



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)

Solution

$$P \approx \frac{m_x}{M_x} \cdot N_A \cdot k \cdot Q(\alpha) = \frac{1}{210 \text{ g}} \cdot \frac{\ln 2}{138.4 \cdot 24 \cdot 60 \cdot 60 \text{ s}} \cdot 5.41 \cdot 10^6 \cdot 96485 \text{ J} = 144 \frac{\text{W}}{\text{g}}$$

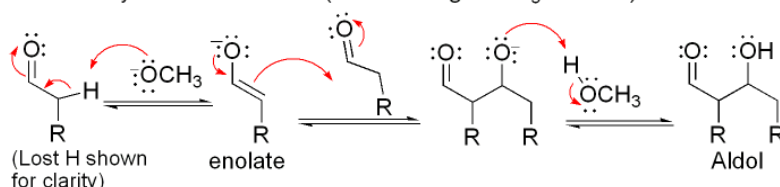
$$m_t = \frac{1000 \text{ W}}{144 \text{ W/g}} = 6.94 \text{ g}$$

$$m_t = m_0 \cdot \exp(-kt) \Rightarrow m_0 = \frac{6.94 \text{ g}}{\exp\left(-\frac{120}{138.4} \cdot \ln 2\right)} \approx 12.7 \text{ g} \text{ (3-4 significant figures acceptable)}$$

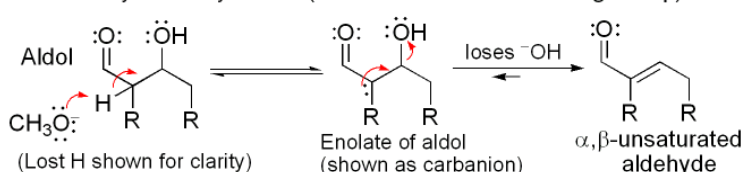
Problem 2 Aldol condensation gone wrong! (25 points)

1. The problem was about aldol condensation in base, therefore a base catalyzed mechanism was required:

Base catalyzed aldol reaction (shown using $^-\text{OCH}_3$ as base)

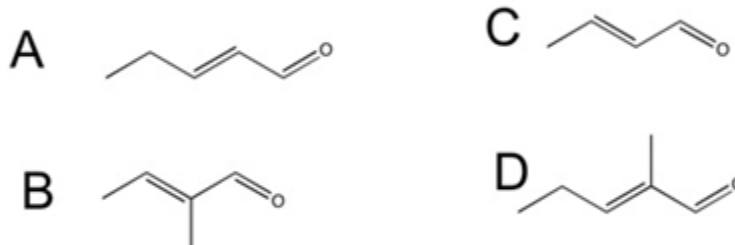


Base catalyzed dehydration (sometimes written as a single step)



Important point in OH elimination is the formation of enolate in the first step and elimination in the second step, the reaction is a 2 step process.

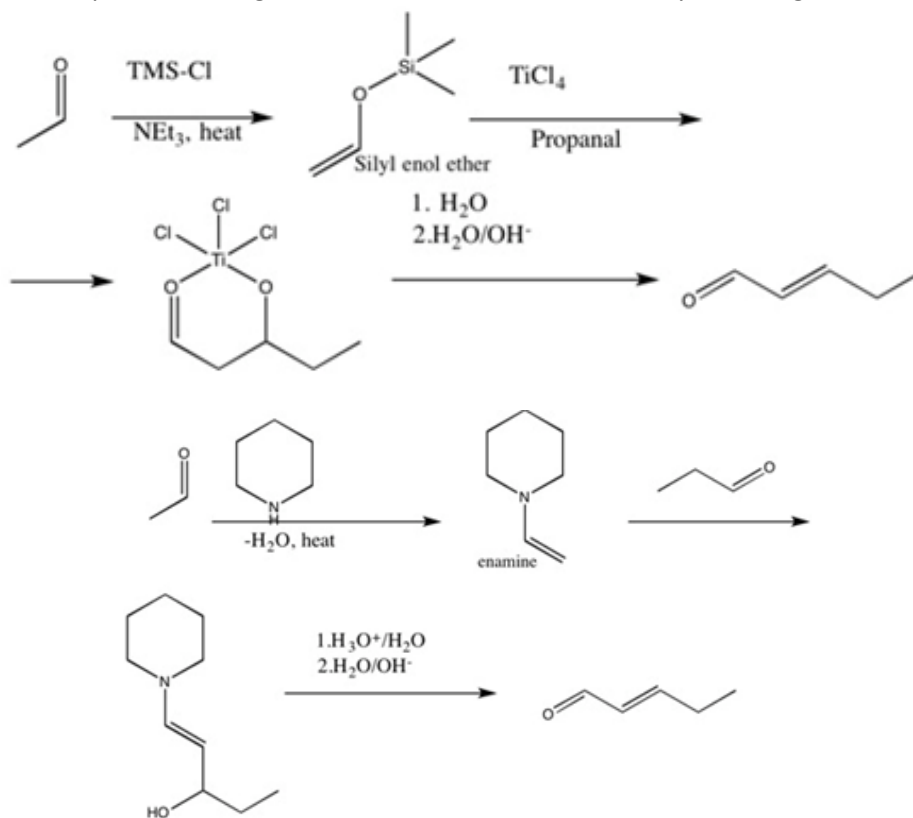
2. From the fact that all products are formed at $\sim 25\%$ it should be evident that it is not due to E Z isomerization as one of the two isomers would be preferred over the other. Geometrical isomerization is ignored in this problem.

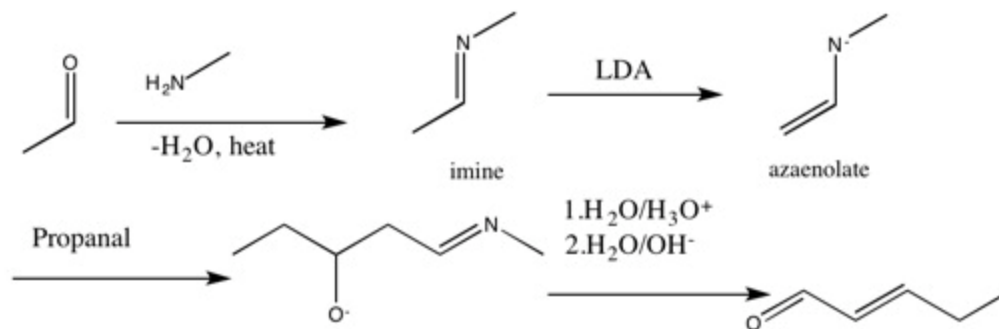


Products are 2 self condensation products and 2 cross condensation products (acetaldehyde enolate + propanal and propanal enolate + acetaldehyde).

A is 2-pentenal because it is the desired product and its structure is actually given in the problem. C and D must be self condensation products because of reasons explained in part 4 of this problem. Since C has lower boiling point than D, C must have lower molar mass than D. Because the structures of the 4 products are very similar their boiling points should increase with increasing molar mass. The remaining product must be B.

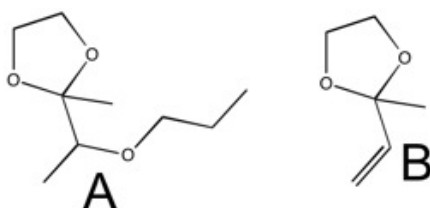
- Due to very similar structures the 2 aldehydes have very similar reactivities and their α protons have very similar acidities. Both have equal probability of getting enolized and the enolate have an equal probability of attacking either of 2 aldehydes. The result is 4 products in equal amounts determined by probability. The reaction is done at equilibrium conditions, at any one time the reaction mixture contains a very low concentration of enolate which means that it is easy for the enolate to attack any of the aldehydes.
- It was intended to form an enolate of one aldehyde so that unwanted self or cross condensation cannot happen, however, due to high reactivity of aldehydes the moment the first base is added the aldehyde enolizes and attacks non-enolized aldehyde before the base can deprotonate it. The result is self condensation product C. Only half of the base is consumed because only 1 equivalent of base is required for 2 equivalents of aldehyde. This means that when the second aldehyde is added to what is supposed to be an enolate it is self condensed as well (product D). At low temperature enolate attack on aldehyde is still faster than deprotonation and different base makes no difference because the problem of this method is the high reactivity of aldehyde.
- Using aldehyde directly is problematic due to its high reactivity. An enol equivalent must be used, this adds extra steps but the target molecule can be obtained. 3 ways of doing this are summarized here:





Problem 3 Base vs Nucleophile! (25 points)

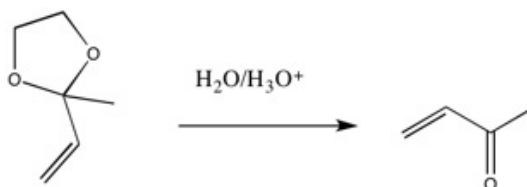
1. The structures are:



2. The first reaction is nucleophilic substitution reaction (S_N2). DMSO is a good solvent for solvating cations, not anions, therefore the sodium ion ends up protected by DMSO envelope while the propionate anion is exposed and therefore very reactive. Propanol as a solvent coordinates around both ions, most importantly around the anion thereby making it bigger and bulkier (harder to attack) and also stabilizing its charge (lower reactivity), both effects decrease the rate of reaction.

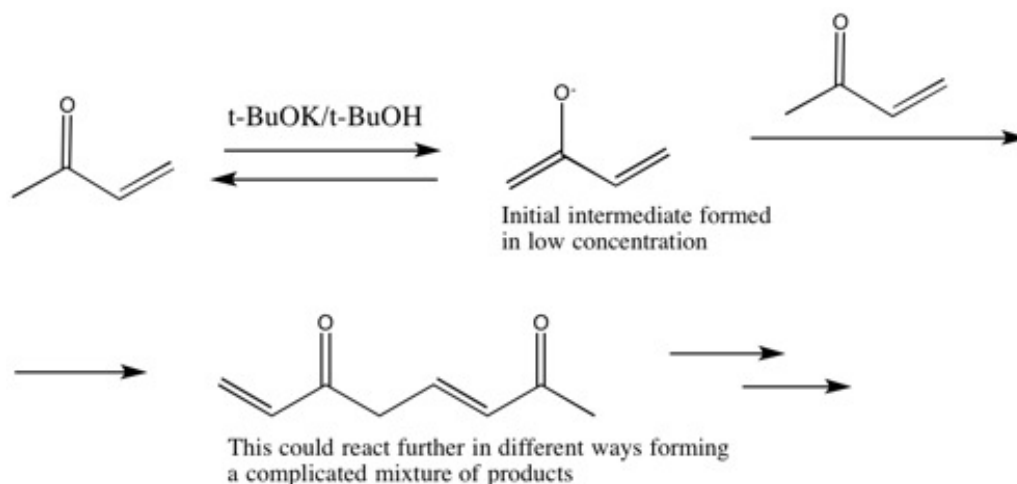
The second reaction involves a very bulky reagent which cannot act as a nucleophile due to steric hindrance. Because it cannot react as a nucleophile it reacts as a base (E2 reaction). The *t*-butanol cannot efficiently coordinate around *t*-butanoate anyway due to bulkiness of both molecules, therefore using DMSO in this case makes little difference.

3. This is a simple hydrolysis:



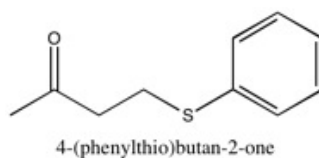
Reactants are product B and water and the catalyst is an acid.

4. Reaction with *t*-BuOK would lead to a complicated mixture of products, one of possible outcomes is shown here:



In this case maximum points were awarded for noting that an enolate will be formed in low concentration in equilibrium conditions and that it can react further.

Reaction with benzenethiol is much more predictable and should give:



As a soft nucleophile benzenethiol does 1,4 addition in preference of 1,2 addition.

Problem 4

Charm of physical chemistry (25 points)

① $2d \sin \theta = k \lambda$

$d = \frac{k \lambda}{2 \sin \theta}$

$d_{221} = \frac{154 \cdot 10^{-12}}{2 \sin \frac{52,56}{2}} = 2,75 \cdot 10^{-10} \text{ m}$

$d_{220} = 2,37 \cdot 10^{-10}$

$d_{202} = 2,18 \cdot 10^{-10}$

3 ~~2~~ taskai

② $\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$

$$\left\{ \begin{aligned} \frac{1}{d_{221}^2} &= \frac{2^2}{a^2} + \frac{2^2}{b^2} + \frac{1^2}{c^2} \\ \frac{1}{d_{220}^2} &= \frac{2^2}{a^2} + \frac{2^2}{b^2} + \frac{0^2}{c^2} \\ \frac{1}{d_{202}^2} &= \frac{2^2}{a^2} + \frac{0^2}{b^2} + \frac{2^2}{c^2} \end{aligned} \right.$$

$$\Rightarrow \left\{ \begin{aligned} \frac{1}{d_{221}^2} &= \frac{4}{b^2} + \frac{4}{c^2} \\ \frac{1}{d_{220}^2} &= \frac{4}{a^2} + \frac{4}{b^2} \\ \frac{1}{d_{202}^2} &= \frac{4}{a^2} + \frac{4}{c^2} \end{aligned} \right.$$

↑ is 1 dalies ↓

$a = 5,588 \text{ \AA}$

$b = 2,951 \text{ \AA}$

$c = 6,971 \text{ \AA}$

$V = abc = 348,4 \text{ \AA}^3$

6 taskai

$$\textcircled{3} \quad S = \frac{m}{V} = \frac{n \cdot M \cdot N_A}{V \cdot N_A} \Rightarrow M = \frac{g \cdot V \cdot N_A}{n \cdot N_A}$$

$$M = \frac{2,71 \cdot 348,4 \cdot 10^{-24} \cdot (6,022 \cdot 10^{23})}{4 \cdot 1} = 142 \text{ g/mol}$$

$$M(\text{ile}) = 142 - 96 = 46 \text{ g/mol}$$

tolu metalo nira, radiumi
metalo riuvalentis, tadg

$$M(\text{ile}) = 46 : 2 = 23 \text{ g/mol} \Rightarrow \text{Na} \quad \text{3 tashai}$$

$$\textcircled{4} \quad m_x = 0,1653 \cdot 239,6 \text{ g} = 39,6 \text{ g}$$

$$m_{\text{H}_2\text{O}} = 239,6 \text{ g} - 39,6 \text{ g} = 200 \text{ g}$$

$$\begin{array}{r} 39,6 \text{ g } x \\ ? \end{array} \quad \begin{array}{r} - 200 \text{ g H}_2\text{O} \\ - 100 \text{ g H}_2\text{O} \end{array}$$

$$\rightarrow 19,8 \text{ g}$$

tesotus tirpalas

3 tashai

$$\textcircled{5} \quad \text{20}^\circ\text{C}: \quad \begin{array}{r} 513 \text{ g} \\ x \text{ g} \end{array} \quad \begin{array}{r} - 100 \text{ g H}_2\text{O} \\ - 200 \text{ g H}_2\text{O} \end{array}$$

$$x = 10,6 \text{ g}$$

3 tashai

$$M \text{ precipitated} = 39,6 - 10,6 = \boxed{29}$$

7

7 tashevi

$$5,3 \text{ g Na}_2\text{SO}_4 - 105,3 \text{ g tärpalo}$$
$$\left(39,6 \text{ g} - \frac{70,49 \cdot 14d}{14d + x}\right) \text{ g Na}_2\text{SO}_4 - (239,6 \text{ g} - 70,49 \text{ g}) \text{ g tärpalo}$$

$$5,3 \cdot (239,6 - 70,49) = 105,3 \left(39,6 - \frac{70,49 \cdot 14d}{14d + x}\right)$$

$$x = 180$$

$$n(\text{H}_2\text{O}) = \frac{180}{18} = 10$$

$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ Glauber's salt

Problem 5 Redox reactions (25 points)

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a) Solution of the first three tasks is based on the Nernst equation. The general formula is the following: $\varepsilon = \varepsilon_0 + \frac{RT}{zF} \ln \left(\frac{[ox]}{[red]} \right)$ where ε_0 is the standard, ε is the actual potential; R is ideal gas constant; T is the temperature in Kelvins; z is the stoichiometric number of electrons; F is the Faraday constant; $[ox]$ and $[red]$ are the concentration of oxidized and reduced species – for approaching the chemical activity.

i) The half-cells are standard, $\varepsilon = \varepsilon_0$, therefore the following reaction will take place: $Cd + Ni^{2+} = Cd^{2+} + Ni$, because the Cd^{2+}/Cd half-cell has lower potential.

ii) At pH=11 precipitation should be considered. $[Cd^{2+}]$ can be determined by using the solubility constant:

$$L = [Cd^{2+}][OH^-]^2 \quad x = [Cd^{2+}]$$

$$10^{-13.5} = x \times (10^{-3})^2, \quad x = 10^{-7.5} = 3.162 \times 10^{-8} \text{ mol/L.}$$

Using the Nernst equation the actual potential of Cd^{2+}/Cd half-cell:

$$\varepsilon(Cd^{2+}/Cd) = -0.40 + \frac{8.3145 \times 298.15}{2 \times 96485} \ln \left(\frac{10^{-7.5}}{1} \right) = -0.62 \text{ V}$$

Therefore the reaction is the same as in the previous subtask.

Another reasoning: precipitation means that the $[Cd^{2+}]$ will decrease. According to the properties of logarithms this means that the actual potential of Cd^{2+}/Cd half-cell will be lower than $\varepsilon(Cd^{2+}/Cd)$ so the $Cd + Ni^{2+} = Cd^{2+} + Ni$ redox reaction will take place as well.

(Because of the precipitation: $Cd + Ni^{2+} + 2 OH^- = \underline{Cd(OH)_2} + Ni$)

iii) This case is quite similar to the previous one. Using the same method: $\varepsilon(Ni^{2+}/Ni) = -0.56 \text{ V}$ so the direction of the redox reaction will be different: $Ni + Cd^{2+} = Ni^{2+} + Cd$

($Ni + Cd^{2+} + 2 OH^- = \underline{Ni(OH)_2} + Cd$)

iv) The actual potential of half-cell 1) can be determined similarly, the concentration is known from the masses: $\varepsilon(Cd^{2+}/Cd) = -0.45 \text{ V}$.

$[Ni^{2+}]$ will be lower because of formation of $Ni(CN)_4^{2-}$. The initial amounts are stoichiometric and the equilibrium constant is a large number, so $[Ni(CN)_4^{2-}]$ could be approached by $[Ni^{2+}]$.

$$10^{31.11} = \frac{1.021 \times 10^{-3}}{x \times (4x)^4}$$

where $x = [Ni^{2+}] = 4.991 \times 10^{-8} \text{ mol/L}$

Using the Nernst equation: $\varepsilon(Ni^{2+}/Ni) = -0.45 \text{ V}$. $\varepsilon(Ni^{2+}/Ni) \cong \varepsilon(Cd^{2+}/Cd)$ therefore no redox reaction will be expected.

b) The main difficulty of this task is that none of the complexes are negligible. The equilibrium constants are given for each complex: $\beta_n = \frac{[\text{CdI}^{(n-2)-}]}{[\text{Cd}^{2+}][\text{I}^-]^n}$ $[\text{CdI}^{(n-2)-}] = \beta_n[\text{Cd}^{2+}][\text{I}^-]^n$

Using these correspondences $[\text{Cd}^{2+}]$ and $[\text{I}^-]$ could be written by the linear combination of concentrations of species. This results a system of equations for $[\text{Cd}^{2+}]$ and $[\text{I}^-]$:

$$[\text{Cd}^{2+}]' = [\text{Cd}^{2+}] \left(\sum_{n=0}^4 \beta_n [\text{I}^-]^n \right) \quad \beta_0 = 1 \quad (1)$$

$$[\text{I}^-]' = [\text{I}^-] + [\text{Cd}^{2+}] \left(\sum_{n=1}^4 \beta_n n [\text{I}^-]^n \right) \quad (2)$$

This could be solved by computer or an iterative method.

Considering the $[\text{I}^-]$ it must be between 0.031 and 0.035 mol/L. Let us suppose that $[\text{I}^-] = 0,031$ mol/L. Using equation (1): $[\text{Cd}^{2+}] = 4.445 \times 10^{-5}$ mol/dm³. Substituting these for equation (2) $[\text{I}^-] = 0.03327$ mol/L. Repeating this method until $[\text{I}^-]$ will not change during the cycle the solutions are $[\text{I}^-] = 0.03321$ mol/L and $[\text{Cd}^{2+}] = 3.937 \times 10^{-5}$ mol/L. The actual potential of this half-cell: $\varepsilon(\text{Cd}^{2+}/\text{Cd}) = -0,53$ V. If there is no difference between these half-cells $\varepsilon(\text{Ni}^{2+}/\text{Ni})$ must be -0.53 V.

$$\varepsilon(\text{Ni}^{2+}/\text{Ni}) = -0.53 \text{ V} = -0.23 + \frac{8.3145 \times 298.15}{2 \times 96485} \ln \left(\frac{[\text{Ni}^{2+}]}{1} \right)$$

so $[\text{Ni}^{2+}] = 7.050 \times 10^{-11}$ mol/L.

In basic solution of $[\text{Ni}^{2+}]$ there must be equilibrium between precipitate and free $[\text{Ni}^{2+}]$, therefore:

$$[\text{OH}^-] = \sqrt{\frac{L}{[\text{Ni}^{2+}]}} = \sqrt{\frac{10^{-17,19}}{7,050 \times 10^{-11}}} = 3,026 \times 10^{-4} \frac{\text{mol}}{\text{dm}^3}$$

Almost the entire amount of Ni^{2+} is in precipitate so $2 \times 0,1 \times 1 \times 10^{-4}$ mol NaOH is necessary for it. Besides this additional $0,1 \times 3,026 \times 10^{-4}$ mol NaOH is needed to set the pH value of the solution. As result **2,011 mg** NaOH must be added.