Baltic Chemistry Competition

Link: http://www.kdc.lu.lv/skoleniem/konkurss/baltija/

ROUND 2 2013

Focus on physical and organic chemistry

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Basic rules:

- any school student can participate in Baltic Chemistry Competition (BCC), copy of valid school student card may be required;
- participants cannot be University students till the end of February 2013;
- participants register for participation by sending answers in one of first two rounds;
- all answers and parts of solutions **must** be written in specially designed answer sheets according to directions (grading will be done automatically by analyzing answer sheet file);
- students must submit their own work; completely identical solutions will be graded with 0 points;
- **working language is English** (problems are in English and students are expected to answer them in English);
- **deadline for submission of answers is 28th February 2013; 24:00 Latvian time**
- if you have more questions or you would like to submit answers, you have to write to bchem@inbox.lv
- this is final round of competition, students after grading problems from both rounds will receive diplomas from University of Latvia.

Organizers and problem authors wish you success and enjoy competition!!

Problem 1 Spaceship (10 points)

Problem in English

Energy of α-particles (5.41 MeV) of isotope X is used in a battery at a spaceship. For one of such spaceships a battery with power of at least 1 kW is needed to be functional for 120 days. Half-life of isotope X is 138.4 days.

Calculate the minimal mass of X in gramms required for the spaceship.

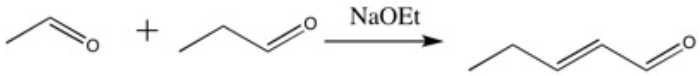
Problem in Russian

Энергия α-частиц (5.41 МэВ) одного из изотопов элемента **X** используется в батареях космических кораблей. Для одного из таких кораблей необходима батарея мощность не менее 1 кВт на срок в 120 дней. Период-полураспада изотопа **X** – 138.4 дней.

Рассчитайте минимальную массу **X** в граммах необходимую для космического корабля.

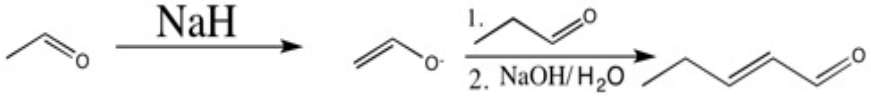
Problem 2 Aldol condensation gone wrong! (25 points)

E-2-pentenal was to be produced in a single step by an aldol condensation. Sodium etoxide (NaOEt) was the base chosen to catalyze the reaction.



After the reaction 4 major products (A, B, C, D) were isolated each at a yield ~25%, the desired product A was amongst them. Yield this low was not acceptable therefore an alternative method was used.

This time a two stage process was employed:

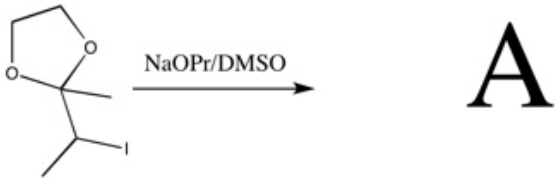


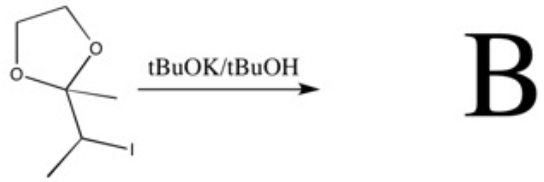
NaOH was supposed to eliminate water from the aldol intermediate to give the final product. This time a 1:1 mixture of C and D was obtained, where C had slightly lower boiling point than D. Change of base from NaH to LDA made no difference. Lowered temperature (-78^0C) in the first step also did not have any effect on the overall outcome of the reaction.

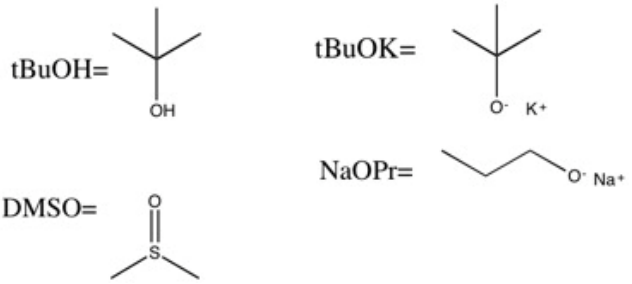
1. *Provide the reaction mechanism for the formation of the intended product A in the first synthesis.*
2. *Provide structures for A, B, C, D.*
3. *Explain what was the problem in the first synthesis*
4. *Explain why the second synthesis did not work.*
5. *How would you make A form the 2 aldehydes provided?*

Problem 3 Base vs Nucleophile! (25 points)

Following reactions were carried out:



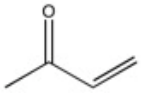




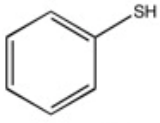
DMSO and tBuOH are solvents. A and B are the main products in the reactions.

1. Provide structures for A and B.

2. It was observed that if DMSO is used as a solvent the first reaction goes much faster compared to propanol as a solvent, it had much smaller effect therefore a simpler solvent was used. Why is that?

3. How would you make :  *the product B, what is, formally speaking, a reactant and a catalyst in this reaction?*

4. How would this unsaturated ketone (question 3) react with a reagent such as tBuOK and how would you expect it to react with: ?



benzenethiol

Problem 4 Charm of physical chemistry (25 points)

Unknown anhydrous metal sulphate **X** was examined using X-ray diffraction (Cu K_α, λ = 154 pm). Diffraction from Miller planes with indices (022), (220), (202) was observed at 2θ angles 32,56°, 37,96 °, 41,40 ° respectively.

1. *Calculate d_{022}, d_{220}, d_{202} spacing between planes.*

Sulphate density ρ = 2.71 g/cm^3. It has orthorombic crystal lattice with 4 formular units in it.

2. *Calculate lattice volume.*
3. *Identify metal.*

X solubility in water at 30 °C is 49,6 g in 100g H_2O, at 0 °C 5,30 g in 100 g H_2O.
16.53% 239,6 g **X** solution was prepared at 30 °C and cooled to 0 °C.

4. *Is the solution saturated at 30 °C?*
5. *What mass of **X** should precipitate at 0 °C?*
6. *In reality the mass of precipitate was 70.49 g. Explain why. Calculate the formula of precipitate. Write its trivial name.*

Problem 5 Redox reactions(25 points)

The explanation of redox reaction is often based on standard electrode potentials. In most cases this concept results in correct conclusions, but it is important to know that the electrode potential depends on other circumstances as well.

a) Consider the following galvanic cells. What redox reactions take place? Why?
   - *i.* *Standard* Ni^{2+}/Ni *and standard* Cd^{2+}/Cd *half-cells*
   - *ii.* *Standard* Ni^{2+}/Ni *half-cell, and* Cd^{2+}/Cd *half-cell at pH=11*
   - *iii.* Ni^{2+}/Ni *half-cell at pH=11, and standard* Cd^{2+}/Cd *half-cell*
   - *iv.* *Following half-cells at 25°C:*
     1) Cd(s) *in 1.00 L solution containing 5.814 g of* $CdSO_4$
     2) Ni(s) *in 1.00 L solution containing 158.0 mg of* $NiSO_4$ *and 200.0 mg of* NaCN.

b) Consider the following half-cells at 25°C:
   1) Cd(s) in a solution that has 25.02 mg of $CdSO_4$ dissolved in 100.0 mL of distilled water and 20.00 mL of KI solution (c = 0,2100 mol/L) was added.
   2) Ni(s) in 0.1000 L solution that has a $1.00 \cdot 10^{-4}$ mol/L concentration of Ni^{2+}.

   Calculate the mass of NaOH *added to* Ni^{2+} *electrolyte, if there is no potential difference between the two half-cells.*

The volume contraction is negligible.

$\varepsilon^0(Ni^{2+}/Ni)$ = –0,23 V, $\varepsilon^0(Cd^{2+}/Cd)$ = – 0,40 V; $pL[Cd(OH)_2]$ = 13,5; $pL[Ni(OH)_2]$ = 17,19;

$lg\beta_4([Ni(CN)_4]^{2-})$ = 31,11; $lg\beta_1([CdI_4]^{2-})$ = 2,48; $lg\beta_2([CdI_4]^{2-})$ = 3,92; $lg\beta_3([CdI_4]^{2-})$ = 5,00; $lg\beta_4([CdI_4]^{2-})$ = 6,10.