# Problem 1 (author Likhanov M.S.)

1. The problem can be solved in different ways, knowing the chemical properties of an unknown metal, or by calculating from the given data of the interaction of substance **C** with sodium fluoride in hydrochloric acid solution. It is easy to assume that the first two reactions are the sequential decomposition of **X** oxalate crystallohydrate, the first one passed with splitting out of water molecule (up to 100ºC) and the last one is subsequent formation of **X** oxide (substance **C**). Looking through the oxidation state of an unknown metal, we find that with an oxidation state of +3, we can write down the following reactions with 6 and 12 equivalents of sodium fluoride:

$$X_2O_3 + 6NaF + 6HCl = 2XF_3 + 6NaCl + 3H_2O$$

$$X_2O_3 + 12NaF + 6HCl = 2Na_3XF_6 + 6NaCl + 3H_2O$$
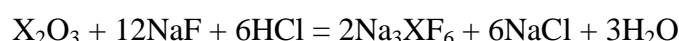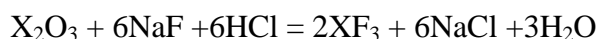
Solving the equation of the ratio of weights for complex and simple fluoride of **X**, we find the mass of an unknown metal: $\frac{3 \cdot 23 + x + 6 \cdot 19}{x + 3 \cdot 19} = 2.235$, $x = 44.98$, therefore, unknown metal – Sc. This is also confirmed by the properties of scandium, since its fluoride and oxalate are insoluble in water.

Thus **C** – Sc_2O_3, **D** – ScF_3, **E** – Na_3ScF_6. Stepwise decomposition of scandium oxalate crystallohydrate:

$$Sc_2(C_2O_4)_3 \cdot nH_2O = Sc_2(C_2O_4)_3 + nH_2O$$
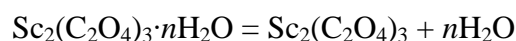
based on the calculation of the mass loss of 20%, we get that $n = 5$, then **A** – $Sc_2(C_2O_4)_3 \cdot 5H_2O$, **B** – $Sc_2(C_2O_4)_3$. Decomposition of scandium oxalate on the air:

$$2Sc_2(C_2O_4)_3 + 3O_2 = 3Sc_2O_3 + 12CO_2$$
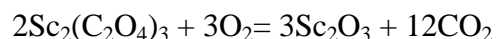
Synthesis of scandium from fluoride by calcium thermic reaction:

$$2ScF_3 + 3Ca = 3CaF_2 + 2Sc$$
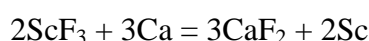
(0.6 points for each compound and 0.5 points for each equation of reaction, 6.1 points in total)

2. The easiest way to determine the composition of subchloride **F**:

$$4ScCl_3 + 3Sc = Sc_7Cl_{12}, \textbf{F} - Sc_7Cl_{12} \text{ or } ScCl_{1.714}$$
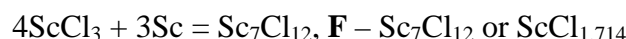
It is interesting to note that the crystal structure of Sc_7Cl_{12} contains a cluster fragment of Sc_6Cl_{18}. Scandium atoms form an octahedron, and chlorine atoms occupy bridged or terminal positions:
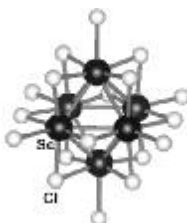
From the loss of mass during the decomposition of Sc_7Cl_{12}, it is not difficult to show the composition of compound **I**: $Sc_7Cl_{12} = 7ScCl_x + yCl_2$. Thus, decomposition of 1 mol of Sc_7Cl_{12} leads to formation of 2.5 mol of Cl_2, from that formula of **I** – ScCl immediately follows.

Given that in the range of subchlorides **F** – **I** the mass fraction of scandium increases, therefore, the oxidation state of scandium should decrease. The oxidation state of scandium in **F** +12/7, then in **G** it will be: $\frac{12}{7}(1 - \frac{2}{30}) = 1.6$, then **G** – ScCl$_{1.6}$ or Sc$_5$Cl$_8$. Similarly, we find the oxidation state of scandium in **H**. Based on the condition, the oxidation state of scandium in **H** is 12% higher than in **G**, then it will be: $\frac{1.6}{1 + 0.12} = \frac{160}{112} = \frac{10}{7}$, thus **H** – Sc$_7Cl_{10}$.

Reaction of coproportionation of **F** and **H**:

$$3Sc_7Cl_{12} + 2Sc_7Cl_{10} = 7Sc_5Cl_8$$

(0.6 points for each subchloride and 0.5 points for each equation of reaction, 3.9 points in total)

Problem 2 (author Hvalyuk V.N.)

1. When the mole fraction of **X** is equal 25% the substances **A1** – **A3** should have the formula (**XZ$_3$**)$_n$, where **Z** – designation of anion, n = 1, 2, 3 … (formally n can be considered as valency of **X**). Since **A1** – **A3** have ionic structure, it is very likely the **X** is an active metal (alkaline or alkaline earth one). The binary substances with ionic structure consisting of non-metal only or containing less reactive metal are extremely rare.

Let's analyze the variant **X** – alkaline metal (therefore n = 1 and **A1** has formula **XZ$_3$**). According to the problem, **A1** can be obtained through the reaction of hydroxide **XOH** and gaseous simple substance at ambient conditions. The following simple substances are gaseous at ambient conditions (apart from noble gas) H$_2$, N$_2$, O$_2$, O$_3$, F$_2$ and Cl$_2$. From this list only O$_3$ forms the substance with alkaline metals with formula **XZ$_3$**. Therefore, this gas is ozone O$_3$ and the reaction of **A1** synthesis (taking into account that the number of **X** atoms should be retain) should be:

$$XOH + O_3 \circledR \; XO_3.$$
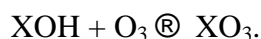
Denote the molar mass of **X** as $M(X)$, then $M(XOH) = (M(X) + 17)$, and $M(XO_3) = (M(X) + 48)$. According to the problem from $\frac{1.000}{M(X) + 17}$ mole of XOH $\frac{1.207}{M(X) + 48}$ mole of XO$_3$ should be formed. From above noted scheme one can see that from 1 mole **XOH** the same quantity of (i.e. 1 mole) **XO$_3$** is formed. Therefore, $\frac{1.000}{M(X) + 17} = \frac{1.207}{M(X) + 48}$. Solving this equation, we get $M(X) = 132.8$ and then the element **X** is caesium Cs. The substance **A1** is caesium ozonide CsO$_3$.

Due to the problem the mass fraction of caesium in **A2** is equal approximately to mole fraction, i.e. 25%. It means that the molar mass $M(Z)$ should be close to the molar mass of caesium Cs, i.e. to 132.8. Moreover this element should form a binary compound with caesium with formula CsZ$_3$. The analysis of molar mass of elements from Periodic Table gives that the most reasonable element is iodine – $M(Z) = 126.9$, formed the compound with caesium CsI$_3$. Therefore, **A2** is caesium triiodide CsI$_3$.

The lightest analog of Cs is Li. The existence of "mirror twin" for **A3** with mole fraction of analog of **X** equal to 75 % means the existence of "twin" Li$_3$**Z** for Li**Z**$_3$. The stoichiometry suggests that **Z** is nitrogen. Then **B3** – nitride, and the "mirror twin" is respectively **A3** – caesium azide CsN$_3$ (0.75 point for each compound, 3 points in total)

2. The oxide Cs$_2$O, peroxide Cs$_2$O$_2$ and superoxide CsO$_2$ have the same qualitative content as CsO$_3$ (0.5 point for compound, 1.5 points in total).
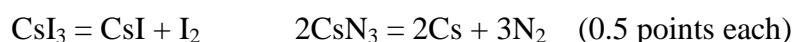
3. The sum of mass fractions of C, H and N in **D1** is equal to 39.33 + 9.90 + 11.47 = 60.70%. Given that in **D1** the anion is the same as in **A1** (i.e. **D1** – ozonide), let's take that the rest is oxygen. Its mass fraction is 100 – 60.70 = 39.30%. Denote the formula of **D1** as C$_a$H$_b$N$_c$O$_d$.

$$a:b:c:d = \frac{39.33}{A_r(C)} : \frac{9.90}{A_r(H)} : \frac{11.47}{A_r(N)} : \frac{39.30}{A_r(O)} = 3.275 : 9.821 : 0.8187 : 2.456 = 4 : 12 : 1 : 3.$$

The formula **D1** – C$_4$H$_{12}$NO$_3$ or (CH$_3$)$_4$NO$_3$ – tetramethylammonium ozonide.

Since according to the task **D2** do not contain carbon, but it is ozonide too, therefore it is ammonium ozonide, **D2** – NH$_4$O$_3$. The only substance that can be melt without decomposition (above 100°C) and which may include chemical elements in various combinations and quantities from ammonium azide is ammonium nitrate. Therefore, it is a product of decomposition of **D2**. It is easy to check on lack of mass mentioned in task (1.5 points for each compound, 3 points in total).

4. The reaction equations mentioned in the task (4.5 points in total):

$$2CsO_3 = 2CsO_2 + O_2 \text{ (приемлемы Cs}_2\text{O и Cs}_2\text{O}_2\text{)} \quad (0.5 \text{ points})$$

$$CsI_3 = CsI + I_2 \qquad 2CsN_3 = 2Cs + 3N_2 \quad (0.5 \text{ points each})$$

$$2CsOH + 5O_3 = 2CsO_3 + H_2O + 5O_2 \qquad 4NH_4O_3 = 2NH_4NO_3 + 4H_2O + O_2 \quad (1.5 \text{ points each})$$

5. In **A1** (CsO$_3$) anion has angular structure (the angle O–O–O is approximately equal to 117°). In **A2** (CsI$_3$) anion has approximately linear structure (the angle I–I–I is approximately equal to 178°). In **A3** (CsN$_3$) anion has linear structure (the angle N–N–N is approximately equal to 180°). (0.5 point for each anion, 1.5 points in total).

6. All of three substances **A1** – **A3** can be synthesized from the simple substances:

$$Cs + O_3 = CsO_3 \qquad 2Cs + 3I_2 = 2CsI_3 \qquad (0.75 \text{ points for each reaction, 1.5 points in total})$$
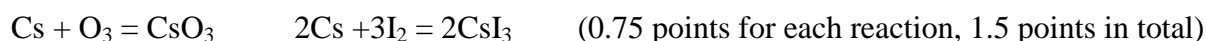
Problem 3 (author Карпушкин Е.А., Лукьянова М.А.)

1. 3LiOH + H$_3$PO$_4$ + FeSO$_4$ → LiFePO$_4$ + Li$_2$SO$_4$ + 3H$_2$O ratio LiOH : FeSO$_4$ = 3 : 1. (It is incorrect to give the LiOH + H$_3$PO$_4$ + FeSO$_4$ → LiFePO$_4$ + H$_2$SO$_4$ + H$_2$O as the reaction and the corresponding ratio 1:1, since pH of such mixture is well below 7, which contradicts the task) (0.7 point for the reaction, 0.3 point for the ratio, 1 point in total).

2. In a weakly acidic medium, where the concentration of PO$_4^{3-}$ is sufficiently high, the formation of insoluble Fe$_3$(PO$_4$)$_2$ phase and poorly soluble Li$_3$PO$_4$ is possible; in more acidic

medium, poorly soluble Li_2HPO_4 can be formed. In alkaline medium, $Fe(OH)_2$ can be formed, besides Li_3PO_4 and $Fe_3(PO_4)_2$ (for each question *a* and *b*: 0.5 point for three phases, 0.4 point for two phase, 0.2 point for one phase; 0.1 point penalty for each incorrect phase, 1 point in total).

3. 1 g of the cathode material contains $1/M$ mol of its formula units, which corresponds to passing x/M mol of electrons through it during the charging. The charge of this amount of electrons is $F·x/M$ Q, which equals $F·x/M$ A·s or $(1000·F·x)/(3600·M)$ mA·h. Finally $q_m = (F·x)/(3.600·M)$ mA·h/g.

For lithium iron phosphate q_m = 168 mA·h/g и M = 157.8 g/mol, and x = 0.99. It is to be seen that almost complete reversible charging is possible for $LiFePO_4$ in the battery (1.5 point for the equation, 0.5 point for calculation of *x*, 2 points).

4. By analogy with lithium iron phosphate:

$$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 \rightarrow xLi^+ + xe^- + Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$$
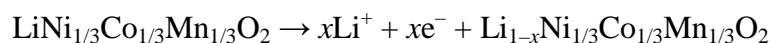
Molar mass of the formula unit M = 96.49 g/mol, and x = 0.58. In is to be seen that the cathodic reaction is incomplete, in contrast to the case of $LiFePO_4$. (*Notice: in fact, deeper charging is possible at higher potential, but this leads to the irreversible transformation of the cathode material and damage of the battery. Therefore, modern charging devices include a special electronic system controlling the charging potential, to avoid the battery damage, overheating, and explosion.*)

To calculate specific energy density, we should remember that $E = U·I·t$ and $E_m = U·I·t/m$ (*m* being the mass of cathode material). In view of the units for the respective values, $q_m = I·t/m$, and, hence, $E_m = U·q_m$ (since q_m is in mA·h/g, and E_m is in W·h/kg, no numerical coefficient is required). Then for the modified material E_m = 3.8 V·160 mA·h/g = 608 W·h/kg. Now, we only need to calculate the average charging potential for the lithium iron phosphate battery to complete the table. The calculation gives $U = E_m/q_m$ = 580 W·h/kg/168 mA·h/g = 3.45 V. Therefore, the advantages of the modified cathode are the increased charging potential and increase specific energy density. The reduced (160 vs 168 mA·h/g) specific charge capacity cannot be treated as the advantage, and the higher conversion in the reaction does not suit the obtained values. In view of the abundance of the elements (Fe vs Ni, Co, and Mn), the price of the modified cathode should be higher. Moreover, higher toxicity of Ni, Co, and Mn can be expected in comparison with Fe (1 point for the reaction, 0.5 points for calculation of *x*, 1.4 point for calculation of E_m, 6·0.1 = 0.6 point for the table, 3.5 points in total).

5. By analogy with the cathodic reactions, the equation of the anodic one is as follows: $C + xLi^+ + xe^- \rightarrow CLi_x$. For carbon, M = 12.01 g/mol, hence, at specific charge capacity 372 mA·h/g the equation derived in question 3 gives x = 0.167, and the formula of the formed compound is $CLi_{0.167}$ (or C_6Li) (1 point for the equation, 0.5 points for the formula = 1.5 points)

6. The maximum battery capacity will be achieved when the charge capacity is equal and fully used. Then, 1 g of the cathode material should correspond to 1 g/(372 mA·h/g)·160 mA·h/g = 0.43 g of the anode material, the specific capacity of this combination of the electrodes being equal to 160 mA·h/(1 g + 0.43 g) = 111.9 mA·h/g. The total capacity of the battery of 3·3500 mA·h required therefore the use of 93.8 g of the electrode materials, and finally, the total mass of the battery is 93.8/0.8 = 117.3 g (1 point).

Problem 4 (author Kuzin S.V.)

1. Calculation of instantaneous rates in case (a):

$$r_1 = k_1[\mathbf{X}]^2 = 2.44 \text{ M/min}; \quad r_2 = k_2[\mathbf{X}] = 0.164 \text{ M/min}; \quad r_3 = k_3[\mathbf{X}][\mathbf{Y}] = 2.0 \cdot 10^{-4}[\mathbf{Y}] \text{ M/min}$$

It is clear that as **X** reacts in parallel ways the fastest **step 1** determines the rate (1 point). In case (b):

$$r_1 = k_1[\mathbf{X}]^2 = 6.1 \cdot 10^{-5} \text{ M/ min}; \quad r_2 = k_2[\mathbf{X}] = 8.2 \cdot 10^{-4} \text{ M/min}; \quad r_3 = k_3[\mathbf{X}][\mathbf{Y}] = 1.0 \cdot 10^{-6}[\mathbf{Y}] \text{ M/min}$$

Step 1 cannot be rate-determining. Steps 2 and 3 are consecutive and at any reasonable concentration of **Y** (not greater than several mol/L) the **step 3** will be the slowest and will be rate-limiting (1 point).

2. Reaction 1: $CH_3COOH \rightarrow CH_4 + CO_2$ (0.5 points)

Reaction 2: $CH_3COOH \rightarrow CH_3OH + CO$ (0.5 points).

3. The slope of the plot $\ln k$ *vs* $1/T$ equals to $-E_a/R$. The continuation of the lines to the intersection with the y-axis shows logarithm of pre-exponential factors, so the line with the slope -17000 corresponds to the 1st reaction ($A_1 > A_2$) and with the slope -5300 to the 2nd reaction. A_1 and A_2 can be calculated from coordinates of intersection of two straight lines:
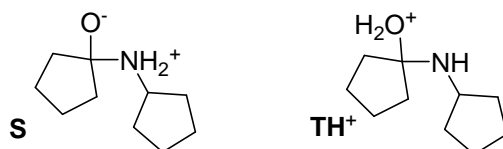
$$\ln A_1 - \frac{E_{a1}}{R}\frac{1}{T} = \ln A_1 - 17000 \cdot 6.25 \cdot 10^{-4} = 5.4 \Rightarrow \ln A_1 = 16 \Rightarrow A_1 = 9 \cdot 10^6 \text{ H}^{-1}$$

The same calculation for A_2.

Finally: $E_{a1} = 141$ kJ/mol, $A_1 = 9 \cdot 10^6$ h^{-1}, $E_{a2} = 44$ kJ/mol, $A_1 = 6 \cdot 10^3$ h^{-1}.

(0.75 points for each correct result, 3 points in total)

4. (0.5 point for each structure)

5. The mechanism has two slow steps (with rate constants k_1 and k_2) and it can be rewritten in equivalent scheme with 2 consecutive steps only (see next point). This means that rate-determining step is the slowest one. With pH decrease amine is significantly protonated, so the 1st reaction slows down. Simultaneously equilibrium K_2 is shifted to **TH**$^+$ side, which increases the rate of the 2nd step.

Similar arguments can be found in the case of high pH. **At low pH amine addition is limiting. At high pH H_2O elimination is limiting** (0.5 point for every correct indication of rate-determining step).

6. One should find the dependence of k_3 and k_4 on the acidity:

$$k_3 = k_1[RNH_2] = k_1 \frac{K_a}{K_a + [H^+]} C(RNH_2)$$

$$k_4([T] + [TH^+]) = k_2[TH^+]$$

$$k_4 = k_2 \frac{[TH^+]}{[T] + [TH^+]} = k_2 \frac{K_2[H^+]}{1 + K_2[H^+]}$$

The assumption $k_3 = k_4$ leads to the following quadratic equation:

$$K_2[H^+]^2 + K_a K_2 (1 - \frac{k_1}{k_2}C(RNH_2))[H^+] - \frac{k_1}{k_2}K_a C(RNH_2) = 0,$$

Solving the equation we obtain $[H^+]_{max} = 8.7 \cdot 10^{-5}$ M, $pH_{max} = 4.1$ (2 points).

Problem 5 (author Garifullin B.N.)

1. The spectrum of biogenic elements is limited. Upon combustion, most of these either afford substance absorbed by alkali (S, Se, halogens) or those having different aggregation state at STP (H, Se, elements of electrolyte ground like Na, K, Ca, Mg). Thus, only nitrogen is left under consideration disclosing the gaseous elementary compound **X** as N_2 (0.75 points).

Examples include reactions of glycine and urea combustion:

$$2 NH_2–CH_2–COOH + 4.5O_2 \rightarrow 4CO_2 + N_2 + 5H_2O \qquad \text{(0.5 point)}$$

$$CO(NH_2)_2 + 1.5O_2 \rightarrow CO_2 + N_2 + 2H_2O \qquad \text{(0.5 point, 1.75 points in total)}$$
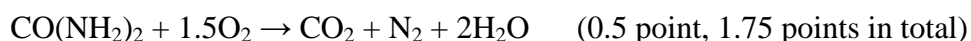
2. Let us calculate the amount of substance for carbon $n(C)$ and nitrogen $n(N)$, molar C:N ratio, and the residual mass $m(res)$, available for the rest of the elements in **B** – **E**.

Compound	$n(C)$, mmol	$n(N)$, mmol	$n(C) : n(N)$	$m(res)$, g
B	49.4	19.7	5:2	0.131
C	50.2	18.8	8:3	0.134
D	45.4	22.6	2:1	0.138
E	40.4	27.0	3:2	0.137

Taking into account that the residual masses are quite small and close to each other, one can suppose that these correspond to hydrogen in **B** – **E**. If so, the simplest chemically consistent formulae are: **B** – $C_{10}H_{26}N_4$, **C** – $C_8H_{21}N_3$, **D** – $C_4H_{12}N_2$, **E** – $C_3H_{10}N_2$ (0.5point for each formula, 2 points in total).

3. It is clearly seen that the compounds are saturated polyamines (free of multiple bonds and cycles) with the general formula of $C_nN_mH_{2n+m+2}$ (1 point).

4. The net formulae of polyamines are determined unambiguously. Multiplying of element indexes by factor k in the general formula $C_nN_mH_{2n+m+2}$ results in $(2n + m + 2)\cdot k$ hydrogen atoms. Still, the number of hydrogen atoms equals $(2n + m)\cdot k + 2$ to meet the general formula, which is possible only if k equals 1 (1 point, 0 point if no calculation shown).

5. With due account for linear character of **D** and **E** molecules, the number of types of atoms present, and instability of compounds with two amino groups attached to one carbon atom, only the hereunder structures are left under consideration (0.25 for each structure, 1.25 points in total):
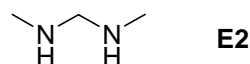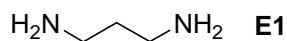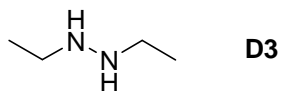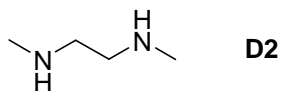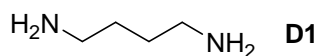

6. The imino group (the third nitrogen atom) in **C** must be positioned so that the maximum symmetry is attained. The final choice for **D** and **E** of the above structures is unambiguous (0.25 point for **D** and **E**, 0.5 point for **C**, 1 point in total):


C, homospermidine   **D**, putrescine   **E**
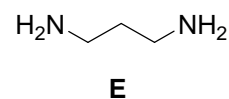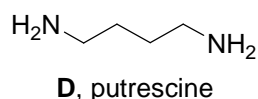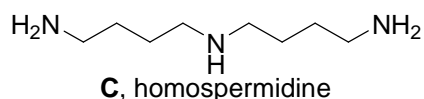
7. The molecular formula of **A** is: $C_3H_{10}N_2 + C_8H_{21}N_3 - C_4H_{12}N_2 = C_7H_{19}N_3$.

The structure of **A** is found with due account for the order of the substituent exchange in the enzymatic reaction **A** (spermidine):
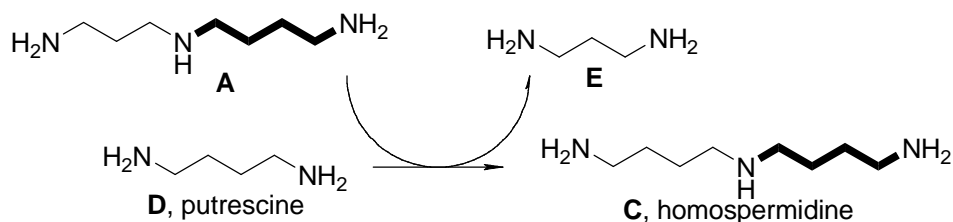

Comparison of the **A** and **D** suggests the structural fragment to be duplicated in **B** (spermine) to attain the maximum symmetry (the initial fragment of putrescine is highlighted bold). The structure is double checked with respect to the molecular formula found earlier (1 point for each structure, 2 points in total):
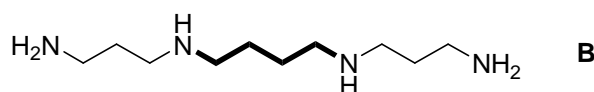
Problem 6 (author Bakhtin S.G.)

1. The molecular formula of **A** corresponds to isomeric chloropropenes and chlorocyclopropane. The product **B** is the result of the nucleophilic substitution of Cl in **A**. Then 1-chloropropene and 2-chloropropene are not suitable in a view of the impossibility of S_N2 reaction at the vinyl C atom under the action of $C_2H_5O^-$. **C** is formed from **B** by deprotonation with a strong base. Taking into account the existence of **C** as two resonance structures, the presence of C=C bond in **D** (there is $C(sp^2)$ atom), only allyl chloride is a suitable compound, and since a carbanion formed exists as two resonant structures **C1** and **C2**, deprotonation of **B** should occur in allyl position. Accordingly, the major alkylation product of **C** can be represented by two isomeric structures:
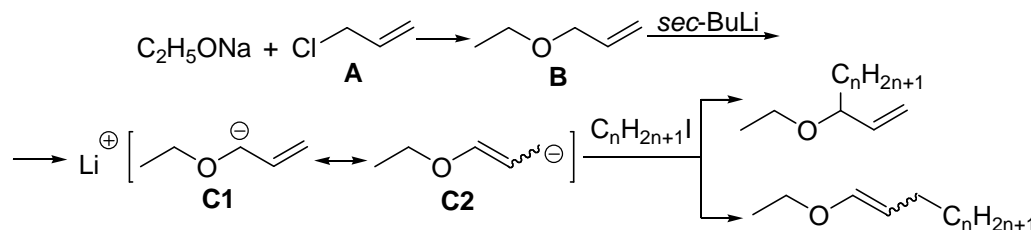

If **D** is formed through the first path, then $n_H[C(sp^3)]/n_H[C(sp^2)] = (5+1+2n+1)/3 = 10.0$, $n = 11.5$ – impossible, if the second one proceeds, then $(5+2+2n+1)/2 = 10.0$, $n = 6$, $C_6H_{13}I$. The transformation of **D** into **E** involves hydrolysis with further isomerization of enol into nonanal:
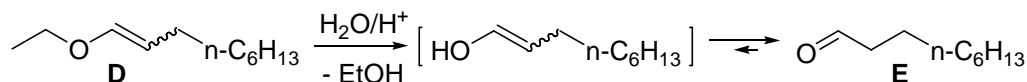

(structural formulas of **A** – **E** and RI – 0.5 points, 3.5 points in total).

2. The analysis of the scheme in first question indicates that the use of the nucleophile **C** results in the introduction of a fragment containing three carbon atoms, one of which becomes carbonyl group. Then, from the variants proposed in the answer sheet, only one structure is suitable for the synton **S** (the so-called homoenolate (0.25 points)), where X = H (0.25 points):
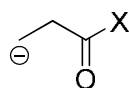

3. According to the scheme, **F** is able to attach HBr (there is a C=C bond); according to the IR spectrum it contains an OH group ($\nu = 3300–2500$ cm^{-1}) and a C=O group($\nu = 1710$ cm^{-1}). These three fragments could be uniquely linked to form acrylic acid. If we add HBr to it in the usual way according to the Markovnikov's rule, the 2-bromopropanoic acid formed will be optically active, which contradicts the condition. Hence for this compound Markovnikov's rule doesn't hold (this is characteristic of all α,β-unsaturated carbonyl compounds and is associated with electronic effects). When the first equivalent of BuLi acts on **G**, the carboxyl group is deprotonated, the second mole of the base leads to the substitution of Br for Li, which can be guessed from the molecular formula of **I**. Further, the usual nucleophilic addition of carbanion **I** to the carbonyl group of propanal occurs to form **J**, the hydrolysis of which initially should give 4-hydroxyhexanoic acid. However, the molecular formula of the final product **K** differs from that for the acid mentioned above by one

molecule of water (dehydration occurred). Since **K** does not have C=C bonds (does not decolorize bromine water), dehydration has occurred intramolecularly forming the lactone cycle (structures of **F** – **K** – 0.5 points each, 3 points in total):
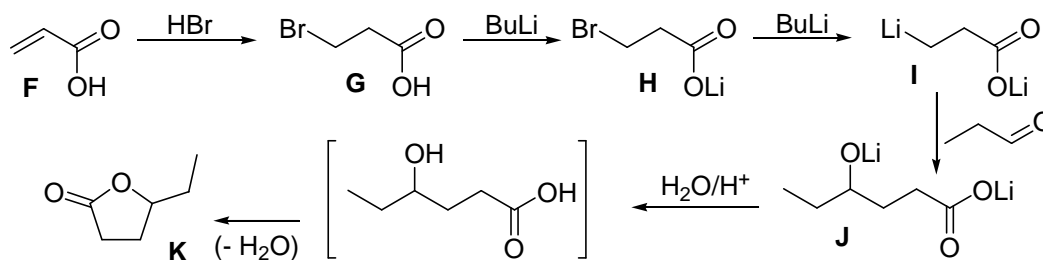

4. **Ia** is the isomer of **I** (tautomer according to the condition). Then the molecular formula $Li_2C_3H_4O_2$ with all four identical H atoms (one singlet in the ^1H NMR spectrum) can correspond only to the structure (1 point):
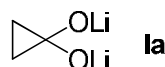

5. According to the condition the final product **K** was formed from **O** by transesterification. Since **K** is a lactone, the transesterification proceeded intramolecularly. This conversion was accompanied by the loss of 2 C atoms (as ethanol). This allows us to establish the structure of **O** - ethyl 4-hydroxyhexanoate:
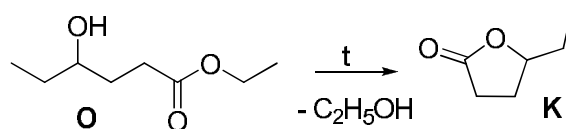

Now in the structure of **O** it is easy to find out a fragment of propanal from the condition (electrophile) and nucleophilic synthon **S**:
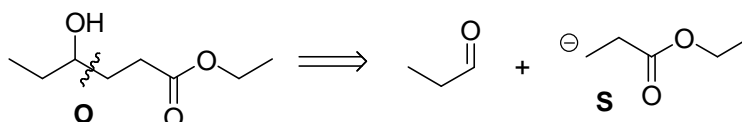

The molecular formula of this found specific **S** differs from that of **N** by the $TiCl_3$. Since **N** is an analog of the homo-enolate form **I** and the QN of Ti in it is equal to 5, the structure of **N**:
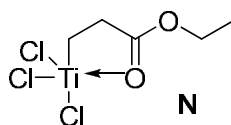
Similarly, the molecular formula of the found **S** differs from the that of **L** by one Cl atom. This allows us to establish the structure of **L**:
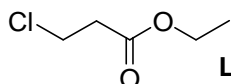
Analysis of molecular formulas shows that the transformation of **L** to **M** was accompanied by the replacement of Cl with C_3H_9Si – this is a group Me_3Si. However, in the condition it is said that **M** is not an analog of the non-linear homonenolate **I**, but its cyclopropane tautomer **Ia**:
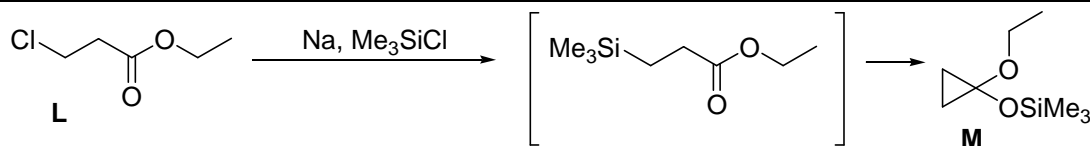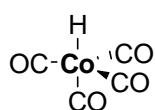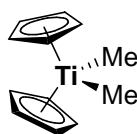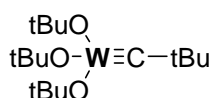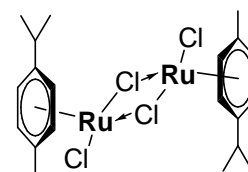
(structural formulae of **L** – **O** –0.5 points each, 2 points in total).

Problem 7 (author Shved A.M., Volochnyuk D.M.)

General comment. This problem DOES NOT require deep knowledge of participants in organometallic chemistry and catalysis. The first part of it can be solved using the information about total number of valence electrons in the complexes. To solve the second part general knowledge of organic chemistry and basic information about spectroscopy are needed. Below you can find the logical reasoning which can be used to solve the problem correctly.

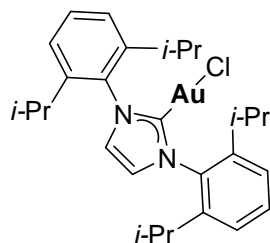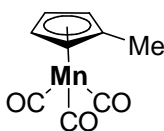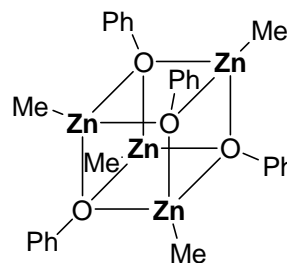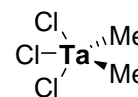**1.** Having calculated the number of electrons donated by the ligands, the electron configuration of the metal atom can be easily found. For example, in the compound **I** the number of electrons donated by the ligands equals to 4·2(CO) + 1(H) = 9. Then the number of electrons of the metal is 18 – 9 = 9, that for 3*d* elements corresponds to cobalt ($3d^74s^2$).[1] The rest 9 compounds can be determined in a similar way, their structures with mass fractions of the metal and the calculation of the number of electrons of the metal are provided below. It should be noted that there are different approaches to the counting of the number of valence electrons in metal complexes. The approach used in the solution is called covalent model. An alternative is the ionic model, more details on this approach you can find in the listed literature (0.25 points for each right metal, 2.5 points in total).

I	**II**	**III**	**IV**	**V**
18*e*⁻, 3*d*	16*e*⁻, 3*d*	12*e*⁻, 5*d*	16*e*⁻, 3*d*	18*e*⁻, 4*d*
18–4·2–1=9	16–2·5–2·1=4	12–3·1–3=6	16–2·3=10	18–6–2·1–2=8
(34.27% **Co**)	(23.00% **Ti**)	(38.92% **W**)	(41.67% **Ni**)	(33.01% **Ru**)
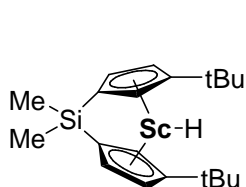
VI	**VII**	**VIII**	**IX**	**X**
14*e*⁻, 3*d*	14*e*⁻, 5*d*	18*e*⁻, 3*d*	18*e*⁻, 3*d*	10*e*⁻, 5*d*
14–2·5–1=3	14–1–2=11	18–5–3·2=7	18–1–1–2·2=12	10–3·1–2·1=5
(13.05% **Sc**)	(31.72% **Au**)	(25.19% **Mn**)	(37.68% **Zn**)	(54.27% **Ta**)

2. According to the task, if we know the metal mass fractions in complexes, we can easily match the reactions with the compounds, which catalyze them (0.25 points for each catalyst matching, 2.5 points in total):

| Reaction	1	2	3	4	5	6	7	8	9	10
Catalyst	[Sc] (**VI**)	[Ti] (**II**)	[Mn] (**VIII**)	[Au] (**VII**)	[Ru] (**V**)	[Co] (**I**)	[Zn] (**IX**)	[W] (**III**)	[Ni] (**IV**)	[Ta] (**X**)

3. The next part of the solution of this problem is the determination of reaction products using data from the table. Moreover, you will find some information about the properties of the catalysts and the types of reactions. But this information was NOT required for the solution of the task and it is given here to open the mind of future participants of the Olympiad.

Reaction 1. Based on the molecular mass of the product ($M^+ = 84$) and the fact that only hydrocarbon and hydrogen participated in the reaction, the molecular formula of **A** is C_6H_{12}. The degree of unsaturation is 1, i.e. there is either one double bond or one cycle in the structure. Among the compounds with a double bond, there are no compounds that have 4 signals in ^{13}C NMR spectrum; moreover, their formation is unlikely, since the reaction occurs in hydrogen atmosphere. Among the cycles, two compounds **1** and **9** have 4 signals in ^{13}C NMR spectrum. Compound **1** can be discarded, as cyclopropanes can "open up" under harsh catalytic hydrogenation conditions. So, the compound **A** is methylcyclopentane.
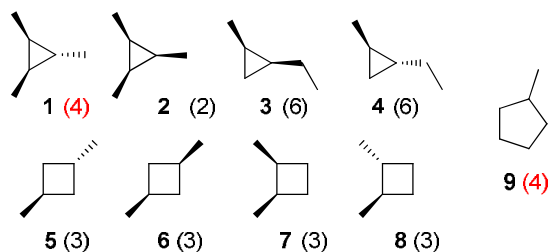
Indeed, the compound **VI** catalyzes this reaction. The compound **VI** (abbreviated in scientific literature as **DpSc-H**) is a Ziegler-Natta polymerization catalyst. The process is driven by the activation of C=C bond by the addition of Sc-H with a subsequent metathesis through a four-membered transition state. When dienes with "separated" double bonds are used, their isomerization is possible (see the figure), and carrying out a similar reaction in hydrogen atmosphere leads to the hydrogenation of Sc–C bond.[2]
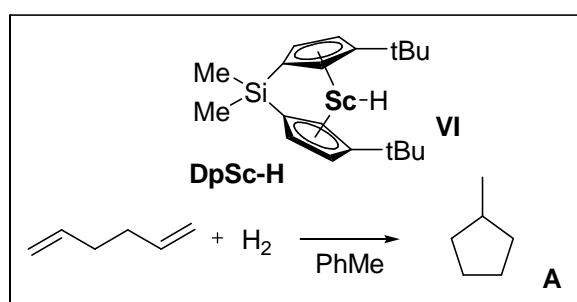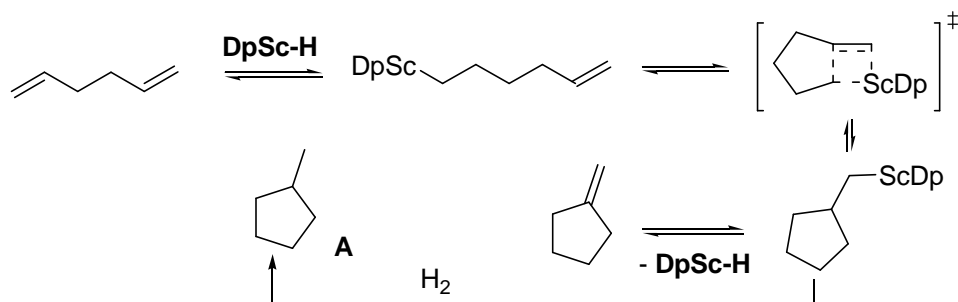
Reaction 2. As in the previous case, based on the mass spectrum, we can find the molecular formula of the compound **B** – C_5H_9N, which has a degree of unsaturation 2. The information about hydrogenation product **10** immediately gives us the information about the order of atoms in the molecule **11**. There are six possible ways to insert a double bond in it, giving the isomers **12** – **17**. Among these compounds, only the compounds **16** and **17** have an intense band at 1650 cm^{-1} in IR spectrum (vibrations of C=N bond). Upon further selection, the compound **16** is rejected due to the fact that it evidently has a signal of aldimine proton in the region of $\delta > 4$ ppm. So, the compound **B** is 5-methyl-3,4-dihydro-2H-pyrrole. This transformation is the intramolecular hydroamination of the triple bond, which is catalyzed by titanium compounds. Compound **II** is dimethyl titanocene, which is widely used in organic synthesis.[3a] In this case the reaction occurs through the formation of an intermediate with Ti=N bond, which can react with the acetylene moiety.[3b]
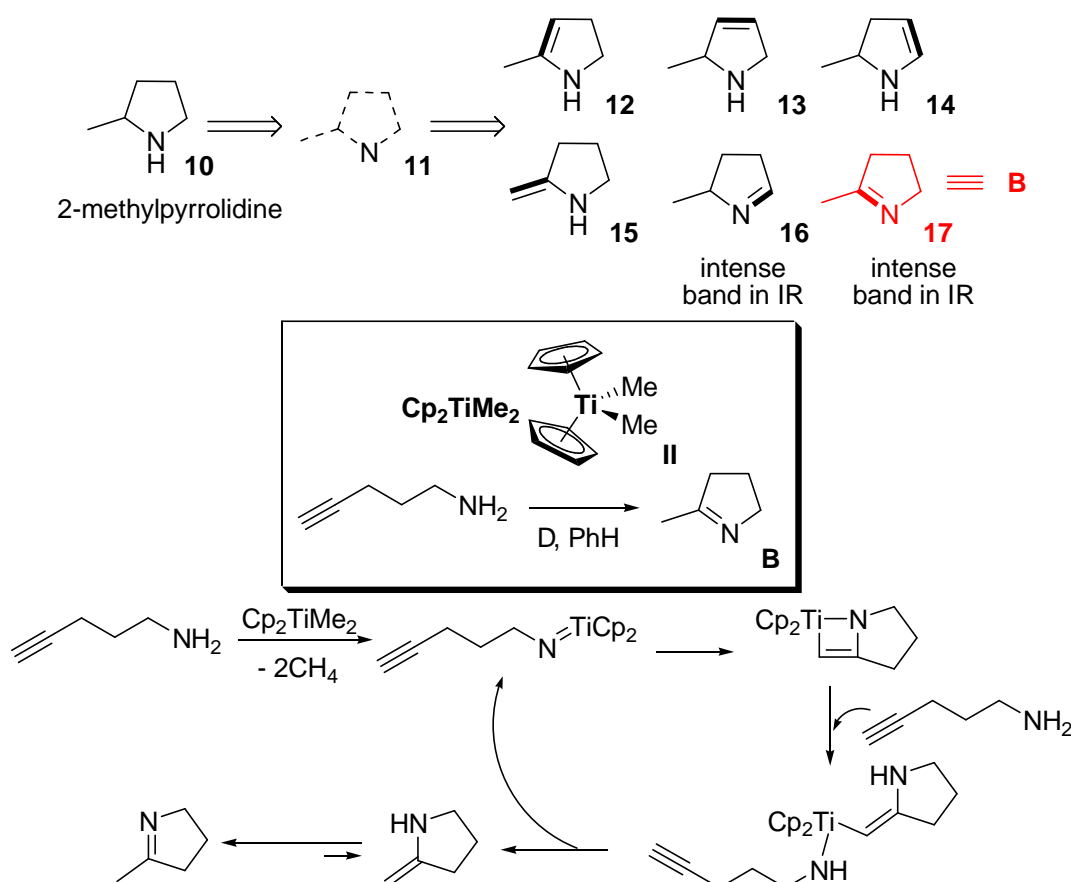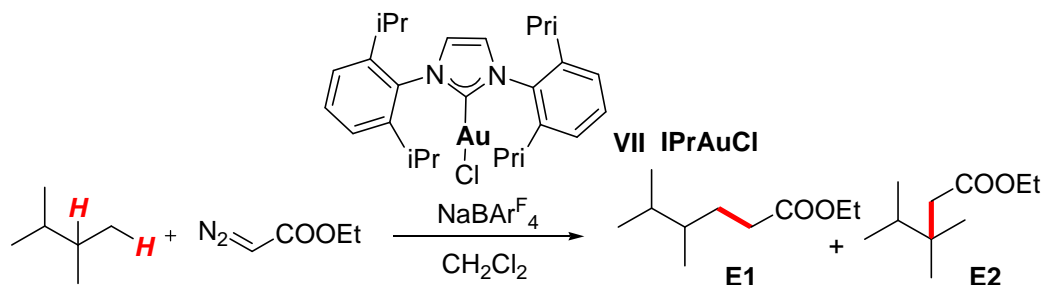
Reaction 3. The analysis of the molecular mass of the product gives that it is equal to two molecular masses of the initial isocyanate minus 44. This clearly indicates that the gas **C** is CO_2,

and the compound **D** is dicyclohexylcarbodiimide (DCC). DCC is a substance that is actively used to create a peptide bond. The conversion of isocyanates to carbodiimides is catalyzed by a large number of compounds, one of which is **VIII** – methylcyclopentadienyl manganese tricarbonyl (in scientific literature it is found under the abbreviation **MMT**).[4] It should be noted that **MMT** is produced in large quantities, though not as a catalyst, but as an additive to gasoline, which increases the octane rating, having replaced tetraethyl lead.
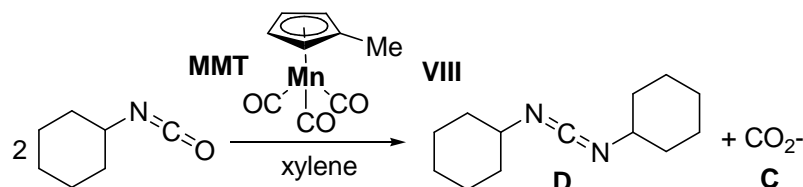

Reaction 4. In this case the molecular mass analysis shows that only one carbene molecule was inserted into the hydrocarbon. Since the initial hydrocarbon (2,3-dimethylbutane) has only two types of C–H bonds where this insertion can occur, the isomeric products become obvious. When choosing the major of two isomeric products, we should be guided by the fact that there are more "primary" C–H bonds in a molecule than "tertiary" (6:1). Accordingly, the attack on the "primary" CH, i.e. methyl group will prevail if the insertion of carbene is statistical. This type of transformation is catalyzed by various transition metal complexes, including gold derivative **VII** (IPrAuCl). In addition to complexes of gold, the compounds of rhodium, silver, copper, palladium and ruthenium can also be used.[5]

Reaction 5. The molecular mass of the product **F** indicates that the isomerization of allyl alcohol has been occurred. An additional analysis of the NMR spectrum, namely the presence of a one-proton doublet at 9.80 ppm, clearly indicates that it is propanal. This transformation of allyl alcohols into aldehydes is catalyzed by ruthenium complex **V** (abbreviation **[(*p*-cymene)RuCl$_2$]$_2$**)[6a], which is used to generate aldehydes in reaction medium, that are prone to self-condensations, unlike allyl alcohols.[6b]
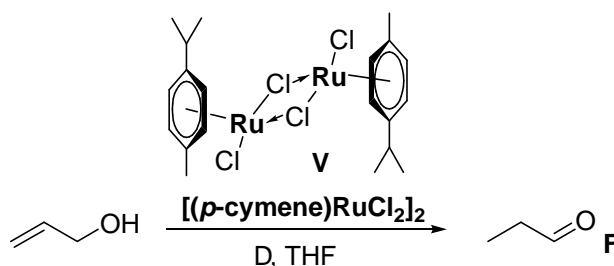
Reaction 6. A positive test with 2,4-dinitrophenylhydrazine (on aldehydes and ketones) and participation in silver mirror reaction clearly indicate that **G** is an aldehyde. The information about molecular mass and unbranched structure leads us to the fact that **G** is *n*-heptanal. The use of synthesis gas (CO + H$_2$) in the reaction indicates that this is a hydroformylation or oxo-synthesis reaction, which was discovered in 1938 by Otto Roelen. The first industrial catalyst for this reaction was actually HCo(CO)$_4$.[7a] At the moment HCo(CO)$_4$ is no longer used in this reaction. Since 1970 rhodium complexes have been used in oxo-synthesis, however HCo(CO)$_4$ has found its application in fine organic synthesis.[7b]
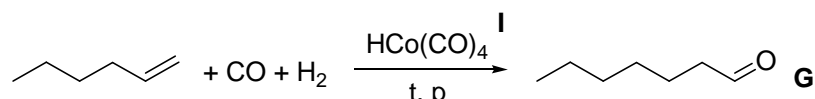

Reaction 7. From the mass spectrum it can be seen that a carbonyl group has been reduced (M(product) = M(initial) + 2); in addition, a positive Lukas test indicates that it is α-phenylethanol. In this case, zinc complex [(MeZnOPh)$_4$] (**IX**) acts as an activator (coordinates to the carbonyl group of acetophenone) of the addition of (EtO)$_3$SiH to acetophenone.[8]
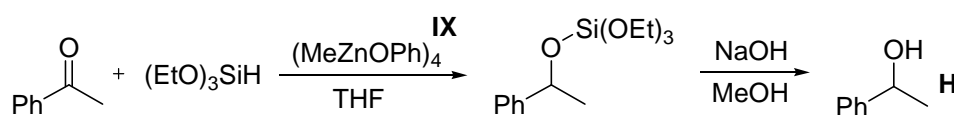

Reaction 8. The analysis of molecular mass of product **J** shows that it can contain three phenylene and three acetylene fragments (300 = 3·76 + 3·24 = 3·M(C$_6$H$_4$) + 3·M(C$_2$)). Given the symmetry (3-fold symmetry axis) of the compound **J**, it is not difficult to "construct" its structural formula (see the figure). Such a reaction product indicates that acetylene metathesis has occurred and the second reaction product is dimethylacetylene **I**, which is actually a low-boiling liquid having 1 signal in ^{1}H NMR spectrum. Tungsten carbyne complex (tBuO)$_3$W≡CCMe$_3$ (**III**) is among the early generation catalysts for this reaction, discovered by Schrock in the early 1980s.[9]
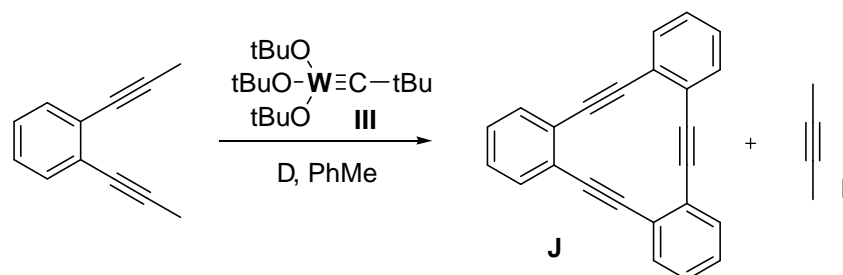
Reaction 9. The information that the reducing ozonolysis of the compound **K** results only in the formation of succinic dialdehyde gives us the general structural formula for the product **K**. To choose n, one can use the information that **K** gives a product with a 3-fold symmetry axis with borane, which is possible only for n = 3. Indeed, such an unusual trimerization of butadiene, catalyzed by the nickel allyl complex [Ni(allyl)]$_2$ (**IV**), was discovered by Wilke in the 1960s.[10]
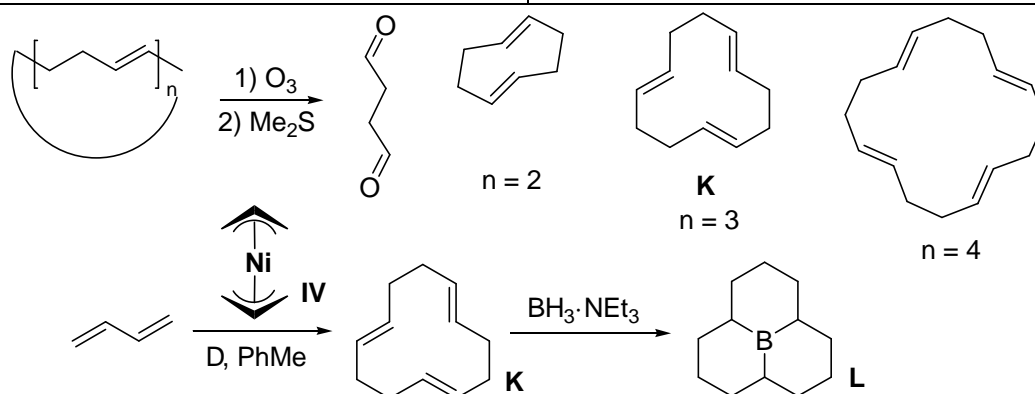
Reaction 10. In the last reaction, the structure of a product is interpreted on the assumption that it is a substrate for oxo-synthesis (reaction **6**), where *n*-heptanal is formed. This compound is hexene-1. Such a process for the selective trimerization of ethylene was recently developed using tantalum-based catalysts.[11] This selectivity is due to the fact that TaCl$_3$ is generated in the reaction medium, being a true catalyst. It reacts with three ethylene molecules to form a seven-membered metallocycle, which decomposes to form hexene-1 and catalytically active TaCl$_3$. The formation of larger metallocycles is disadvantageous.
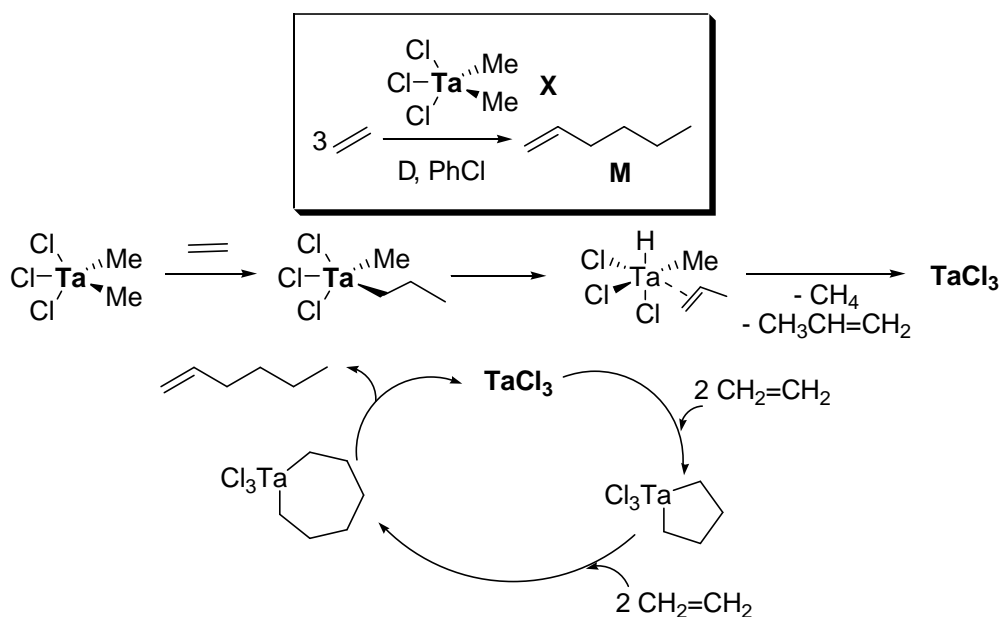
(for the right structural formulas of **A**, **B**, **F**, **G**, **H**, **M** – 0.5 point each, for the right structural formulas of **C**, **D**, **E1**, **E2**, **I**, **J**, **K**, **L** – 0.25 point each, 5 points in total)

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Problem 8 (author Beklemishev M.K.)

1. a) $CO_2 + 2NH_3 + H_2O = (NH_4)_2CO_3$

b) $4NH_3 + 6CH_2O = (CH_2)_6N_4 + 6H_2O$

c) $4NH_4^+ + 6CH_2O + 4OH^- = (CH_2)_6N_4 + 10H_2O$ (1 point for each, 3 points in total)

2. Plugging $[H^+] = 1 \cdot 10^{-8}$ into the expressions for the first and second ionization constants of carbonic acid, we can get: $[HCO_3^-] / [H_2CO_3] = 43$ and $[CO_3^{2-}] / [HCO_3^-] = 0.0047$, which implies that at pH 8 hydrocarbonate ion dominates (1 point).

3. a) A part of alkali reacts with ammonium carbonate, the amount of which is equivalent to the amount of absorbed CO_2 (ammonia is then bound by formaldehyde): $OH^- + NH_4^+ = NH_3 + H_2O$ (0.5 points).

Barium precipitates carbonate ion: $Ba^{2+} + CO_3^{2-} = BaCO_3^-$ (0.5 points; it can be shown that at pH 8 carbonate is quantitatively precipitated from ~ 0.1 M Ba^{2+} salt solution).

After precipitation of carbonate, HCl is consumed only for the titration of the excess of alkali ($H^+ + OH^- = H_2O$, 1 point), but not for the titration of carbonate. Thus, the barium salt eliminates the side reaction of HCl with carbonate ion (0.5 points).

b) Hydrochloric acid would be spent, firstly, for the titration of excess alkali: $H^+ + OH^- = H_2O$ (0.5 points) and, secondly, for the reaction with carbonate (with the formation of hydrocarbonate, because, according to paragraph 2, this is the predominant form at the end point of the titration): $H^+ + CO_3^{2-} = HCO_3^-$ (1 point; a total of 2.5 points for items **3**a, b).

4. a) The difference between the volumes of the acid and the alkali is 0.20 mL. Since the concentrations of the acid and the alkali are equal, the difference corresponds to the volume of alkali spent for the deprotonation of ammonium ion. Thus, $c(CO_2) = 0.20$ mL $\cdot 0.5000$ M NaOH / 5.00 mL of the sample $\cdot$ 2 (from the stoichiometry of the ammonium carbonate formation reaction) $= 0.010$ M (1 point).

b) In the absence of a barium salt, as shown above, the following reaction would proceed: $H^+ + CO_3^{2-} = HCO_3^-$, i.e. an amount of acid equal to carbonate would be additionally spent (0.01 M); therefore, the volume of HCl would be: 0.01 M $\cdot$ 5 mL (sample volume) / 0.50 M (HCl concentration) = 0.10 mL HCl, totally 9.80 + 0.10 = 9.90 mL of HCl (1 point).

5. a) Hydrolysis of hexamethylenetetramine occurs; it is a reaction reverse to its formation, in which the protons are spent:

$$(CH_2)_6N_4 + 4H^+ + 6H_2O = 4NH_4^+ + 6CH_2O \text{ (1 point)}$$
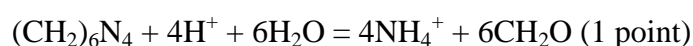
b) Answer *2* (it would grow, and grow stronger than for a mixture with pH 4.0), since, judging by the reaction equation, hydrolysis will proceed faster in a more acidic medium (0.5 points).