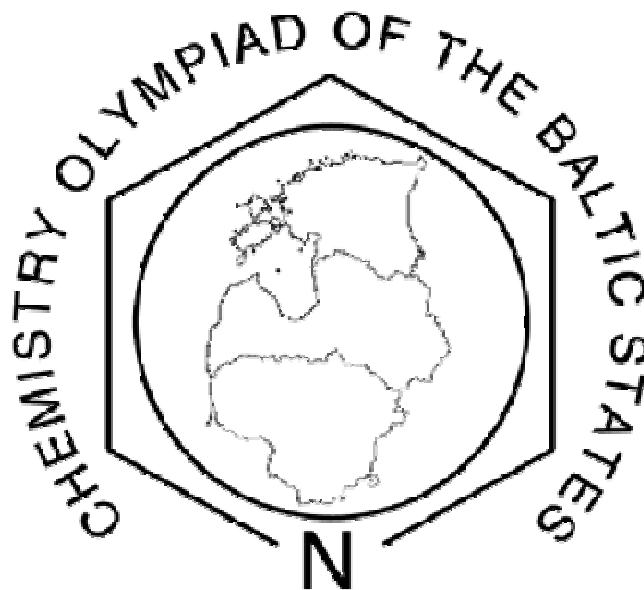




17th Chemistry Olympiad of the Baltic States

Riga, Latvia, 2009

Theoretical examination

Answers



Problem 1. Hydrolysis of pyrophosphate (10 pts).

$$a) \quad K_1 = \frac{[\text{HP}_2\text{O}_7^{3-}][\text{H}^+]}{[\text{H}_2\text{P}_2\text{O}_7^{2-}]}$$

$$K_2 = \frac{[\text{P}_2\text{O}_7^{4-}][\text{H}^+]}{[\text{HP}_2\text{O}_7^{3-}]}$$

$$c = [\text{H}_2\text{P}_2\text{O}_7^{2-}] + [\text{HP}_2\text{O}_7^{3-}] + [\text{P}_2\text{O}_7^{4-}]$$

$$b) \quad c = \left(1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2} \right) [\text{P}_2\text{O}_7^{4-}]$$

$$\alpha = \frac{[\text{P}_2\text{O}_7^{2-}]}{c} = \frac{K_1 K_2}{K_1 K_2 + K_1 [\text{H}^+] + [\text{H}^+]^2}$$

$$\alpha = \frac{10^{-6,12} \cdot 10^{-8,95}}{10^{-6,12} \cdot 10^{-8,95} + 10^{-6,12} \cdot 10^{-7} + (10^{-7})^2} = 0,00979$$

$$k = \frac{k_7^*}{\alpha_7} = \frac{0,0010 \text{ s}^{-1}}{0,00979} = 0,102 \text{ s}^{-1}$$

$$c) \quad \alpha_6 = \frac{10^{-6,12} \cdot 10^{-8,95}}{10^{-6,12} \cdot 10^{-8,95} + 10^{-6,12} \cdot 10^{-6} + (10^{-6})^2} = 0,000484$$

$$\alpha_8 = \frac{10^{-6,12} \cdot 10^{-8,95}}{10^{-6,12} \cdot 10^{-8,95} + 10^{-6,12} \cdot 10^{-8} + (10^{-8})^2} = 0,0997$$

$$k_6^* = \alpha_6 k = 0,000484 \cdot 0,102 \text{ s}^{-1} = 4,93 \cdot 10^{-5} \text{ s}^{-1}$$

$$k_8^* = \alpha_8 k = 0,0997 \cdot 0,102 \text{ s}^{-1} = 1,0 \cdot 10^{-2} \text{ s}^{-1}$$



Problem 2. Iodine and polyiodides (12 pts).

a)

A – KI

B – HIO₃

C – I₂O₅

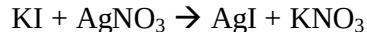
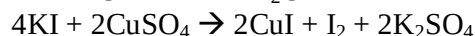
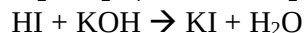
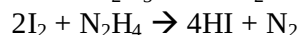
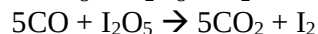
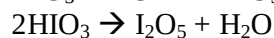
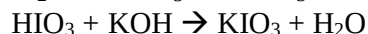
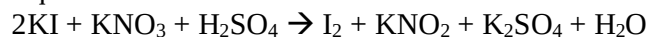
D – KIO₃

E – HI

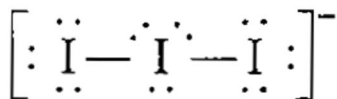
F + **G** – CuI + I₂

H – AgI

Equations:

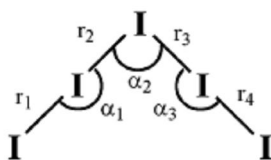


b)



Linear I — I — I

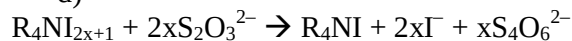
c) Possible geometries:



V-shaped and L-shaped:

Linear pentaiodides also are possible.

d)



$$n(\text{S}_2\text{O}_3^{2-}) = 0.01023 \text{ L} \times 0.112 \text{ mol/L} = 0.001146 \text{ mol}$$

if $x=1$ $n(\text{R}_4\text{NI}_{2x+1}) = 0.001146/2 = 0.0005729 \text{ mol}$; $M = 0.219 \text{ g}/0.0005729 \text{ mol} = 382.3 \text{ g/mol}$
M too small for R_4NI_3 . Only I_3 gives 381 g/mol.



if $x=2$ $n(R_4NI_{2x+1}) = 0.001146/4 = 0.0002865 \text{ mol}$; $M = 0.219 \text{ g} / 0.0002865 \text{ mol} = 764.5 \text{ g/mol}$

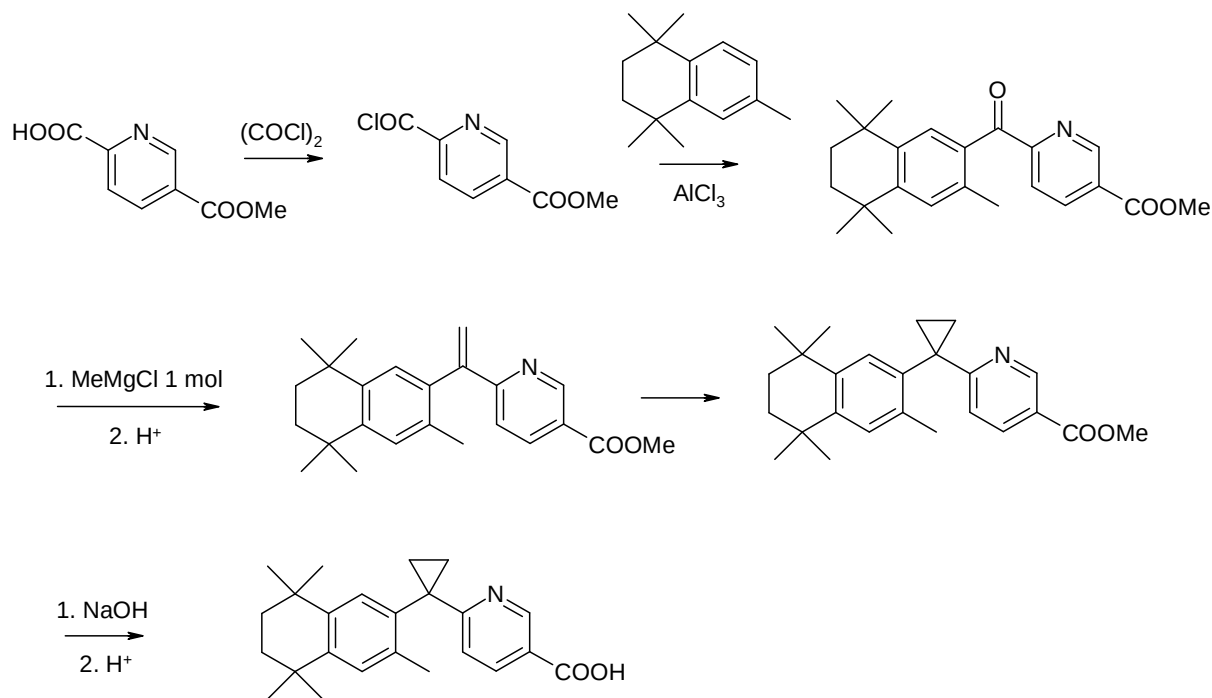
(in general $M = 382.3x$)

R_4NI_5 $M = (14n+1) \cdot 4 + 14 + 127 \cdot 5 = 764.5$ $n=2$

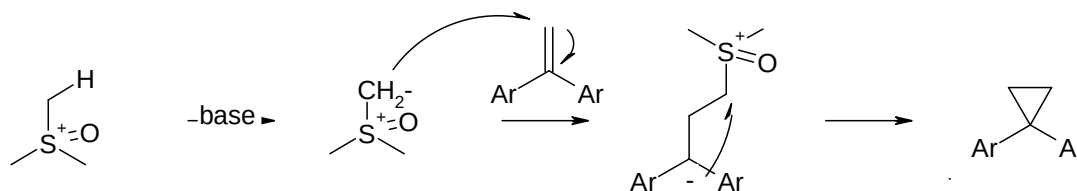
Molecular formula $(C_2H_5)_4NI_5$.

Higher values of x doesn't fit any plausible R .

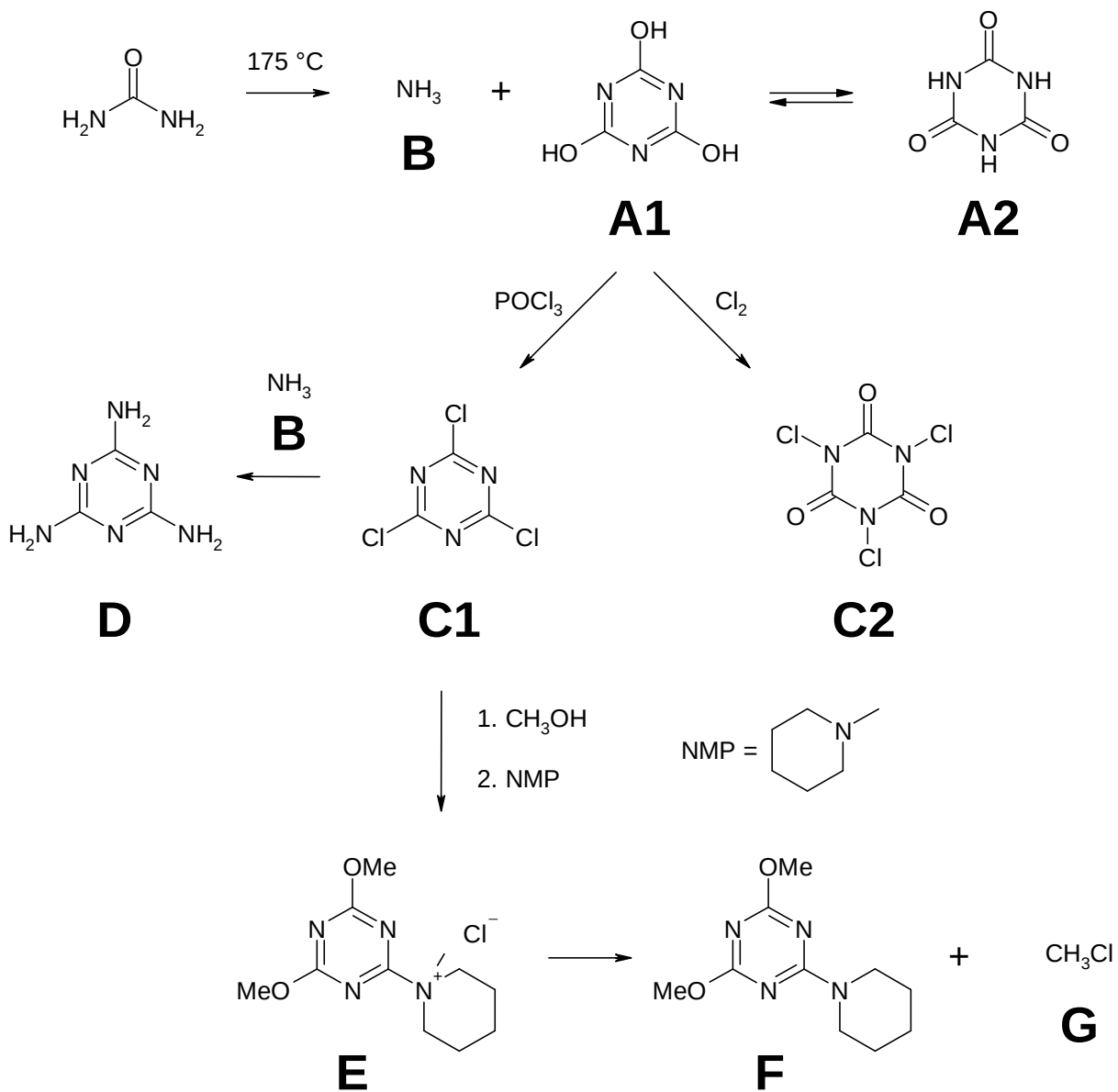
Problem 3. Small rings fighting diabetes (10 pts).



2.

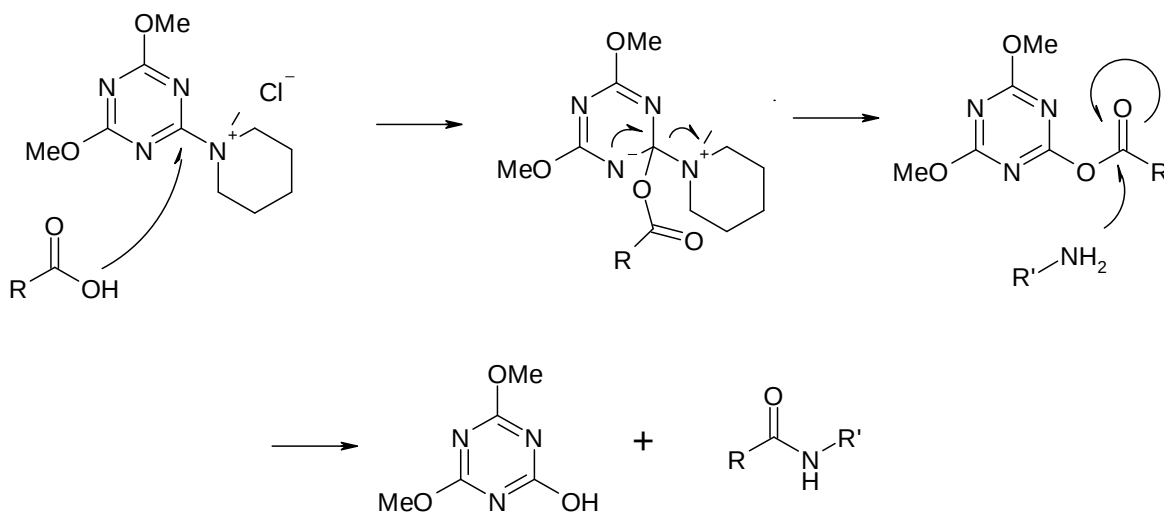


Problem 4. Uses and misuses of nitrogen compounds (10 pts).



2. Replace chloride with a nonnucleophilic anion (BF_4^- , PF_6^-)

3.



Problem 5. Kinetics and equilibrium (8 pts).

$$\text{a) } K = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right) = 0.00264$$

$$K^{298} = \exp\left(-\frac{4730}{8.314 \cdot 298} - \frac{33.5}{8.314}\right) = 0.00264$$

$$K^{273} = \exp\left(-\frac{4730}{8.314 \cdot 273} - \frac{33.5}{8.314}\right) = 0.00221$$

$$\text{b) } k_2^{298} = \frac{0.0375 \text{ s}^{-1}}{0.00264} = 14.2 \text{ s}^{-1}$$

$$k_2^{273} = \frac{0.0021 \text{ s}^{-1}}{0.00221} = 0.95 \text{ s}^{-1}$$

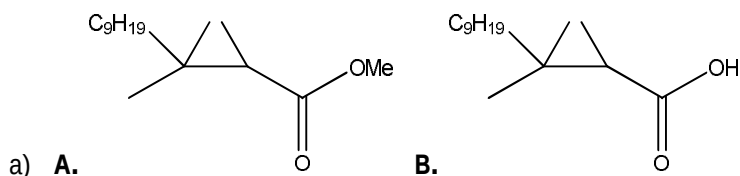
$$\ln \frac{k_1}{k_2} = -\frac{\Delta E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\Delta E_a = \frac{T_1 T_2}{T_1 - T_2} R \ln \frac{k_1}{k_2}$$

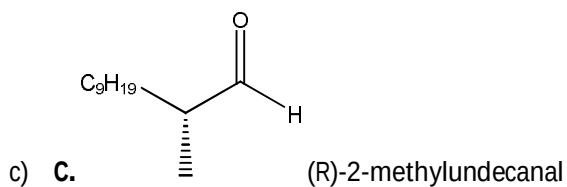
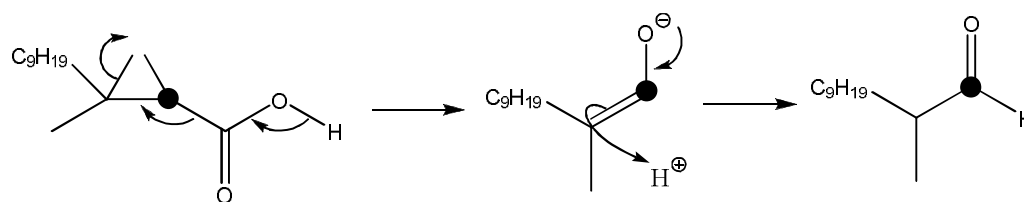
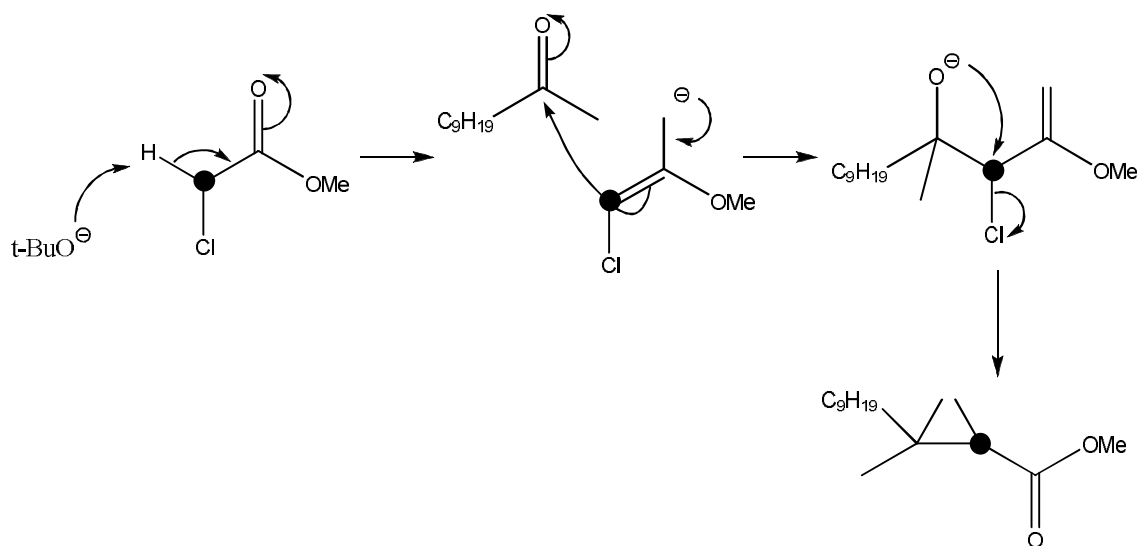
$$\Delta E_1 = \left(\frac{298 \cdot 273}{25} \right) \text{K} \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot \ln \frac{0.0375}{0.0021} = 78 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta E_2 = \left(\frac{298 \cdot 273}{25} \right) \text{K} \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot \ln \frac{14.2}{0.95} = 73 \text{ kJ} \cdot \text{mol}^{-1}$$

Problem 6. Chanel №5 (10 pts).



b)



- d) (S) enantiomer is used. After imine **D** is formed, methoxy group sterically blocks methyl addition to the imine in enolic form from the Si face. Methyl adds to the imine's unhindered face and after hydrolysis (R)-methylundecanal is formed.

