



Name: _____

Student Number _____

This paper consists of **13 pages (10 questions)** (including this title page).

Ensure that you have a complete paper (data pages will be provided).

Molecular models and a non-programmable calculator may be used during this examination.

Time: 3 hours (180 minutes)

Marking Scheme For The Exam

QUESTION #

1	2	3	4	5	6	7	8	9	10
14	11	13	12	20	18	35	16	14	15

168		
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Total

Grade

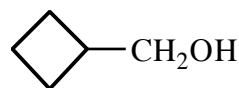
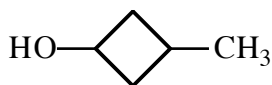
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Budget your time carefully and best wishes for the holidays!!

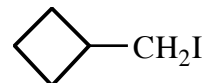
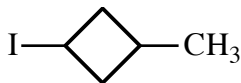
I hope you enjoyed the course and all the best for 2005!!!

Question 1. (14 Marks) A. Circle the correct answer. (4)

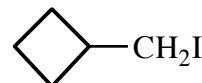
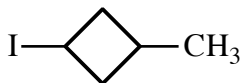
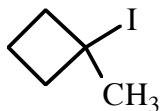
a) The compound that requires the lowest temperature for an E1 reaction with concentrated H_2SO_4 .



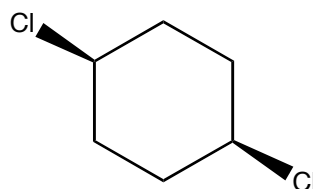
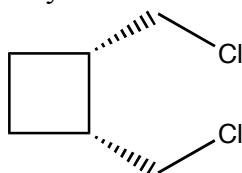
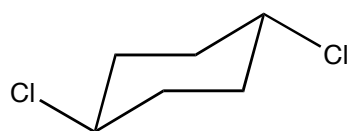
b) The compound that will give the least amount of E2 product with $\text{CH}_3\text{O}^-/\text{CH}_3\text{OH}$.



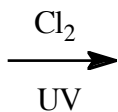
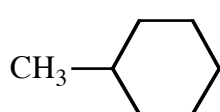
c) The compound that will give the fastest solvolysis reaction with H_2O .



d) Is a constitutional isomer of trans-1,4-dichlorocyclohexane



B. The following achiral compound was subjected to Cl_2/UV . Provide the number for each of the listed terms to describe the outcome of the **monochlorination reaction**; i.e., each product contains only one Cl atom. (5)



monochlorination products

___ positional isomers

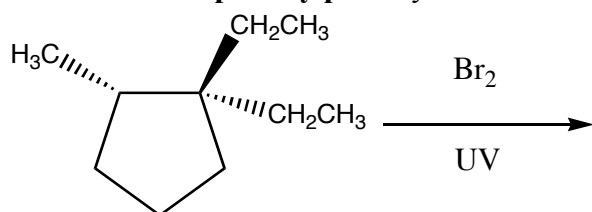
___ pairs of enantiomers

___ achiral compounds

___ pairs of geometric isomers; i.e., cis/trans pairs

___ peaks in the GC trace (you may assume that enantiomers **cannot** be separated)

C. Provide the structure (including any necessary stereochemistry) of the **two** major products formed in the reaction of the **optically pure** hydrocarbon and then circle the correct answer. (5)



This reaction is regioselective:

T

F

This reaction is stereoselective:

T

F

The starting material can have a diastereomer:

T

F

The starting material can have an enantiomer:

T

F

The reactive intermediate is a:

bromonium ion

carbocation

free radical

The reactive intermediate is:

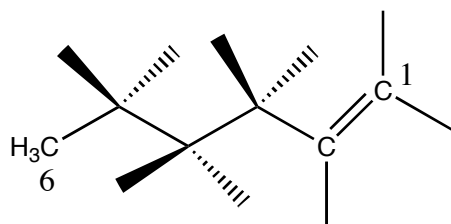
achiral

racemic

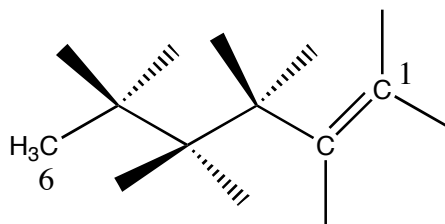
optically pure

Question 2. (11 Marks) A. Compound A is (E)-3S, 4S, 5R-tribromo-1-chlorohexene (4)

- complete the partial sawhorse projection of A to clearly show its stereochemistry
- complete the partial sawhorse projection to show the enantiomer of A

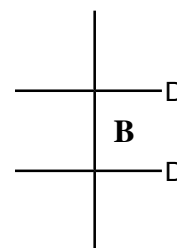
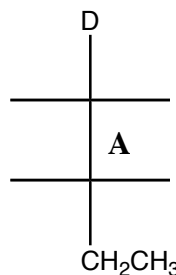
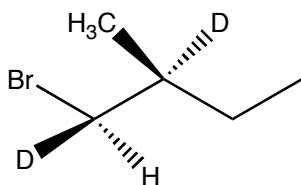
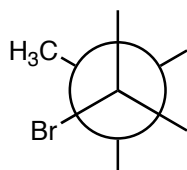


A



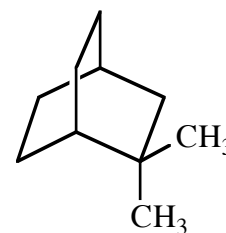
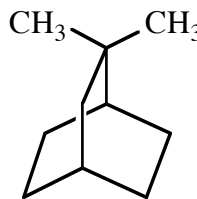
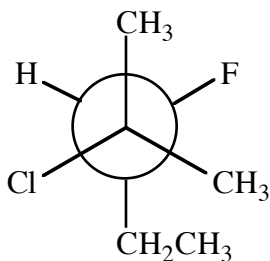
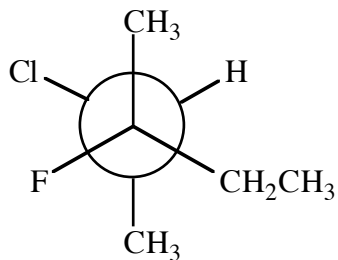
enantiomer of A

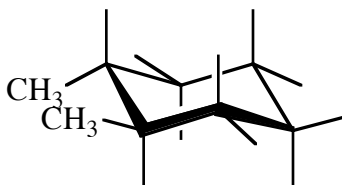
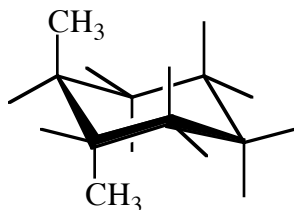
B. Complete the Newman Projection formula (on the left) and its Fischer Projection formula (A) and the Fischer Projection formula of a diastereomer (B) of the compound shown in the sawhorse projection formula. (3)

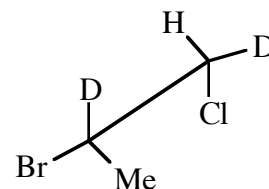
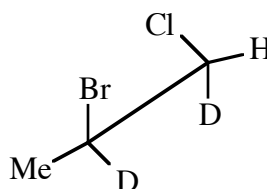


C. Given below are structural diagrams for several pairs of molecules. From the following list of 5 terms, choose the term that best describes each pair. The terms may be used more than once or not at all. (4)

enantiomers diastereomers conformers constitutional isomers identical

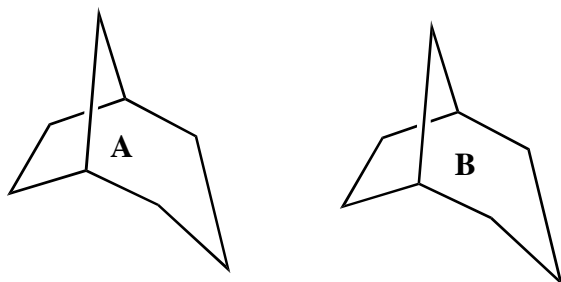






Question 3. (13 Marks) A. Complete the structures below to illustrate the listed terms. (8)

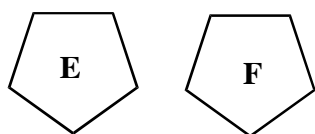
A and B - a pair of enantiomers
(add two Cl atoms and a C=O group)



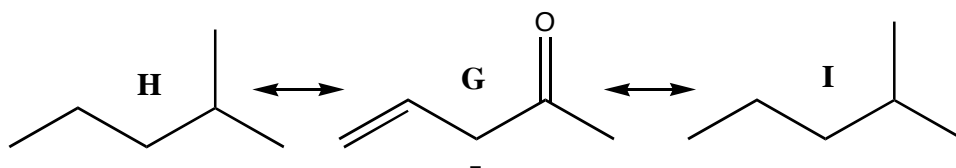
C and D - a pair of diastereomers
(add a Me group and a Br atom)



E and F - a pair of tautomers
(use the formula $C_6H_{10}O$)

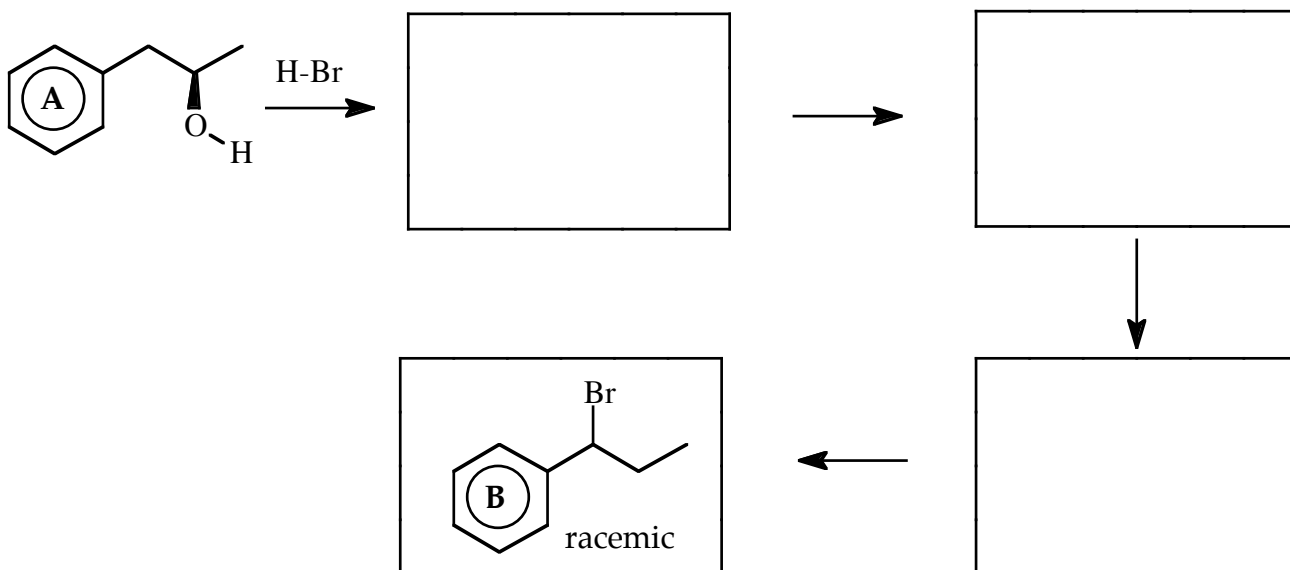


H and I - 2 different localized resonance structures of **G**
(all atoms must have a completed valence shell of e's)



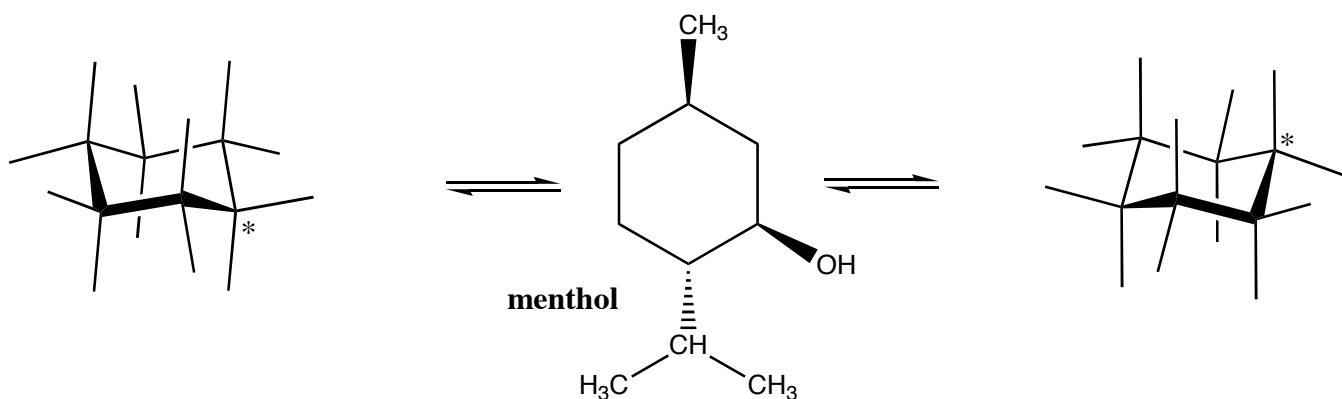
B. Provide (with any appropriate stereochemical prefixes) the IUPAC name of your compound A above. (1)

C. The reaction of the optically pure alcohol A below with concentrated HBr produces the final product B (as a racemic mixture). Briefly sketch the mechanistic steps involved in this conversion, including the correct direction for any arrows representing the movement of electrons. The boxes should contain the three reactive intermediates involved in the process. (4)



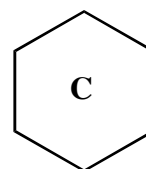
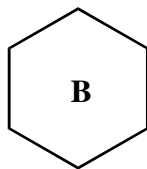
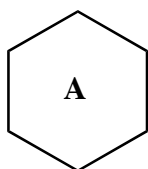
Question 4. (12 Marks) The structure of the natural product menthol (isolated from peppermint) is shown below. The stereoisomer shown has a boiling point of 207 °C and a specific rotation of -28°.

A. Complete the two chair conformational isomers below and then circle the more stable one. The * is where I would like you to place the OH group on each structure. (3)



B. Menthol is best labelled as: { **cis, cis / trans, trans / cis, trans / trans, cis** } (1)

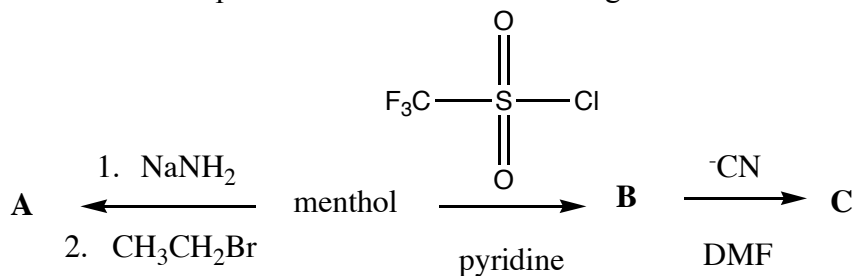
C. Complete the structures (**clearly indicating any necessary stereochemistry**) for: (3)
 a constitutional isomer of menthol which has a specific rotation of 0° (**compound A**)
 a stereoisomer of menthol which has a specific rotation of +28° (**compound B**)
 a stereoisomer of menthol which has a boiling point not equal to 207 °C (**compound C**)



D. A synthetic sample of menthol has a specific rotation of +6.2°. Determine the optical purity of the sample and the % of (+)-menthol and (-)-menthol molecules in the synthetic sample. (2)

optical purity: ____ % (+)-menthol: ____ % (-)-menthol: ____ %

E. Complete the structures of the compounds formed in the following reactions of menthol: (3)

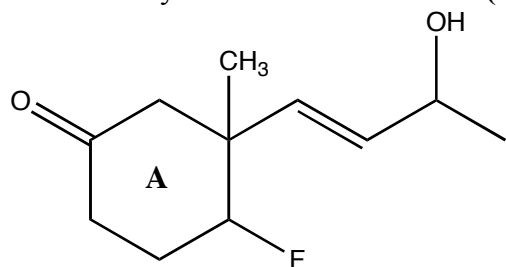


A: _____

B: _____

C: _____

Question 5. (20 Marks) A. Provide the IUPAC name for the following compound A and provide the necessary answers. (4)



How many degrees of unsaturation are present? _____

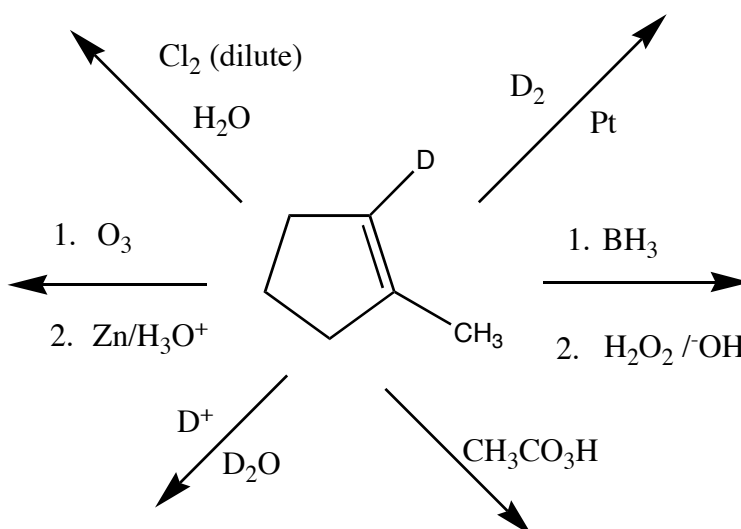
How many pairs of non-bonding electrons are present? _____

How many vinyl C atoms are present? _____

How many 2° H atoms are present? _____

IUPAC name: _____

B. Propose the structure of the major product formed in each of the following reactions on the same starting material. Include any pertinent stereochemistry and **indicate whether the product is a single achiral compound, a racemic mixture or some other mixture of isomers.** (12)



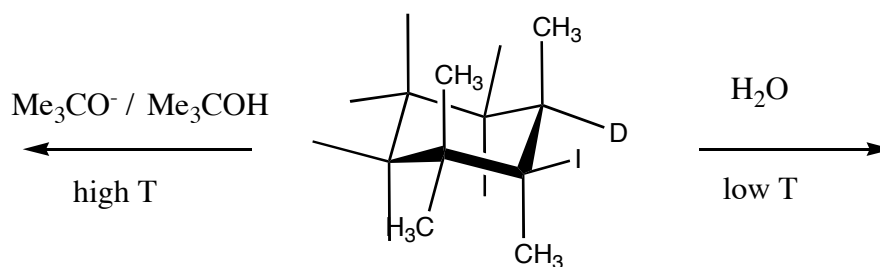
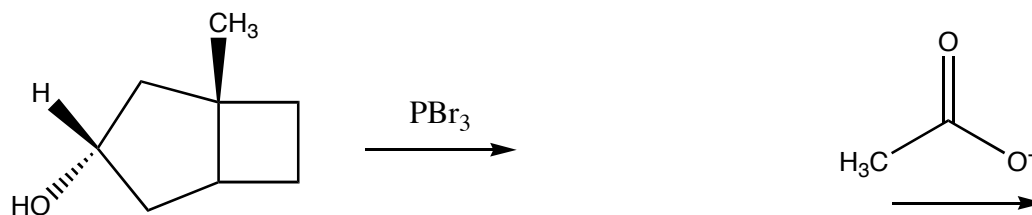
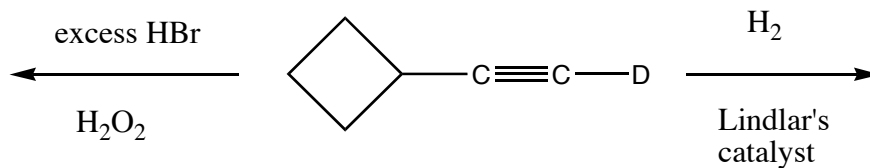
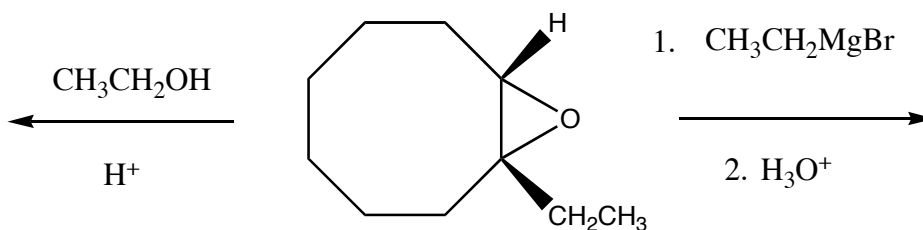
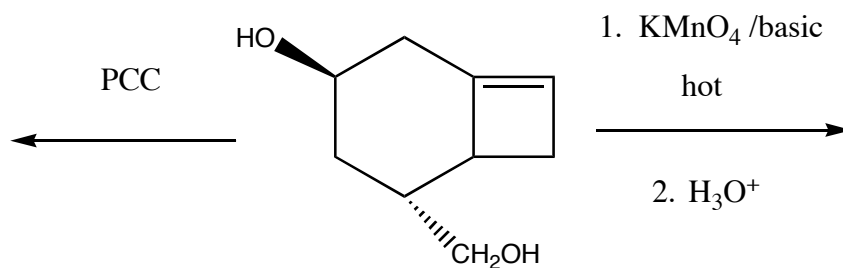
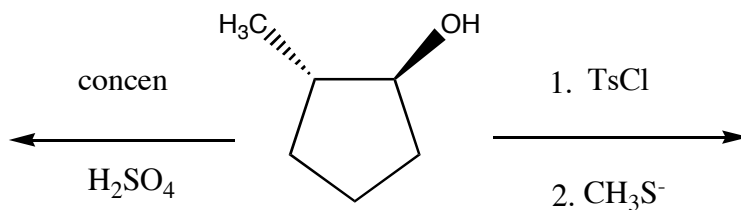
C. The D^+/D_2O process in part B is a { **concerted** / **nonconcerted** } { **stereoselective** / **regioselective** } reaction best described as { **an electrophilic** / **a nucleophilic** } { **addition** / **substitution** }. (2)

D. Indicate the type of intermediate involved in the: (1)

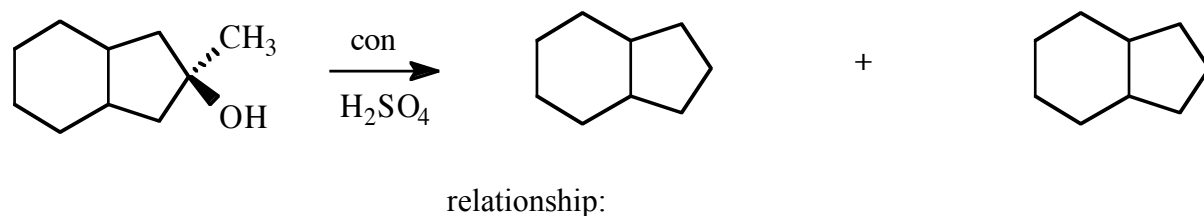
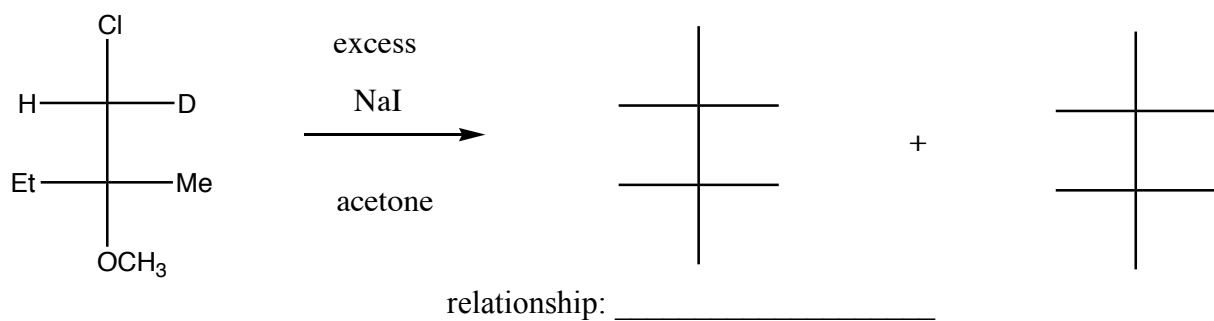
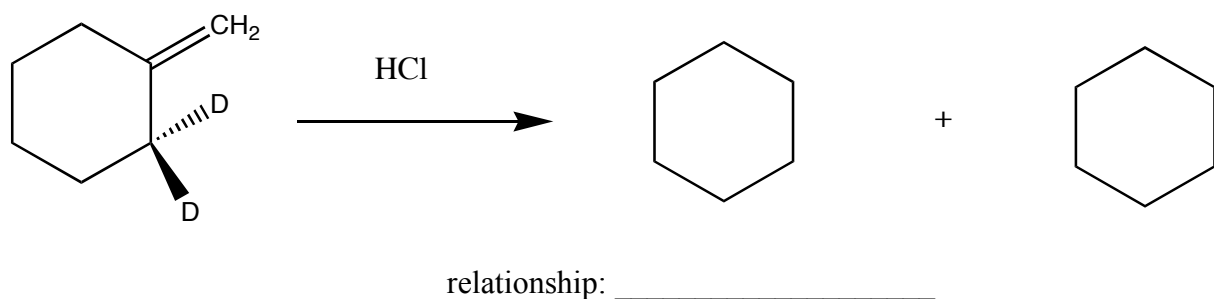
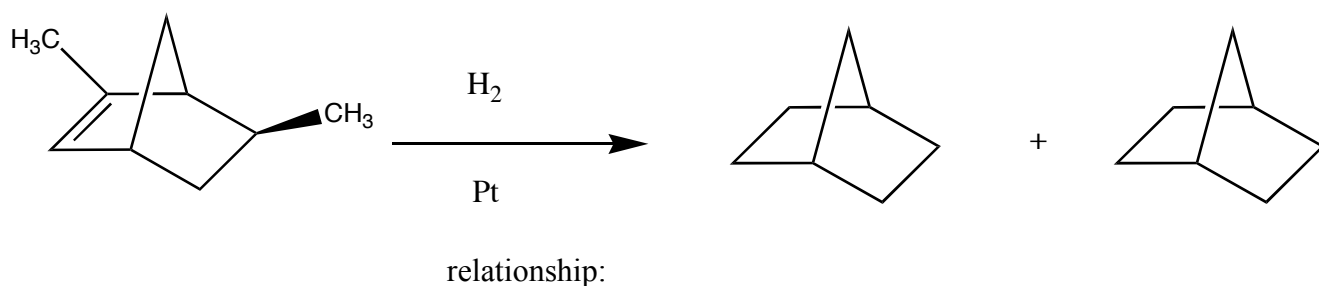
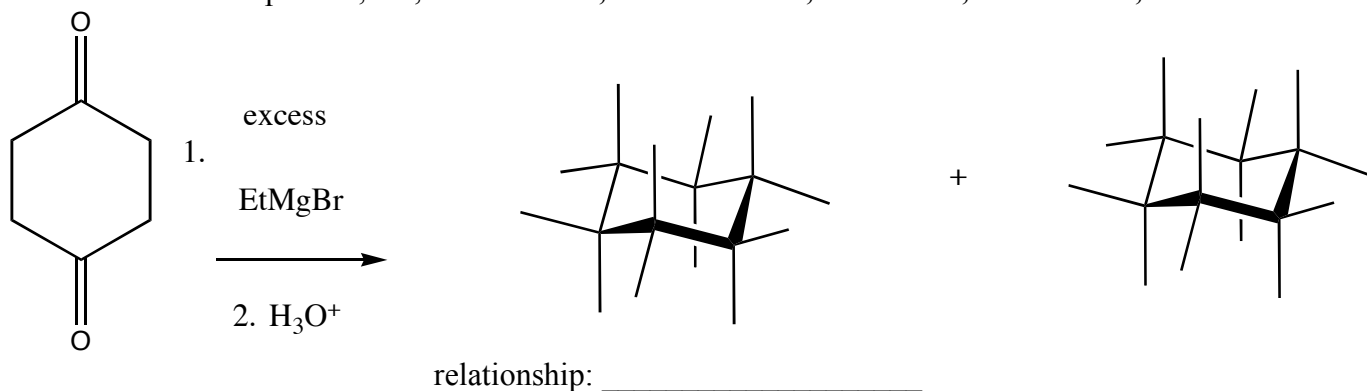
Cl_2 / H_2O reaction in part B: _____ O_3 reaction in part B: _____

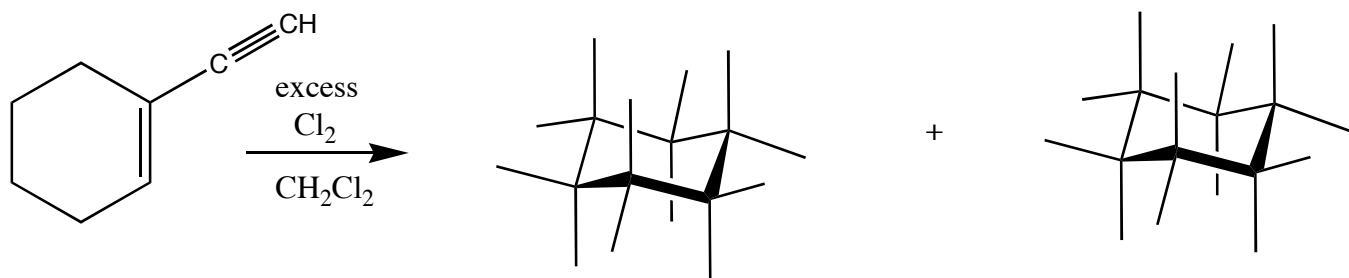
E. The BH_3 reaction in part B is { **a syn** / **an anti** } { **Markovnikov** / **anti-Markovnikov** } process. (1)

Question 6. (18 Marks) Provide the structure of the **major product** expected in each of the following reactions. **Include any pertinent stereochemistry** where important.

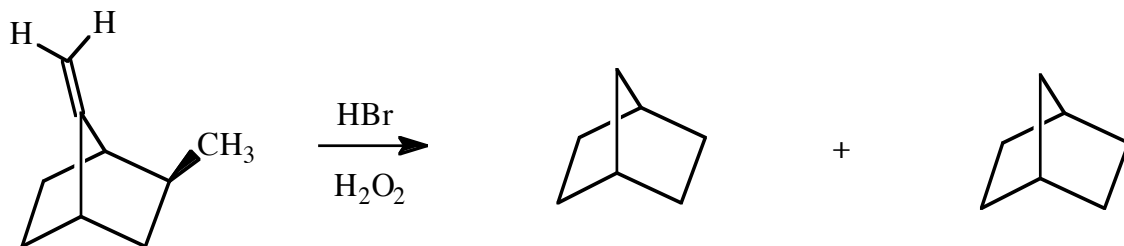


Question 7. (35 Marks) Each of the following reactions produces **2 major products**. Complete the structure of each product (**clearly showing any pertinent stereochemistry**) and indicate the relationship between the two compounds; i.e., **enantiomers, diastereomers, tautomers, not isomers, etc....**

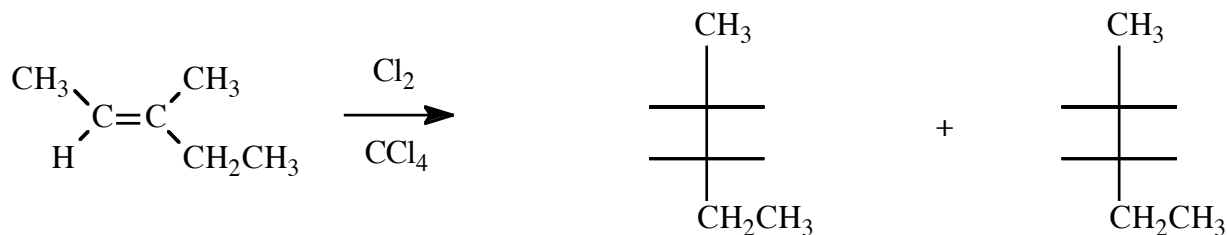




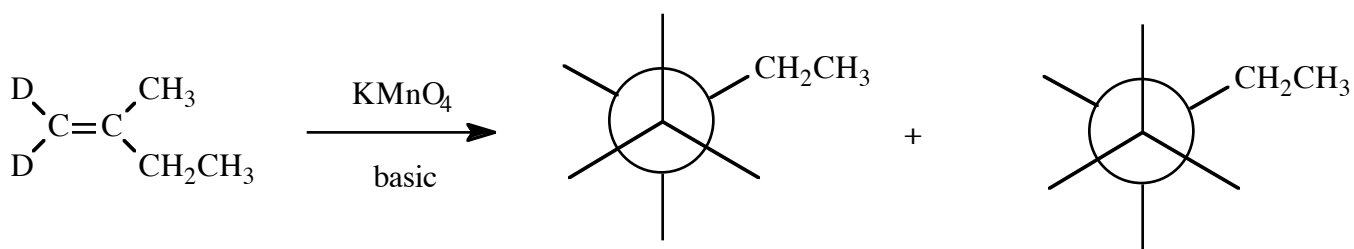
relationship: _____



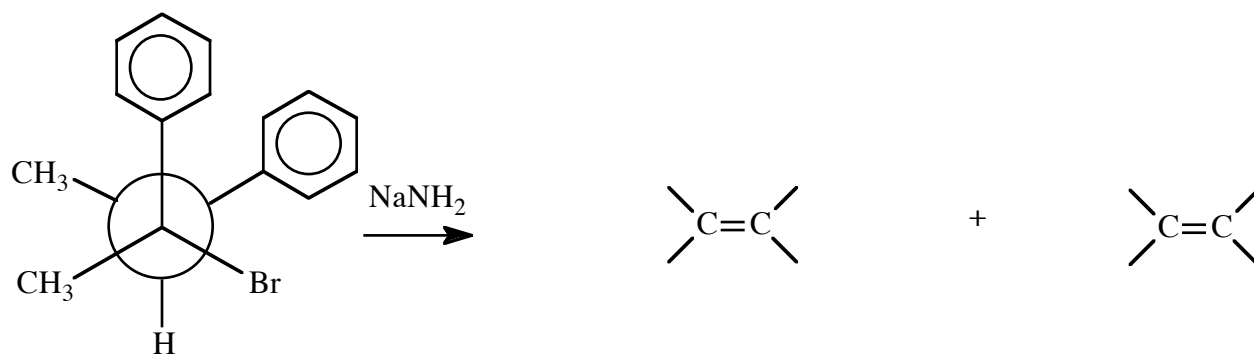
relationship: _____



relationship: _____



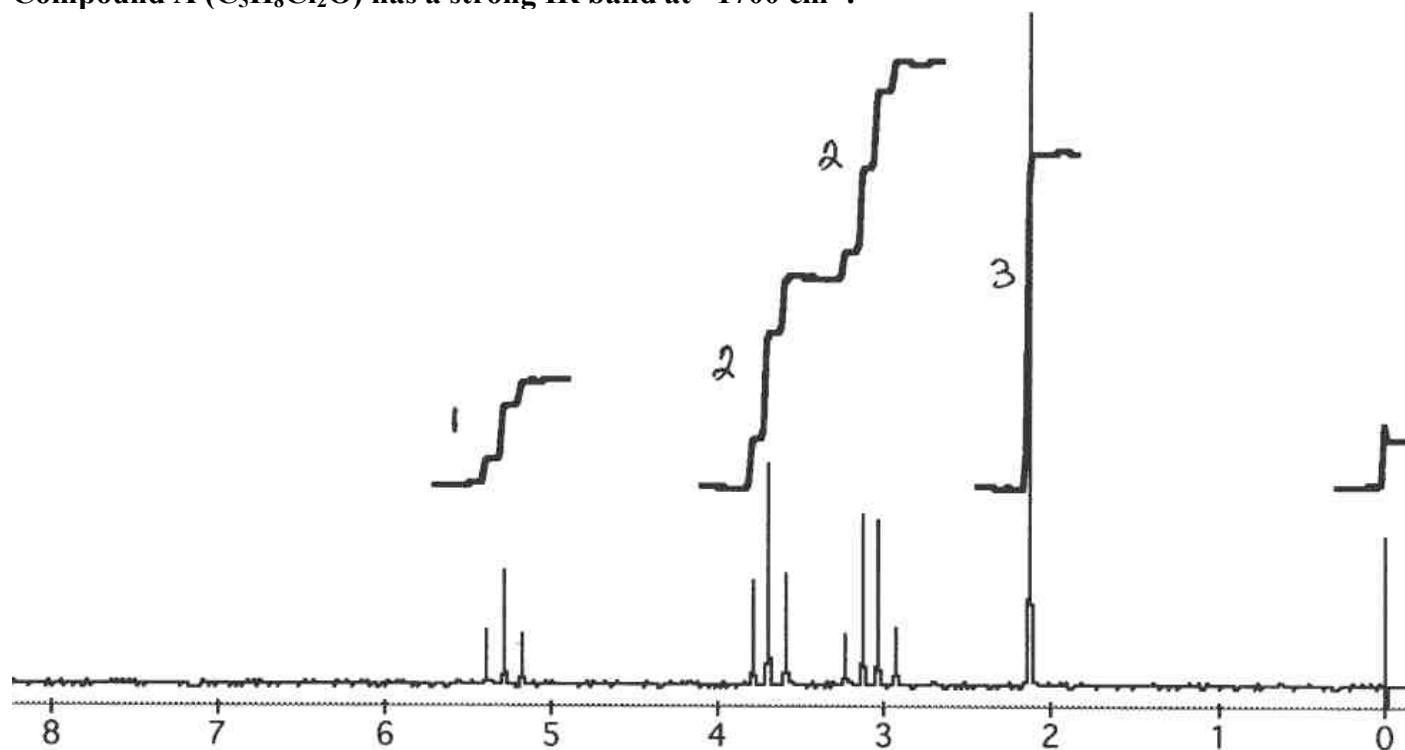
relationship: _____



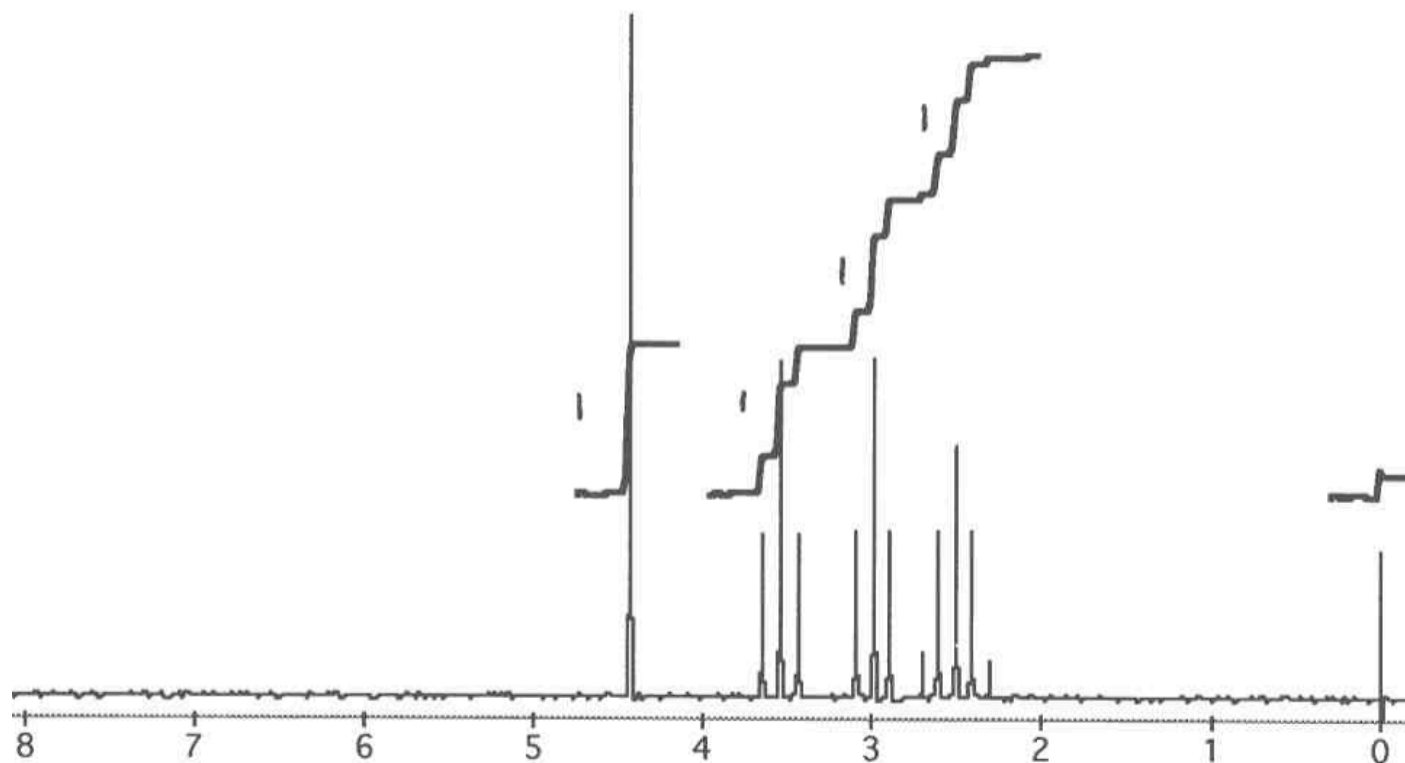
relationship: _____

Question 8. (16 Marks) Provide the structures of the compounds based upon the IR and ^1H -NMR information provided below.

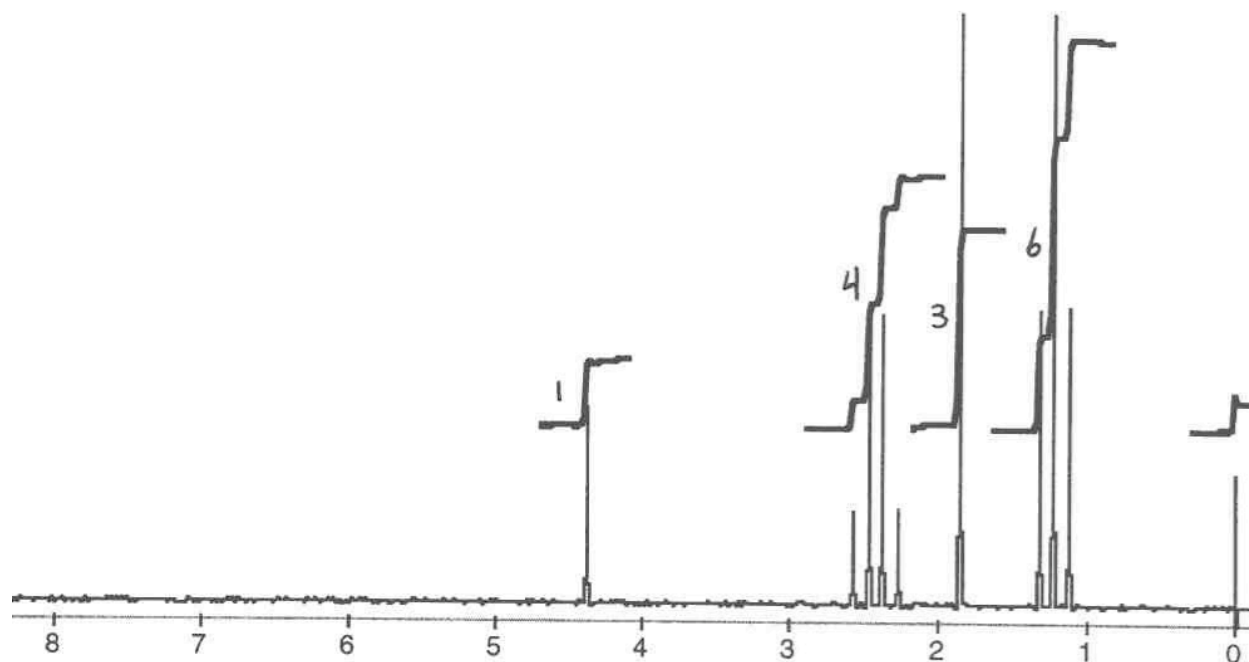
Compound A ($\text{C}_5\text{H}_8\text{Cl}_2\text{O}$) has a strong IR band at $\sim 1700\text{ cm}^{-1}$.



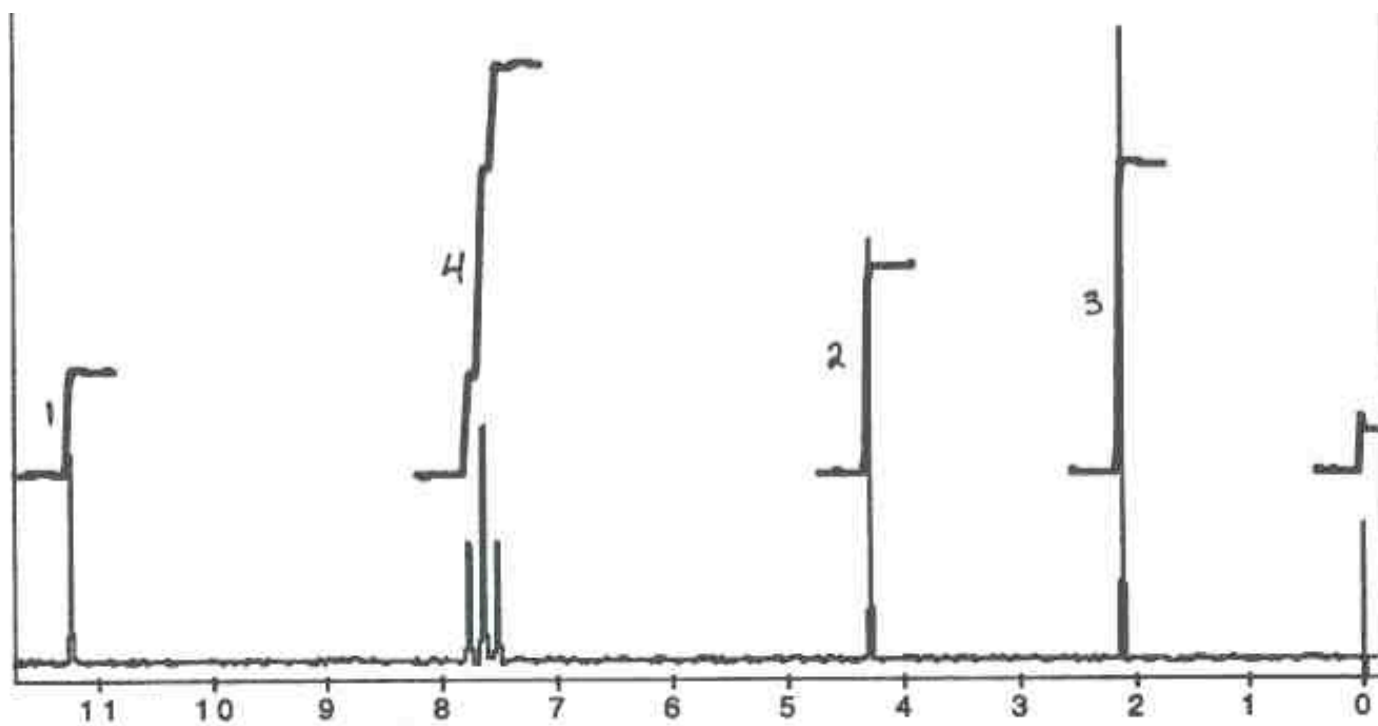
Compound B ($\text{C}_5\text{H}_8\text{Cl}_2\text{O}$) has a strong IR band at $\sim 1700\text{ cm}^{-1}$.



Compound C ($\text{C}_6\text{H}_{14}\text{O}$) has a strong IR band at $\sim 3400\text{ cm}^{-1}$.



Compound D ($\text{C}_9\text{H}_{10}\text{O}_2$) has a strong IR band at $\sim 1700\text{ cm}^{-1}$ and a broad band from 2500 to 3400 cm^{-1} .

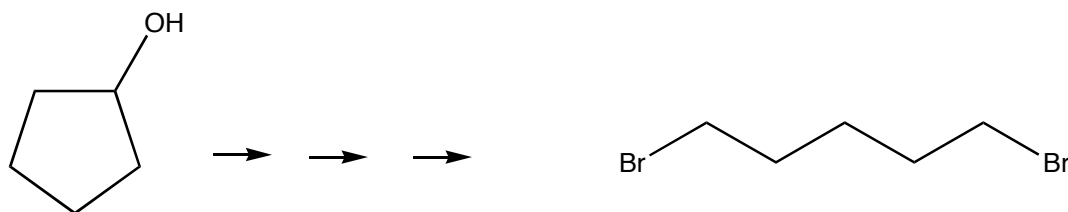
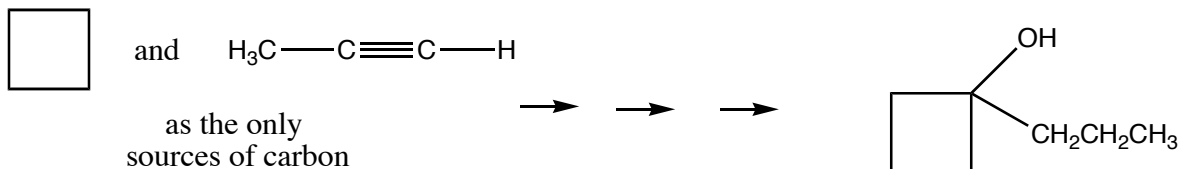


Question 9. (14 Marks) A. Compounds X and Y (C_xH_yF) have the same parent peak (88) in the MS. Compound X contains only primary H atoms, while compound Y contains only secondary H atoms. Determine the molar mass and propose a suitable structure for each of the compounds. **(4)**

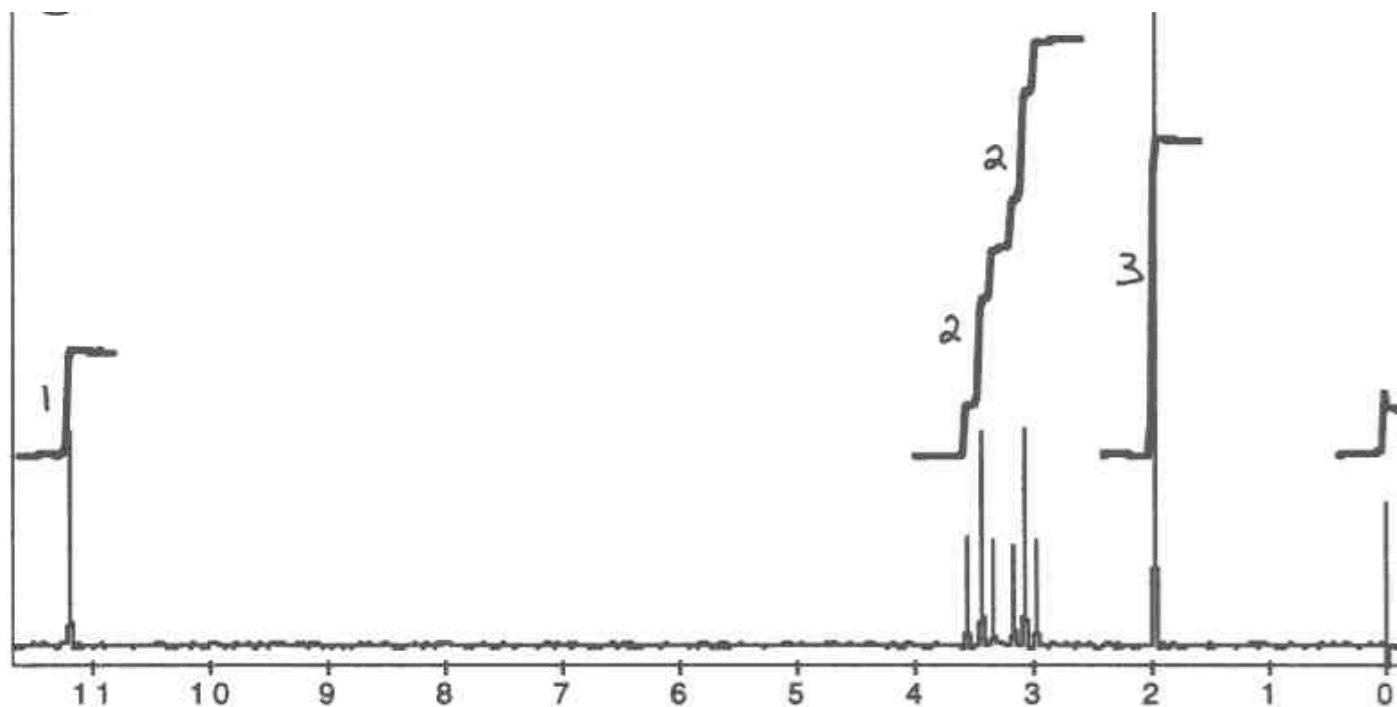
X: _____

Y: _____

B. Perform the following sequences. You may use any inorganic reagents in addition to the original starting materials (which you can use as many times as you need to). Show the structure of the **major product** formed after each reaction. **(10)**



Question 10. (15 Marks) The optically pure compound A (C_5H_7Br) was converted to compounds B and C (both C_5H_9Br and diastereomers of each other) upon reaction with hydrogen gas in the presence of a Pt catalyst. Compounds B and C were separated from each other and both were found to be optically pure. When compound A was converted to the corresponding Grignard reagent and then hydrolyzed with a dilute solution of hydrochloric acid, the achiral compound D (C_5H_8) was produced. Treatment of compound D with a hot basic solution of $KMnO_4$, followed by acidification, led to the formation of the achiral compound E ($C_5H_8O_3$). The IR spectrum of compound E showed two strong bands around 1700 cm^{-1} and a broad band from $\sim 2500\text{ cm}^{-1}$ to 3400 cm^{-1} . The 1H -NMR spectrum of compound E is provided below. Provide structures (in the boxes below) for compounds A through E.



A	B	C
D	E	