Chem. 310N, Spring 2008, Professor Krische

Final Exam Key

Last Name:_____

First Name:_____

Problem

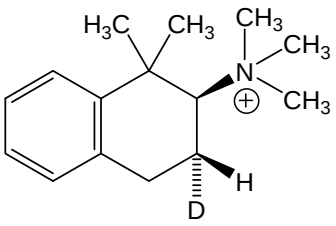
1. (30 points)_____
2. (12 points)_____
3. (10 points)_____
4. (14 points)_____
5. (15 points)_____
6. (10 points)_____
7. (24 points)_____
8. (20 points)_____
9. (15 points)_____

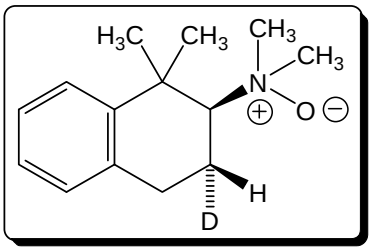
Total Points: /150

Letter Grade	T-Score
A+	100-96
A	95-92
A-	91-90
B+	89-86
B	85-82
B-	81-80
C+	79-76
C	75-72
C-	71-70
D+	69-66
D	65-62
D-	61-60
F	60-0

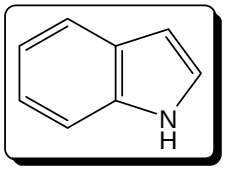
1. (30 Points) For the following compounds, circle the one that embodies the indicated property. (2 pts each)

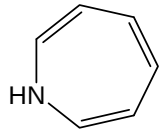
a. Retains deuterium upon elimination



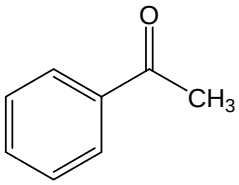


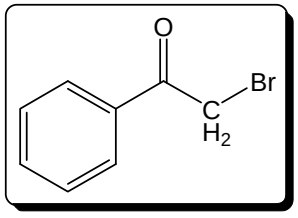
b. Aromatic Stabilization



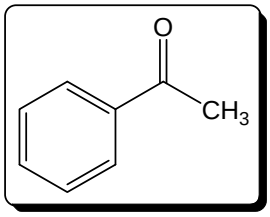


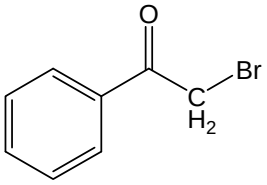
c. Faster Rate of Reaction with Br_2/NaOH



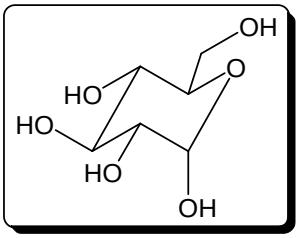


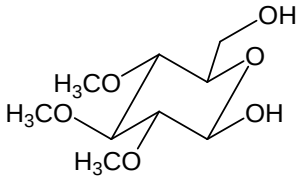
d. Faster Rate of Reaction with Br_2/HBr



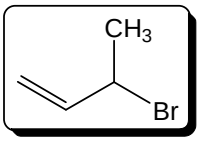


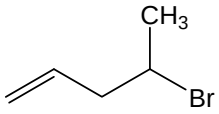
e. Anomeric Hydroxyl in α-configuration



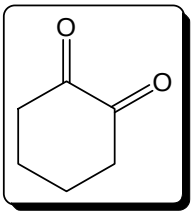


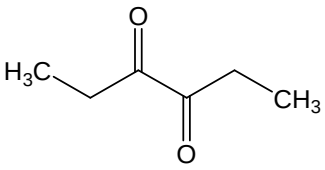
f. Faster Rate of Reaction with CH_3OH through an S_N1 Mechanism



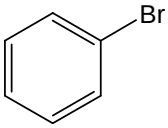


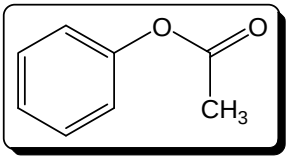
g. Greater Dipole Moment



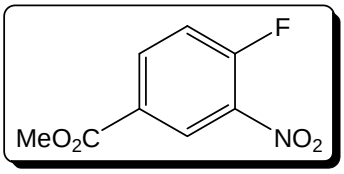


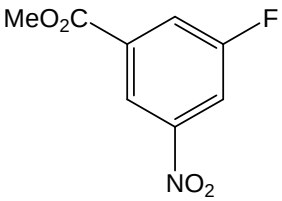
h. Faster Rate of Reaction with HNO_3/H_2SO_4



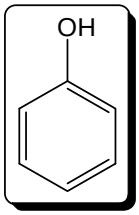


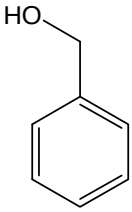
i. Faster Rate of Reaction with $NaOCH_3/HOCH_3$



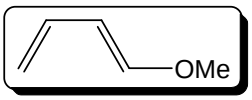


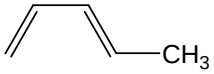
j. Greater Acidity



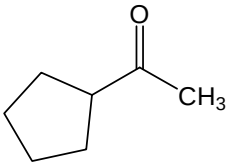


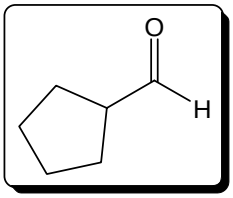
k. Faster Rate of Reaction in Diels-Alder Cycloaddition with cyclohexenone



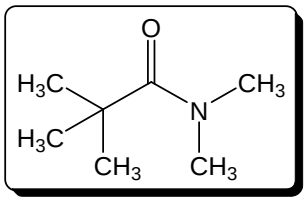


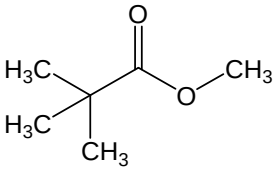
j. Greater Concentration of Hydrated Form at Equilibrium in water



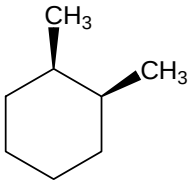


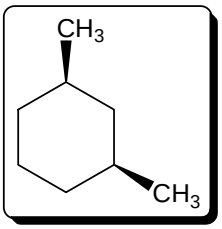
h. Greater Basicity of the Carbonyl Oxygen



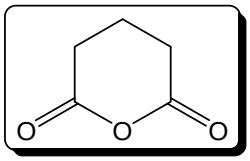


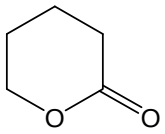
i. Greater Number of Signals in the ^{13}C NMR





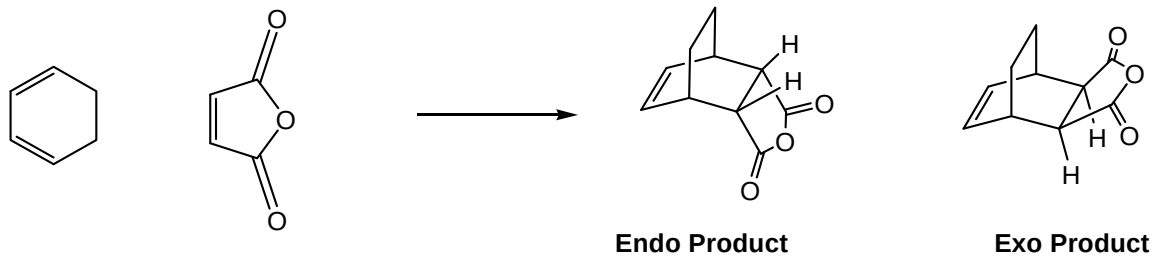
j. Faster Rate of Reaction with CH_3NH_2 through an Addition-Elimination Mechanism





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

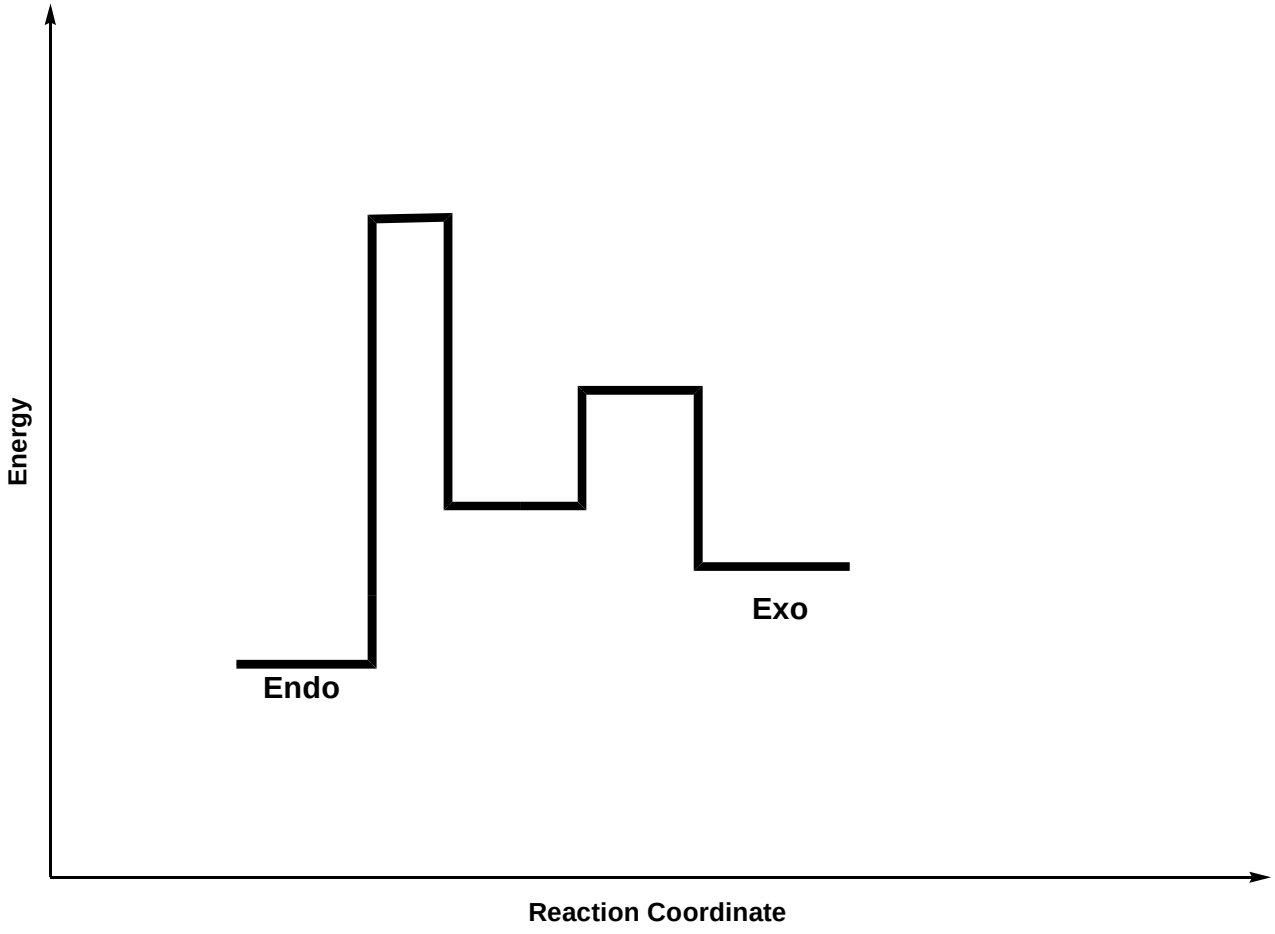
A. (8 Points) Draw the endo- and exo products.



Endo Product
Major Product at
Low Temperature

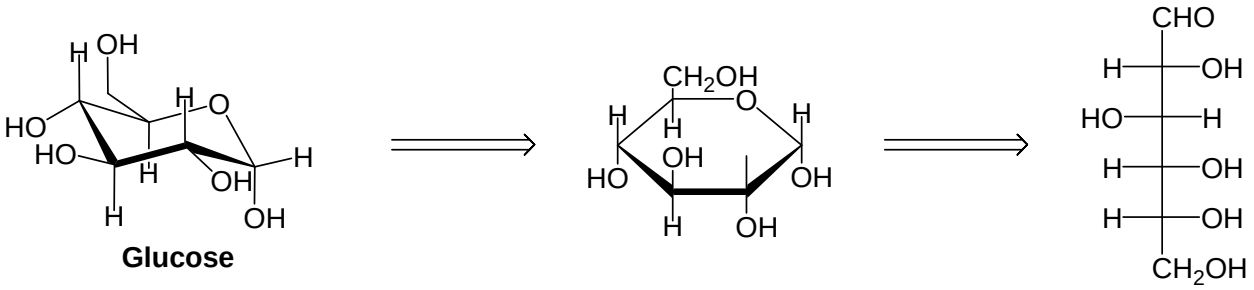
Exo Product
Major Product at
High Temperature

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



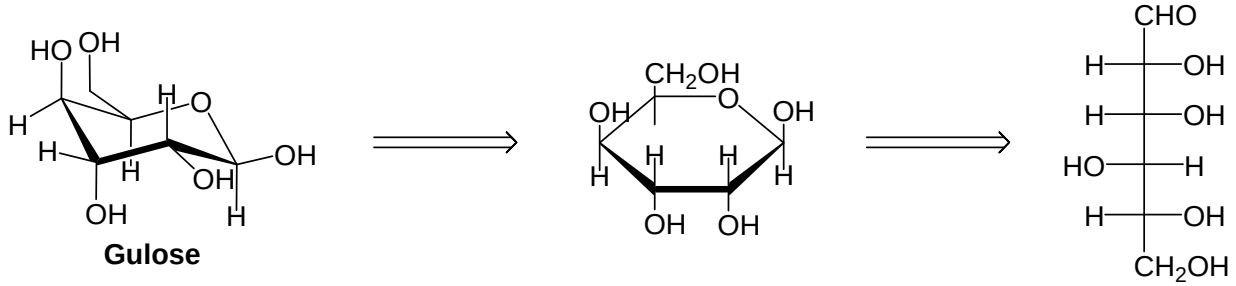
3. (10 points) Consider the following hexoses.

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



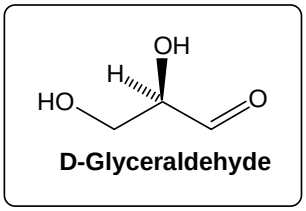
Glucose depicted as the... **a-anomer** **or** **β-anomer.**

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

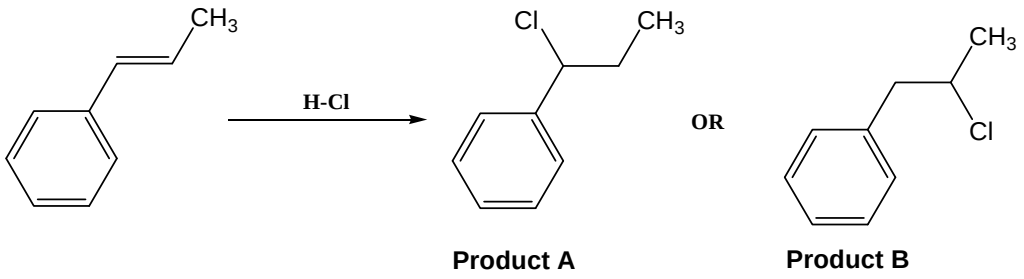


Gulose is depicted as the... **α-anomer** **or** **β-anomer.**

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

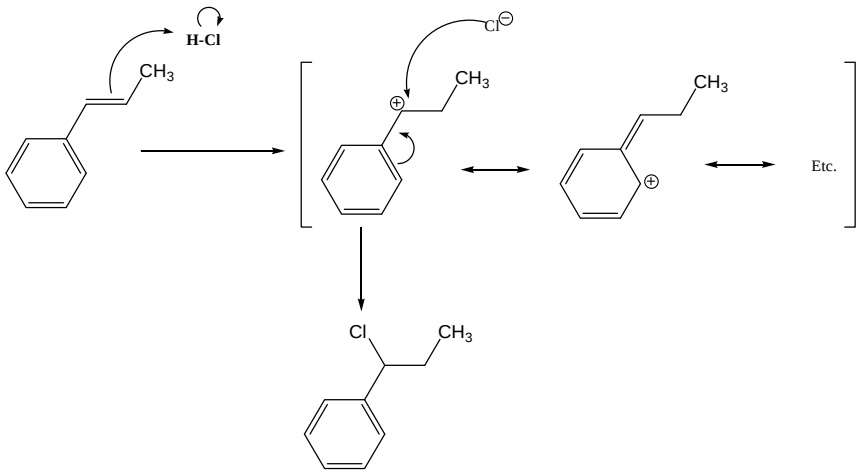


4. (14 points) Consider the hydrochlorination of the following alkene. Write separate mechanisms to account for the formation of each product, indicating any relevant resonance structures. Based on a comparison of the two mechanisms, predict which product is expected to be the major product. Circle the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

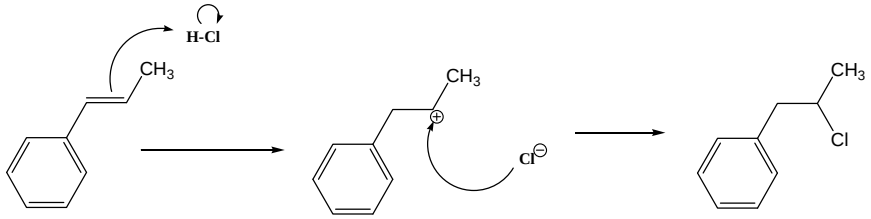


Product A **Product B**

Mechanism for formation of Product A: (5 pts)



Mechanism for formation of Product B: (5 pts)

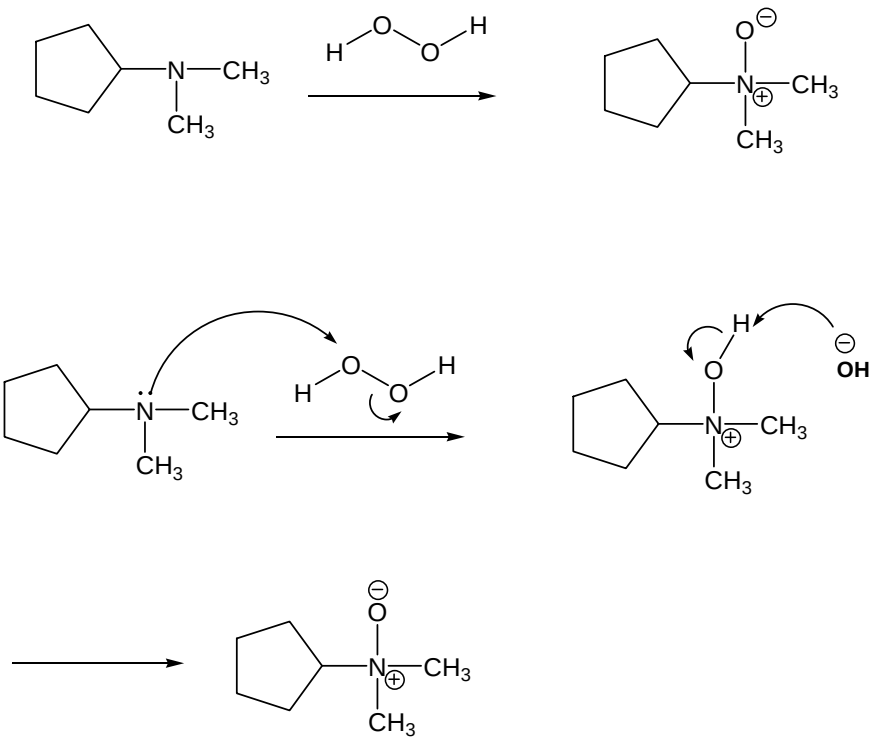


Justification (One sentence): (4 pts)

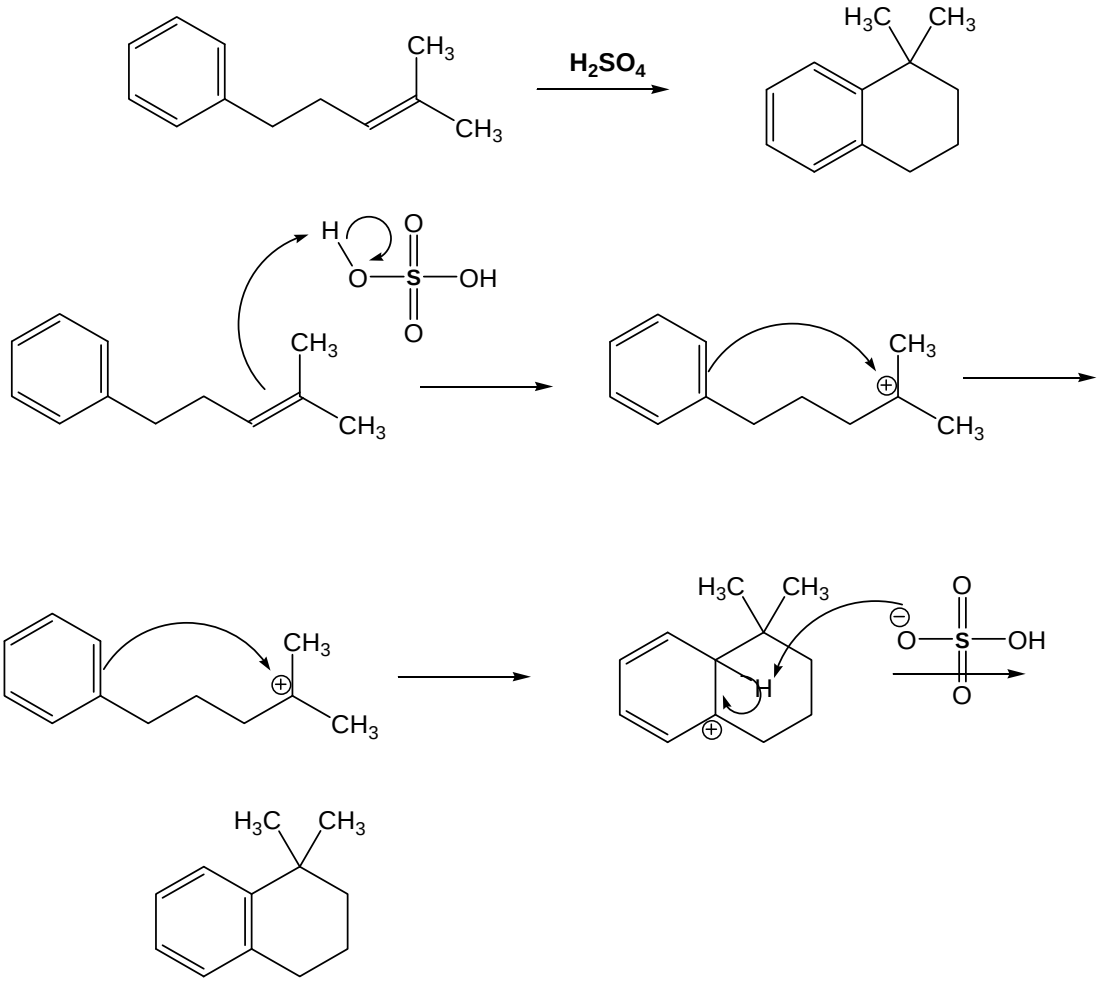
Resonance stabilization of the carbocation from the aromatic ring causes A to be favored.

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)

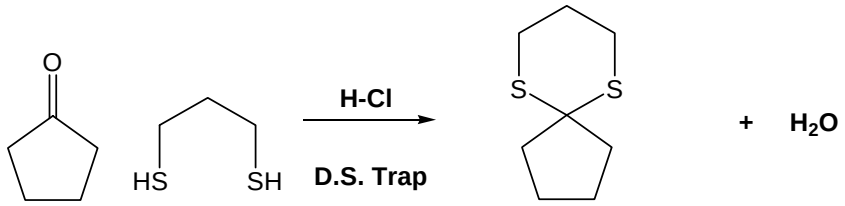
A.

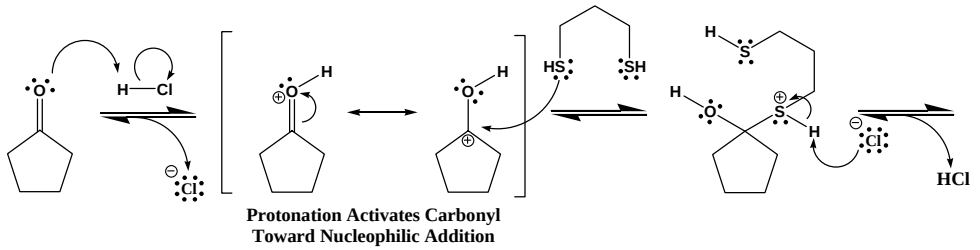


B.

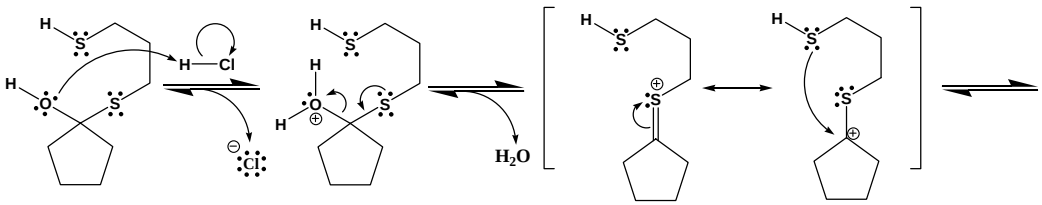

CH3
CH3
H2SO4
H3C
CH3
H
O
S
OH
O
O
CH3
CH3
CH3
CH3
CH3
CH3
H3C
CH3
O
O
S
OH
O
H
H3C
CH3

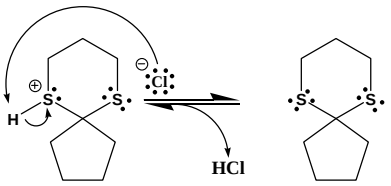
C.





Protonation Activates Carbonyl Toward Nucleophilic Addition

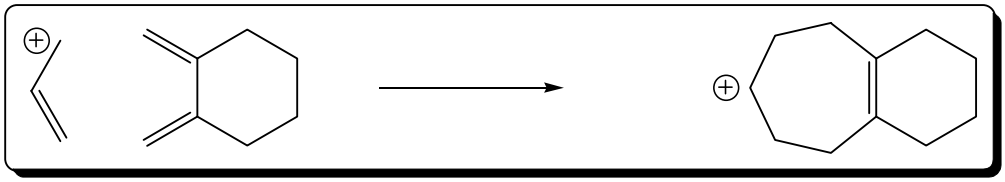


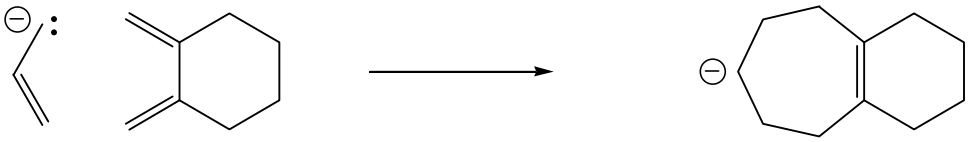


6. (10 points) Consider the proposed pericyclic reactions.

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 <u>one sentence</u>.

(4 pts)



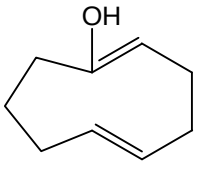


<u>Explanation</u>: (2 pts)

Aromatic stabilization of transition state.

B. Draw the **<u>final</u>** product of the following Cope rearrangement. (4 pts)

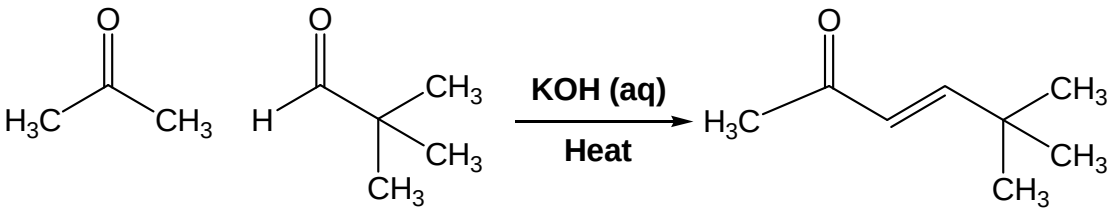
or



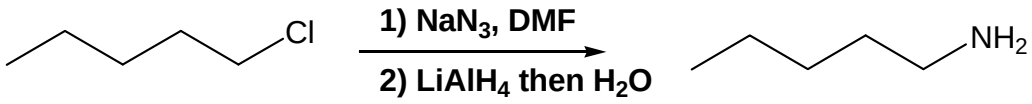
-1 pt

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.

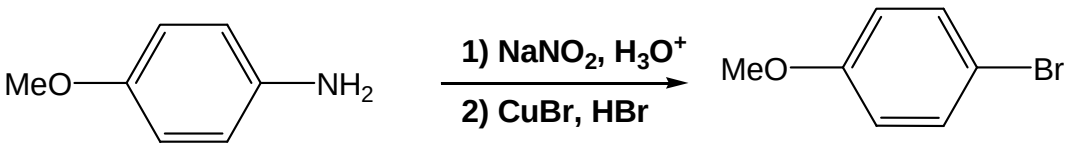
A.



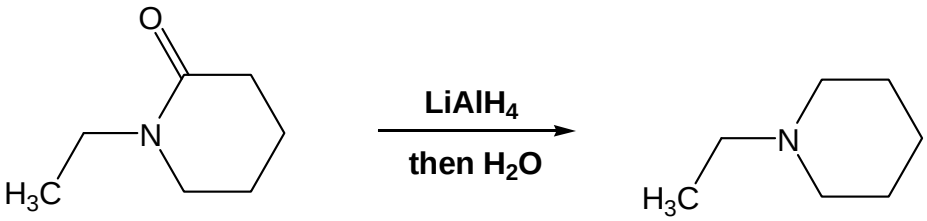
B.



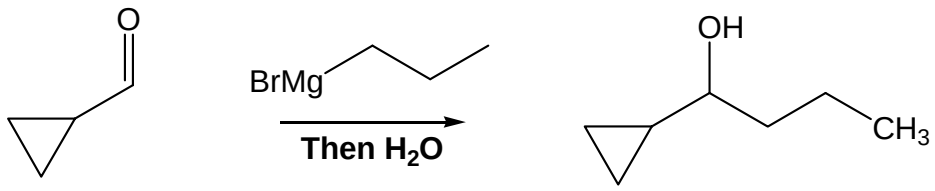
C.



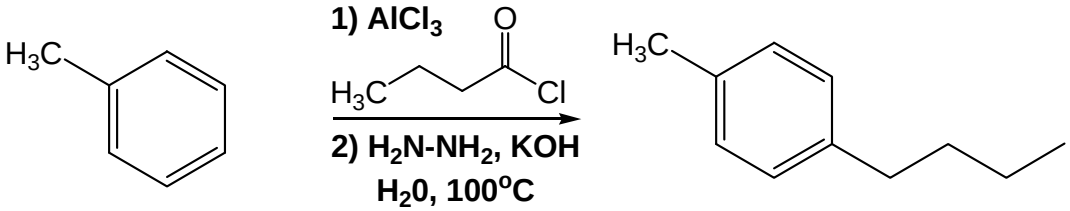
D.



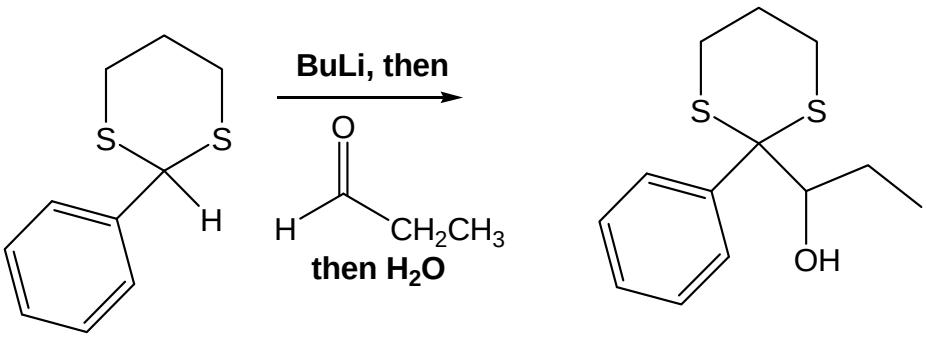
E.


O
BrMg
Then H_2O
OH
CH_3

F.

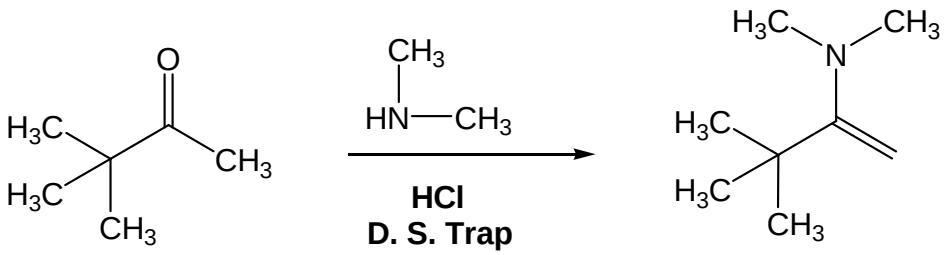

H_3C
1) $AlCl_3$
O
H_3C
Cl
2) H_2N-NH_2, KOH
H_20, 100°C
H_3C

G.

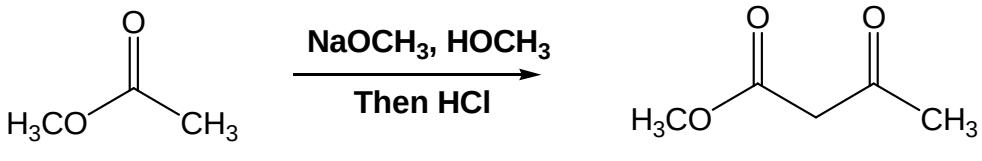

S
S
H
BuLi, then
O
H
CH_2CH_3
then H_2O
S
S
OH

H.

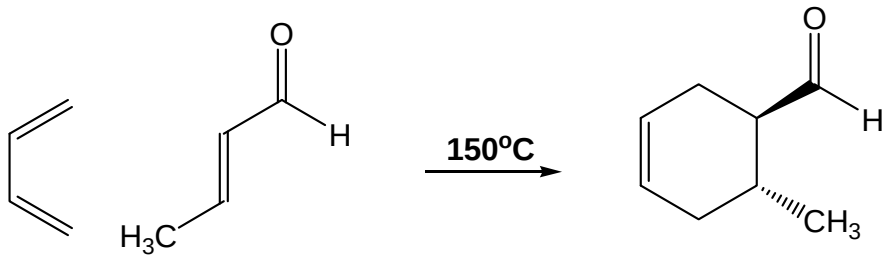
I.


O
H3C
CH3
H3C
CH3
CH3
HN
CH3
HCl
D. S. Trap
H3C
N
CH3
H3C
H3C
CH3

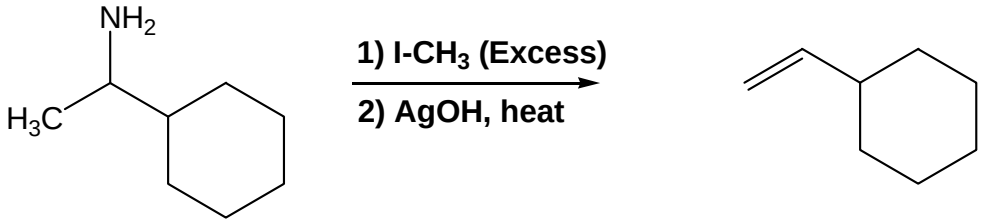
J.

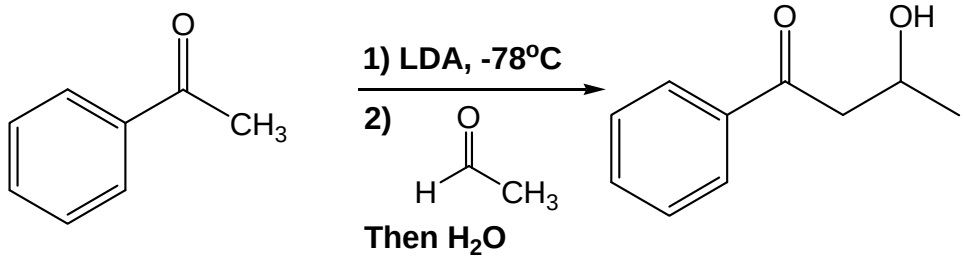

O
H3CO
CH3
NaOCH3, HOCH3
Then HCl
O
O
H3CO
CH3

K.


O
H
H3C
150°C
O
H
CH3

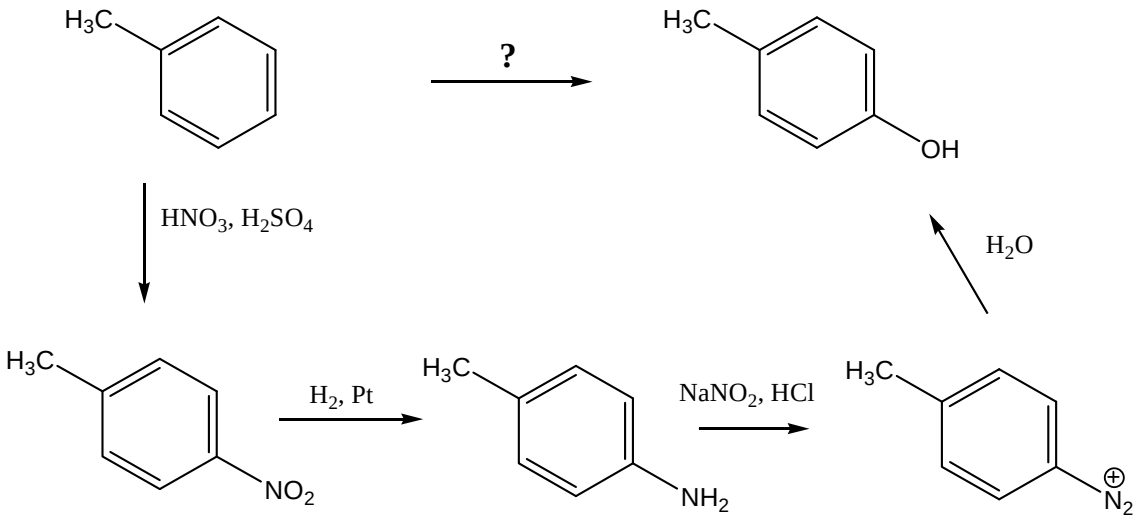
L.


NH2
H3C
1) I-CH3 (Excess)
2) AgOH, heat

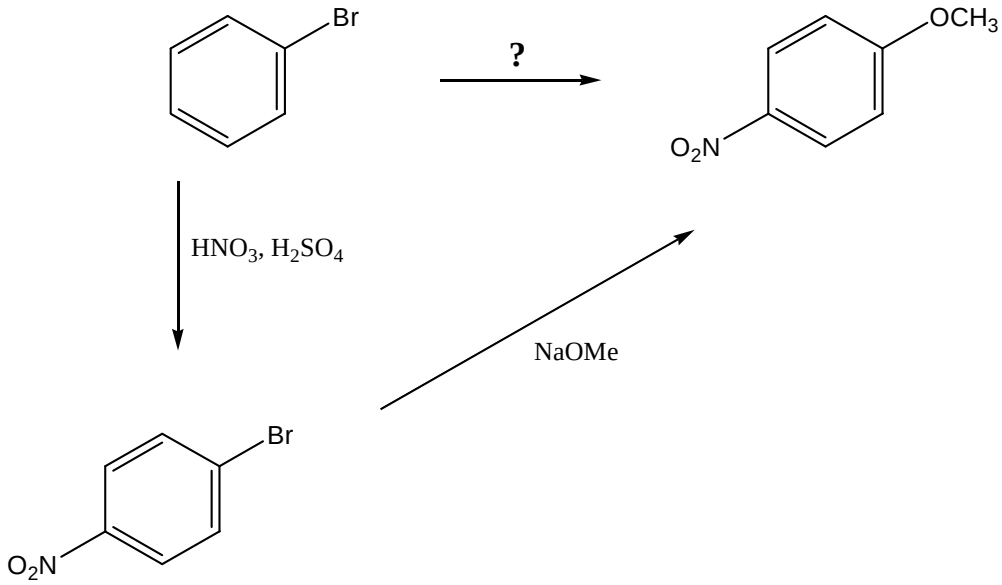

O
CH3
1) LDA, -78°C
2)
O
H
CH3
Then H2O
O
OH

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).

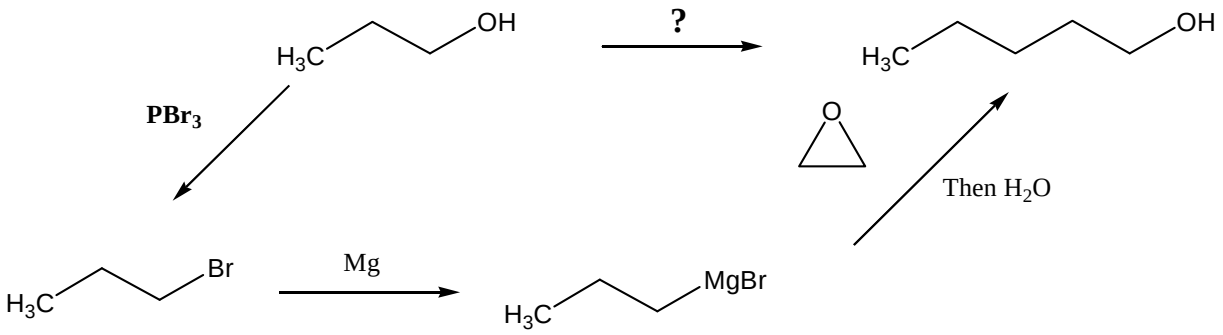
A. (5 pts)



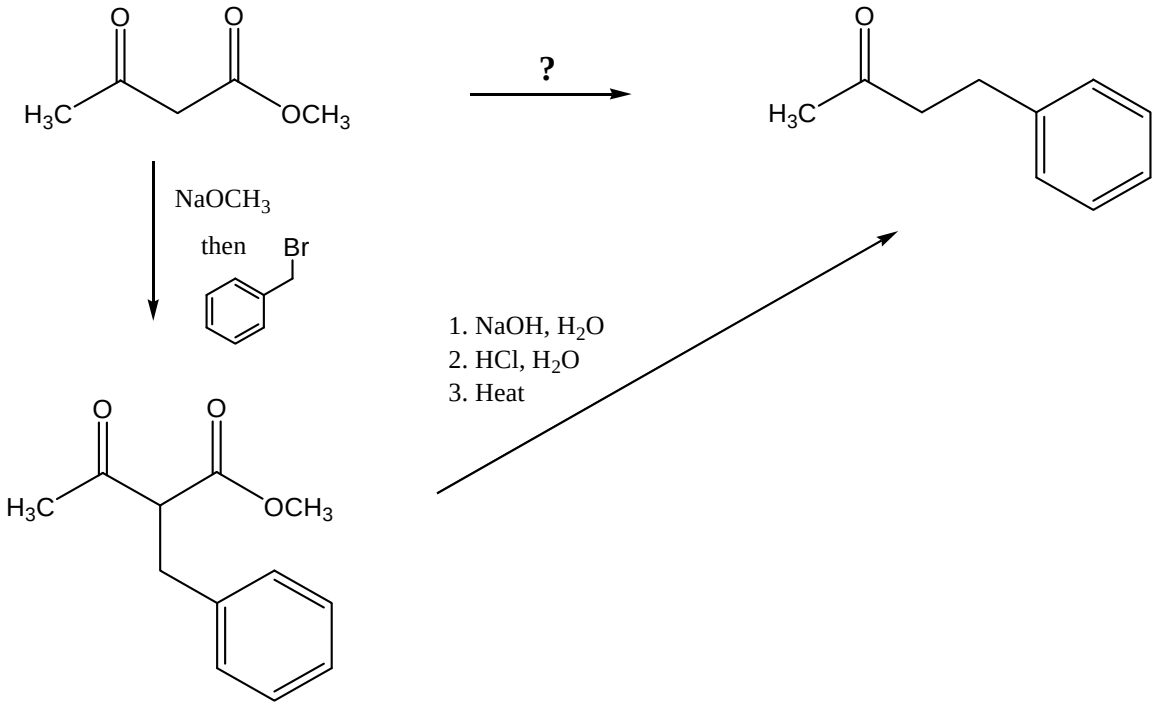
B. (5 pts)



C. (5pts)

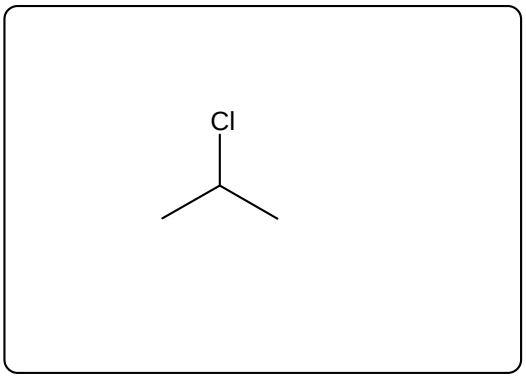

OH
H3C
?
PBr3
O
Then H2O
Br
Mg
MgBr

D. (5 pts)

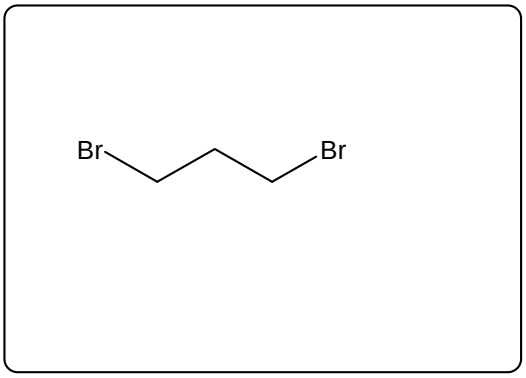

O
O
H3C
OCH3
?
NaOCH3
then
Br
1. NaOH, H2O
2. HCl, H2O
3. Heat

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

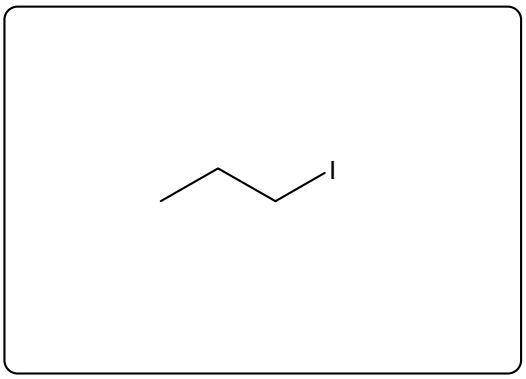
Compound A) C_3H_7Cl



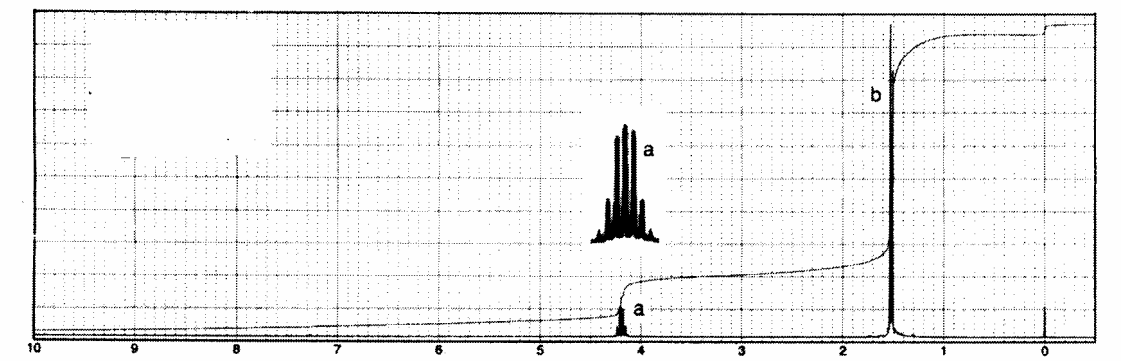
Compound B) $C_3H_6Br_2$



Compound C) C_3H_7I

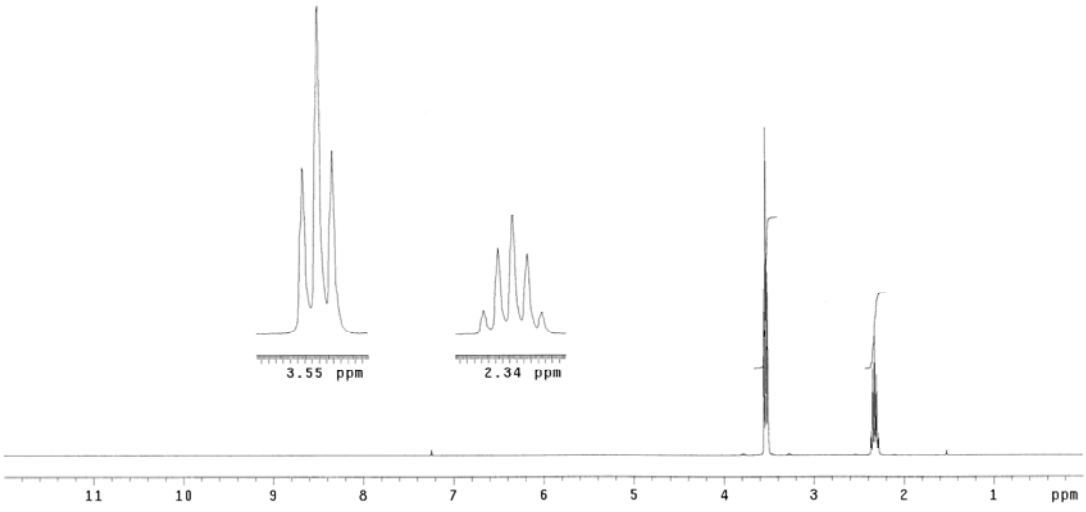


A. C_3H_7Cl



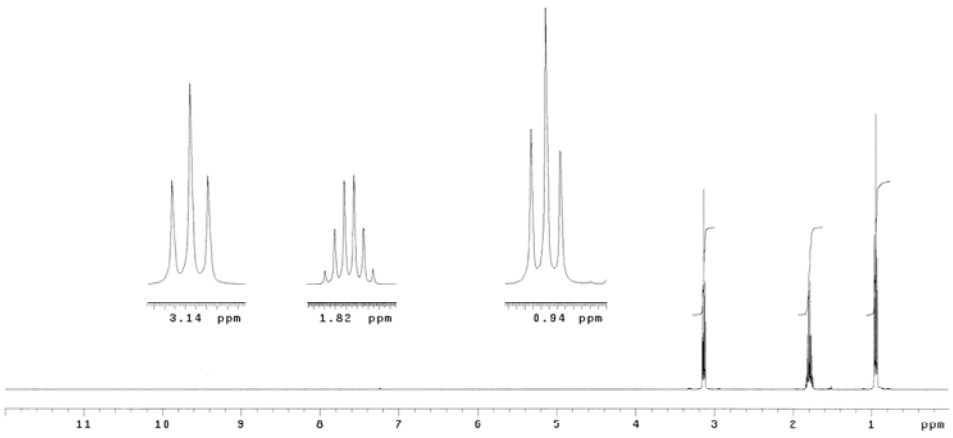
(4.2 ppm, 1H, septet), (1.5 ppm, 6H, doublet)

B. $C_3H_6Br_2$



(3.55 ppm, 4H, triplet), (2.34 ppm, 2H, pentet)

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