper layers; temperature at 50–180 meters depth approximately equals 23°C . $K_{a1}(\text{H}_2\text{CO}_3) = 3.57 \cdot 10^{-7}$, $K_{a2}(\text{H}_2\text{CO}_3) = 4.40 \cdot 10^{-11}$, $K_{sp}(\text{FeCO}_3) = 5.91 \cdot 10^{-11}$.

- Calculate the constants $K_H = [\text{H}_2\text{CO}_3(\text{aq})]/p(\text{CO}_2(\text{g}))$ value at 23°C .
- Calculate the pH at **i)** 50 and **ii)** 180 meters depth.
- Determine the maximum solubility of CO_2 at **i)** 50 and **ii)** 180 meters depth.
- Assuming the linear dependence of concentration on depth (50-180 meters), evaluate the maximum quantity, mass, and volume at 30°C of CO_2 that could be emitted from the lake.