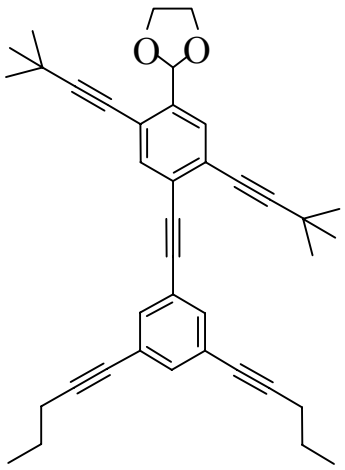


Translated by

Yuriy Kholin,

mentor of the Ukrainian team at the 37th IChO

Problems of the 42nd Ukrainian Chemistry Olympiad

(March 2005, Kherson, Ukraine)

More information can be obtained from our web-site

http://www.bestnet.kharkov.ua/olympiad

Problem 1

For each task mark right statement(s).

1. At irradiation with the sun light, the fastest reaction occurs between gaseous Br_2 and hydrocarbon (great excess of hydrocarbon):

a) CH_4 b) C_6H_{12} (cyclohexane) c) C_4H_{10} (isobutane) d) C_2H_6

2. The reaction constant depends on

a) concentration of reagents b) temperature c) pressure d) activation energy

3. Geometrical isomers can be called:

a) enantiomers b) diastereoisomers c) tautomers d) conformers

4. The nickel-cadmium cell generates electricity due to reaction

$Cd(s) + NiO_2(s) + 2H_2O(l) = Cd(OH)_2(s) + Ni(OH)_2(s)$,

that is based on

a) oxidation of cadmium b) oxidation of NiO_2

c) reduction of cadmium d) reduction of $H_2O(l)$.

5. The temperature coefficient $\left(\frac{\partial E}{\partial T}\right)_p$ of galvanic cell can be used to calculate:

a) coefficient of efficiency b) operation time of the cell

c) ΔS^0 for reaction taking place in the cell d) operation temperature of the cell

6. Mark the right statement(s)

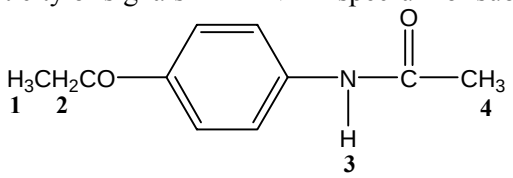
a) internal energy of an ideal gas depends on temperature but does not depend on pressure;

b) entropy measures the age of Universe;

c) during spontaneous chemical reaction entropy is increased (no exceptions exist);

d) standard entropy of elementary substances is equal to 0 by definition.

7. Absorbance (optical density) of solution depends on
a) concentration b) temperature c) wavelength of light
d) material of the cell e) nature of soluted substance.
8. Reacting with an excess of the HI concentrated aqueous solution, anisole gives:
a) phenol and methyliodide b) phenyliodide and methyliodide
c) phenyliodide and methanol.
9. Determine the multipleticity of signals in ^{1}H-NMR specrum of substance



a) 1: triplet 2: doublet 3: singlet 4: triplet b) 1: doublet 2: doublet 3: singlet 4: triplet
c) 1: triplet 2: quartet 3: singlet 4: singlet d) 1: quintet 2: quintet 3: singlet 4: квартет
10. Activity coefficient of the Ag^+ ion in 0.001 M the aqueous $AgNO_3$ solution:
a) is calculated with the Debye-Huccel equation
b) is calculated with the Nernst equation
c) is determined experimentally through the measurement of the surface tension of solution
d) is close to 1
11. To tranform *p*-nitrobenzoylchloride to *p*-nitroacetophenone it is necessary to use:
a) CH_3MgCl b) $(CH_3)_2Cd$ c) CH_3MgCl or $(CH_3)_2Cd$ d) CH_3Cl
12. Density of a physical body:
a) is defined as quotient of volume and mass of the body
b) is changed in one elementary cell
c) under one conditions is the intensive property and under conditions is the extensive one
d) always is the intensive property
13. Arrange in ascending basicity following ions: 1) NH_2^- 2) $R–C\equiv C^-$ 3) RO^- 4) $RCH=CH^-$.
a) 1, 2, 3, 4 b) 3, 1, 4, 2 c) 2, 3, 1, 4 d) 3, 2, 1, 4
14. $\Delta G^0_{formation}$ of a compound:
a) characterizes its stability at 0K
б) characterizes its stability in an ideal solution
в) >0 if the compound decomposes spontaneously to elementary substances
г) characterizes its stability at 298K with regard to the transitions crystal – liquid – gas.

Problem 2

As everybody knows, silver practically is not oxidized with oxygen, but “tarnishes from medicinal waters and salty winds”.

At long storage, sliver goods (plate, jewelries and so on) lose their glance due to the formation on the surface of compound **X**. There are many ways to return the lost glance, for instance

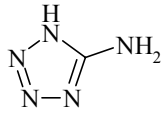
- to boil the good in the soda solution in an aluminium pot;
- to put the good into the KSCN or NH_4SCN aqueous solution for few minutes;
- to treat the good with the water-ethanol solution of thiourea, HCl or H_3PO_4 and soap powder.

1. Determine compound **X**. Write down the chemical equation of reaction responsible for the of the glance.
2. Write down the chemical equations of all mentioned above reactions which allow to return the glance of silver goods.
3. Calculate the solubility of compound **X** in aqueous solution at pH 7 ($K_{S0} = 6{,}3\cdot10^{-50}$, stepwise dissociation constants of the corresponding acid $K_{a1} = 9{,}5\cdot10^{-8}$, $K_{a2} = 1{,}0\cdot10^{-14}$).
4. Compare the solubility of compound **X** in aqueous 6M HNO_3 solution and 6M HCl solutions? Substantiate your answer.

Problem 3

At treating with aqueous $NaNO_2$ and HCl solutions 5-aminotetrazol **A** turns into compound **B** (CHN_6Cl). At careful heating this compound turns into extremely reactive intermediate **X**. If ethylene is present in the

reacting mixture, hydrocarbon **C** (C_5H_8) is formed. This hydrocarbon has only one signal in the ^{1}H-NMR spectrum.

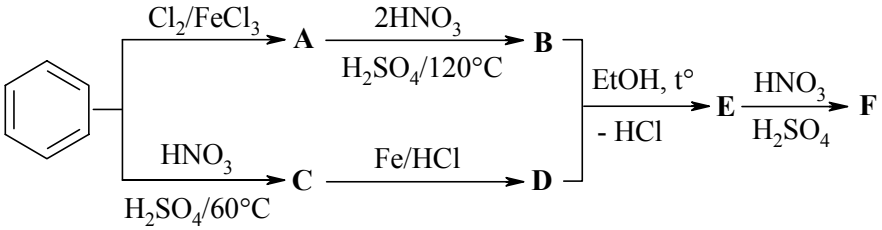


A

1. Determine substances **B**, **C** and **X**.
2. Write down the chemical equation for formation of **X**.
3. If *trans*-2-butene is present in the reacting system instead of ethylene, the mixture of 3 enantiomeric pairs is formed. Draw the spatial structure of the molecules.
4. Characterize the symmetry elements in the **C** molecule.

Problem 4

For the first time, substance **F** was obtained in 1874 by German chemist Piter Austen. Due to interesting properties of substance **F**, its industrial production began soon. Now substance **F** is obtained according to the following scheme:

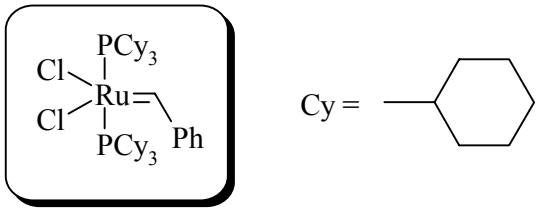


Only 2 signals are observed in the ^{1}H-NMR spectrum of **F**, while one of them disappears after addition of D_2O.

1. Determine substances **A** – **F**.
2. What are interesting properties of substance **F**? For what utilization it was produced?
3. Is it possible to obtain **F** in a more simple way, without changing the skeleton of the molecule?
4. Describe the formation mechanism of **E**?
5. At present, **F** is used to determine the K^+, Rb^+ and Cs^+ ions. Describe, in what way?

Problem 5

Modern organic chemistry attends to developing new methods for creation of C–C bonds. In particular, reactions of alkene metathesis under the influence of ruthenium containing catalysts are intensively studied During the last decade. The structure of one such catalyst (Grubbs' catalyst) is shown below.



Grubbs' catalist

The synthesis of one isomers of derivatives of allyl alcohol (**X**, $C_6H_{10}O_2$) presents one example of using this reaction. Substance **A** is the product of cycloaddition of furan and acetylene. Substance **B** was obtained from **A** through the partial hydrogenation on Pt. Reacting with alkaline ethanolic solution, this compound gives optically inactive mixture of isomers **X1** and **X2**.

It is possible to obtain the third isomer **X3** from substance **C**. The last is the product of reaction between succinaldehyde with an excess of the Norman's reagent C_2H_3BrMg (plain anion) in ether at – 78 °C. Under the of Grubbs' catalyst, substance **C** undergoes cyclization in the CH_2Cl_2 solution producing optically inactive mixture of isomers **X1**, **X2** and **X3** and gas **D**.

1. Determine all ciphered substances and draw the schemes of transformations.
2. Using R,S-notation, mark configuratons of all chiral centers in the molecules of **X1**, **X2** and **X3**.

3. Characterize optical activity of **X3** and explain your opinion.
4. Propose the possible mechanism for the Grubbs' catalyst action.

Problem 6

To make the calomel reference electrode it is necessary to place on the mercury layer contacting with an out cell the layer of paste prepared by grinding calomel (Hg_2Cl_2) and mercury in presence of potassium chloride. After that the potassium chloride solution is poured on top. Usually, 0.1 M, 1 M or saturated potassium chloride solutions are employed. The standard electrode potentials (V) for some half-reactions are reported in the Table.

i	Half-reaction	$E_i°$, V
1	$Hg_2Cl_{2(s)} + 2e^- = 2Hg_{(l)} + 2Cl^-$	0.2676
2	$Hg^{2+} + 2e^- = 2Hg_{(l)}$	0.8540
3	$Hg_2^{2+} + 2e^- = 2Hg_{(l)}$	0.7986

1. Calculate the solubility product of Hg_2Cl_2 at 25°C. Determine the dimensionality of this equilibrium constant.
2. Calculate the potential of calomel electrode, made with the use of the 0.1 M KCl solution (accept $\left[Cl^-\right] = a_{Cl^-}$).
3. Explain, why the mention above paste is employed rather than pure calomel.
4. Calculate E° for half-reaction $2Hg^{2+} + 2e^- = Hg_2^{2+}$.
5. Calculate equilibrium constant for reaction $Hg_2^{2+} = Hg^{2+} + Hg$. In what direction the state of its equilibrium will be shift in presence of KCN; Na_2S; NH_3 solutions? Explain your answers giving the corresponding chemical equations.

Problem 7

Amino acids have the zwitter-ion structure (in solution cation and anion are in equilibrium with zwitter-ion). The isoelectric point (IP) is considered to be the important characteristic of an amino acid. IP is the pH values of aqueous solution in which concentrations of cation and anion are equal.

1. Give the definition of acids and bases according to the Arrenius, Bronsted and Lewis theories. What theory (theories) allows to consider amino acids as amphoteric substances?
2. Explain, what substance – glycine or its ethyl ester – demonstrates more basic properties.
3. Draw the general forms of amino acid cation, anion and zwitter-ion.
4. Deduce formula that allows to calculate the IP value of amino acid, if the equilibrium constants for the following reactions are known:

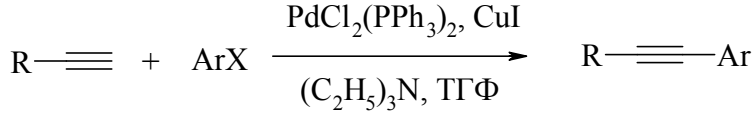
$X + H^+ = XH^+$ (K_1) and

$X = H^+ + X^-$ (K_2).

5. Calculate the IP value for phenylalanine ($\log K_1 = 1{,}83$; $\log K_{a2} = -9{,}13$).

Problem 8

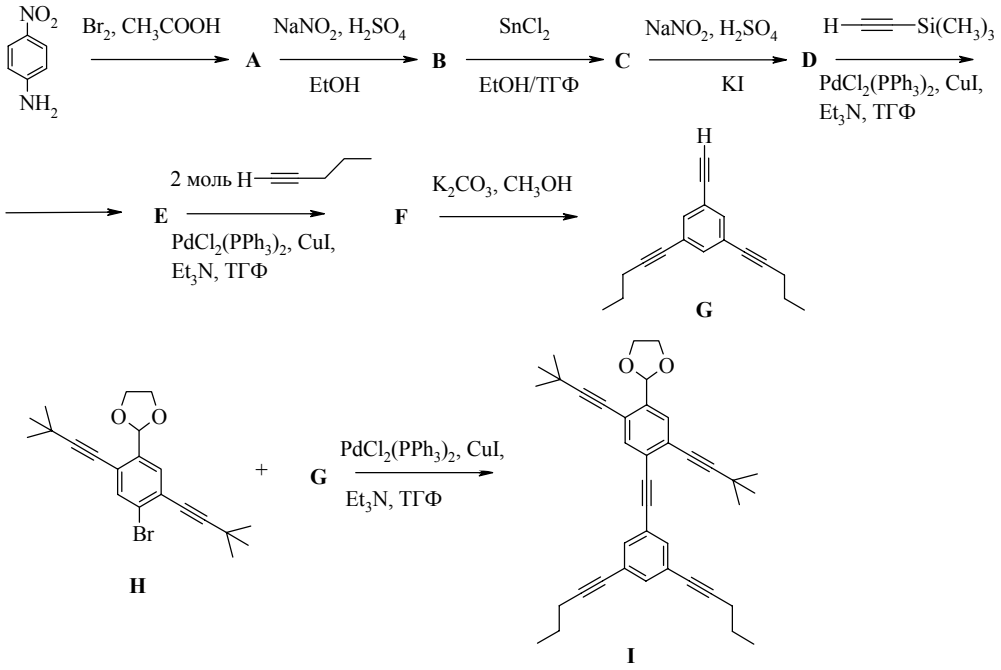
Pd, Rh, Ru complex compounds are often used as catalysts. Among many reactions catalyzed with these catalysts, formation of C–C bond is of special interest for organic chemists because the reactions provide high yields and demonstrate very high selectivity. The Sonogoshira's reaction is the typical example. This reaction is the interaction of aryl halides with mono substituted acetylenes that produces alkyne arenes:



The catalytic system consists of three phosphine complex of Pd(II), CuI and triethylamine while tetrahydrofurane is used as solvent. The potential of this reaction is illustrated brightly by the recent work of American scientists in which the elegant synthesis of the "NanoPutian" molecules was described. The partial synthetic scheme to obtain one of NanoPutians (structure **I**, so-called "NanoKid") is presented below.

1. Draw the structures for all substances denoted with letters if it is known that each molecule **B**-**F** contains 3 hydrogen atoms (2 of them are chemically equivalent) at the aromatic ring while molecule **A** contains 2 chemically equivalent hydrogen atoms.
2. Explain the application of trimethylsilylacetylene at the stage of **D→E** transformation. Is it possible to replace this compound with acetylene?

3. The Sonogoshira's reaction with aryl iodides is known to pass much more easier as compared to aryl bromides. What information about the reaction mechanism can be extracted from this fact? How this difference in reactivity is used in synthesis of compound **G**?
4. Propose your own scheme to synthesize substance **H** from 1,4-dibromine-2,5-diiodine benzene and any another nonaromatic substances with the use of the Sonogoshira's reaction.



Problem 9

For a certain nuclide **Ω** (the half-life time $T_{½}$ = 0,18 c) the following nuclear reactions are known:

$$ {}^{12}_{?}\mathbf{A} + {}^{?}_{1}\mathbf{x} = \mathbf{\Omega} + 5\,{}^{?}_{1}\mathbf{x}\,; \qquad (1) $$

$$ {}^{26}_{?}\mathbf{B} + {}^{?}_{?}\mathbf{y} = \mathbf{\Omega} + {}^{22}_{?}\mathbf{B} \qquad (2) $$

$$ \mathbf{\Omega} = {}^{?}_{?}\mathbf{z} + {}^{8}_{?}\mathbf{C}, \qquad (3) $$

$$ {}^{8}_{?}\mathbf{C} = {}^{?}_{?}\mathbf{z} + {}^{8}_{?}\mathbf{D}, \qquad (4) $$

$$ {}^{8}_{?}\mathbf{D} = 2\,{}^{?}_{?}\mathbf{y}, \qquad (5) $$

where **x**, **y**, **z** are the stable particles (anti-neutrinos, stable particles with zero mass and charge, are not shown in equations).

The atomic number of element **B** is known to exceed twice the atomic number of element **A**.

1. What nuclides are denoted by letters **A** – **D**? What particles are denoted by letters **x**, **y**, **z**?
2. Give the complete equations for all nuclear reactions.
3. How many atoms are every second decayed in 1 mg of **Ω**?

Problem 10

4.8215 g of mixture containing NaH_2PO_4 and Na_2HPO_4. were soluted in 200.0 cm^3 of 0.1982 M HCl aqueous solution. 20.00 cm^3 of obtained solution were titrated with 0.25000 M NaOH solution in presence of phenolphthalein, and 21.00 cm^3 of titrant solution were consumed.

1. Calculate the mass fraction of Na_2HPO_4 in the mixture.

To titrate at pH 2 aqueous solution, containing Fe(II) and Fe(III), 13.70 cm^3 of 0.0552 M Trilon B solution were consumed, while at pH 6 23.50 cm^3 of the same solution are necessary for titration.

2. Determine masses of Fe(II) and Fe(III) in the titrated solution.