

Final Exam

Last Name: _____

First Name: _____

Problem

1. (30 points) _____

2. (12 points) _____

3. (10 points) _____

4. (14 points) _____

5. (15 points) _____

6. (10 points) _____

7. (24 points) _____

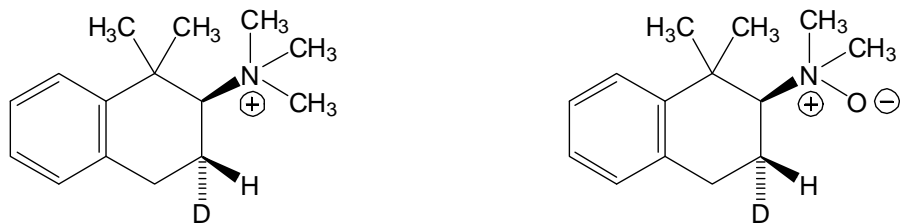
8. (20 points) _____

9. (15 points) _____

Total Points: _____ **/150**

1. (30 Points) For the following compounds, circle the one that embodies the indicated property. (2 pts each)

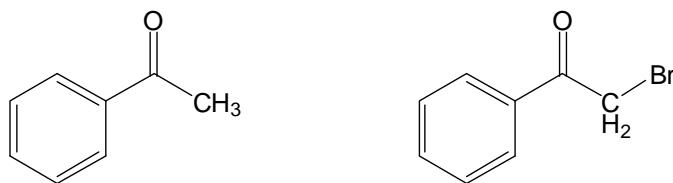
a. Retains deuterium upon elimination



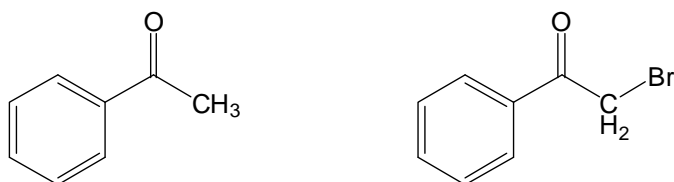
b. Aromatic Stabilization



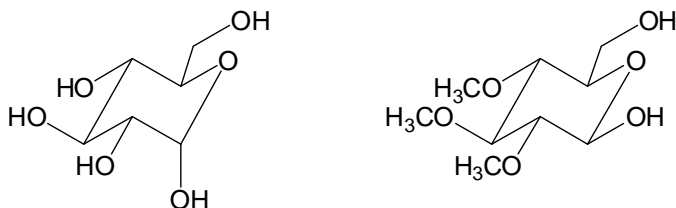
c. Faster Rate of Reaction with Br₂/NaOH



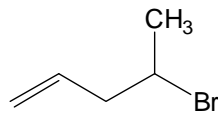
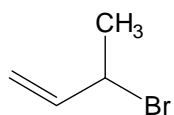
d. Faster Rate of Reaction with Br₂/HBr



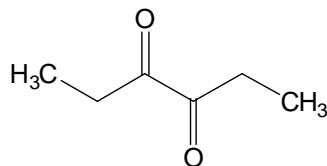
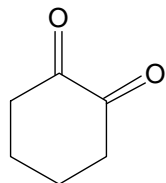
e. Anomeric Hydroxyl in α -configuration



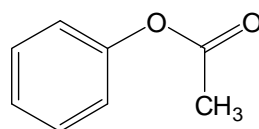
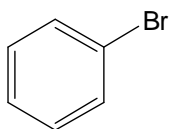
f. Faster Rate of Reaction with CH₃OH through an S_N1 Mechanism



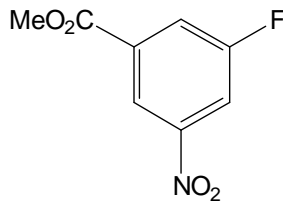
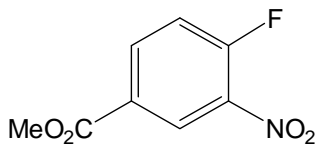
g. Greater Dipole Moment



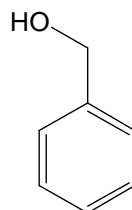
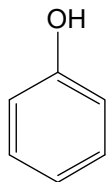
h. Faster Rate of Reaction with $\text{HNO}_3/\text{H}_2\text{SO}_4$



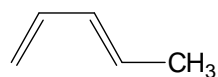
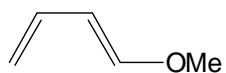
i. Faster Rate of Reaction with $\text{NaOCH}_3/\text{HOCH}_3$



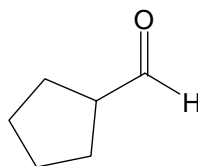
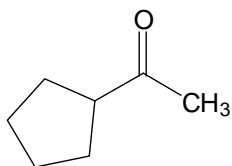
j. Greater Acidity



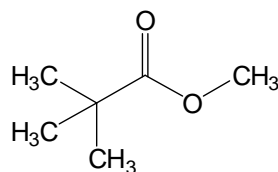
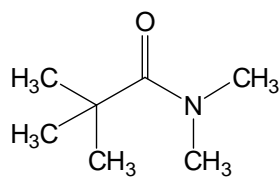
k. Faster Rate of Reaction in Diels-Alder Cycloaddition with cyclohexenone



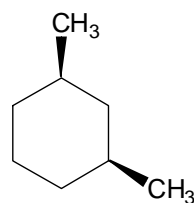
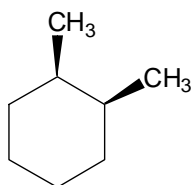
j. Greater Concentration of Hydrated Form at Equilibrium in water



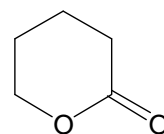
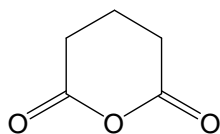
h. Greater Basicity of the Carbonyl Oxygen



i. Greater Number of Signals in the ^{13}C NMR

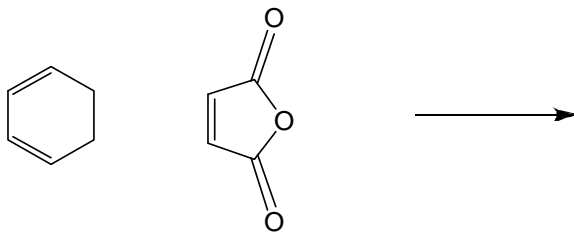


j. Faster Rate of Reaction with CH_3NH_2 through an Addition-Elimination Mechanism



2. (12 points) At low temperature the following Diels-Alder reaction provides mainly the endo product, while at high temperature the exo product predominates.

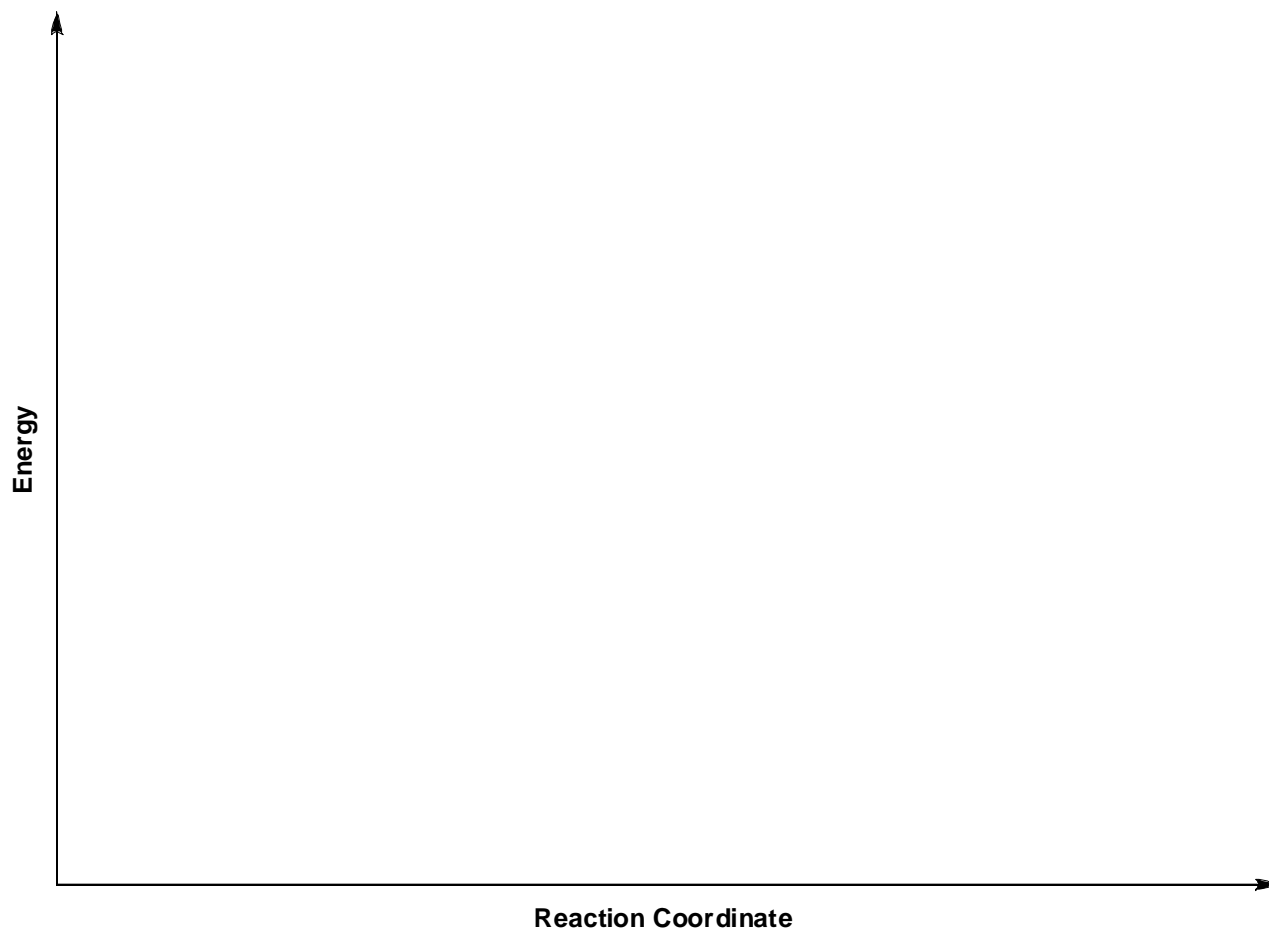
A. (8 Points) Draw the endo- and exo products.



Endo Product
Major Product at
Low Temperature

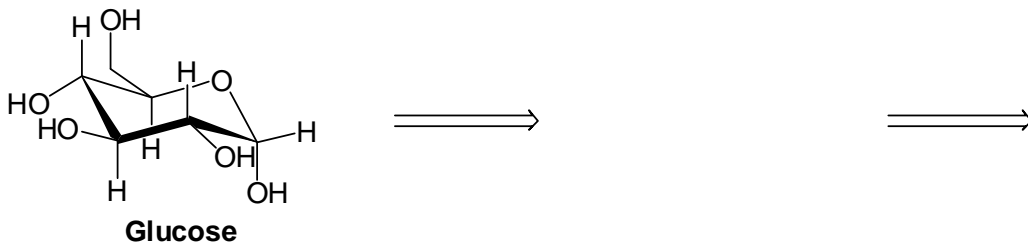
Exo Product
Major Product at
High Temperature

B. (4 Points) Draw an energy *versus* reaction progress diagram that accounts for the observed change in product distribution as a function of temperature.



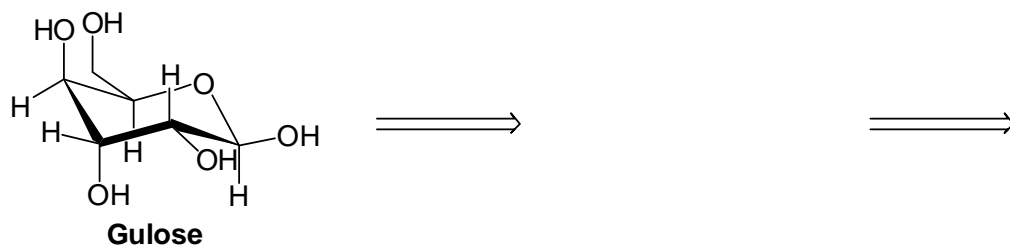
3. (10 points) Consider the following hexoses.

The hexoses indicated below are drawn as Kekulé type structures. Convert these hexoses to Haworth projections and, finally, Fischer projections (in their acyclic forms). Answer the questions by circling the correct response. (5 pts each)



Glucose depicted as the... α -anomer or β -anomer.

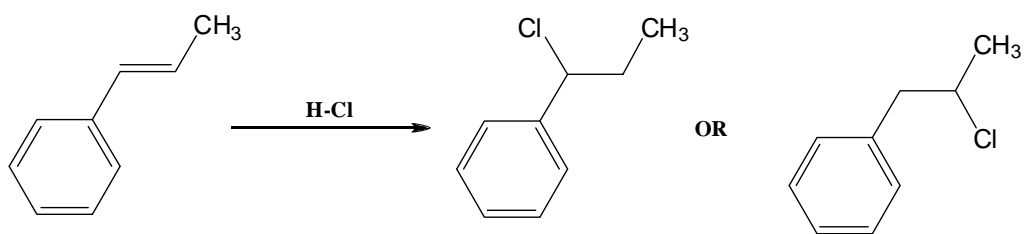
The compound above is... D-Glucose or L-Glucose.



Gulose is depicted as the... α -anomer or β -anomer.

The compound above is... D-gulose or L-gulose.

4. (14 points) Consider the hydrochlorination of the following alkene. Write separate mechanisms to account for the formation of each product, indicating any relevant resonance structures. Based on a comparison of the two mechanisms, predict which product is expected to be the major product. Circle the major product and justify your prediction in writing.



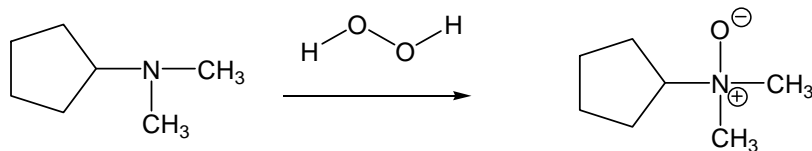
Mechanism for formation of Product A: (5 pts)

Mechanism for formation of Product B: (5 pts)

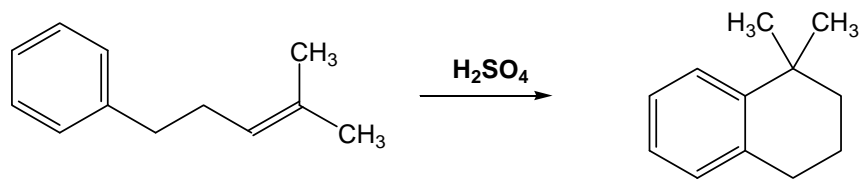
Justification (One sentence): (4 pts)

5. (15 points) Propose mechanisms to account for the following transformations. For each intermediate, draw all lone pair electrons, any formal charges, and all important resonance structures. Use the arrow pushing formalism to interconvert intermediates. (5 pts each)

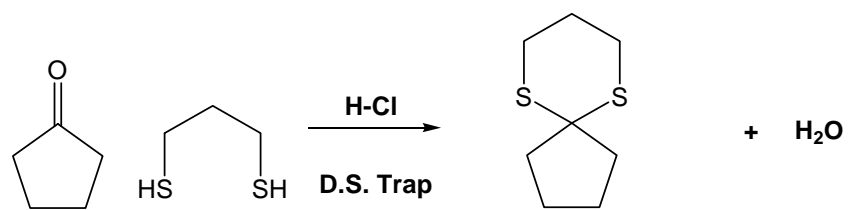
A.



B.



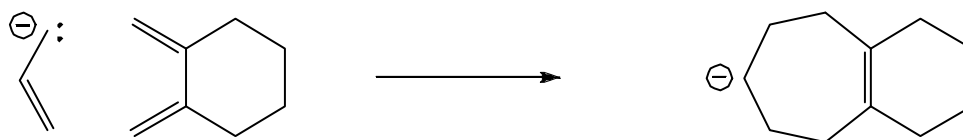
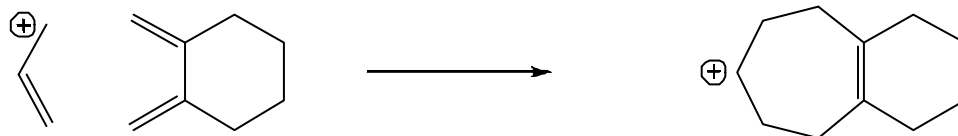
C.



6. (10 points) Consider the proposed pericyclic reactions.

A. (5 Points) Based on your understanding of transition state aromaticity, predict which of the two reactions should be successful. Circle the reaction that you expect to proceed most readily. Explain your answer in one sentence.

(4 pts)



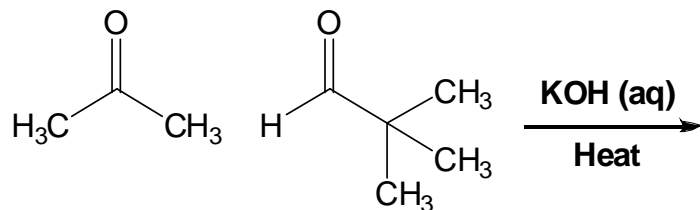
Explanation: (2 pts)

B. Draw the **final** product of the following Cope rearrangement. (4 pts)

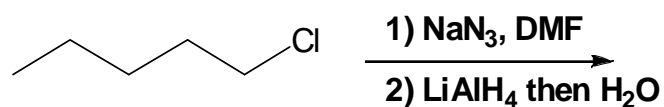


7. (24 points) Draw the major product(s) expected when the indicated starting materials are subjected to the following transformations. Be sure to indicate stereochemistry when relevant.

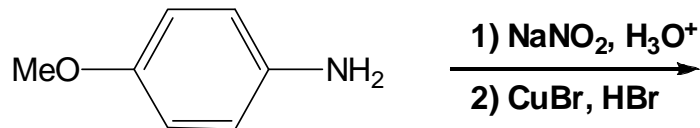
A.



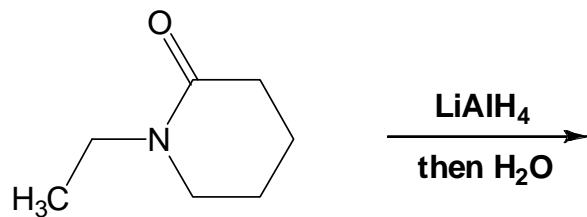
B.



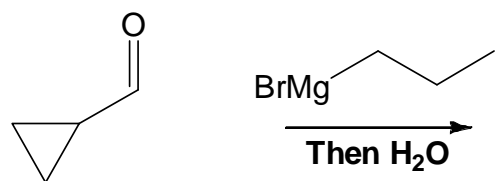
C.



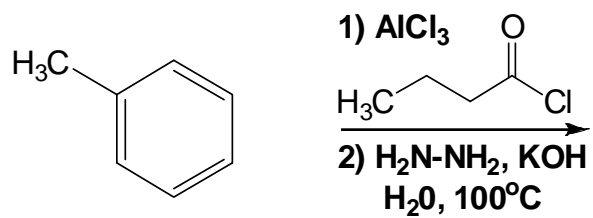
D.



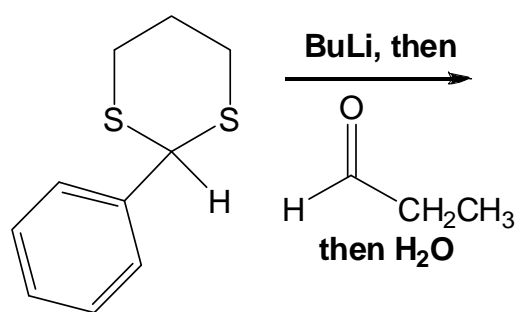
E.



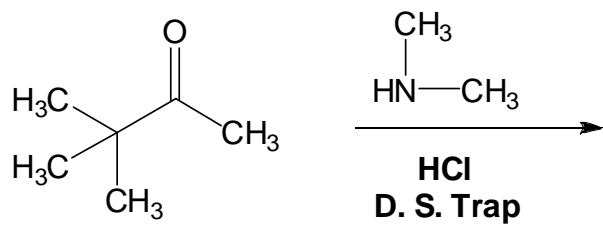
F.



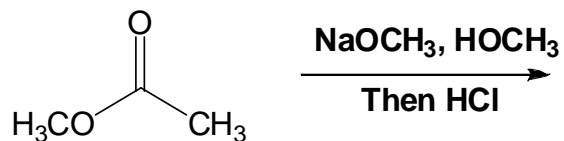
G.



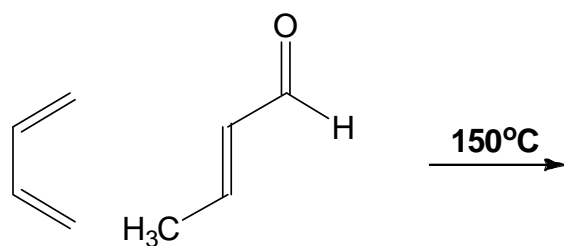
H.



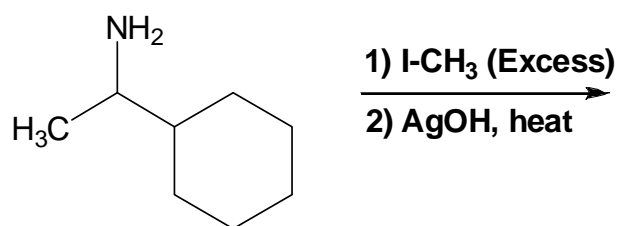
I.



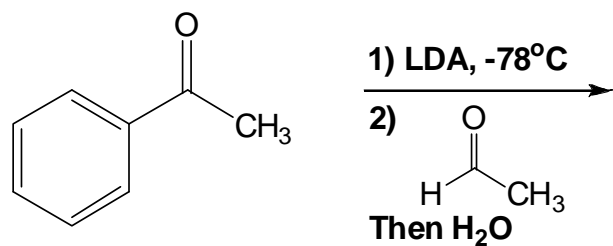
J.



K.

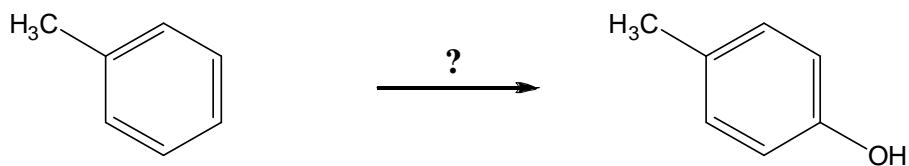


L.

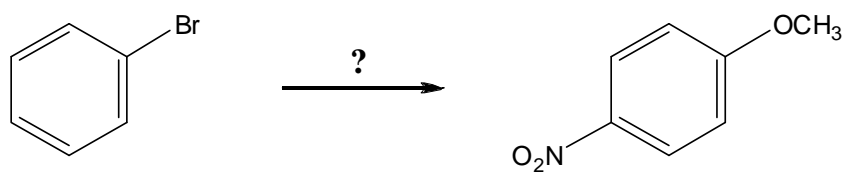


8. (20 points) Devise a synthetic route to accomplish the following transformations. Clearly number each step of your proposed sequence and **Draw all Intermediates**. (Hint: Try to work backwards).

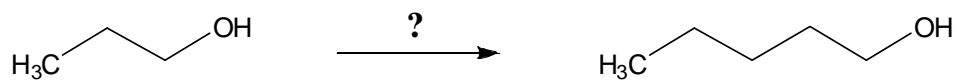
A. (5 pts)



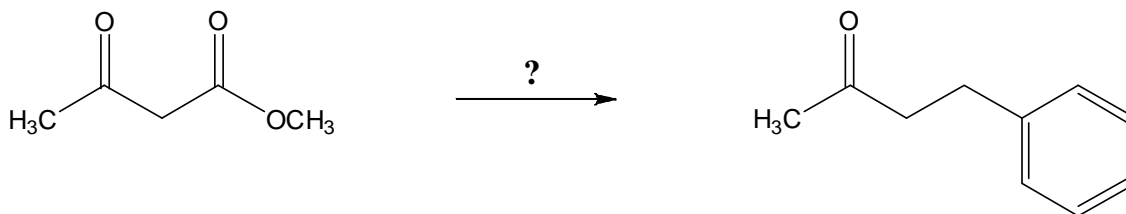
B. (5 pts)



C. (5pts)



D. (5 pts)



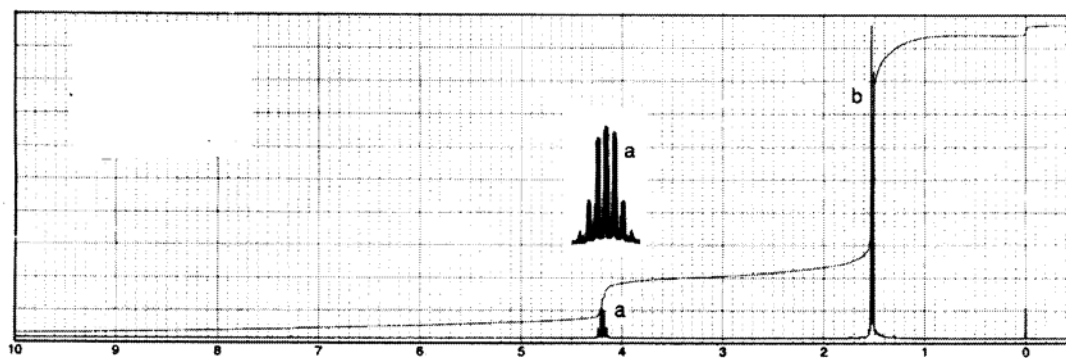
9. (15 points) The molecular formulas of three compounds determined by combustion analysis are given below. By considering the ^1H NMR spectra of these compounds (found on the following page), formulate structural assignments. Indicate your answer by drawing the compound (5 pts each)

Compound A) $\text{C}_3\text{H}_7\text{Cl}$

Compound B) C₃H₆Br₂

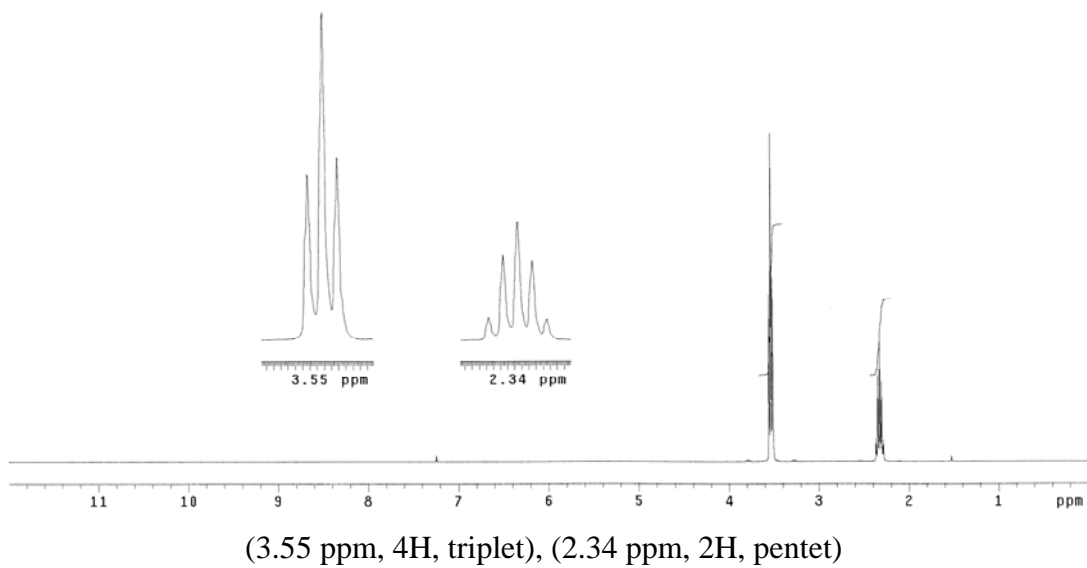
Compound C) C₃H₇I

A. C₃H₇Cl

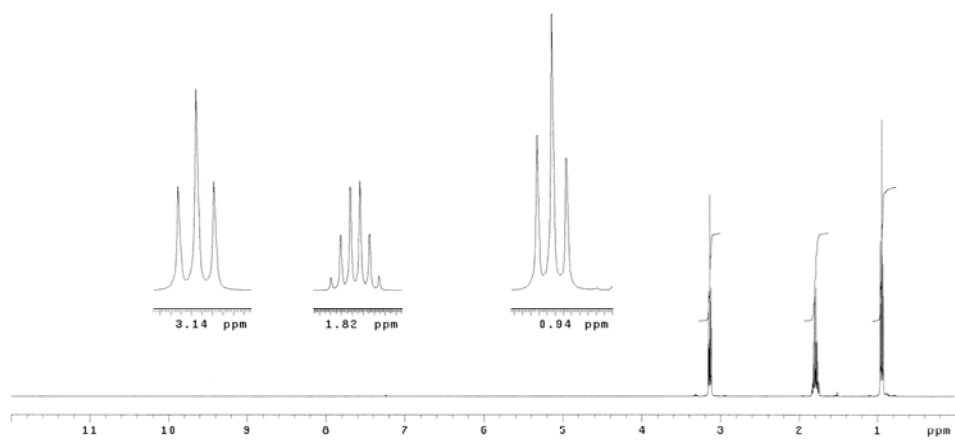


(4.2 ppm, 1H, septet), (1.5 ppm, 6H, doublet)

B. $C_3H_6Br_2$



C. C_3H_7I



(3.14 ppm, 2H, triplet), (1.82 ppm, 2H, sextet), (0.94 ppm, 3H, triplet)

Scratch Paper

Scratch Paper

Scratch Paper