55th Lithuanian National Chemistry Olympiad
Selected Problems
Problem 1. How Lukas was trying to squeeze the curd from water.

A well-established chemist Lukas had known well that urea is an abundant compound with application as a fertilizer for soil. In his perspective future work place – Achema – urea is synthesised via a two step synthesis, starting from ammonia and carbon dioxide. Gasses are mixed and heated at an elevated pressure to form ammonium carbamate $CO_2N_2H_6$. Second step is a dehydratation reaction of carbamate to give carbamide CON_2H_4.

1) Calculate mass percentage of nitrogen in two most common nitrogen fertilizers – urea and ammonium nitrate.

2) Draw the structural formula of urea, as Lukas forgot it.

3) Write down and balance both reactions involved in carbamide synthesis. (use structural formulas)

Barbiturates are a well known central nervous system depressants (discovered by A. Bayer in XIX century). Their synthesis is quite trivial (Lukas could perform it with his eyes shut): malonic acid ($CH_2\,(COOH)_2$) reacts with carbamide to form cyclic barbituric acid molecule.

4) Use structural formulas to write and balance a reaction between malonic acid and carbamide forming barbituric acid.

Barbiturates belong to carbonylic compound's class, thus they should exibit keto-enol tautomerism.

5) Lukas was too lazy to draw all tautomers, hence you have to suggest all possible tautomers of acid obtained in 4) question.

If you were to exchange one oxygen atom to sulphur, you would get thiobarbiturates. Sodium thiopental – a thiobarbiturate – is more well known as the truth serum in pop culture. Below you see a possible synthetic pathway for it's synthesis.
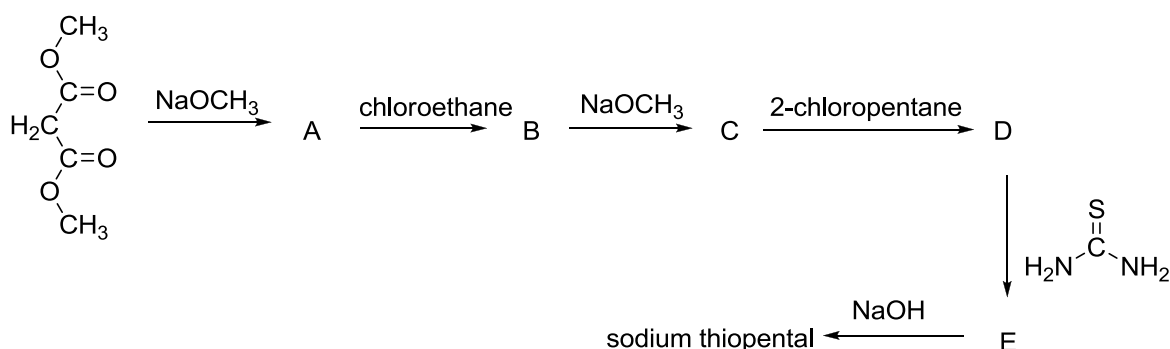
6) Draw structures of compounds A-E and suggest the sturcture for sodium thiopental.

Note:
- *A and C are intermediate products – they are non-isolatable salts which further react with chloroalkanes;*
- *B proton NMR spectra has these signals 3H, triplet, 0.9 ppm; 2H, doublet of quartets, 2.07 ppm; 1H, triplet, 3.31 ppm, 6H, singlet, 3.68 ppm.*
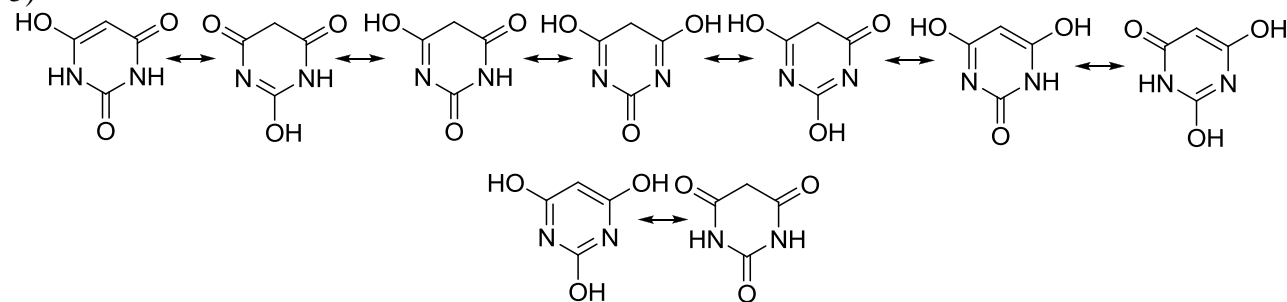
SOLUTION:
1) Urea: w(N) = 28 g/mol / 60 g/mol * 100 % = 46,67 %
Ammonium nitrate: w(N) = 28 g/mol / 80 g/mol * 100 % = 35 %

2) or any other correct representation.
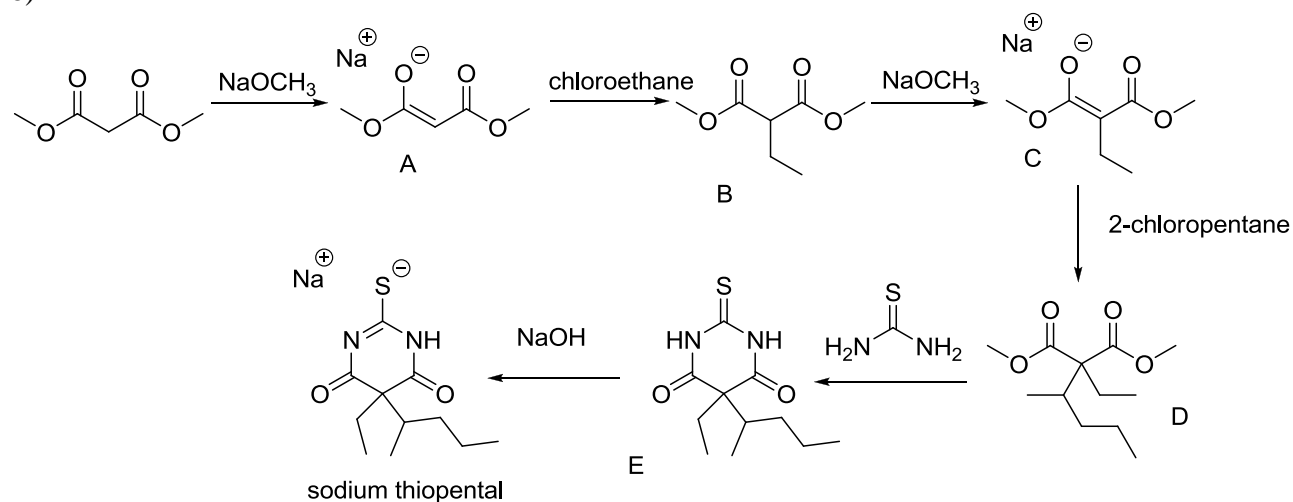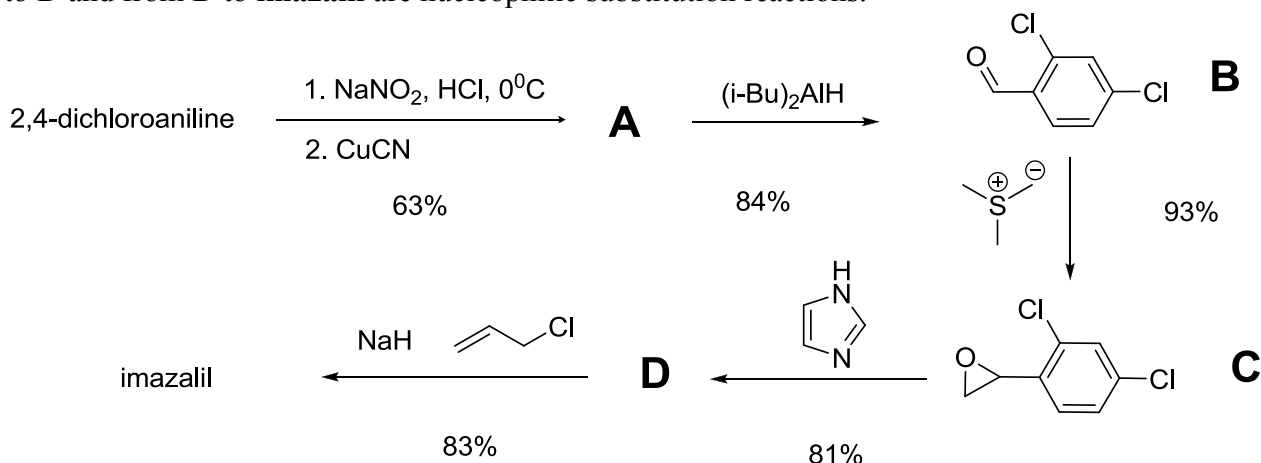
3)
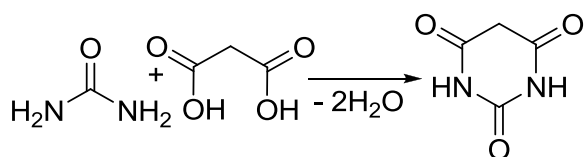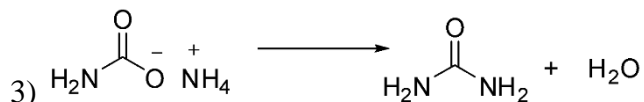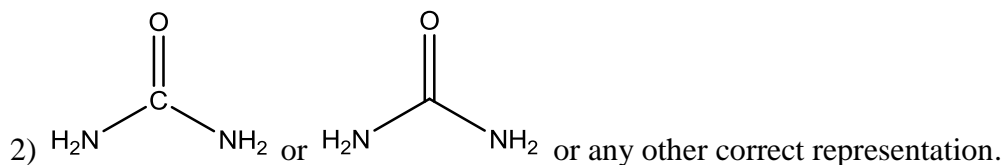
4)

5)

6)

Problem 2. Mantas has two oranges: one of them is big, the other is a lemon

Being in a shop Mantas, who is a great chemist, decided to buy some juicy oranges and squeeze them to get a cup of fresh orange juice. Putting oranges into his bag Mantas noticed a note in a label saying 'TREATED WITH IMAZALIL'. Mantas highly interested in imazalil, because he was a deeply curious chemist. After coming back home he found some information on the internet that imazalil is a widely used fungicide for citrus fruits. This fungicide is often called enilconazole or chloramisole in various countries. A chemist Mantas came up with an idea to synthesize this fungicide because he had an intention to treat with imazalil his lemon tree, which was sick with a fungous disease. A scheme of imazalil synthesis is given below. A molar mass of compound **A** is **172** g/mol. Reactions from **C** to **D** and from **D** to **imazalil** are nucleophilic substitution reactions.

2,4-dichloroaniline → 1. $NaNO_2$, HCl, 0^0C 2. CuCN 63% → **A** → (i-Bu)$_2$AlH 84% → **B**

B ↓ 93% → **C**

C ← 81% ← **D** ← (imidazole) ←

D → NaH, allyl chloride 83% → **imazalil**

5.1. Give a structural formula of 2,4-dichloroaniline.

5.2. Draw structures of compounds **A**, **D** and **imazalil**.

5.3. Reaction from **B** to **C** is called Johnson–Corey–Chaykovsky reaction. Using curve arrows for the depiction of the electron pairs' movement, draw the mechanism of this reaction.

5.4. Suggest a reagent (or a mixture of reagents) which could help Mantas to convert 2,4-dichloro-1-ethenylbenzene to the compound **C**.

5.5. A cyclic compound having two nitrogen atoms is used in the reaction from **C** to **D**. How is it called? (Only one answer is correct.)
    a) Pyrrole   b) Imidazole   c) Pyridine   d) Pyrimidine

5.6. How many stereoisomers can exist for compound **C**? (Only one answer is correct.)
    a) 1   b) 2   c) 3   d) 4

Another possible scheme for compound **D** production is given below. Imazalil could be produced form the compound **D** as indicated in the upper picture.

X → Br$_2$, dichloromethane 43% → **Y** ($C_8H_5OCl_2Br$) → (imidazole) 84% → **Z** → $NaBH_4$ 95% → **D**
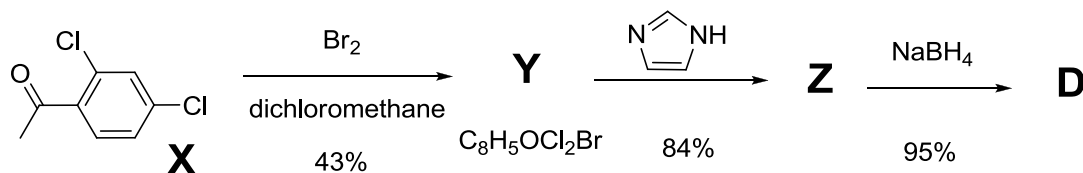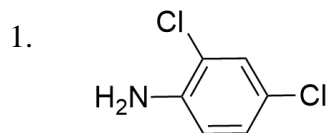
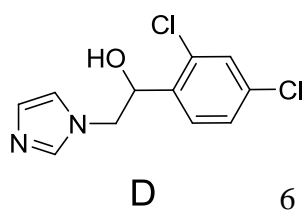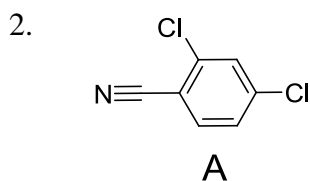5.7. Draw structures of compounds **Y** and **Z**.

5.8. In both pictures you can see the yields of all the reactions, which Mantas have performed. Which way of imazalil production is more effective: from 2,4-dichloroaniline or from compound **X**? Prove the answer with your calculations.
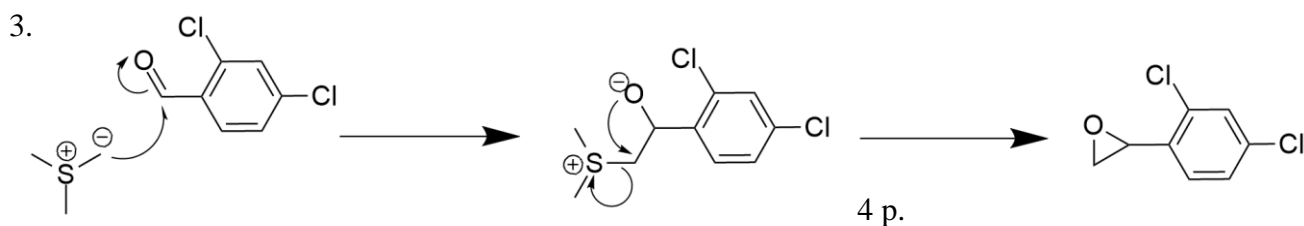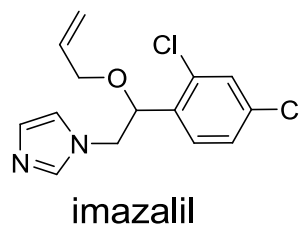
SOLUTION

1.

2 p.

2.

A   D   6 p.   imazalil

3.

4 p.

4. m-CPBA, H_2O_2/NaOH or other logical answer.   2 p.
5. b   1 p.
6. b   1 p.
7.

Y   Z   4 p.

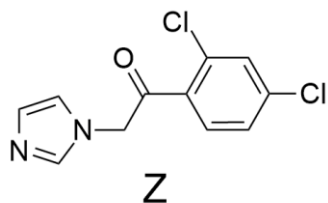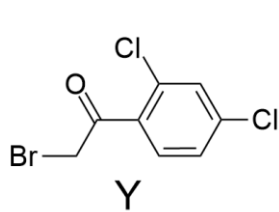8. To evaluate the effectiveness of the synthesis, the yields of all steps of the synthesis should be multiplied.
From 2,4-dichloroaniline: 0,63*0,84*0,93*0,81*0,83 = 0,33
From compound X: 0,43*0,84*0,95*0,83 = 0,28
All in all, although there are more steps it is clearly seen that the synthesis from 2,4-dichloroaniline is more effective.   2 p.

22 points overall

Problem 3. Power of Thermodynamics

Solubility chart states that $CaSO_4$ is hardly soluble. Alice decided to figure out what does *hardly soluble* mean. Alice figured out it would be cheaper to work out the problem using calculations rather than experimentations, thus, she tried to find the solution using her knowledge in thermodynamics. To begin with Alice found some useful data (Table 1). You too join Alice with her calculations.

a. Write down the equation, showing how $CaSO_4$ dissolves in water. Identify the states of matter.
b. Calculate thermodynamic potentials of equation in part *a* at 25 °C:
    i) $\Delta H°$;   ii) $\Delta S°$;   iii) $\Delta G°$.
c. Calculate molar concentration of saturated $CaSO_4$ solution.
d. Without using any computations figure out how calcium sulfate's solubility changes when temperature is increased. Explain you choice.
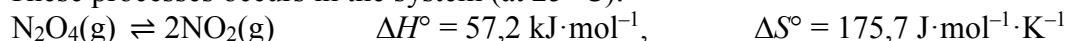
So what does *hardly soluble* mean? Alice gave this definition: substances will be named hardly soluble if their solubility is similar to calcium sulfate and differs from it no more than ±20%.

e. Using Alice criteria specify the solubility range for hardly soluble substances. (answer denoted in mol/L and having only one significant figure).

Table 1. Thermodynamic data (25 °C)

	$\Delta H°_f$, kJ·mol^{-1}	$S°$, J·mol^{-1}·K^{-1}
Ca^{2+}(aq)	–542,8	–53,1
SO_4^{2-}(aq)	–909,3	20,1
$CaSO_4$(s)	–1434,1	106,7

After dealing with a solubility problem Alice tried to put her knowledge in thermodynamics to a test estimate the change in entropy. During some research Alice found an article about a system, that after pouring 0,035 mol N_2O_4 gases and 0,030 mol n-pentane C_5H_{12} gases into 1.0 L empty closed volume system is in non-equilibrium state. However, as the system goes into equilibrium some parameters of the system does not change – temperature, enthalpy – and there is no energy flow to or from the system. These processes occurs in the system (at 25 °C):

N_2O_4(g) $\rightleftharpoons$ 2NO_2(g) $\Delta H° = 57,2$ kJ·mol^{-1}, $\Delta S° = 175,7$ J·mol^{-1}·K^{-1}

C_5H_{12}(g) $\rightleftharpoons$ C_5H_{12}(l) $\Delta H° = -26,2$ kJ·mol^{-1}, $\Delta S° = X$

f. Find the change of entropy (X) of n-pentane's condensation (the change in volume due to liquid forming is negligible).

a. $CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$ (5 Pts.)

b. Changes in enthalpy and in entropy will be found using table 1:

   i) $\Delta H° = 1 \cdot \Delta H°(Ca^{2+}_{(aq)}) + 1 \cdot \Delta H°(SO_4^{2-}_{(aq)}) - 1 \cdot \Delta H°(CaSO_{4\,(s)})$

     $\Delta H° = -542,8 - 909,3 + 1434,1 = -18,0$ kJ/mol (2 Pts.)

   ii) $\Delta S° = 1 \cdot S°(Ca^{2+}_{(aq)}) + 1 \cdot S°(SO_4^{2-}_{(aq)}) - 1 \cdot S°(CaSO_{4\,(s)})$

     $\Delta S° = -53,1 + 20,1 - 106,7 = -139,7$ J/mol/K (2 Pts.)

   iii) The change in Gibb's free energy will be found using:

     $\Delta G° = \Delta H° - T\Delta S°$

     $\Delta G° = -18000 + 41630,6 = 23630,6$ J/mol $\approx 23,6$ kJ/mol (3 Pts.)

c. Saturated solution will be only when maximum amount of $CaSO_4$ will dissolve at that temperature.

   To find molar concentration we need to find $CaSO_4$ solubility constant K_{sp}: (1 Pt.)

   $\Delta G° = -RT \ln K_{sp}$

   $K_{sp} = \exp\left(-\dfrac{\Delta G°}{RT}\right)$

   R - ideal gas constant, equal to 8,314 J/mol/K.

   $K_{sp} = \exp(-9,538) = 7,21 \cdot 10^{-5}$ (3 Pts.)

   From chemical reaction (part *a*) equilibrium constant K_{sp} is also equal to:

   $K_{sp} = [Ca^{2+}_{(aq)}][SO_4^{2-}_{(aq)}]$

   Because $[Ca^{2+}_{(aq)}] = [SO_4^{2-}_{(aq)}]$, we get that

   $[Ca^{2+}_{(aq)}] = [SO_4^{2-}_{(aq)}] = 0,00849$ mol/L (2 Pts.)

   In other words, in 1 L of solution 0,00849 mol of $CaSO_4$ has dissolved.

d. If $\Delta G°$ increases, equilibrium constant decreases, so as calcium sulfate's solubility. Because Gibb's free energy increases with temperature (because $\Delta S° < 0$ and $\Delta H° < 0$), we can conclude that calcium sulfate's solubility decreases as temperature increases. (6 Pts.)

e. Using Alice definition hardly soluble substances have to have solubility in this range:

   $0,8 \cdot 0,00849$ M < SOLUBILITY < $1,2 \cdot 0,00849$ M

   After multiplying and doing some rounding we get :

   $0,007$ M < SOLUBILITY < $0,01$ M (3 Pts.)

f. Using already mentioned equations ($\Delta G° = \Delta H° - T\Delta S°$ ir $K_p = \exp\left(-\dfrac{\Delta G°}{RT}\right)$) we find N_2O_4 and NO_2 equilibrium constant:

   $K_p = 0,1417$

Also, by using chemical equation we get that K_p is equal to:

$$K_p = \frac{p(NO_2)^2}{p(N_2O_4)}$$

$p(NO_2)$ and $p(N_2O_4)$ are gases' NO_2 and N_2O_4 partial pressures in bars.

During equilibrium there should be left (0,035 mol – x) N_2O_4 and created 2x of NO_2.   (3 Pts.)

Using ideal gas law:

$$p(NO_2) = \frac{2xRT}{Vp^\circ}$$

$$p(N_2O_4) = \frac{(0,035 - x)RT}{Vp^\circ}$$

After some mathematical rearrangements:

$$K_p = \frac{4RT}{Vp^\circ} \cdot \frac{x^2}{0,035 - x}$$

p° = 100 000 Pa/bar.

After putting constants' values into equation above we get:

$x^2 + 0,001430x - 5,00 \cdot 10^{-5} = 0$ (5 Pts.)

x = 0,00640 mol.

Because of formation of NO_2 system's enthalpy should have changed by ΔH_1:

$\Delta H_1 = 57,2 \cdot 0,00640 = 0,366$ kJ = 366 J   (1 Pts.)

But we know, that systems enthalpy remained constant, thus, because of n-propane's condensation there had been enthalpy change of ΔH_2, such that $\Delta H_1 + \Delta H_2 = 0$.

$\Delta H_2 = -366$ J.

Which means that y moles of n-pentane condensed:

$y = \frac{-0,366 \text{ kJ}}{-26,2 \text{ kJ/mol}} = 0,01397$ mol $\approx 0,014$ mol.   (2 Pts.)

Because the whole system is in the equilibrium, the condensation process must be as well:

K_k – condensation-evaporation equilibrium constant.

$$K_k = \frac{1}{p(C_5H_{12(g)})}$$

$$p\left(C_5H_{12(g)}\right) = \frac{(0,030 - 0,014)RT}{Vp_0}$$

$p(C_5H_{12(g)})$= 0,396 bar

$K_k = \frac{1}{0,396} = 2,52$

After using some thermodynamics' identities:

ΔG° = -2292 J/mol ir X = ΔS° = -80,2 J/mol/K   (4 Pts.)