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Problems and Solutions



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Physical Chemistry

1- A spherical He balloon is placed in the freezer. What happens to the size of the balloon? Be as quantitative as possible.

It is reasonable to suppose that the pressure inside the balloon is equal to the outside pressure. Then, it is clear that at constant external pressure the size of the balloon will decrease after cooling independent of the material of its cover.

To give a quantitative estimate, we make two assumptions: 1) the cover is uniform and ideally compressible – it means that the balloon will retain its spherical shape upon cooling; 2) helium is an ideal gas.

Consider the ideal gas equations inside the freezer (parameters – P , T_{in} , V_{in}) and outside it (P , T_{ex} , V_{ex}):

$$PV_{\text{in}} = nRT_{\text{in}},$$

$$PV_{\text{ex}} = nRT_{\text{ex}}.$$

Dividing one equation by another, we get:

$$V_{\text{in}} / V_{\text{ex}} = T_{\text{in}} / T_{\text{ex}}.$$

The volume of the sphere is: $V = \frac{4}{3}\pi r^3$, hence the radius of the balloon inside the freezer, r_{in} , at temperature T_{in} is:

$$r_{\text{in}} = r_{\text{ex}} \left(\frac{T_{\text{in}}}{T_{\text{ex}}} \right)^{1/3}$$

where r_{ex} is the initial radius at temperature T_{ex} .

2- How might you keep a gas at a constant temperature in a thermodynamic process.

Consider the equation for the First Law:

$$dU = \delta Q + \delta W$$

If the gas is ideal (which is supposed by default), then its internal energy depends only on temperature and remains constant in any isothermal thermodynamic process, that is $dU = 0$. So, for the temperature to remain constant the heat supplied to the gas or taken from it, should be equal to the work done by the gas or upon it.

3- Find the internal pressure of the following equation of state

$$P = \frac{RT}{\bar{V}-b} e^{-\frac{aRT}{\bar{V}}}, \text{ where } \bar{V} \equiv \frac{V}{n}$$

The internal pressure, by definition, is the derivative of internal energy with respect to volume at constant temperature: $\left(\frac{\partial U}{\partial V}\right)_T$. To find it, we use the identity:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P.$$

From the equation of state:

$$P = \frac{RT}{\bar{V}-b} \exp\left(-\frac{aRT}{\bar{V}}\right)$$

we find the pressure derivative with respect to temperature:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\bar{V}-b} \exp\left(-\frac{aRT}{\bar{V}}\right) - \frac{RT}{\bar{V}-b} \frac{aR}{\bar{V}} \exp\left(-\frac{aRT}{\bar{V}}\right)$$

Multiplying by T , we get:

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{\bar{V}-b} \exp\left(-\frac{aRT}{\bar{V}}\right) - \frac{RT}{\bar{V}-b} \frac{aRT}{\bar{V}} \exp\left(-\frac{aRT}{\bar{V}}\right) = P - \frac{PaRT}{\bar{V}}$$

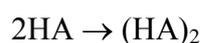
The final expression for the internal pressure of this gas:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = -\frac{PaRT}{\bar{V}}$$

4- The equation of freezing point depression of water in the dilute solution of benzoic acid is $\Delta T = ik_f m$, with value of i between $\frac{1}{2}$ and 1. Give a reasonable explanation.

The freezing point depression is the colligative property of solutions, that is, it depends only on the number of particles in solution, not on their nature. From the fact that isotonic coefficient lies in the range from 0.5 to 1 it follows that the process in solution leads to the decrease of the number of particles – hence, it is association rather than dissociation. (This is true for benzene solutions but in water dissociation will prevail, so the problem is incorrect)

Denote benzoic acid as HA, then association is described by the equation:



Let the initial number of HA molecules in solution be N , and the degree of association – x , then the solution contains $N \cdot (1-x)$ molecules of HA and $N \cdot x/2$ molecules of its dimer $(\text{HA})_2$. The total number of particles in solution is $N \cdot (1-x + x/2) = N \cdot (1 - x/2)$, and the isotonic coefficient is $i = 1 - x/2$.

The degree of association x can vary from 0 to 1, and the corresponding values of isotonic coefficient are in the range from 1 (no association) to 0.5 (complete association).

5- Show that the activation energy can be obtained using activation complex theory as follow:

$$E_a = \Delta H^\ddagger + (RT - \Delta n^\ddagger RT)$$

There is no explanation in the text of the problem, so we first show the designations: E_a is the experimental activation energy of an elementary step, ΔH^\ddagger is the enthalpy of formation of the activation complex (synonym – the transition state), Δn^\ddagger is change in the number of molecules during the activation complex formation ($\Delta n^\ddagger = 0$ for the monomolecular reactions and $\Delta n^\ddagger = -1$ for bimolecular reactions).

According to the activated complex theory, the rate constant of an elementary step is:

$$k = \frac{k_B T}{h} K_c^\ddagger = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta U^\ddagger}{RT}\right)$$

(see any textbook in physical chemistry for designations). The experimentally observed activation energy is defined as:

$$E_a = RT^2 \frac{d \ln k}{dT}$$

Substituting the rate constant into this definition, we get:

$$E_a = RT^2 \left(\frac{1}{T} + \frac{\Delta C_v^\ddagger}{RT} + \frac{\Delta U^\ddagger}{RT^2} - \frac{\Delta C_v^\ddagger}{RT} \right) = RT + \Delta U^\ddagger = RT + \Delta H^\ddagger - \Delta n^\ddagger RT$$

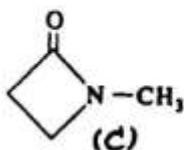
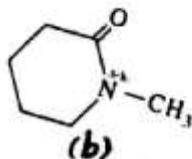
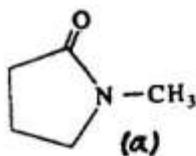
This is a rather trivial exercise for undergraduate students in the course of chemical kinetics.

Inorganic Chemistry

1. Explain briefly the observation that the energy difference between the $1s^2 2s^1, ^2S_{1/2}$ and the $1s^2 2p^1, ^2P_{1/2}$ states for Li is 14904 cm^{-1} , whereas for Li^{2+} the $2s^1, ^2S_{1/2}$ and $2p^1, ^2P_{1/2}$ states differ by only 2.4 cm^{-1} .

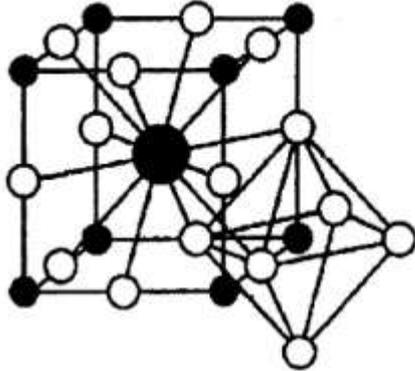
Solution. The large energy difference between two electronic states in a Li atom is due to electron-electron repulsions. Li^{2+} is a hydrogen-like ion with only one electron. So, there are no electron-electron interactions in this ion. The very small difference between energies of the $^2S_{1/2}$ and $^2P_{1/2}$ electronic states is due to spin-orbit interaction which for lithium is much weaker than the electron-electron Coulomb interaction.

2- Compare the carbonyl basicity of the serie given below. Account for the order / explain your reason.



Solution. The difference between these compounds is in the number of atom in a cycle. In case (c), because of the conformation of the cycle p -orbital of nitrogen atom is not parallel to p -orbitals of double $\text{C}=\text{O}$ bond, therefore their conjugation is not complete. When the increase of the number of atoms in a cycle, the orbitals have more opportunities to conjugate. If the orbital of a nitrogen atom is completely conjugated with the $\text{C}=\text{O}$ bond, the electron density on oxygen is higher because oxygen is more electronegative than nitrogen. The higher is electron density on oxygen atom, the larger is the carbonyl basicity of a compound. So, the strongest base is (b), and the weakest – (c).

- 3- (i) For $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, identify which cation (s) is (are) represented by the labels A and B in the general perovskite structure shown below.
- (ii) What is formal oxidation state of Mn in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$?
- (iii) What are the coordination numbers of the large cation (A), small cation (B) and oxygen?
- (iv) How many cubic holes are there per unit cell in a perovskite – based structure?



- Large cation (A)
- Octahedral cation (B)
- Oxygen

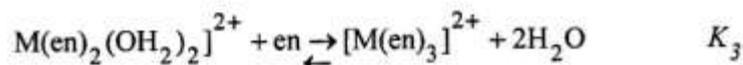
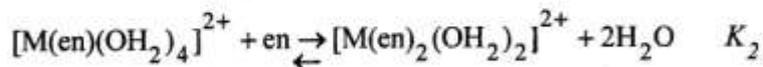
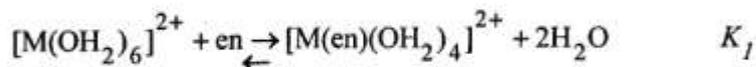
Solution. (i) (A) is a large cation, it should be La or Sr, (B) is Mn because the radii of lanthanides are higher than the radius of Mn.

(ii) La and Sr oxidation states are +3 and +2 respectively, and oxygen oxidation state is -2 , so the formal oxidation state of Mn is: $3 \cdot 2 - 0.7 \cdot 3 - 0.3 \cdot 2 = +3.3$.

(iii) La cation has 12 neighboring oxygen atoms, so its coordination number is 12. Atom of Mn has an octahedral environment, so its coordination number is 6. Oxygen has only 2 nearest neighbors, so its coordination number is 2.

(iv) There are 4 cubic holes.

4- The equilibrium constants for the successive reactions of ethylenediamine with Co^{2+} , Ni^{2+} , and Cu^{2+} are as follows:



Ion	Log K_1	Log K_2	Log K_3
Co^{2+}	5.89	4.83	3.10
Ni^{2+}	7.52	6.28	4.26
Cu^{2+}	10.72	9.31	-1.0

Discuss whether these data support the generalizations about successive formation constants and the Irving-Williams series. How do you account for the very low value of K_3 for Cu^{2+} ?

Solution. These constants support the generalizations about successive formation constants. Also they support the Irving-Williams series.

Because of Jahn-Teller distortion, Cu^{2+} cation prefers to form planar square complexes. So, the square complex with 2 molecules of ethylenediamine is much more stable than the octahedral complex with 3 molecules of ethylenediamine. This is why K_3 is very small for Cu^{2+} .

5. Predict and justify the relative linewidths and intensities of the following electronic transitions:

- $\text{Mn}(\text{H}_2\text{O})_6^{2+}$
- CuCl_4^{2-}
- $\text{Eu}(\text{H}_2\text{O})_8^{3+}$

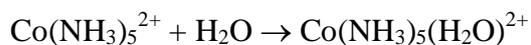
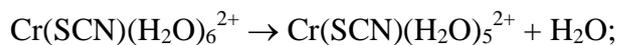
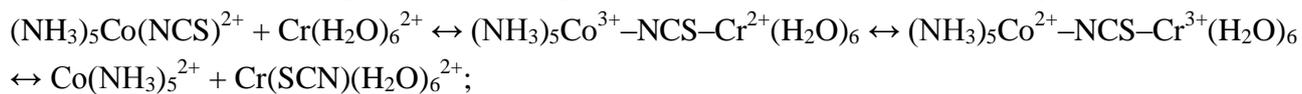
Solution. a) In $\text{Mn}(\text{H}_2\text{O})_6^{2+}$, manganese has 5 unpaired electrons, so there are no spin-allowed electron transitions for this complex. Also there is no charge transfer in this complex in vis-region. So the line in uv-vis spectrum will have low intensity and small linewidth.

b) In tetrahedral CuCl_4^{2-} , copper has one unpaired electron, so there is spin-allowed electron transition between e and t_2 orbitals. There is a charge transfer. So, in the spectrum of the complex there is an intense and wide line.

c) $\text{Eu}(\text{H}_2\text{O})_8^{3+}$ has no spin-allowed electron transitions, so the lines in its spectrum have low intensity and small linewidth.

6. Show a detailed mechanism for the electron transfer reaction of $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ and $(\text{NH}_3)_5\text{Co}(\text{NCS})^{2+}$. Identify precursor and successor complexes and justify why each intermediate forms and the resulting products of the reaction.

Solution. This is an example of the inner-sphere electron transfer. The reaction proceeds as follows:



First, sulfur's electron pair attacks Cr atom. Cr^{2+} has an empty d-orbital which accepts a sulfur's electron pair forming the bridge between two complexes. In the second step, one electron from Cr transfers to Co through $-\text{S}=\text{C}=\text{N}-$ bonds. Now Cr is oxidized and Co is reduced. Then, Co-N bond breaks. And finally, Cr-complex loses one molecule of water resulting in $\text{Cr}(\text{SCN})(\text{H}_2\text{O})_5^{2+}$ whereas Co-complex reacts with water molecule and becomes $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$.

7- Given below is a list of items. Choose from the list the item that completes or is associated with the question.

Note: An item may apply to more than one question and there may be more than one choice although only one answer is required.

- A soft acid:
- A substantially labile complex:
- A carbonylate complex:
- A d^8 square planar complex:
- A good trans-activating or directing species:
- A metallocene complex:
- A potential ligand that is isoelectronic with CO but is a poor σ -donor and a poor π -acceptor ligand:
- A complex having a bridging carbonyl ligand(s):
- An abbreviation for specific ligand having 3 potential sites (or atoms):
- A potential di-hapto (η^2) ligand:
- A complex with a metal-metal bond:
- A complex having an anti-prismatic structure:
- A macrocyclic ligand:
- A complex with a Jahn-Teller distortion:
- A complex with D_3 point group:

List:

AuCl_4^-	F^-
C_2H_4	$\text{Fe}(\text{CO})_5$
CN^-	$\text{Fe}_2(\text{CO})_9$
$\text{Co}_2(\text{CO})_8$	H^+
$\text{Cr}(\text{aq})^{3+}$	H^-
$\text{Cr}(\text{aq})^{2+}$	$\text{Mo}(\text{CN})_8^{4-}$
Crown ether	$\text{Mn}(\text{CO})_5^-$
$(\text{Cp})_2\text{ReH}$	$\text{Mn}_2(\text{CO})_{10}$
Cyclam	N_2
dien	trien
$(\text{Ph}_3\text{P})_3\text{Pt}$	RhCl_6^{4-}
PtCl_6^{2-}	$\text{Ru}(\text{bpy})_3^{2+}$
ReCl_8^{2-}	$[\text{Zr}_6\text{F}_{31}]^{7-}$
RhCl_6^{3-}	NO
en	

Solution. a) $\text{Ru}(\text{bpy})_3^{2+}$

b) $\text{Mo}(\text{CN})_8^{4-}$

c) $\text{Mn}(\text{CO})_5^-$

d) AuCl_4^-

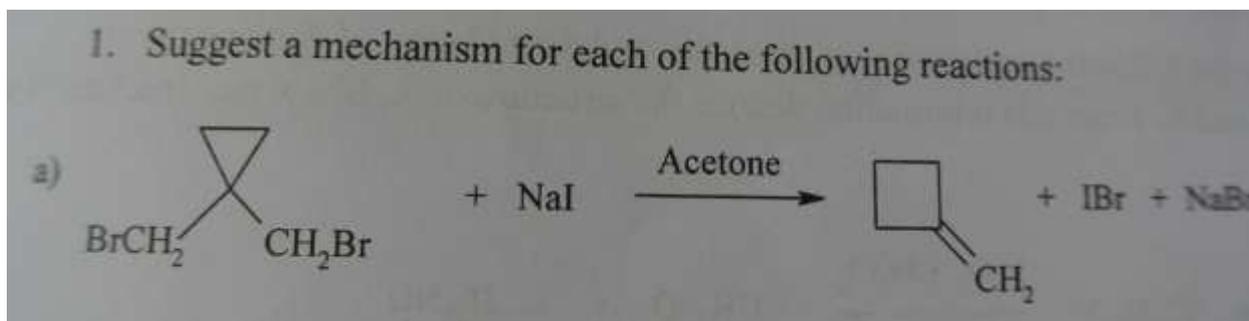
e) NO

- f) $(\text{Cp})_2\text{ReH}$
- g) N_2
- h) $\text{Mn}_2(\text{CO})_{10}$
- i) trien
- j) dien
- k) $[\text{Zr}_6\text{F}_{31}]^{7-}$
- l) ReCl_8^{2-}
- m) crown ether
- n) RhCl_6^{4-}
- o) $(\text{Ph}_3\text{P})_3\text{Pt}$

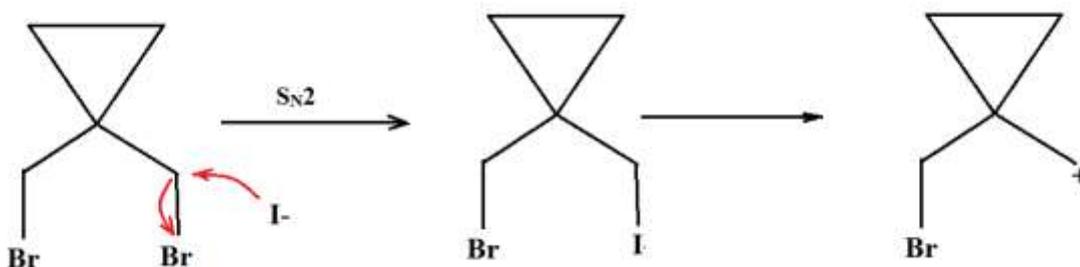
Organic Chemistry

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№ 1.

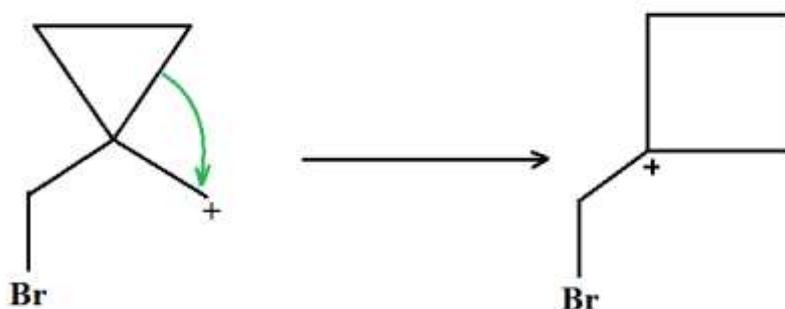


For the first stage we can propose S_N2 reaction with iodide-ion and subsequent formation of a carbocation:

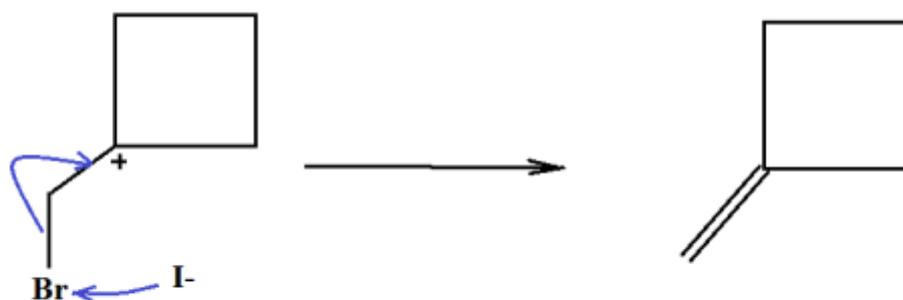


However, the carbocation can be generated directly from the initial substance by the elimination of bromide-anion.

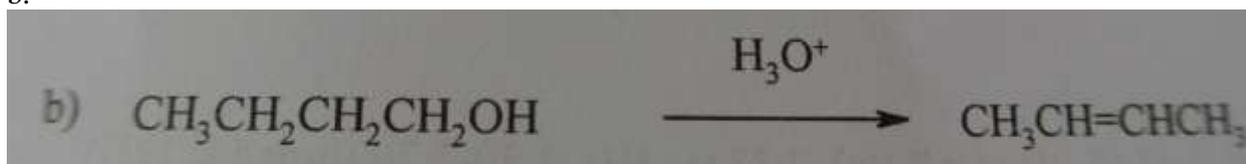
The next step is an alkyl shift, which leads to the formation of the corresponding cyclobutane derivative:



Finally, the elimination of Br^+ in the form of IBr proceeds and the alkene is generated:



b.



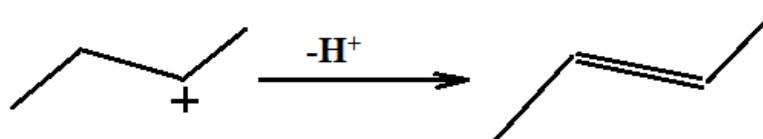
First, the protonation of the hydroxyl oxygen takes place, then the elimination of water to form an unstable primary carbocation:



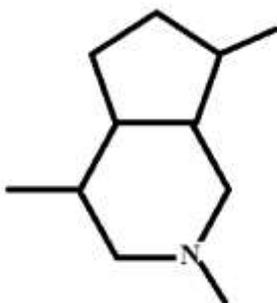
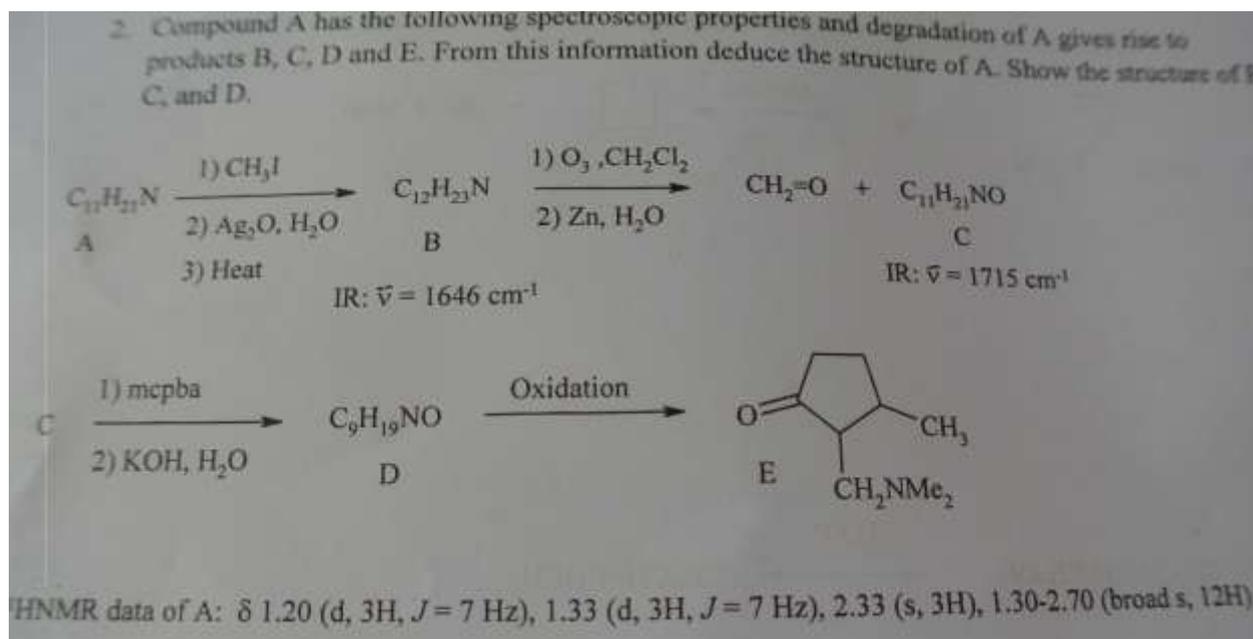
The primary carbocations are significantly less stable than the secondary ones, so this carbocation undergoes hydride shift :



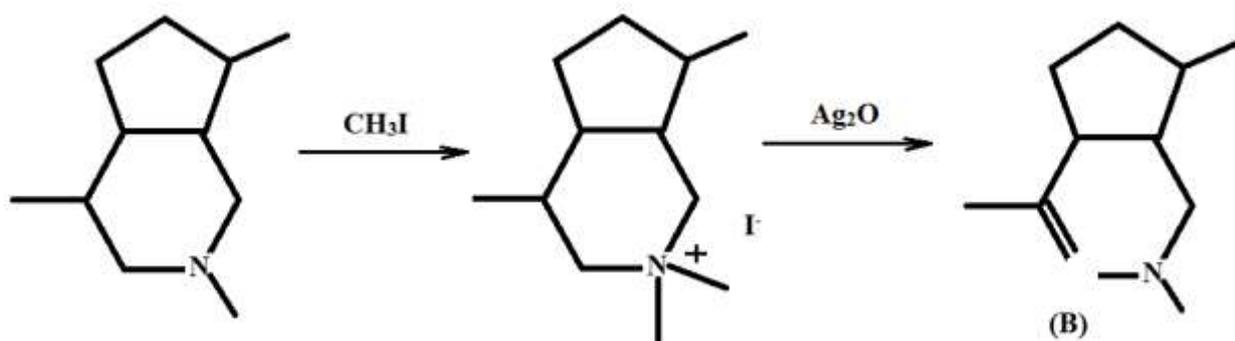
Then, the most stable double-substituted alkene (2-butene) is produced:



№ 2

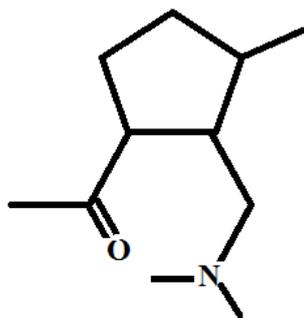


A - Signals at 1.20 and 1.33 ppm correspond to the protons of methyl groups, connected to carbon atoms. Singlet at 2.33 ppm arises from protons of the methyl group, which is connected to nitrogen. Other protons have rather close chemical shifts and complex multiplicity, and so they appear as a broad singlet. The reaction $A \rightarrow B$ is the Hofmann elimination:



The absorbance at 1646 cm^{-1} in the infrared spectrum is due to the presence of carbon-carbon double bond in this compound.

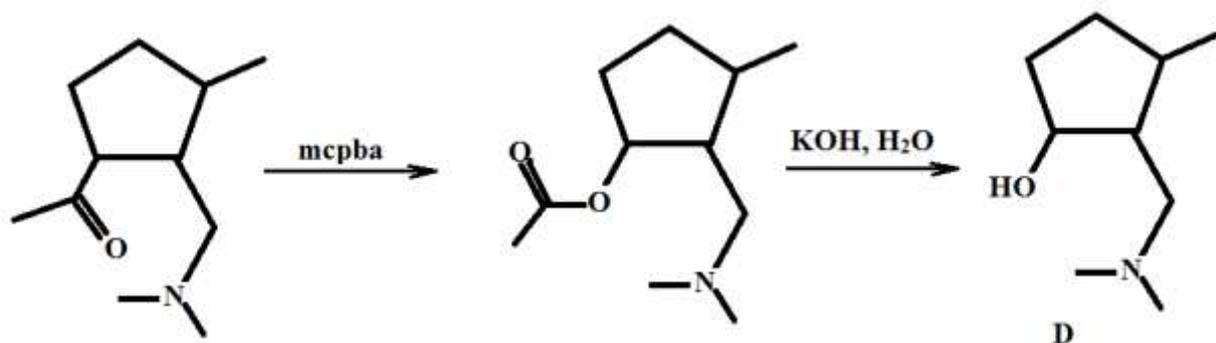
The next step is ozonolysis and the product is a corresponding ketone:



C-

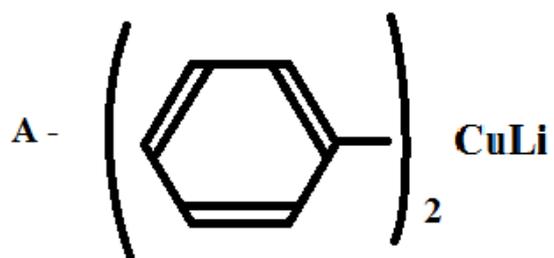
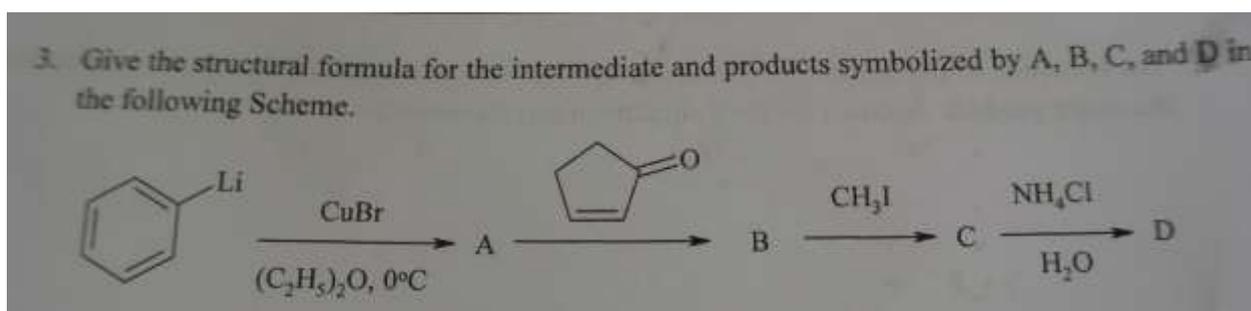
Carbonyl group in this compound gives a signal at 1715 cm^{-1} in IR spectrum

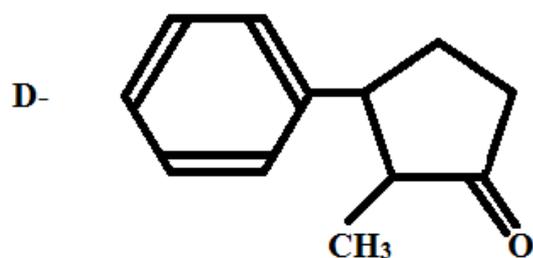
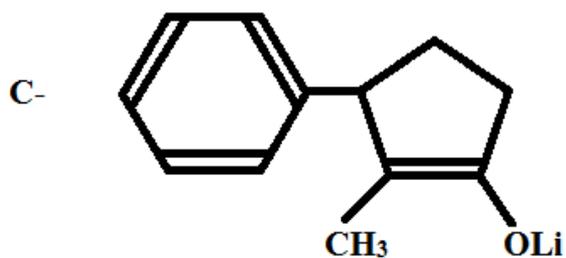
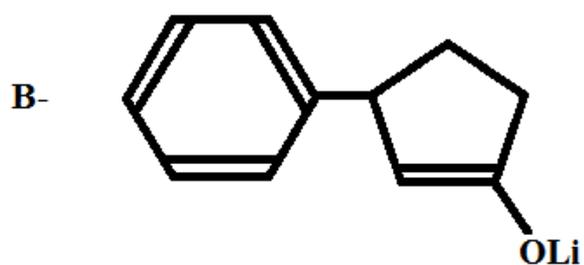
Reaction of this ketone with mcpba (Baeyer–Villiger oxidation) leads to an ester, in which secondary alkyl group migrates easier than primary one, the subsequent hydrolysis of the ester gives an alcohol:



The oxidation of D simply turns the hydroxyl group into carbonyl (product E)

№ 3.

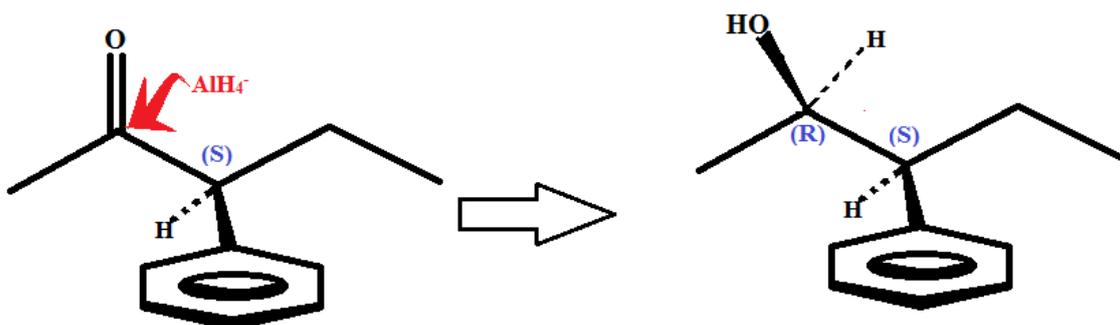




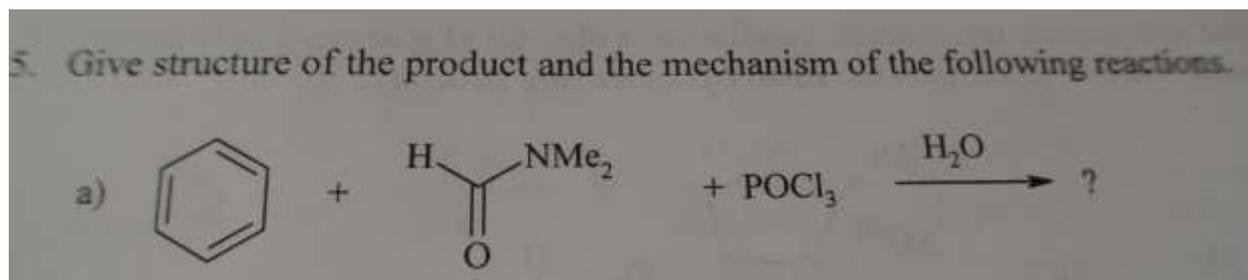
№ 4.

The reduction of (S)-3-phenyl-2-pentanone by LiAlH_4 produces (2R),(3S)-3-phenyl-2-pentanol as the major product. Account for the formation of this stereoisomer as the major product.

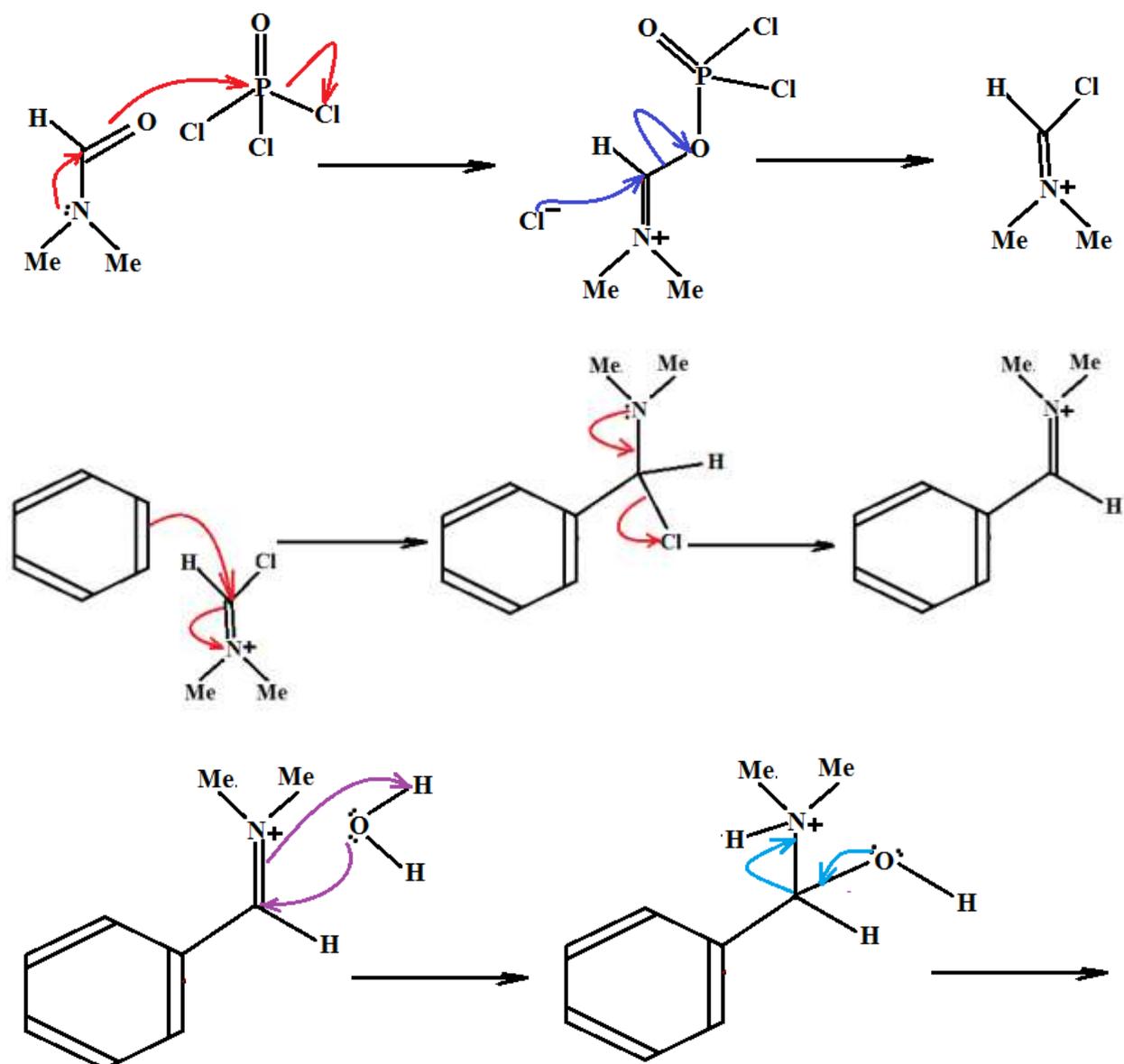
Structural formula of (S)-3-phenyl-2-pentanone is shown in the picture. The attack of an AlH_4^- ion occurs from the less sterically hindered side. A benzene ring is undoubtedly a serious steric hindrance, so attack proceeds from the opposite side, generating a (2R)-stereocenter:

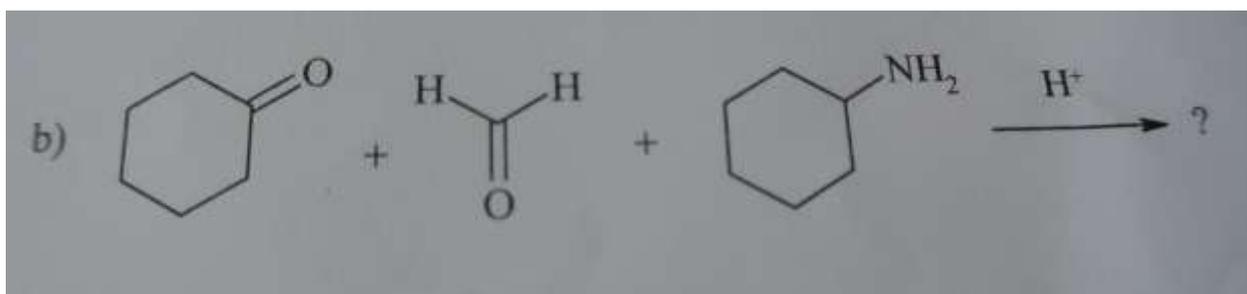
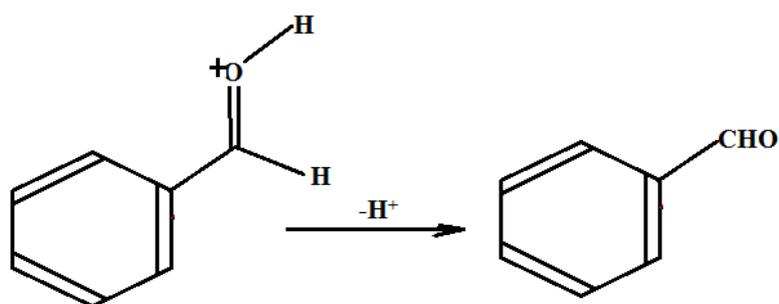


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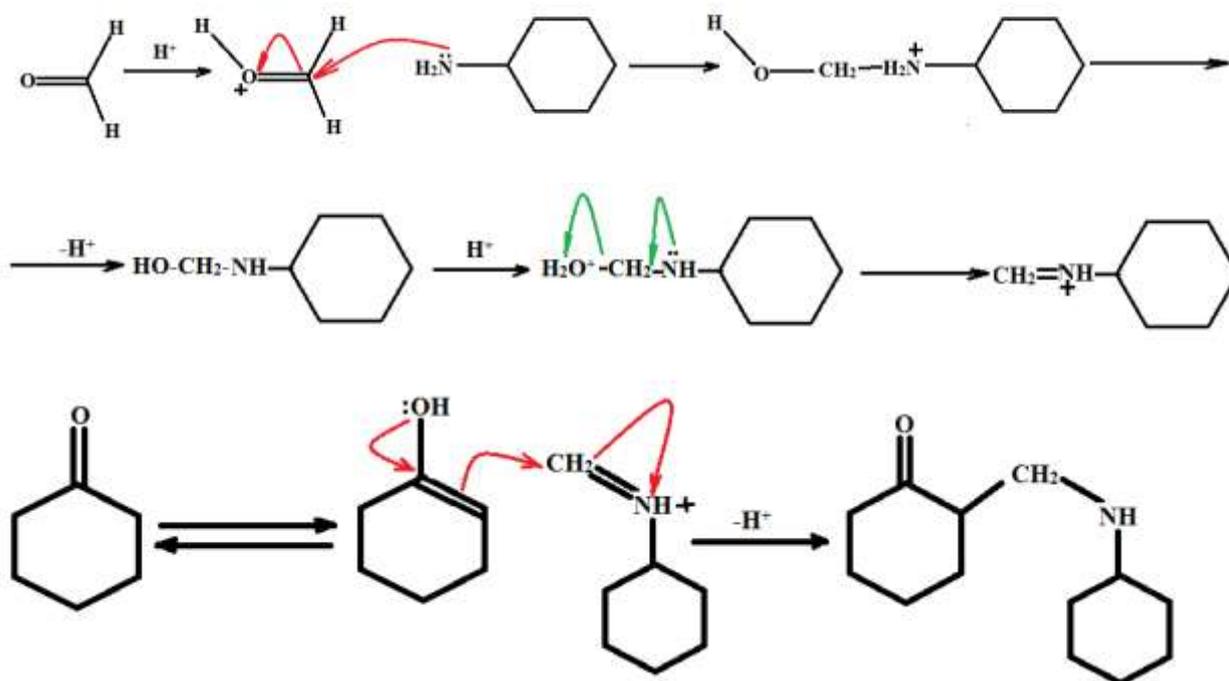


This is the Vilsmeier-Haack reaction. The mechanism of this reaction involves iminium cation as an intermediate. It reacts with benzene to produce a corresponding iminium ion, hydrolysis of which gives benzaldehyde.

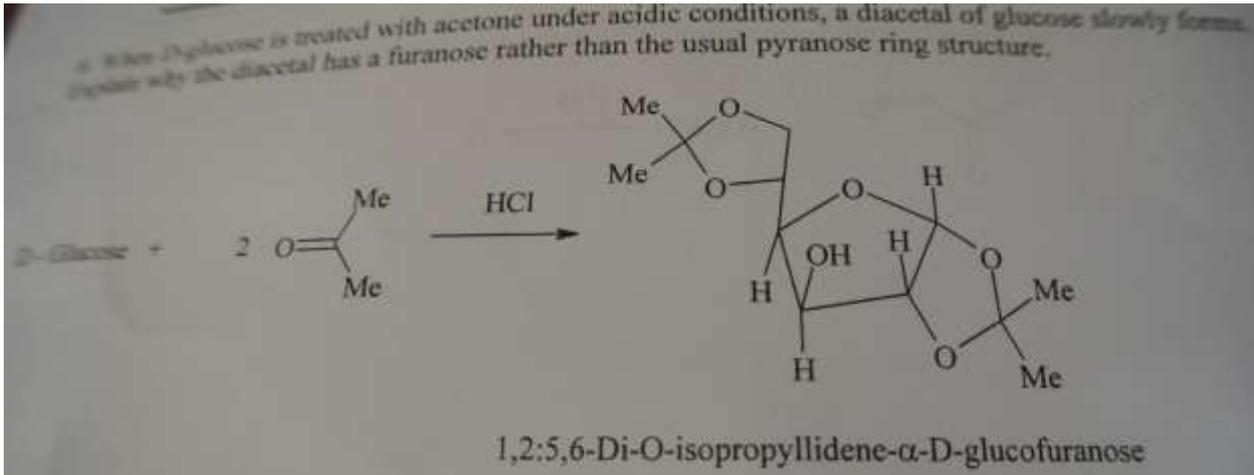




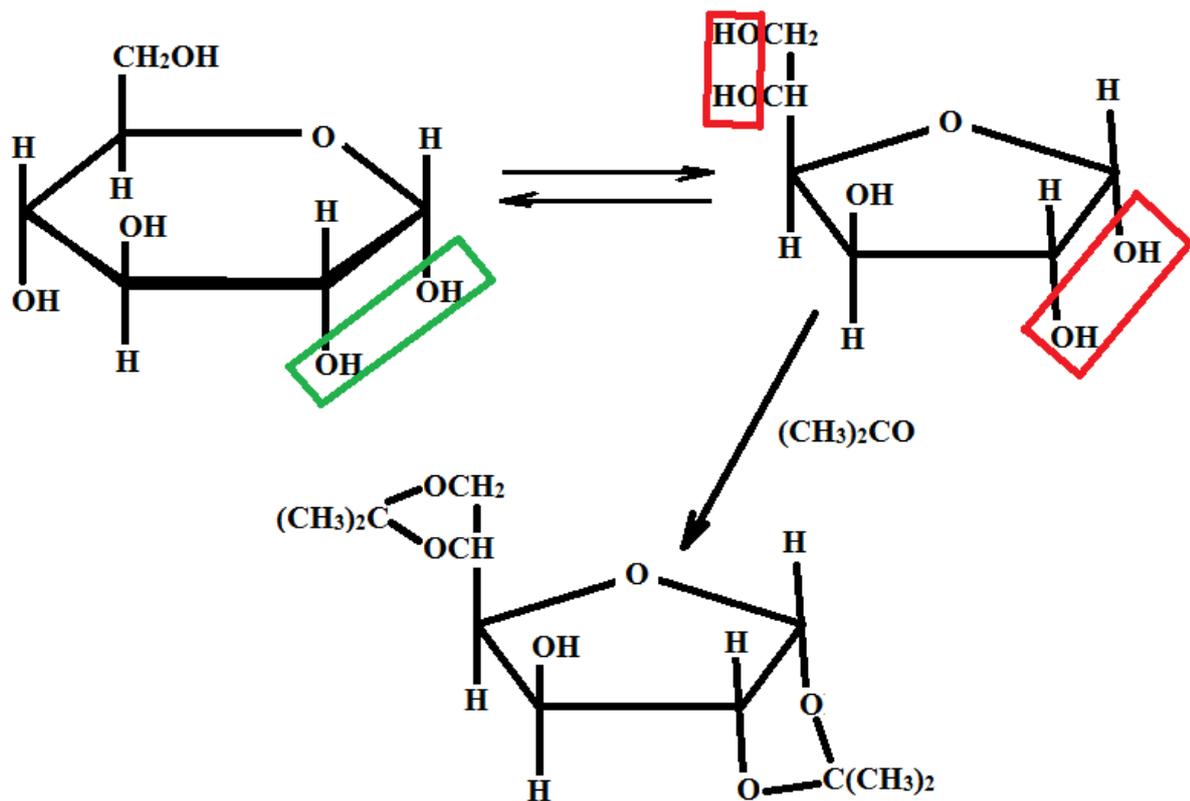
This is the Mannich reaction. First, formaldehyde and amine form an imine, which reacts with the enol form of cyclohexanone. The product is a corresponding amine.



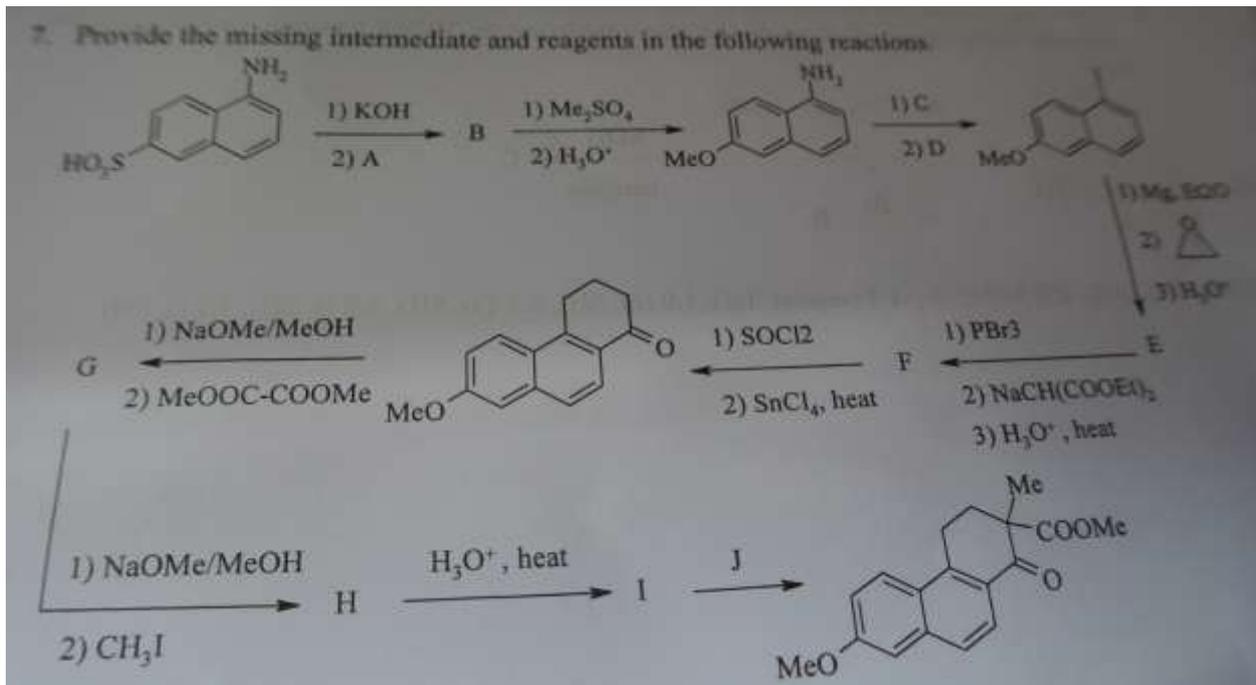
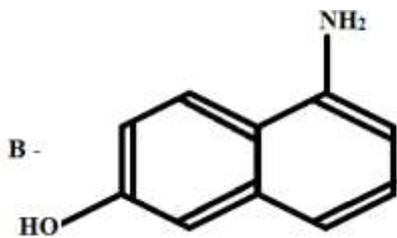
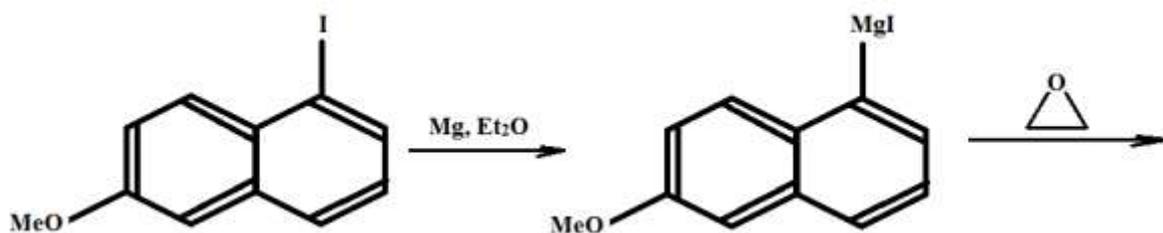
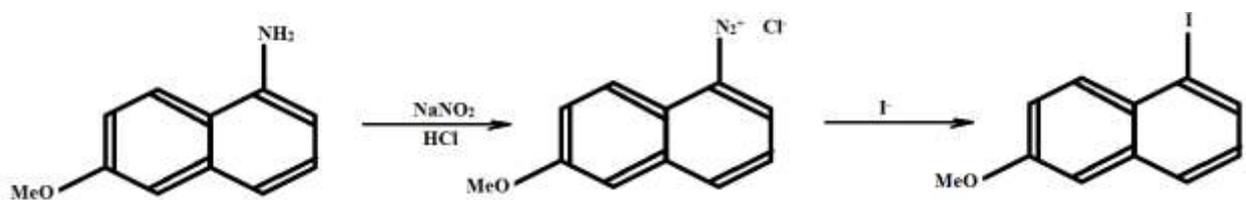
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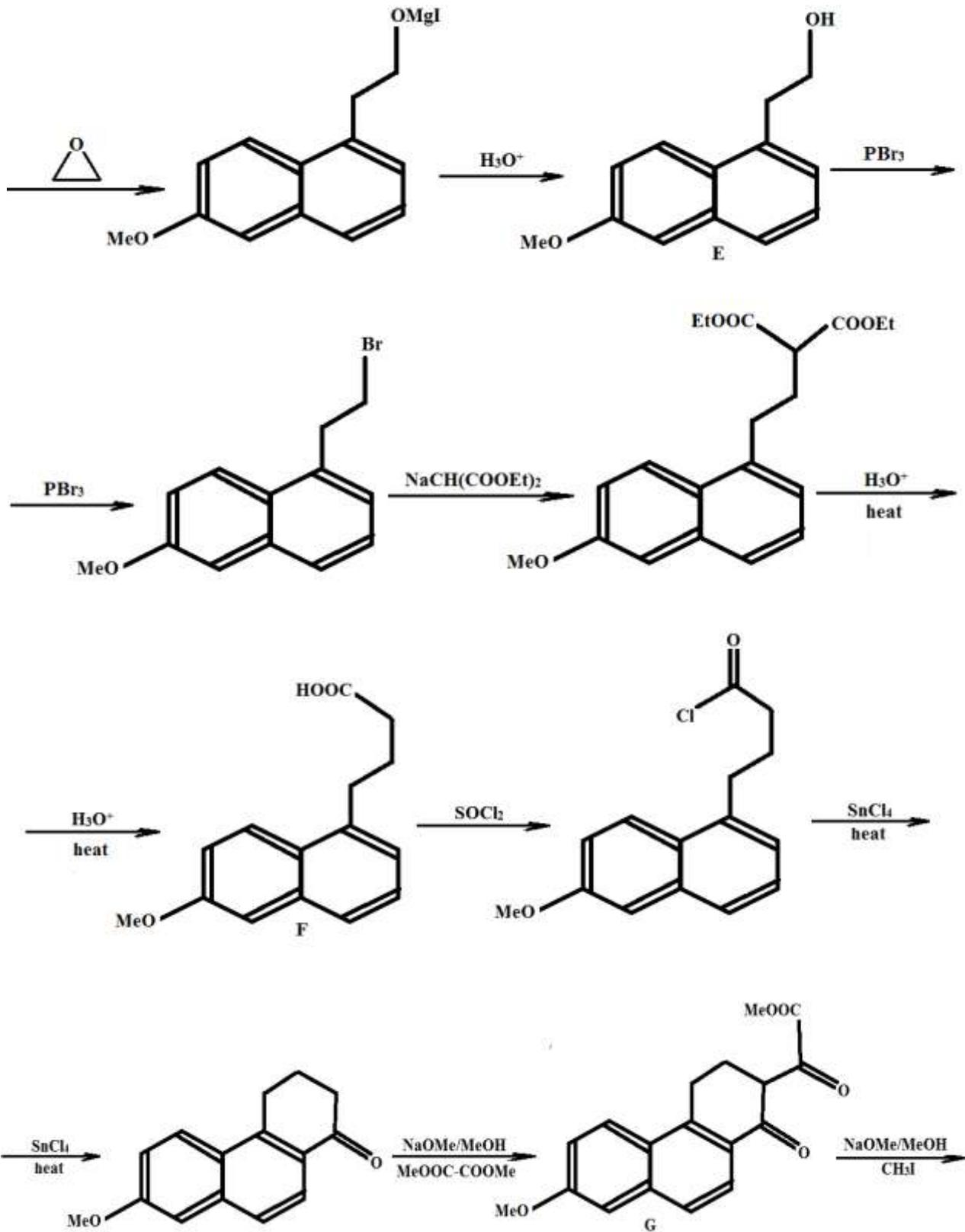


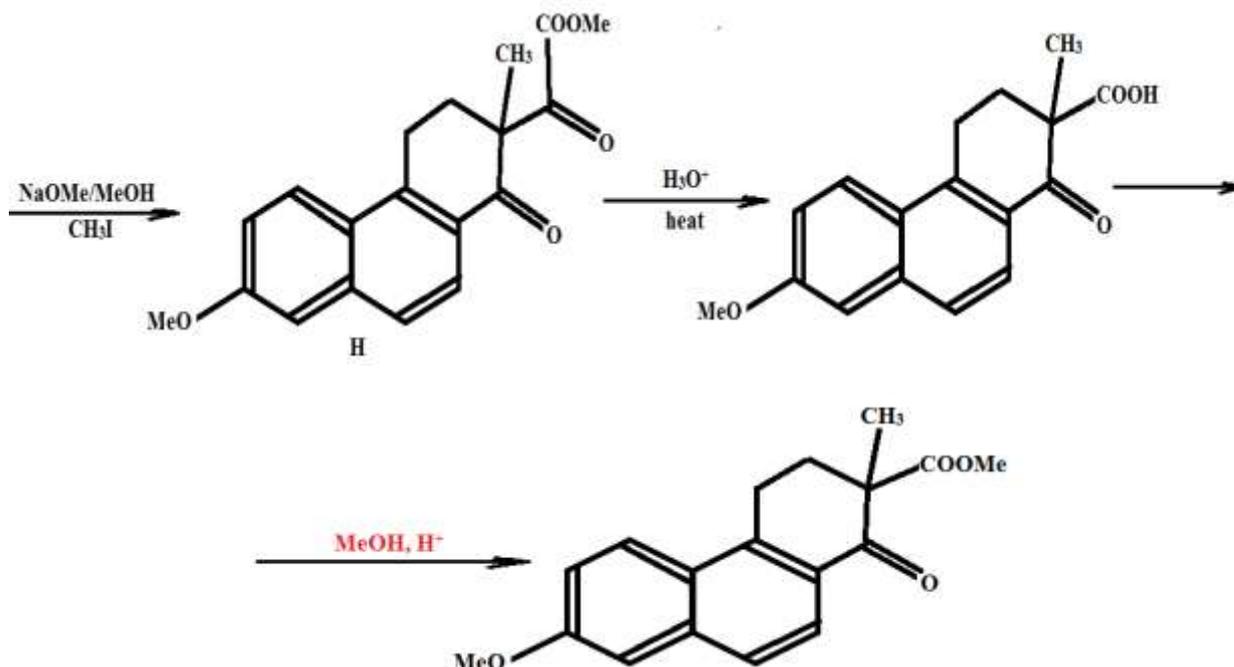
In a pyranose form, α -D-glucose has only vicinal diol group, which is able to react with acetone. It exists in equilibrium with a furanose form, which has two such groups and gives more stable product:



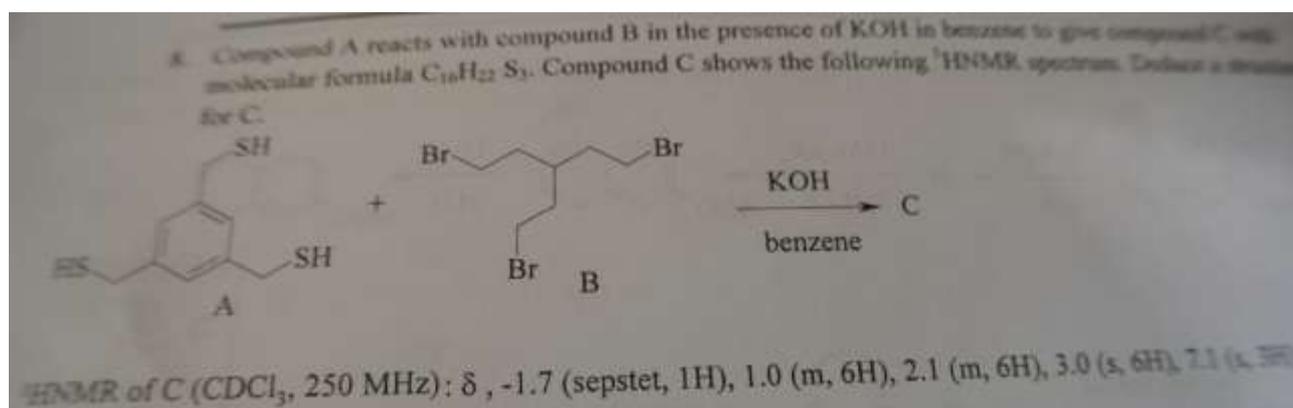
№ 7.

A – H^+ (any diluted acid is appropriate)C – $\text{NaNO}_2 + \text{HCl}$ D – I^- 





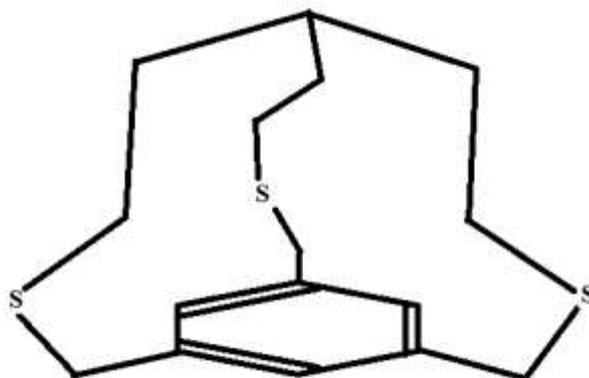
№ 8.



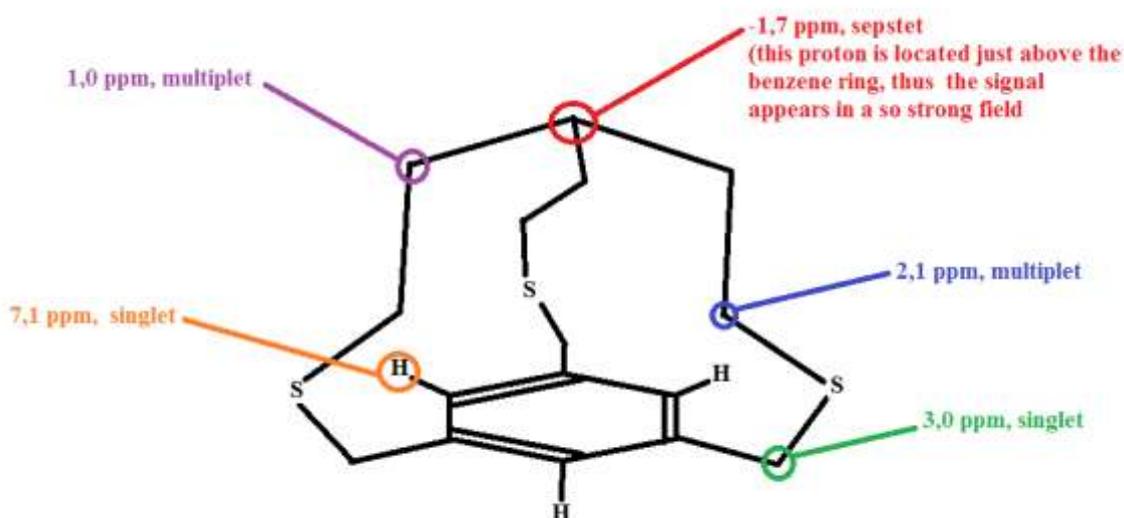
Under alkali conditions, thiole group becomes a good nucleophile. So, nucleophilic substitution can take place:



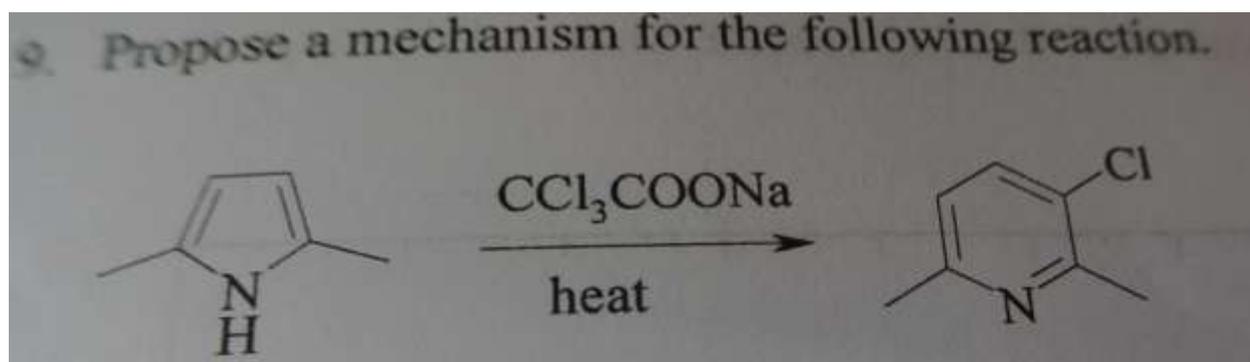
Both molecules have three -SH and -CH₂Br groups. So, nucleophilic substitution can take place three times to form the following product.



As we can see, this product correlates with the given spectral data:



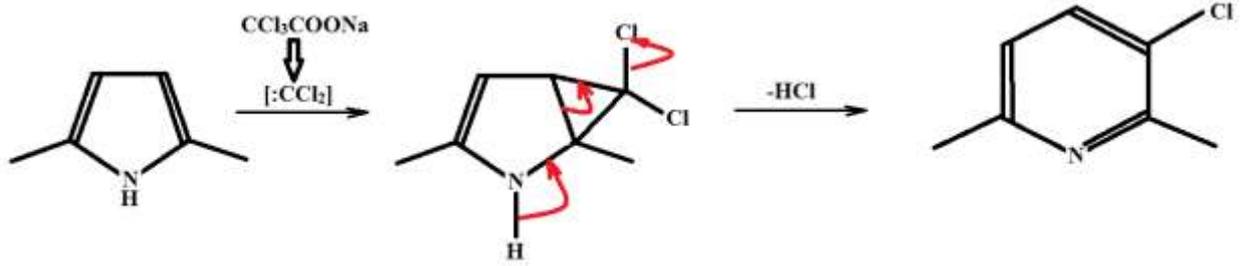
№ 9.



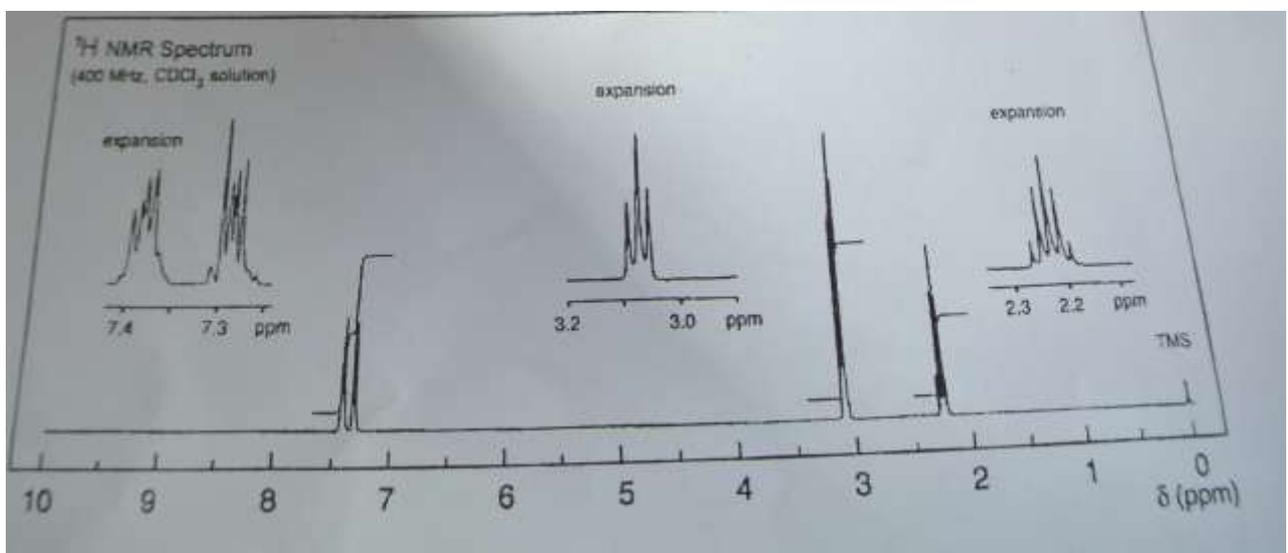
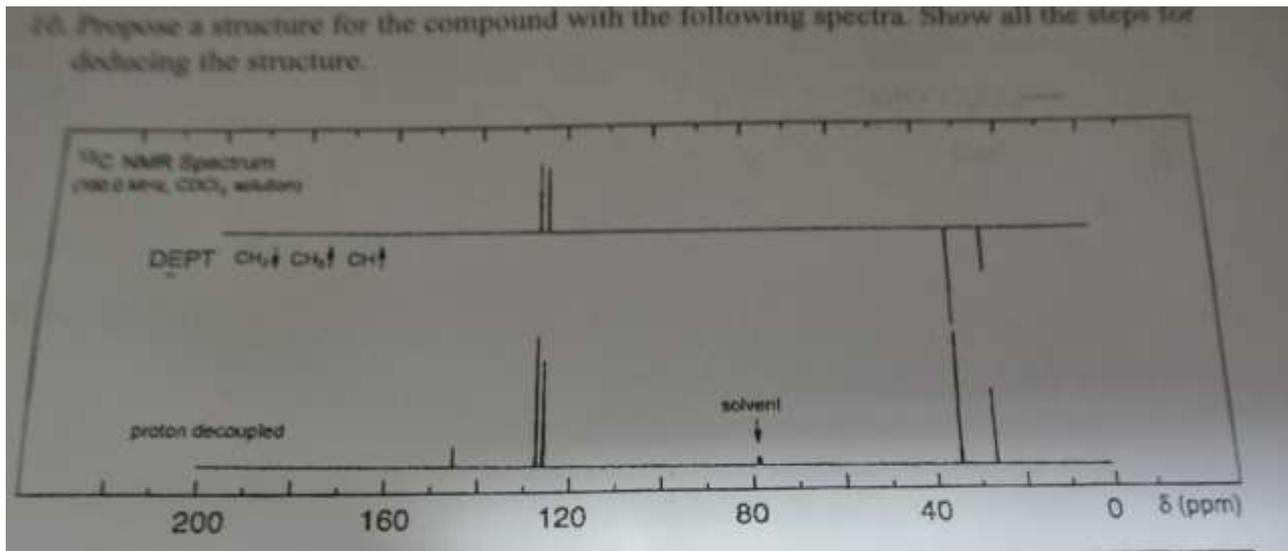
CCl_3COONa while being heated produces dichlorocarbene CCl_2 :

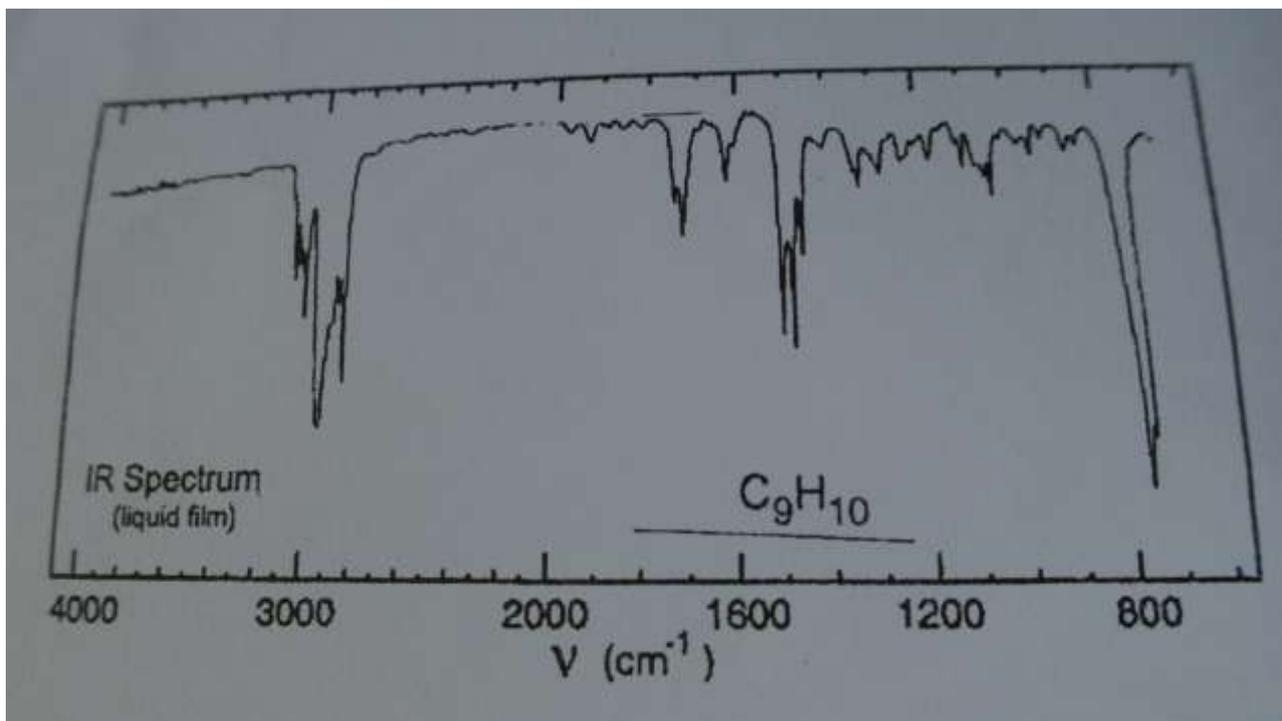


The reaction of a substituted pyrrole with dichlorocarbene proceeds through the dichlorocyclopropane derivative intermediate. The expansion of the cycle leads to the formation of a substituted pyridine.



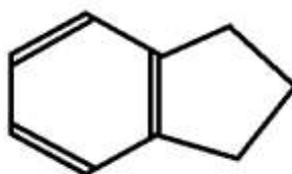
№ 10.



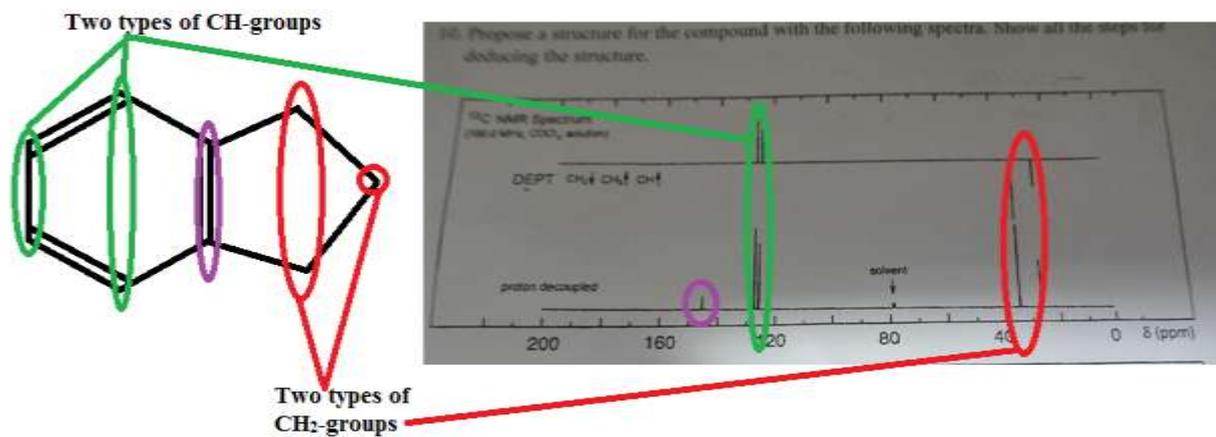


First, look at the molecular formula, C_9H_{10} . The degree of unsaturation is $(9 \cdot 2 + 2 - 10) / 2 = 5$. A benzene ring is likely to be present in this molecule. The 1H -NMR spectrum confirms this assumption: complex multiplets near 7-8 ppm seem to be the signals of aromatic protons. But one benzene ring gives only 4 degrees of unsaturation. Then, we have 3 carbon atoms and one degree of unsaturation left.

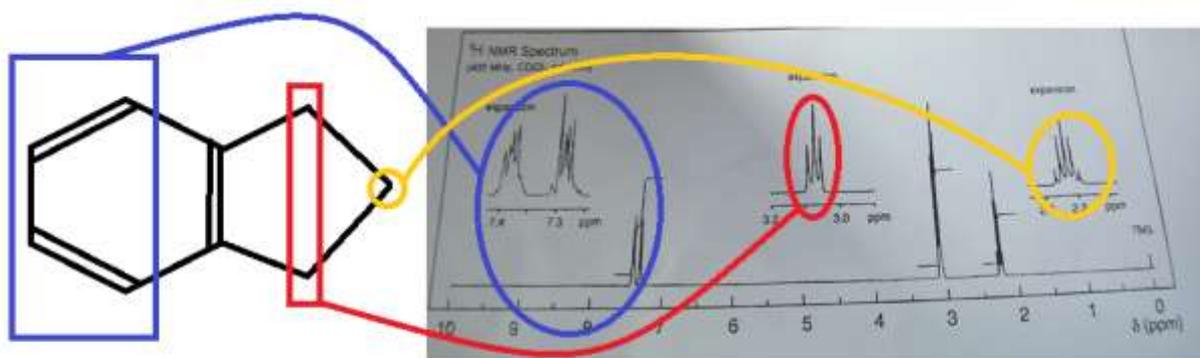
As we see from DEPT spectrum, there are two types of CH_2 -groups. The presence of a triplet at 3.1 ppm and a quintet at 2.2 ppm in the 1H -NMR spectrum with the ratio of relative intensities 2:1 suggests a fragment $-CH_2-CH_2-CH_2-$, in which the first and the last methylene groups are equivalent. So, the only possible structure is:



Assignment of the ^{13}C -NMR spectrum:



Assignment of the ¹H-NMR spectrum:



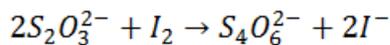
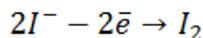
IR spectrum just shows the presence of aromatic and aliphatic protons (near 3000 cm⁻¹) and double carbon-carbon bonds (near 1600 cm⁻¹).

Analytical Chemistry and Instrumental Analysis

تحليل كلام و شيمياء تجزيه

- 1- To determine the purity of a sample of $\text{Na}_2\text{S}_2\text{O}_3$, the sample is titrated coulometrically using Γ as a mediator and I_3^- as the titrant. A sample weighing 0.1342 g is transferred to a 100-mL volumetric flask and diluted to volume with distilled water. A 10.00-mL portion is transferred to an electrochemical cell along with 25 mL of 1 M KI, 75 mL of a pH 7.0 phosphate buffer, and several drops of a starch indicator solution. Electrolysis at a constant current of 36.45 mA requires 221.8 s to reach the starch indicator endpoint. Determine the purity of the sample.
 $\text{Na}_2\text{S}_2\text{O}_3 = 158.1 \text{ g/mol}$

The corresponding processes are:



From these equations, $\nu(\bar{e}) = \nu(\text{S}_2\text{O}_3^{2-}) = \frac{It}{F}$. The overall mass of pure $\text{Na}_2\text{S}_2\text{O}_3$ is:

$$m_0 = \frac{V_{\text{flask}}}{V_{\text{portion}}} \nu(\text{S}_2\text{O}_3^{2-}) M_{\text{Na}_2\text{S}_2\text{O}_3}$$

Expression for purity in %:

$$\text{purity} = \frac{m_0}{m_{\text{sample}}} \cdot 100\% = \frac{V_{\text{flask}}}{V_{\text{portion}}} \frac{It}{F} M_{\text{Na}_2\text{S}_2\text{O}_3} \frac{100\%}{m_{\text{sample}}} = 98.7\%$$

- 2- 1.00 mmole of thionile fluoride (SOF_2) gas was absorbed in 100 mL of water solution.
- Calculate the pH of the solution.
 - What volume of 0.10 M NaOH should be added to the solution to increase the pH up to 4.00?
- ($\text{SOF}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 + 2\text{HF}$)
 H_2SO_3 ; $K_{a1} = 1.70 \times 10^{-2}$, $K_{a2} = 5.00 \times 10^{-6}$
 $K_a = 6.40 \times 10^{-4}$

a) $c_{\text{H}_2\text{SO}_3}^0 = 10^{-2} \text{ M}$, $c_{\text{HF}}^0 = 2 \cdot 10^{-2} \text{ M}$

Assume that $[\text{SO}_3^{2-}]$ and $[\text{OH}^-]$ are negligible at these conditions. Then,

$$[\text{HSO}_3^-] + [\text{H}_2\text{SO}_3] = c_{\text{H}_2\text{SO}_3}^0 = [\text{HSO}_3^-] \left(1 + \frac{[\text{H}^+]}{K_{a1}} \right) \Rightarrow [\text{HSO}_3^-] = \frac{K_{a1} c_{\text{H}_2\text{SO}_3}^0}{K_{a1} + [\text{H}^+]}$$

$$[\text{F}^-] = \frac{K_a c_{\text{HF}}^0}{K_a + [\text{H}^+]}$$

Equation of electroneutrality at the assumptions made:

$$[HSO_3^-] + [F^-] = [H^+] \Leftrightarrow \frac{K_{a_1} c_{H_2SO_3}^0}{K_{a_1} + [H^+]} + \frac{K_a c_{HF}^0}{K_a + [H^+]} = [H^+].$$

This is a cubic equation with respect to $[H^+]$, but we can simplify it.

Since $[H^+] \gg K_a$, $[H^+]^3 + K_{a_1}[H^+]^2 \approx K_{a_1}K_a c_{HF}^0 + (K_{a_1}c_{H_2SO_3}^0 + K_a c_{HF}^0)[H^+]$. Since

$K_{a_1}K_a c_{HF}^0 \sim 10^{-8}$, we can assume it to be negligible. $[H^+]$ can be obtained from the resulting quadratic equation:

$$[H^+] = \frac{-K_{a_1} + \sqrt{K_{a_1}^2 + 4(K_{a_1}c_{H_2SO_3}^0 + K_a c_{HF}^0)}}{2} = 7.47 \cdot 10^{-3}, \text{ so } pH = 2.13.$$

$$b) c_{H_2SO_3}^{i0} = \frac{V_0}{V_0 + V_{NaOH}} c_{H_2SO_3}^0, c_{HF}^{i0} = \frac{V_0}{V_0 + V_{NaOH}} c_{HF}^0, [H^+] = 10^{-4} M, [Na^+] = \frac{c_{NaOH} V_{NaOH}}{V_0 + V_{NaOH}}$$

$$\alpha_{SO_3^{2-}} = \frac{1}{1 + \frac{[H^+]}{K_{a_2}} + \frac{[H^+]^2}{K_{a_1}K_{a_2}}} = 4.74 \cdot 10^{-2}, \alpha_{HSO_3^-} = \frac{\frac{[H^+]}{K_{a_2}}}{1 + \frac{[H^+]}{K_{a_2}} + \frac{[H^+]^2}{K_{a_1}K_{a_2}}} = 9.47 \cdot 10^{-1}$$

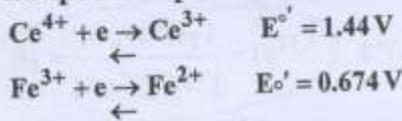
$$\alpha_{F^-} = \frac{1}{1 + \frac{[H^+]}{K_a}} = 8.65 \cdot 10^{-1}$$

Equation of electroneutrality:

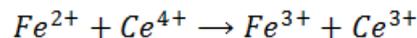
$$2\alpha_{SO_3^{2-}} c_{H_2SO_3}^{i0} + \alpha_{HSO_3^-} c_{H_2SO_3}^{i0} + \alpha_{F^-} c_{HF}^{i0} + [OH^-] = [Na^+] + [H^+]$$

$$\text{Thus, } V_{NaOH} = \frac{(2\alpha_{SO_3^{2-}} c_{H_2SO_3}^0 + \alpha_{HSO_3^-} c_{H_2SO_3}^0 + \alpha_{F^-} c_{HF}^0 + \frac{K_w}{[H^+]}) V_0}{c_{NaOH} + [H^+] - \frac{K_w}{[H^+]}} = 27.6 \text{ ml}$$

3- A 50.00 mL portion of 0.0500 M Fe (II) solution is titrated with 0.1000 M Ce (IV) solution. Both solutions are 1.0 M in H_2SO_4 . Calculate the titration error, if the sodium salt of diphenylamine sulfonic acid is used as indicator (color change midpoint at potential of 0.85 V).



The redox process used for titration is:



Expressions for the redox potentials:

$$E_{Fe^{3+}/Fe^{2+}} = E_{Fe^{3+}/Fe^{2+}}^0 + 0.059 \lg \frac{[Fe^{3+}]}{[Fe^{2+}]}, E_{Ce^{4+}/Ce^{3+}} = E_{Ce^{4+}/Ce^{3+}}^0 + 0.059 \lg \frac{[Ce^{4+}]}{[Ce^{3+}]}$$

At the equilibrium point $[Fe^{2+}] = [Ce^{4+}]$, $[Fe^{3+}] = [Ce^{3+}]$ and $E_{Ce^{4+}/Ce^{3+}}^{eq} = E_{Fe^{3+}/Fe^{2+}}^{eq} = E_{eq}$,

so $E_{eq} = \frac{E_{Fe^{3+}/Fe^{2+}}^0 + E_{Ce^{4+}/Ce^{3+}}^0}{2} = 1.057 \text{ V}$. Since $E = 0.85 \text{ V} < E_{eq}$, titration error is negative.

$$E = E_{Fe^{3+}/Fe^{2+}}^0 + 0.059 \lg \frac{[Fe^{3+}]}{[Fe^{2+}]} \Rightarrow \frac{[Fe^{3+}]}{[Fe^{2+}]} = 10^{\frac{E - E_{Fe^{3+}/Fe^{2+}}^0}{0.059}}$$

The titration error is:

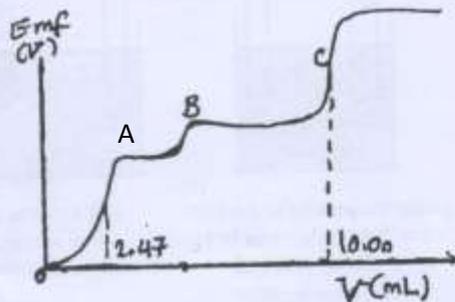
$$Err = - \frac{[Fe^{2+}]}{[Fe^{2+}] + [Fe^{3+}]} \cdot 100\% = - \frac{100\%}{1 + 10^{\frac{E - E_{Fe^{3+}/Fe^{2+}}^0}{0.059}}} = -0.1\%$$

- 4- 25.00 mL of neutral solution containing KCl and KCN is titrated potentiometrically with a 0.100 M AgNO₃ at 25 °C using an Ag-SCE electrode pair. Assume that the protonation of cyanide ion is negligible. The plot of titration curve of E vs. titrant volume is shown in Fig. The following data is available.

$$\beta_2 = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]} = 10^{21.1} \quad E^0(Ag^+/Ag) = 0.800 V \quad E^0_{SCE} = 0.258 V$$

$$K_{sp}(AgCN) = 10^{-15.8}, \quad K_{sp}(AgCl) = 10^{-9.75}$$

- (I) write an ionic balanced reaction for each A, B and C points in titration plot.
 (II) Calculate the concentration of KCl and KCN in the solution.
 (III) Calculate the emf (in volt) at A and C points.



- I) A: $Ag^+ + 2CN^- \leftrightarrow Ag(CN)_2^-$
 B: $Ag(CN)_2^- + Ag^+ \leftrightarrow 2AgCN$
 C: $Ag^+ + Cl^- \leftrightarrow AgCl$

II) $V_{AgNO_3}^1 c_{AgNO_3} = \frac{1}{2} V_0 c_{KCN} \Rightarrow c_{KCN} = \frac{2V_{AgNO_3}^1 c_{AgNO_3}}{V_0} = 0.02 M$
 $V_{AgNO_3}^2 c_{AgNO_3} = V_0 (c_{KCN} + c_{KCl}) \Rightarrow c_{KCl} = \frac{V_{AgNO_3}^2 c_{AgNO_3} - V_0 c_{KCN}}{V_0} = 0.02 M$

III) For point A: $[CN^-] = 2[Ag^+]$, $\beta_2 = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2}$, $[Ag(CN)_2^-] = \frac{V_{AgNO_3}^1 c_{AgNO_3}}{V_0 + V_{AgNO_3}^1}$.

$$\text{Thus, } [Ag^+] = \sqrt[3]{\frac{V_{AgNO_3}^1 c_{AgNO_3}}{4\beta_2 (V_0 + V_{AgNO_3}^1)}} = 1.21 \cdot 10^{-8} M.$$

Expression for emf: $emf = E_{Ag^+/Ag}^0 + 0.059 \lg [Ag^+] - E_{SCE}^0 = 0.075 V$

For point C: $[Ag^+][CN^-] = K_{sp}^{AgCN}$, $[Ag^+][Cl^-] = K_{sp}^{AgCl}$, $[CN^-] + [Cl^-] = [Ag^+]$

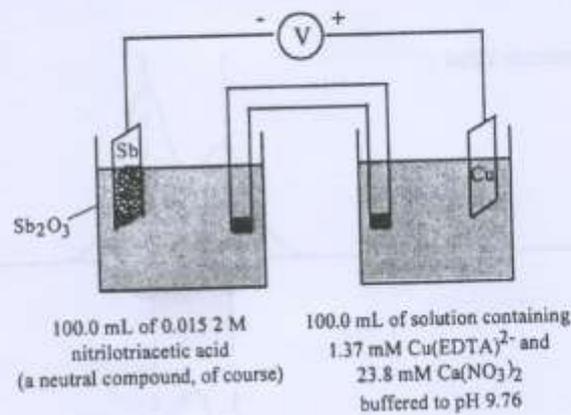
$$\text{Thus, } [Ag^+] = \sqrt{K_{sp}^{AgCN} + K_{sp}^{AgCl}} = 1.33 \cdot 10^{-5} M, \text{ emf} = 0.254 V$$

- 5- The monstrous cell below was set up. Then 50.0 mL of 0.0444 M Na₂EDTA was added to the right-hand compartment and 50.0 mL 0.0700 M NaOH was added to the left-hand compartment. The cell voltage leveled off at +0.418 V. Find the formation constant for CuY²⁻ (where Y = EDTA).

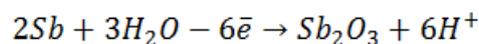
$$E_{Cu^{2+}/Cu}^{\circ} = 0.339 V, E_{Sb_2O_3/Sb}^{\circ} = 0.147 V$$

$$K_f(CaY^2) = 4.9 \times 10^{10}$$

for nitrilotriacetic acid : pK_{a1} = 3.032 , pK_{a2} = 3.071 pK_{a3} = 10.334



Process on an anode:



Expression for its potential:

$$E_{Sb_2O_3/Sb} = E_{Sb_2O_3/Sb}^{\circ} + 0.059 \lg [H^+] = E_{Sb_2O_3/Sb}^{\circ} - 0.059 pH$$

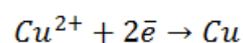
After adding NaOH to the left-hand compartment the buffer solution of Hnta²⁻/nta³⁻ is formed (here nta is nitrilotriacetic acid). The molar quantities of the corresponding species are:

$$v(nta) = 1.52 \cdot 10^{-3} \text{ mol}, v(NaOH) = 3.5 \cdot 10^{-3} \text{ mol} \Rightarrow v(nta^{3-}) = 4.6 \cdot 10^{-4} \text{ mol},$$

$$v(Hnta^{2-}) = 1.06 \cdot 10^{-3} \text{ mol}, [H^+] = \frac{K_{a3} [Hnta^{2-}]}{[nta^{3-}]} = 1.07 \cdot 10^{-10} M \Rightarrow pH = 9.97$$

The corresponding potential is: $E_{Sb_2O_3/Sb} = -0.441 V$

Process on a cathode:



Potential:

$$E_{Cu^{2+}/Cu} = E_{Cu^{2+}/Cu}^{\circ} + \frac{0.059}{2} \lg [Cu^{2+}]$$

Since $emf = E_{Cu^{2+}/Cu} - E_{Sb_2O_3/Sb}$, $E_{Cu^{2+}/Cu} = -0.023 V \Rightarrow [Cu^{2+}] = 5.36 \cdot 10^{-13} M$

Concentrations of complex species after adding the EDTA solution:

$$[CuY^{2-}] = [CuY^{2-}]_0 \frac{V_0}{V_0 + V_{EDTA}} = 9.13 \cdot 10^{-4} M, [CaY^{2-}] = \frac{c_{EDTA} V_{EDTA}}{V_0 + V_{EDTA}} = 0.0148 M,$$

$$[Ca^{2+}] \approx \frac{[Ca^{2+}]_0 V_0 - c_{EDTA} V_{EDTA}}{V_0 + V_{EDTA}} = 1.07 \cdot 10^{-3} M$$

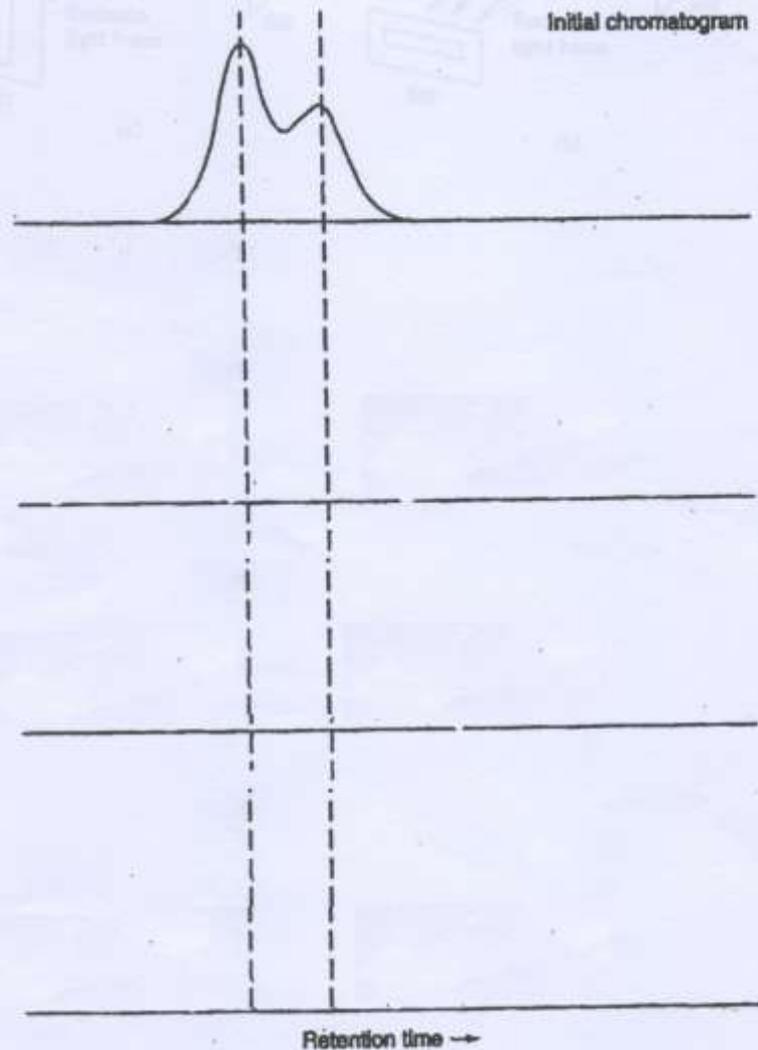
Assume that $K_f^{CuY^{2-}} \gg K_f^{CaY^{2-}}$. Then, $[Y^{4-}] \approx \frac{[CaY^{2-}]}{K_f^{CaY^{2-}} [Ca^{2+}]} = 2.82 \cdot 10^{-10} M$.

$$\text{Thus, } K_f^{CuY^{2-}} = \frac{[CuY^{2-}]}{[Cu^{2+}][Y^{4-}]} = 6.04 \cdot 10^{18}$$

- 6- Two peaks emerge from a chromatography column as sketched in the illustration. According to:

$$\text{Resolution} = \frac{\sqrt{N}}{4}(\alpha - 1) \left(\frac{k'_2}{1 + k'_2} \right) \approx \frac{\sqrt{N}}{4}(\alpha - 1) \left(\frac{k'}{1 + k'} \right)$$

- Sketch what the chromatogram would look like if N and α were kept the same, but k' was increased or decreased.
- Sketch the chromatogram if N and k' were kept the same, but α was increased.
- Sketch the chromatogram if α and k' were kept the same, but N was increased.



- First, $\left(\frac{\partial R}{\partial k'} \right)_{\alpha, N} > 0$. Assume that k' is increased. Therefore, R is increased. Since $\alpha = \frac{k'_2}{k'}$, k'_2 is also increased. Assume V_0 to be constant. Since $k'_i = \frac{V_i - V_0}{V_0} \Rightarrow V_i$ are also increased. Since $N = 16 \left(\frac{V_i}{\omega_i} \right)^2$, where ω_i is the width of the corresponding peak, ω_i are also increased. Thus, chromatogram would look like the Fig. 1a.
- Similar to a), k'_2 , V_2 and ω_2 are increased. Since $\left(\frac{\partial R}{\partial \alpha} \right)_{k', N} > 0$, R is increased. Thus, chromatogram would look like the Fig. 1b.

- c) Since $\left(\frac{\partial R}{\partial N}\right)_{k', \alpha} > 0$, R is increased. Since k'_i and α are kept constant, V_i are also kept constant. Since $N = 16 \left(\frac{V_i}{\omega_i}\right)^2$, ω_i are decreased. Thus, chromatogram would look like the Fig. 1c.

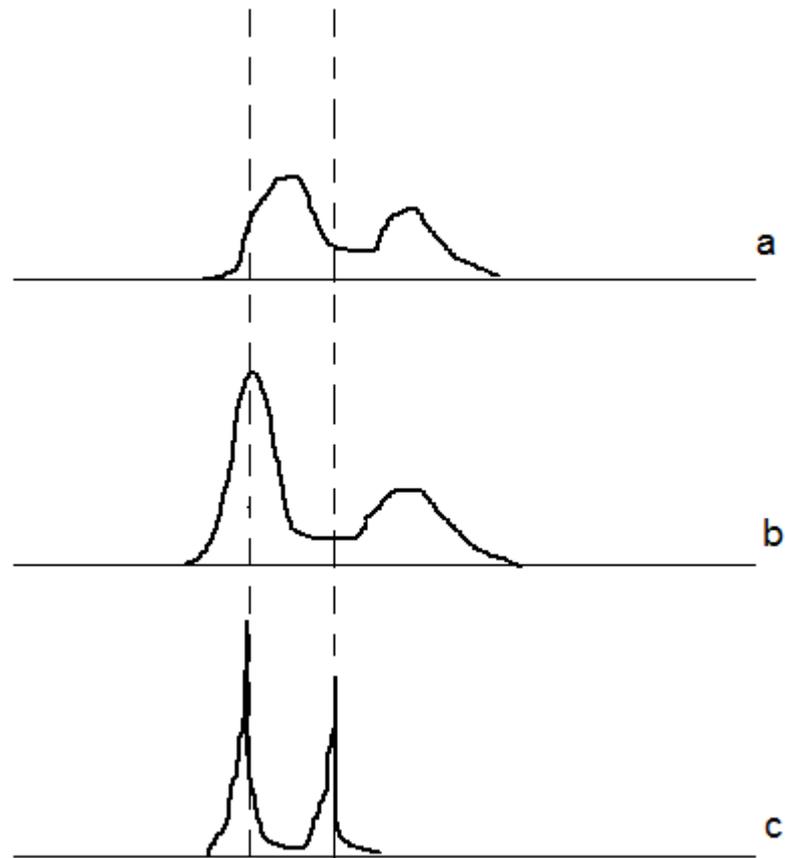
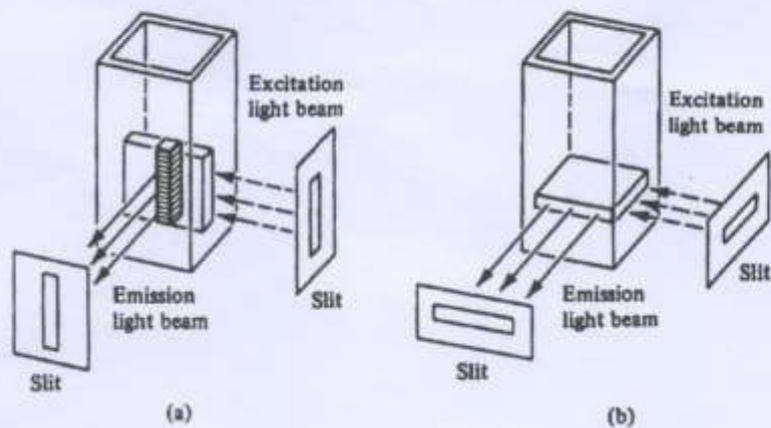


Fig. 1

- 7- Compare luminescence signal intensity in spectrofluorometers with a) a vertical slit configuration and b) a horizontal slit arrangement?



Since the areas of absorption are the same in both cases, we can only consider the thickness of emitting layers. For spectrofluorometers with horizontal slit arrangement it is larger than that with vertical arrangement. Hence, luminescence signal intensity would increase although radiation is partially extinguished. So, the answer is (b).