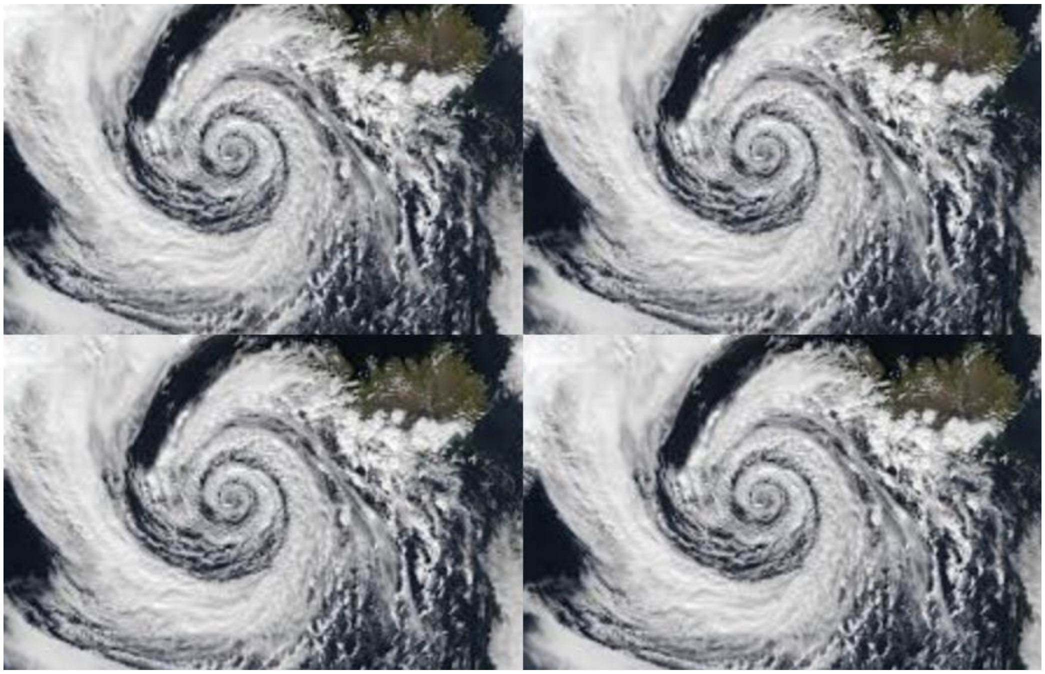


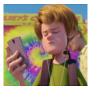
Theoretical Problems

MOCK ICHO 2021

Chemistry Online Discord Server

Pensive Insular and Scoob

Contest Writers
Alec Zhu & Anugrah Chemparathy



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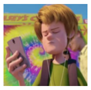
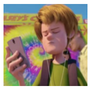


Instructions

- This theoretical exam booklet contains 24 pages.
- You may begin writing as soon as the **START** command is given.
- You have **5 hours** to complete the exam.
- All results and answers not on the premade answer sheets must be clearly written **in the format shown in the templates**.
- You may use as much scratch paper as you want (due to the online format of this competition). Remember that any work that you want to be graded must be done in the format shown in the templates!
- The periodic table is not part of this document; it is provided separately.
- You must use a **scientific calculator**. Graphing calculators are not allowed.
- **This is the official English version** of the exam.
- The supervisor will announce a 30-minute warning before the **STOP** command.
- You must stop your work immediately when the **STOP** command is announced.
- After the **STOP** command has been given, follow the instructions from the instructions document to scan and send your pdfs within the scanning time window.
- In order to ensure impartial grading, you should **not write your name** on any of your pages to be submitted except for the honor code (which should be scanned separately).



Theoretical #1	1.	2.	3.	4.	5.	6.	7.	8.	9.	Total
13% of the total	1	2	3	1	3	3	4	3	3	23

Problem 1. Cool Chemistry

Note: You should **round to at least 4 significant figures throughout this problem** to avoid rounding errors. You will not be graded for significant figures explicitly, but they may affect the accuracy of your answers, which will make grading more difficult and less generous.

A refrigeration cycle is created using a novel refrigerant titled NKT-19, which has a molecular weight of 60 g/mol. Following is some thermodynamic data of NKT-19. Assume NKT follows the properties of ideal gas behavior for the entirety of this question.

NKT-19 (l)	$S^o_{298\ K} = 20.00\ J \cdot mol^{-1} \cdot K^{-1}$
NKT-19 (g)	$S^o_{298\ K} = 140.0\ J \cdot mol^{-1} \cdot K^{-1}$
NKT-19 (l)	$\rho_{270\ K} = 3.400\ g \cdot cm^{-3}$ $\rho_{298\ K} = 3.340\ g \cdot cm^{-3}$ $\rho_{330\ K} = 3.300\ g \cdot cm^{-3}$
NKT-19 (l) → NKT-19 (g)	$\Delta A^o_{298\ K} = -5.100$ kJ/mol
NKT-19 (g)	γ (NKT-19) = 1.333

The Helmholtz free energy ΔA^o of a reaction is a thermodynamic potential that measures the useful work obtainable from a closed thermodynamic system at a constant temperature and volume analogous to Gibbs free energy (which measures useful work at constant temperature and pressure). Consider:

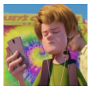
$$\Delta A^o = \Delta U^o - \Delta(T \cdot S^o)$$

(Reminder: round to at least 4 significant figures throughout the problem)

1. Calculate the standard change in internal energy and change in enthalpy for the vaporization of one mole of NKT-19.

Assume that the enthalpy and entropy of vaporization of NKT-19 is constant for the entirety of this problem. *If you were unable to calculate the value of* ΔH_{vap} *in part (1), use* ΔH_{vap} *= 34 kJ/mol.*

(Reminder: round to at least 4 significant figures throughout the problem)



2. Calculate the boiling point of NKT-19 at $P_{ext} = 1$ bar.

Consider a piston which contains 1 mol of NKT-19 at the freezer temperature of 270 K. The molar composition inside the piston is 90% liquid and 10% vapor (call this state **V**).

(Reminder: round to at least 4 significant figures throughout the problem)

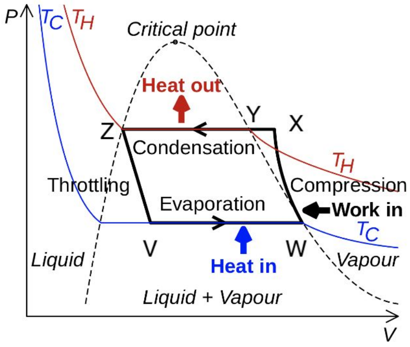
3. What is the vapor pressure of the liquid?

4. Which of the following is true of a reversible process? (*Choose one)*

1. ☐ $P < P_{ext}$
2. ☐ $P = P_{ext}$
3. ☐ $P > P_{ext}$

5. The piston then expands isothermally and reversibly until all the liquid is vaporized, removing heat from the refrigerator. How much work is done by the expanding gas, and how much heat is absorbed?

The refrigeration cycle is thus constructed starting from state **V** (described above). First, the coolant is vaporized. Next, it is adiabatically compressed, followed by isobaric condensation. The hot coolant is then "throttled" to cool it down. These steps are summarized by the diagram on the right. Assume all processes (except throttling) are reversible, and $T_C = 270$ K, $T_H = 330$ K.



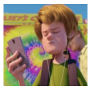
6. What is the vapor pressure of the coolant at T_H?

7. Calculate the work done during the compression step, and the temperature after compression.

8. Finally, the gas must be cooled isobarically from **X** to **Y** before it begins condensing. Calculate the heat removed from the gas and work done on the gas during this step.

Define the "refrigerator efficiency" η of a refrigeration cycle to be the heat absorbed from the fridge divided by the work that must be done by the compressor in each cycle.

9. Compute the refrigerator efficiencies of the NKT-19 refrigerator and that of a maximally efficient heat pump refrigerator operating between 270 K and 330 K.



Theoretical #2	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	Total
15% of the total	6	2	2	2	1	1	2	1	1	2	3	6	9	38

Problem 2. Interesting Oxidation States of Copper

Copper is most frequently found in its ionic forms in either the +2 oxidation state. However some compounds containing copper in its +3 oxidation state exist. A common example of this high oxidation state copper is the square planar copper (III) periodate complex which was synthesized according to the following procedure:

> *"Copper sulfate pentahydrate (1.56 g), potassium persulfate (1.0 g), sodium periodate ($NaIO_4$) (2.67 g) and potassium hydroxide (8.0 g) were added to 250 ml of water. The mixture was shaken thoroughly and heated on a water bath. The mixture turned an intense red after 3 h and boiling was continued for 20 min more to complete the reaction. The mixture was filtered through a sintered glass crucible, cooled and diluted to 250 ml. The complex is soluble and present in the dilution, but upon evaporation of solvent, the complex was isolated as ionic solid **A**."*

The following mass percentage data was obtained for analysis of **A:**

Element	Mass %
Cu	7.4030
I	29.566
O	44.734
H	3.0290

1. Determine the formula of **A**, and write the overall reaction for the formation of the copper (III) periodate complex **A** according to the procedure.

2. Draw the structure of the copper containing ions in the complex and draw a d-orbital splitting diagram for Cu (III) in its coordination environment. Fill in the electrons and label the orbitals.

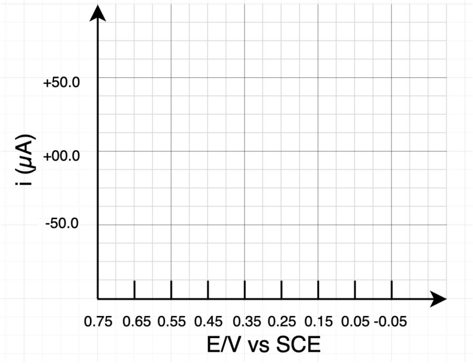
Although the direct coordination environment is typically described as square planar, it is perhaps better described as octahedral owing to the presence of water molecules located axially to the coordination environment.

3. Draw and fill the crystal field of **A** if (a) H_2O is a stronger field ligand than periodate and if (b) H_2O is weaker than periodate. Fill in the electrons and label the orbitals.

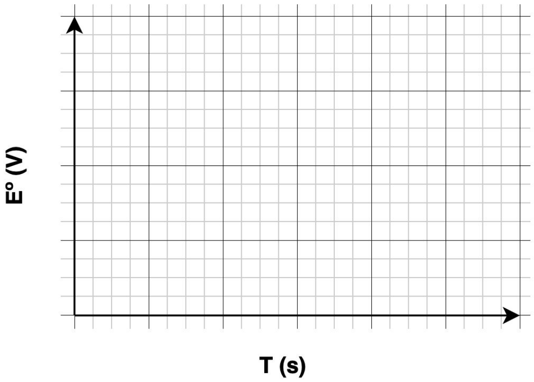
The behavior of this complex can be studied via cyclic voltammetry in which the potential of a working electrode is scanned up and down between 2 values. Samples of copper (III) periodate complex were studied by cyclic voltammetry methods by varying applied potential between 0.00 V and 0.65 V (versus a standard calomel electrode) at a scan rate of 15 mV/s. Anodic peak potential (E_{pa}), cathodic peak potential (E_{pc}), anodic peak current (I_{pa}), and cathodic peak current (I_{pc}) values supplied from related CV graphs depending on the pH are presented in the following table. The complexing ligand for both Cu^{3+} and the Cu^{2+} product is hydrolyzed more easily in the presence of acid.

Trial	*pH*	E_{pa} (V)	E_{pc} (V)	i_{pa} (µA)	i_{pc} (µA)
1	12.43	0.49	0.28	16	10
2	12.75	0.45	0.30	35	25
3	13.17	0.42	0.31	50	40
4	13.30	0.42	0.32	55	41

4. Draw approximately the shape of the cyclic voltammetry curve (i vs E) and the potential waveform (E vs time) *for trial 4*. Label the axes of the potential waveform as you see fit. *(Do this on your answer sheet)*



Cyclic Voltammetry Graph



Potential Waveform

5. Based on the experiment above which of the following can the researchers conclude?
(Check all that apply on your answer sheet)

1. ☐ The reaction is reversible
2. ☐ The reaction is quasi-reversible
3. ☐ The reaction is irreversible
4. ☐ The reaction becomes more reversible at high pH
5. ☐ The reaction becomes less reversible at high pH

6. Which of the following best accounts for your answer to question 5?
(Check all that apply on your answer sheet)

1. ☐ The reaction produces a Cu^{2+} periodate complex, which is more stable than other possible products.
2. ☐ The reaction produces $Cu(OH)_2$ precipitate which is more stable than other possible products.
3. ☐ The reaction produces a Cu^{2+} periodate complex which is more stable in intermediate high pH and competes with the precipitation of $Cu(OH)_2$ which is favorable at highly basic pH.
4. ☐ The reaction produces a Cu^{2+} periodate complex which is more stable at highly basic pH and competes with the precipitation of $Cu(OH)_2$ which is favorable at intermediate high pH.

Cyclic voltammetry can be used to analyze samples to quantitatively determine their composition. It was found that the anodic peak current values scaled linearly with concentration of Cu(III) periodate C_0 within the range 1.10-7.60 mM. The following anodic peak current values for solutions of known concentration with all other conditions constant were recorded:

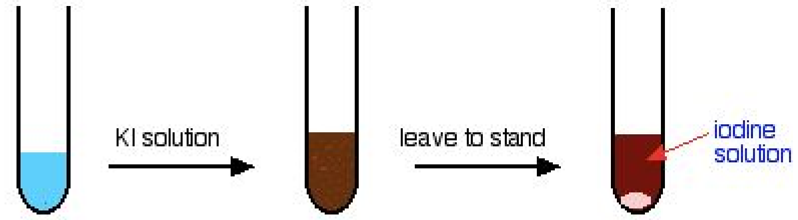
C_0 (mM)	i_{pa} (μA)
2.30	24.78
3.32	34.72
5.54	56.20
6.90	69.38

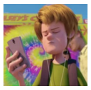
7. Construct a mathematical equation for the calibration curve.

Cyclic voltammetry data was collected for an aqueous sample of copper (III) periodate of unknown concentration. The peak anodic current i_{pa} had a value of 48.34 μA.

8. Determine the concentration of copper (III) periodate in the sample.

Another interesting oxidation state of copper is copper (I); a very well known compound of this type can be made by the reaction of Cu^{2+} and I^-.





9. Write the balanced equation for the reaction of Cu^{2+} and I^-.

The potentiometric titration of a $Cu(NO_3)_2$ is modeled by adding different amounts of solid KI in 10 mmol increments to 3 different beakers containing 1 L of 10 mM $Cu(NO_3)_2$ at 298 K (such that the beakers have 10, 20, and 30 mmol KI added respectively).

An indicator electrode is placed in each beaker, and the potential is calculated relative to the standard calomel electrode (SCE). *Because the KI was added as a solid, the volume of the solution is 1 L in each of the beakers.* ***FORMATION OF I_3^- SHOULD BE NEGLECTED!***

$Cu^{2+} + e^- \rightarrow Cu^+$.. $E^o = 0.15$ V
$I_2 + 2e^- \rightarrow 2I^-$.. $E^o = 0.54$ V
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$ (SCE)..................... $E = 0.25$ V *when* $[Cl^-] = 4.58$ M
$CuI \rightleftharpoons Cu^+ + I^-$.. $K_{sp} = 1.1 \cdot 10^{-16}$

10. Calculate standard reduction potentials of Cu^{2+} and I_2 *with respect to the SCE*.

11. Calculate the voltage read by the indicator electrode in the beaker with 30 mmol added KI.

12. Calculate the voltage read by the indicator electrode in the beaker with 10 mmol added KI.

13. Calculate the voltage read by the indicator electrode in the beaker with 20 mmol added KI.

Theoretical #3	1.	2.	3.	4.	5.	6.	7.	8.	Total
8% of the total	1	2	3	5	1	7	8	2	25

Problem 3. Wolfram, 钨, вольфрама, التنغستن

Tungsten forms a variety of polymeric oxyanions in its (VI) oxidation state. The formation of these polytungstates may be considered to be a polymerization reaction where two terminal W-O$^-$ groups combine to form a W-O-W linkage.

1. Draw the lewis structure of tungstate (WO_4^{2-}).

2. Draw the structure of a tungstate polymer, and write a generic formula in terms of X_n, the number of monomer units in the polymer (henceforth referred to as the polymer length).

3. Many cyclic oxyanions are known. Draw 3 examples, each based on a different group of the periodic table.

In the remainder of this problem we will only consider linear polytungstates. Let us consider polytungstate equilibria in acidic solution. For simplicity, we will assume that all polymerization reactions have the same equilibrium constant. The general reaction for polymerization is:

$$R^1OW(O)_2\text{-}O^- + R^2OW(O)_2\text{-}O^- + 2H^+ \rightleftharpoons R^1OW(O)_2\text{-}O\text{-}W(O)_2OR^2 + H_2O \qquad K_{eq}$$

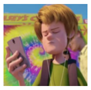
If 100.0 mmol of sodium tungstate is added to a 1.00 L pH = 4.00 buffer, it is found that the statistical average molecular mass of tungstate species is 2200 g/mol.

4. Calculate the value of the equilibrium constant K_{eq}.

At a higher temperature, $K_{eq} = 1.2 \cdot 10^9$. The sample described in part 3 is heated to this new temperature, and the pH is readjusted to exactly 4.00 once more.

5. Pick the statements that are true regarding reaction (1).
(Check all that apply on your answer sheet)

1. ☐$\Delta H_{298} > 0$	2. ☐$\Delta H_{298} < 0$	3. ☐$\Delta G_{298} > 0$	4. ☐$\Delta G_{298} < 0$



6. Compute the statistical average molecular mass of tungstate species in this new system.

Tungsten-Nickel alloys typically contain between 0.5-5 wt% tungsten. A 272.56 mg sample of a tungsten-nickel alloy is assessed for tungsten content as follows:

First, the sample is dissolved in excess concentrated nitric acid (1), releasing a brown gas and leading to the formation of a white precipitate. An excess of concentrated potassium hydroxide is added to the beaker until the beaker turns clear (2). The resulting solution is diluted to 40 ml and two 20 ml aliquots are taken.

To the first aliquot is added an excess of concentrated HCl which leads to a white precipitate (3) which is then filtered, calcined, and quickly weighed to be 8.3±0.5 mg. The second aliquot is passed through an ion exchange column to separate the tungsten and the nickel ions. The released effluent is diluted to 20 ml and further separated into 5 ml and 15 ml aliquots. An excess of concentrated HCl is added to the 5 ml aliquot which leads to a white precipitate which is then filtered, and quickly weighed to be 2.1±0.5 mg.

Some amount of metallic lead is added to the 15 ml aliquot along with some ammonium chloride (4). The titration procedure may not be as accurate if ammonium chloride is omitted. After several minutes, the solution is filtered and the filtrate is acidified and titrated with 17.23 ml of 0.000765 M $K_2Cr_2O_7$ (5).

7. Determine the weight % of Tungsten in the alloy sample and write balanced chemical equations for steps (1)-(5).

8. Propose a reason why the titration procedure is less accurate without ammonium chloride.

Theoretical #4	**1.**	**2.**	**3.**	**4.**	**5.**	**6.**	**7.**	**8.**	**9.**	**10.**	**11.**	**12.**	**Total**
16% of the total	1	2	2	7	2	2	2	3	2	4	2	6	35

Problem 4. Quantum Kinetics

Note: **You should round to at least 4 significant figures throughout this problem** to avoid rounding errors. You will not lose points if you forget, but grading may be less generous.

CH_3COOH (referred to as HOAc throughout the rest of the problem) is an acid with pKa = 4.74. Using the harmonic oscillator model, we can estimate the behavior of its deuterated analog, DOAc in heavy water (D_2O). You may use units of cm^{-1} for frequencies.

1. Write down the acid-base reaction between HOAc and H_2O. Draw structures indicating the relevant bonds being broken and formed.

(Reminder: round to at least 4 significant figures throughout the problem)

2. Calculate, in amu, the reduced mass of the O-H bond and the O-D bond respectively. You should use integer molar masses: m(H) = 1 amu, m(O) =16 amu.

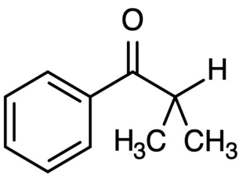
$\tilde{\nu}$O-H (H_3O^+) = 3000 cm^{-1} $\tilde{\nu}$O-H (HOAc) = 2800 cm^{-1}

3. Calculate the stretching frequency of the O-D bond in DOAc and D_3O^+, respectively.

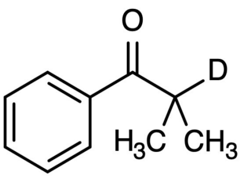
4. Compute the approximate pK_a of DOAc in D_2O using the harmonic oscillator model.

One reaction catalyzed by acid is bromination of phenyl isopropyl ketone (referred to as K and K-D in its deuterated form throughout the rest of the problem) with Br_2, to form bromo-K. The proposed mechanism is as follows:

$K + H^+ \rightleftharpoons HK^+$ K_{eq}, k_1, k_{-1}
$HK^+ \rightarrow Enol + H^+$ k_2
$Enol + Br_2 \rightarrow K\text{-}Br + H^+ + Br^-$ k_3



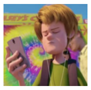
K



K-D

The reaction is studied at 298 K, producing the experimental data shown below:

Trial	Buffer pH	[K] (M)	[Br_2] (M)	Initial rate (M/h)
1	2.7	$1.0\cdot10^{-3}$	$1.0\cdot10^{-3}$	$2.3\cdot10^{-4}$
2	2.7	$2.0\cdot10^{-3}$	$1.0\cdot10^{-3}$	$4.6\cdot10^{-4}$
3	3.7	$1.0\cdot10^{-2}$	$1.0\cdot10^{-2}$	$2.3\cdot10^{-4}$
4	3.7	$1.0\cdot10^{-2}$	$2.0\cdot10^{-2}$	$2.3\cdot10^{-4}$



Throughout all the experiments, Br_2 containing only the Br-79 isotope was used.

(Reminder: round to at least 4 significant figures throughout the problem)

5. Determine the rate law and rate constant for this reaction.

6. Using the steady state approximation, derive the rate law for the proposed mechanism. Under what conditions does it match the experimental rate law? What step of the mechanism do you think is rate-limiting? Justify your answers.

7. К has a pK_b of approximately 21. Estimate the value of the rate constant of the rate limiting step.

8. The reaction К + H^+ → $HК^+$ has $\Delta H \approx 30$ kJ/mol. If the rate of bromination doubles at 308 K, maintaining the same buffer pH, estimate the activation energy and pre-exponential factor of the rate limiting step for the non-deuterated reaction.

9. Calculate initial rate of bromination in H_2O solution containing 1M HOAc, 0.1M NaOAc, 0.001M К, and 0.001M Br_2.

(Reminder: round to at least 4 significant figures throughout the problem)

Assume for the remainder of this question that К and К-D have the same pK_b and pK_a.

10. Calculate initial rate of bromination in a D_2O solution containing 1M DOAc, 0.1M NaOAc 0.001M К-D, and 0.001M Br_2. $\tilde{\nu}$(C-H) = 2950 cm^{-1}.

Under basic conditions, the rate law and mechanism for the chlorination of К are different. The rate law for this reaction is k[Cl_2][OH^-][К]. When natural [Cl_2] is kept constant at .50 M in a pH = 8 buffer, an effective half life in К of 3400 s is observed.

11. Write the mechanism for this reaction. Note that the step involving Cl_2 is rate limiting.

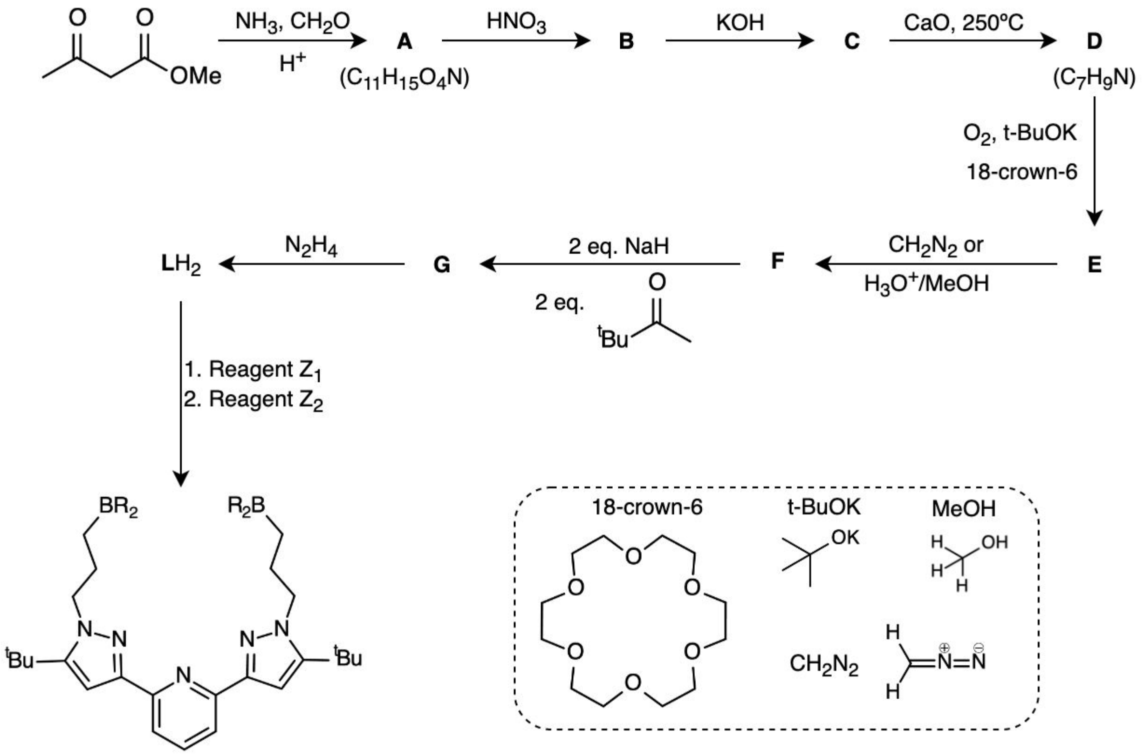
A buffer solution is prepared at pH = 8, with a ratio of hydrogen to deuterium being 2000:1, the same as the natural ratio. To this buffer an equimolar mixture of .001 M К and .001 M К-D is added. Finally, natural Cl_2 is added with a total concentration of .10 M, which contains the Cl-35 and Cl-37 isotopes randomly distributed in a 3:1 ratio. Cl_2(35-35) reacts 7% faster than Cl_2(35-37) and 14% faster than Cl_2(37-37). It may be assumed that Cl_2(35-37) reacts at either chlorine atom with equal probability.

12. Calculate the concentrations of all isotopic variants of К and К-Cl^{35}/К-Cl^{37} after 3 hours, ignoring species of negligible concentration (i.e. less than 1 μM).

Theoretical #4	**1.**	**2.**	**3.**	**4.**	**5.**	**6.**	**7.**	**8.**	**9.**	**Total**
16% of the total	14	1	2	3	22	2	4	2	10	60

Problem 5. Three in One

Scientists are investigating the metal complexes of some potentially useful ligands. The synthesis of two such ligands, **L**H_2 and **X** are shown below.



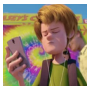
1. Give the structures of compounds **A-G**. The NMR spectrum of **A** is as follows: ^{1}H NMR: δ 2.45 (6H, s), 2.95 (2H, s), 3.71 (6H, s). One proton on **A** is labile and is not visible in the NMR.

2. What is the primary purpose of HNO_3 in step **A** → **B**:
(Check all that apply on your answer sheet)

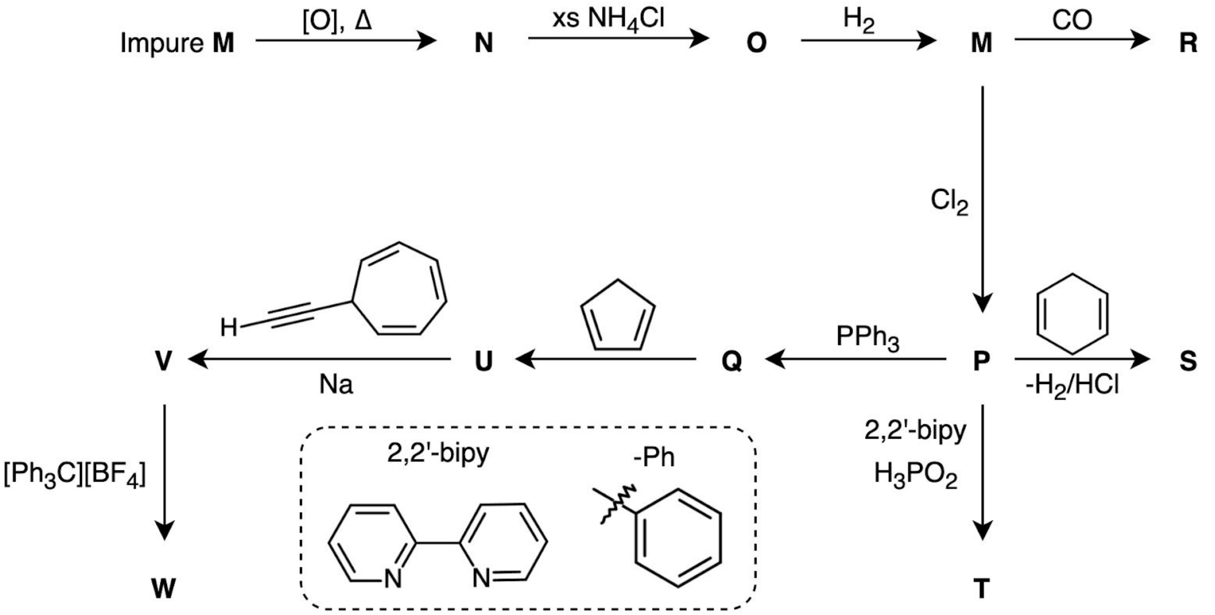
1. ☐Oxidant	2. ☐Nitration Reagent	3. ☐Acid Catalyst	4. ☐Reductant

3. Reagent $\mathbf{Z_1}$ is made by reaction of BH_3 in THF with cycloocta-1,5-diene. Draw its structure.

4. Draw ligand **L**H_2, and provide the identity of reagent(s) $\mathbf{Z_2}$.



Metal **M** is a very interesting metal, and forms a wide variety of organometallic compounds. Metal **M** is usually found as a component of "cathode sludge," and must be purified. Some of its reactions are shown in the scheme below. *Reagents and products are not necessarily shown stoichiometrically or at all.*

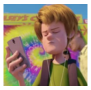


Information:

- **N** is quite volatile.
- **O** is 27.478% **M** by mass, and does not contain oxygen.
- **P** is 48.735% **M** by mass.
- Compounds **Q**, **S**, **T**, **U**, **V**, and **W** all contain **M** in the same oxidation state.
- **Q** is 10.544% **M** by mass, and contains 2 chlorine atoms.
- **S** is dimeric and is 40.420% **M** by mass.
- **U** is tetrahedral at **M**; it is non-ionic.
- **U**→ **V** involves formation of a metal-carbon bond.
- **V** is nonionic.
- **W** may be described as a "metallocumulene." A cumulene is a hydrocarbon with three or more cumulative double bonds (a long allene).

5. Draw structures of the molecular compounds in the scheme, and identify metal **M**. *For non-molecular compounds, a chemical formula is sufficient.*

6. What is the phosphorus-containing byproduct of the reaction **P** → **Q**? Note that this reaction is usually done in the presence of water.

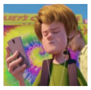


7. Reaction of **Q** with ligand **L**H_2 gives cationic octahedral complex **I** (contains 1 chlorine ligand), which when treated with K_2CO_3 gives neutral complex **II**. Draw the structures of **I** and **II** (feel free to abbreviate the structure of **L** as something similar to RN-N∼N∼N-NR, but draw any hydrogens bonded to nitrogen!)

8. Both **I** and **II** react with MeOH in the presence of $KN(SiMe_3)_2$ to give **III**. Draw the structure of **III**; again feel free to abbreviate the structure of **L**.

Ligand **X** reacts with $FeCl_2$ to give **IV**, which is pentacoordinate. Reaction of **IV** with hydrazine gives **V**, which contains a macrocycle. Reaction with KC_8 gives compound **VI**, which only has 2 N-N bonds. KCl and graphite are byproducts of this reaction. Interestingly, **VI** reacts with KCH_2Ph to form anionic complex **VII**, which reacts with I_2 to give a structure very similar to **VI**, but with one of the aromatic positions substituted.

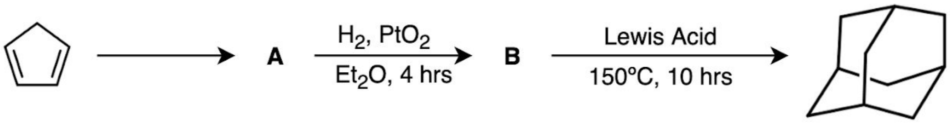
9. Draw structures of complexes **IV-VII**; again feel free to abbreviate the structure of **X**; you do not need to draw out the -R groups.



Theoretical #6	**1.**	**2.**	**3.**	**4.**	**5.**	**6.**	**7.**	**8.**	**9.**	**Total**
9% of the total	3	4	18	1	7	7	3	2	3	48

Problem 6. Compound X, Symmetry, and NMR

Compound **X** can be synthesized in 3 elegant steps as follows:

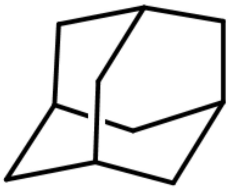


X

1. How many hydrogen NMR signals are theoretically expected for compound **X** according to its molecular symmetry? Draw in and label at least 3 of each chemically distinct hydrogen atom by environment H_a, H_b, H_c etc. (Hydrogen atoms in the same environment should have the same label). State the integration values expected for each environment.

(On your printer paper solutions, write your answers with this formatting. It doesn't need to be incredibly neat or have a carefully drawn table, but it should be approximately this layout)

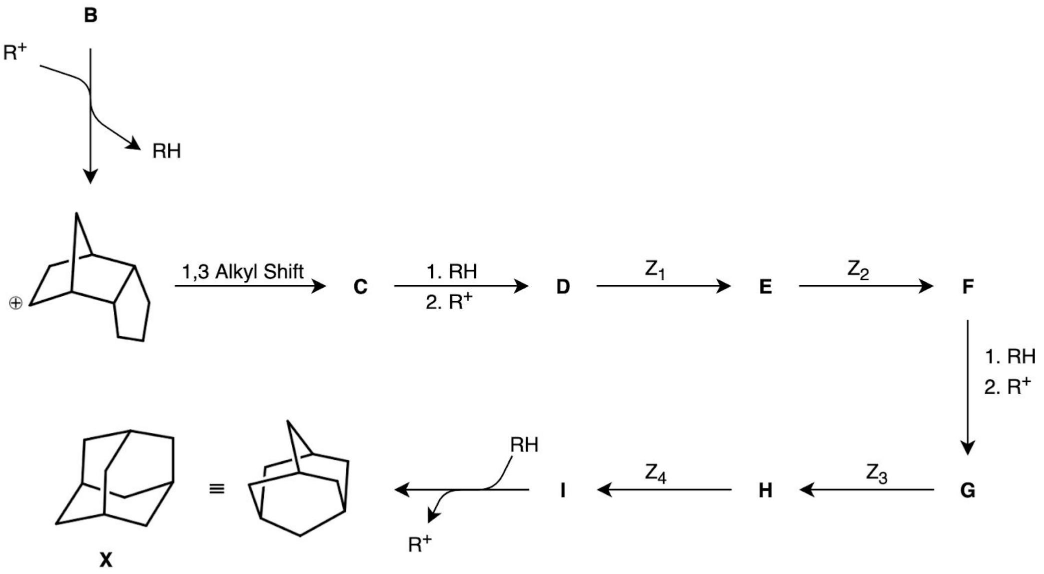
Number of Signals = ___________



	H_a	H_b	H_c	H_d	H_e	H_f
Integration Values						

(There are not necessarily 6 distinct environments)

The last step in the synthesis is the lewis acid isomerization of **B** into compound **X**. This isomerization occurs according to the following mechanism:



The mechanism for conversion of the first drawn intermediate to form carbocation **I** (which is then quenched by addition of hydride) can be completely described using just 3 different steps: carbocation rearrangement, intramolecular hydride shifts between adjacent carbon atoms, and intermolecular hydride transfers (labeled as 1. RH, 2. R^+) which allow for transfer of carbocations at greater distances, i.e. beyond adjacent atoms. (Z_1 though Z_4 represent either carbocation rearrangements or intramolecular hydride shifts which you must decipher). Note that carbocation **I** does not rearrange. *In the scheme shown above, all intermolecular hydride transfers (which move carbocations beyond adjacent carbon atoms) are shown.*

2. Draw the structures of **A** and **B** with stereochemistry.

3. Draw the structures of intermediates **C**-**I** (in 3D) and state whether each step Z_1-Z_4 you have proposed is a carbocation rearrangement or intramolecular hydride shift. There may be more than one unique answer, so all reasonable solutions that are consistent with the chosen Z_1-Z_4 will be accepted. A chemically reasonable answer will receive full points, while a suspect one will only obtain partial.

Compound **X** (the same as before) is notable for the unusual stability of its tertiary cation. A sample of compound **X** (M.W. = 136.228 g/mol) is brominated according to the following procedure:

> *"21st camper Harrison takes 2.0 g of compound* ***X*** *and adds it to a flask, along with about 0.3 g of iron powder and suitable solvent. Finally, approximately 2 ml of bromine are added (ρ(Br_2) = 3.12 g/ml). He then heats the flask for a while at 50 ℃, and once the solution turns virtually colorless, he stops the reaction. He then takes 20 μL of the reaction mixture, adds it to an NMR tube, dilutes to 700 μL with chloroform-d, and obtains the following ^{1}H NMR spectrum. ^{4}*J *and higher couplings have been neglected."*

Label	δ, ppm	Integration	Shape	Label	δ, ppm	Integration	Shape
a	8.20	34.30	m	h	2.006	2.000	s
b	7.71	17.15	m	i	1.976	4.000	dd, J -12 4
c	7.52	34.30	m	j	1.894	1.164	d, J 4
d	7.24	3.917	s	k	1.857	4.000	dd, J -12 4
e	2.056	0.582	d, J -13	l	1.803	2.000	sept, J 4
f	2.038	0.194	sept, J 4	m	1.651	2.000	t, J 4
g	2.060	0.582	d, J -13				

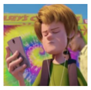
4. Which solvent would 21st camper Harrison have used to carry out the reaction?
(Check all that apply on your answer sheet)

1. ☐ Benzene 2. ☐ Toluene 3. ☐ THF 4. ☐ Nitrobenzene
5. ☐ Phenol 6. ☐ Pyridine 7. ☐ Pentane

5. Based on the data given above, determine all products formed in this reaction and their molar ratios in the NMR sample.

6. Assign *every* NMR peak to a compound and the correct proton on that compound.

7. How much Br_2 actually reacted with compound **X**? Explain this result, with regard to the amount (≈2 ml) of Br_2 added.



Recent computational chemistry studies were used to assess the stability of **J**, a highly unusual and unstable "epimer" of compound **X** (**J** is expected to decompose into compound **X** with a half life of 30 ms at room temperature!) Decoupled ^{1}H and ^{13}C NMR were computed for the hypothetical structure. Special peaks corresponding to the epimerized position were expected at 7.5 ppm and 21 ppm in ^{1}H and ^{13}C NMR respectively. The hypothetical "epimer" **J** exhibits C_3 symmetry, i.e. a 3-fold rotation axis.

8. Draw the structure of **J** with the correct orientation of atoms/stereochemistry.

The computationally derived enthalpy of activation $\Delta H^{‡}$ for the conversion between the epimers is 81 kJ/mol at 298 K.

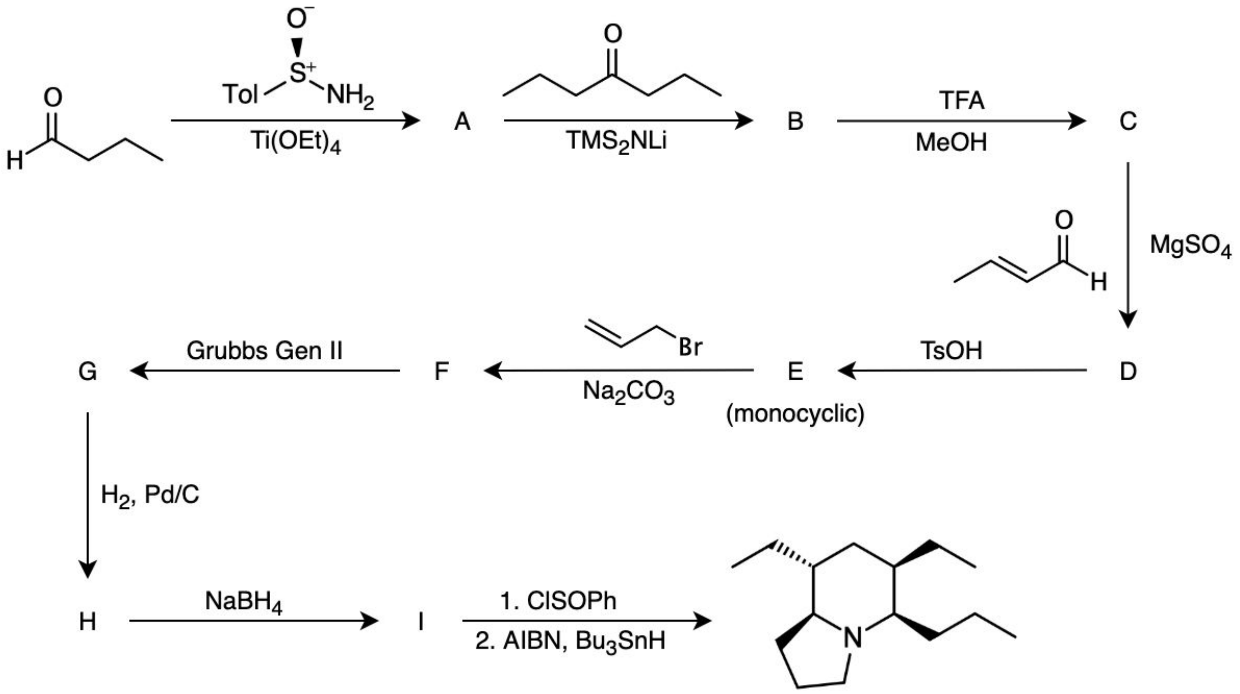
9. Estimate the entropy of activation $\Delta S^{‡}$ for the conversion. Assume that conversion of the transition state to the product occurs with 100% probability.

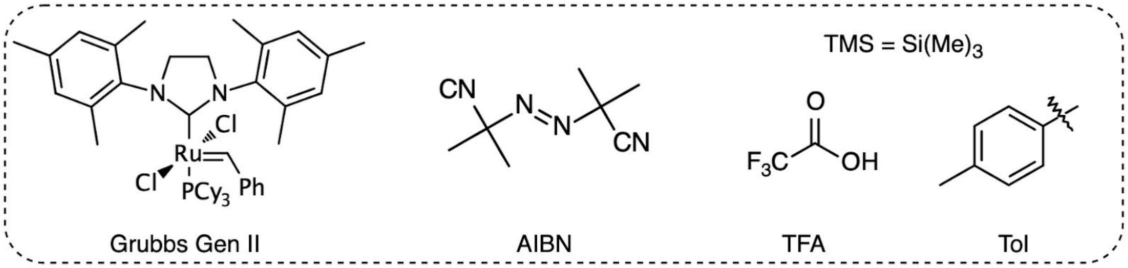
Theoretical #7	1.	2.	3.	Total
15% of the total	27	6	30	63

Problem 7. Build Your Own Frogger

The alkaloid shown below was isolated from frogs in the late 90s. In this problem you will be responsible for deciphering the synthetic methods used in the stereoselective total synthesis of its (+) and (-) isomers.

Consider first the following synthesis of the (-) isomer:

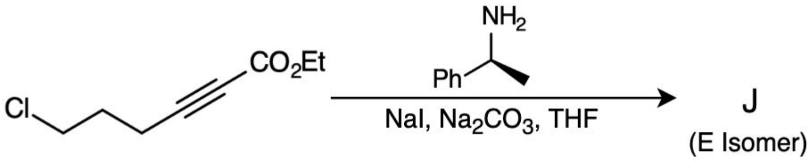




Note that the final step converting intermediate **I** to the target molecule are dehydroxylation conditions (i.e. they remove an OH group).

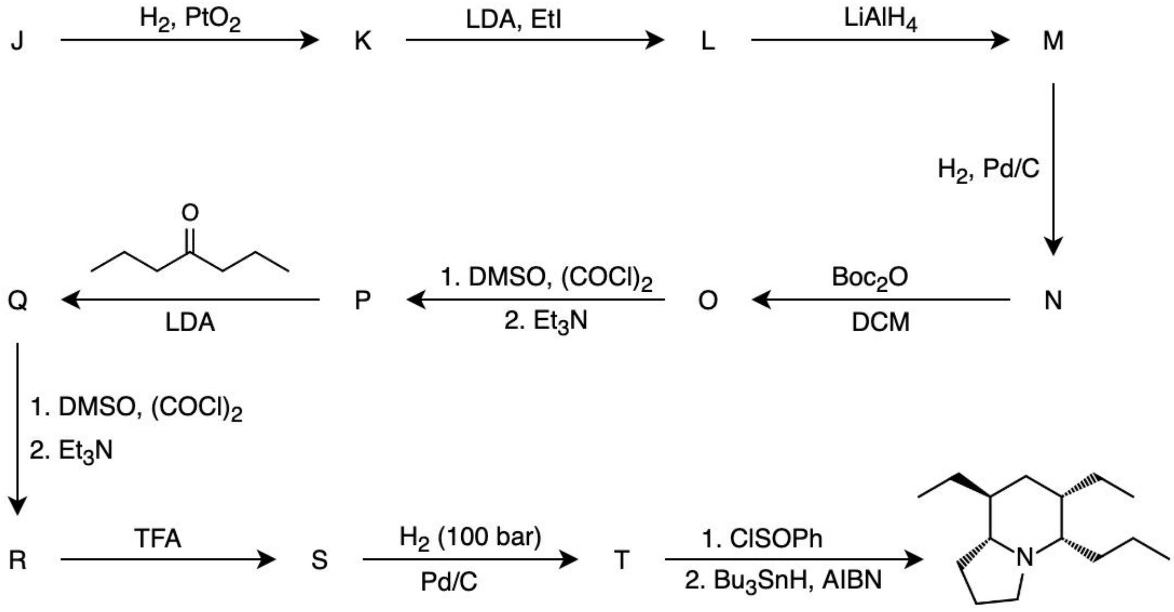
1. Draw the structures of compounds **A-I** with stereochemistry

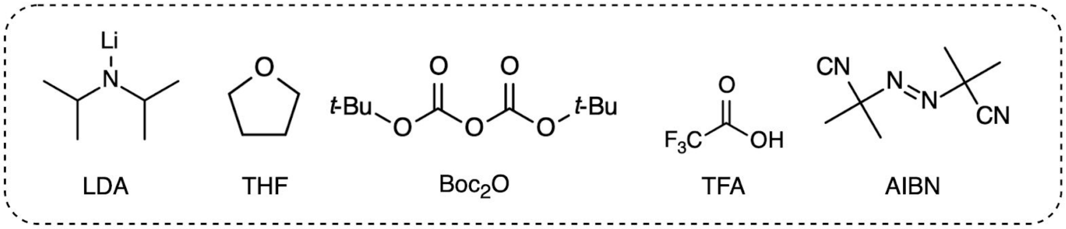
The (+) enantiomer on the other hand began with the synthesis of the *E* isomer of precursor **J**:



2. Draw the structure of **J** with stereochemistry.

The researchers then used **J** to complete the rest of the synthesis:





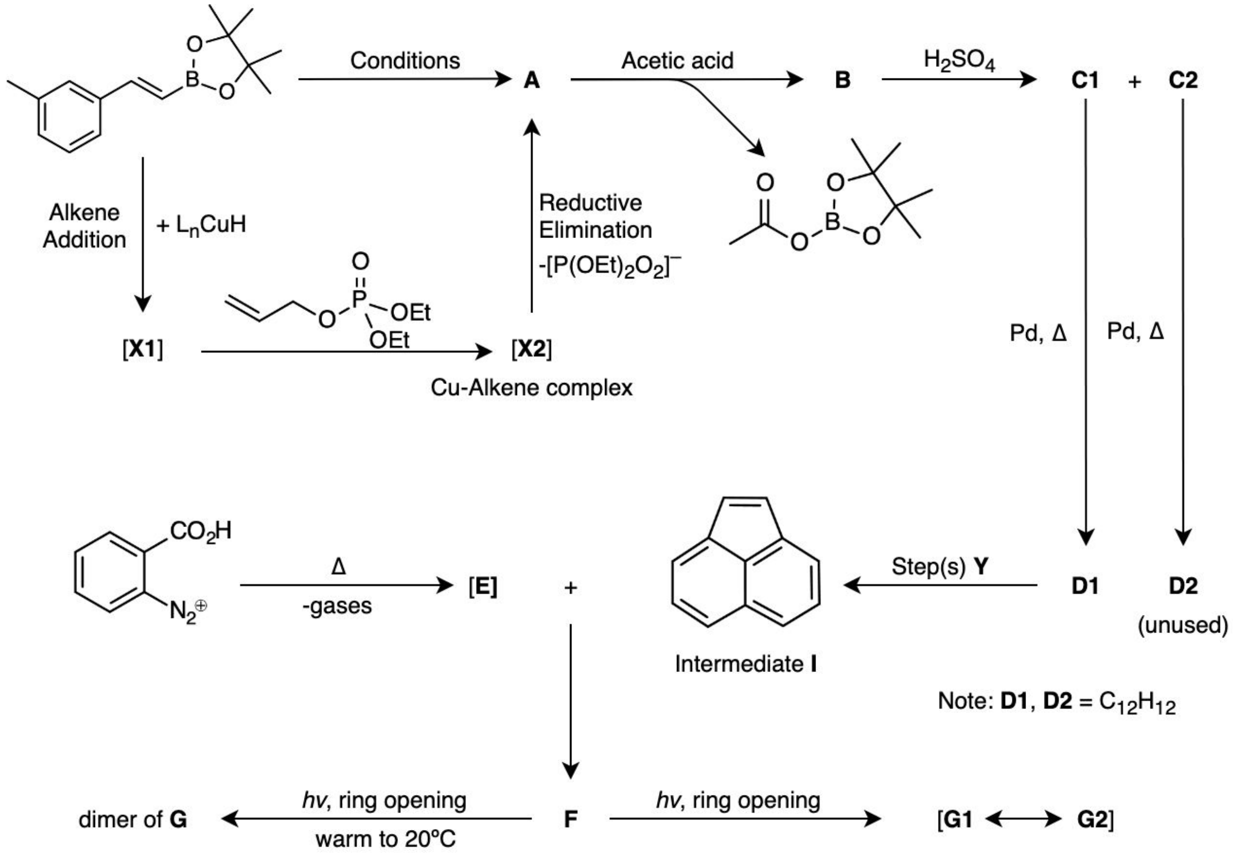
The reaction conditions for **T**→Product also cause dehydroxylation (removal of OH).

3. Draw the structures of compounds **K**-**T** with stereochemistry.

Theoretical #8	1.	2.	3.	4.	Total
8% of the total	6	10	5	9	30

Problem 8. Non-Classical Chemistry

The synthesis of a very interesting molecule **G** was carried out according to the following scheme. Compounds **C** and **D** were formed as a mixture of isomers; however, only **C1** and **D1** are useful in the synthesis. In the synthesis, **D1** is converted in some number of steps which you must propose (step(s) **Y**) into intermediate **I**, and **D2** is discarded.



Note: **D1**, **D2** = $C_{12}H_{12}$

1. Draw the structure of intermediates of **X1** and **X2**, which are intermediates in the mechanism for the synthesis of **A**.

2. Draw structures of compounds **A** through **D1/2**.

3. Propose reagent(s) **Y** (note that reagent(s) **Y** may involve many steps).

4. Draw the structures of reactive intermediate **E**, **F**, and the “classical” and “non-classical” resonance structures **G1** and **G2**. Draw the dimer of **G** as well.

Congratulations for finishing the mock IChO!

Secret Messages (for those who are both gamers and also taxpayers):

Если Вы закончили этот тест в указанное время, Вы уже достигли пика «Нью Эйдж». Если Вы не знаете, что это значить, не беспокойтесь, эпический геймер! И всегда помните, великие ученые думают без носа!