

# KWANTLEN UNIVERSITY COLLEGE

## CHEMISTRY 2320 - R10

### Organic Chemistry I

December 14, 2001

**180 Total Marks Time: 3 hours (180 minutes)**

**Budget your time and good luck!!**

NAME: \_\_\_\_\_

This paper consists of **12 pages (11 questions)** (including this title page).

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

Molecular models may be used during this examination.

### Grading Scheme For The Exam Question

1	2	3	4	5	6	7	8	9	10	11
14	18	18	18	13	16	24	20	14	10	15

**Mark**

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**Maximum**

180
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**Total**

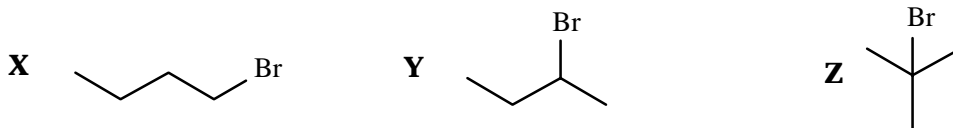
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**Percent**

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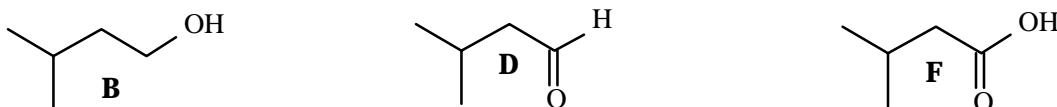
**Question 1. (14 Marks)** Circle the correct answer for each of the following:

a) For the following three constitutional isomers (all  $C_4H_9Br$ ): (5)



Which would give the fastest reaction with $I^-$ in acetone (solvent)?	<b>X</b>	<b>Y</b>	<b>Z</b>
Which would require the lowest temperature for solvolysis ( $H_2O$ )?	<b>X</b>	<b>Y</b>	<b>Z</b>
Which could produce the largest number of $E2$ products?	<b>X</b>	<b>Y</b>	<b>Z</b>
Which could be formed from an alkene with $HBr/H_2O_2$ ?	<b>X</b>	<b>Y</b>	<b>Z</b>
Which could not be formed from an alkane with $Br_2/_?$	<b>X</b>	<b>Y</b>	<b>Z</b>
Which could not be easily formed from an alcohol with $PBr_3$ ?	<b>X</b>	<b>Y</b>	<b>Z</b>

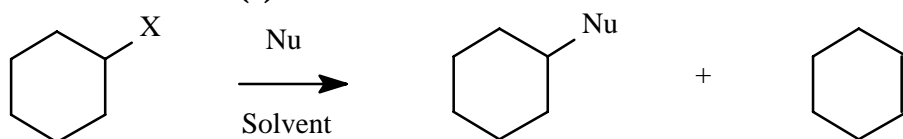
b) This question is based upon the three compounds (B, D and F) shown below:



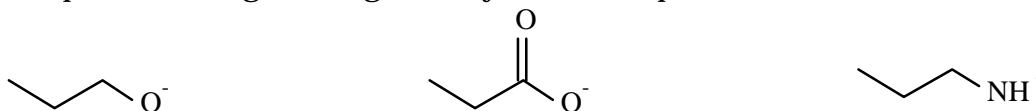
Which compound would have the: (4)

highest boiling point:	<b>B</b>	<b>D</b>	<b>F</b>	highest vapour pressure:	<b>B</b>	<b>D</b>	<b>F</b>
lowest water solubility:	<b>B</b>	<b>D</b>	<b>F</b>	largest $pK_a$ value:	<b>B</b>	<b>D</b>	<b>F</b>

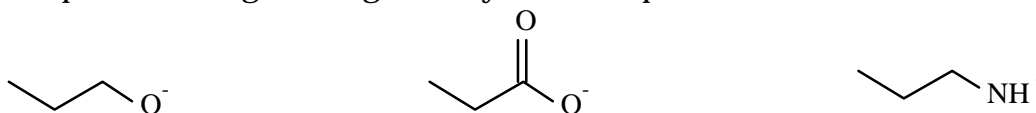
c) For the reaction below: (5)



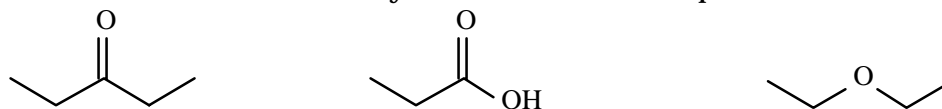
- i) Which leaving group (X) would yield the fastest reaction? **Cl**      **Br**      **I**  
 ii) Which would be the better nucleophile?       **$CH_3O^- \cdot CH_3OH$**        **$CH_3OH_2^+$**   
 iii) Which nucleophile would give the greatest yield of  $S_N2$  product?



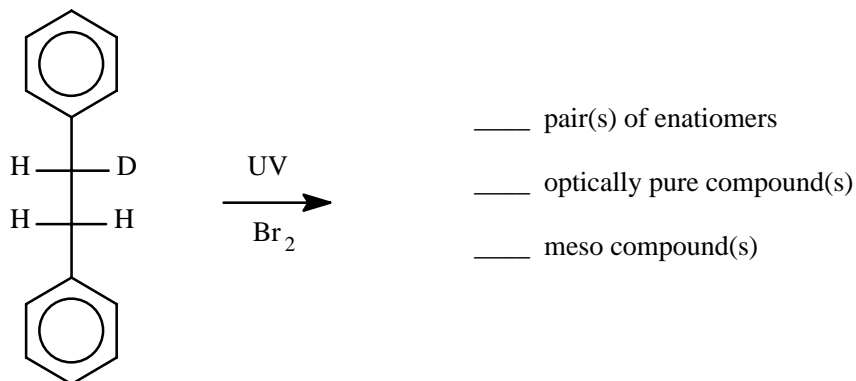
iv) Which nucleophile would give the greatest yield of  $E2$  product?



v) Which solvent would be better for solvolysis; i.e., no other Nu present?



**Question 2. (18 Marks)** The following optically pure compound was treated with Br<sub>2</sub> in the presence of UV radiation to produce a mixture of monobrominated compounds. Provide the correct number for each of the terms indicated. (4.5)



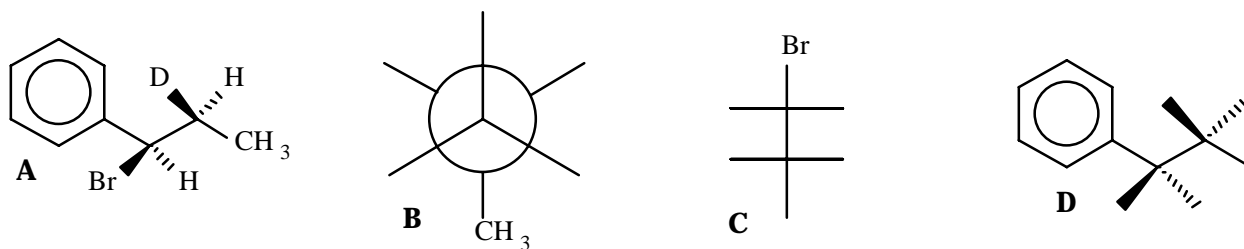
The products were formed as a result of a { **concerted / non-concerted** } process best described as { **regioselective / stereoselective** } in which the { **intermediate / transition state** } was most likely a { **bromonium ion / free radical / carbocation** }. (4)

The following compound A was isolated from a similar bromination process. (4.5)

Complete structure B so that it is the **enantiomer** of compound A.

Complete structure C so that it is a **conformational isomer** of compound A.

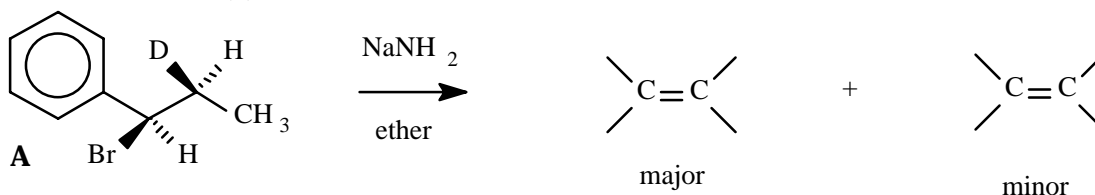
Complete structure D so that it is a **diastereomer** of compound A.



In compound A, the carbon atom containing the Br atom is best labelled as: (1) R S

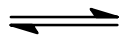
In compound A, the carbon atom containing the D atom is best labelled as: (1) R S

Complete the structure of the major product and the minor product formed in the E2 reaction of compound A with NaNH<sub>2</sub>. (3)

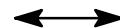


**Question 3. (18 Marks)** Provide/complete the structures to illustrate the following:

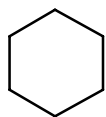
a) keto-enol tautomerism



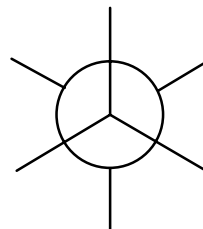
b) a resonance stabilized cation



c) an achiral dimethylcyclohexane which requires no stereochemical prefixes



d) a gauche conformer of hexane (C<sub>3</sub> to C<sub>4</sub>)



e) an unsaturated C<sub>6</sub>H<sub>12</sub> isomer which contains only allylic H atoms

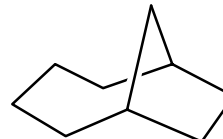
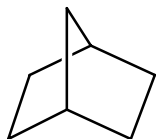
f) a saturated C<sub>6</sub>H<sub>10</sub>Br<sub>2</sub> isomer which is a meso compound

g) an isomer of C<sub>5</sub>H<sub>11</sub>Br which could not undergo an E2 reaction with <sup>-</sup>NH<sub>2</sub>

h) a stronger base than CH<sub>3</sub>CH<sub>2</sub>O<sup>-</sup>

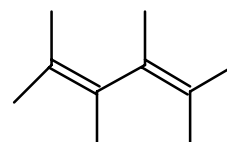
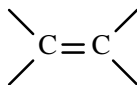
i) a chlorobicyclo[2.2.1]heptan-2-one isomer that requires the prefix endo

j) a methylbicyclo[4.2.1]nonene isomer that requires the prefix anti

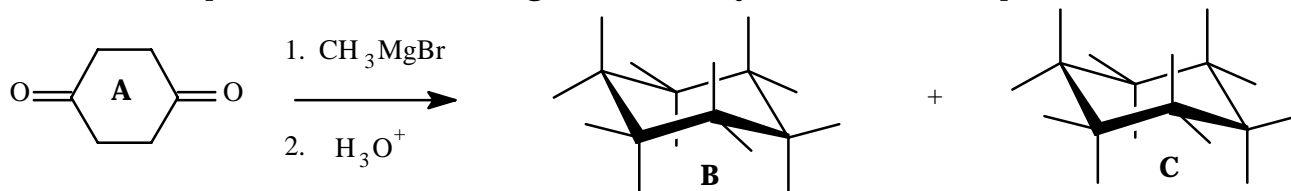


k) an unsaturated isomer of C<sub>4</sub>H<sub>6</sub>F<sub>2</sub> which is non-polar

l) the E,Z stereoisomer of 3,5-dichloro-2,4-pentadienal



**Question 4. (18 Marks)** a) Complete the structures of compounds B and C, each formed from the reaction of compound A excess  $\text{CH}_3\text{MgBr}$  followed by an acidic work-up. (3)



Compound A is a meso compound: (1) Yes No

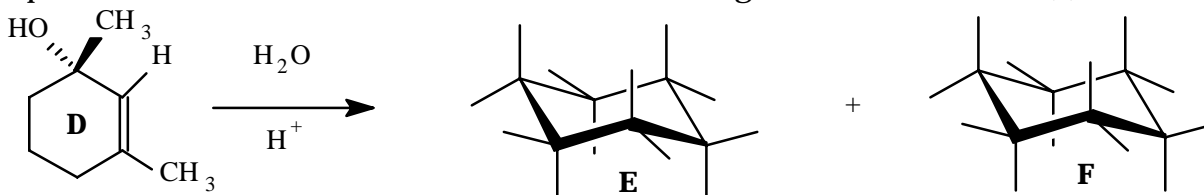
Compounds B and C are: (1) diastereomers enantiomers conformers

Compounds B and C are each: (1) optically pure achiral racemic

The reaction with  $\text{CH}_3\text{MgBr}$  is best described as a(n): (1)

electrophilic addition of  $\text{CH}_3^+$  nucleophilic addition of  $\text{CH}_3^-$   
 electrophilic addition of  $\text{CH}_3^-$  nucleophilic addition of  $\text{CH}_3^+$

b) Complete the structures of compounds E and F, each formed from the reaction of the optically pure compound D with dilute acid. Assume that no rearrangements occur. (3)

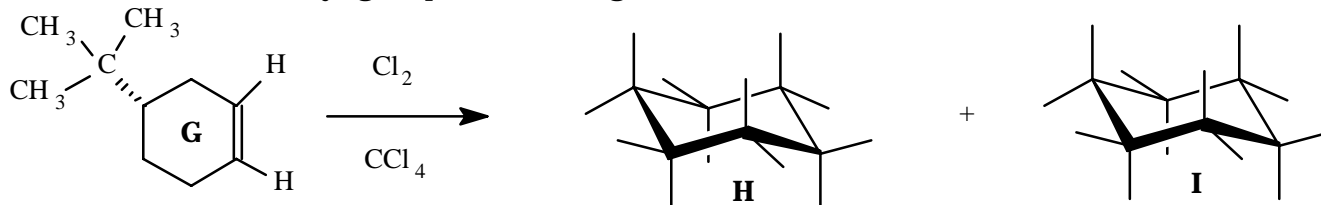


Which compound is optically pure? (1) E F

The reaction is best described as the: (1)

electrophilic addition of  $\text{H}^+$  nucleophilic addition of  $\text{H}^+$

c) Complete the structures of compounds H and I, each formed from the reaction of compound G with  $\text{Cl}_2$ . NOTE: The t-butyl group is much larger than a Cl atom. (3)

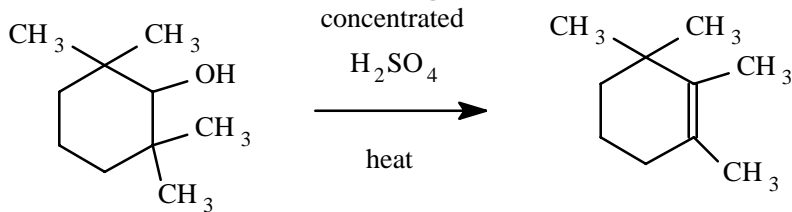


Which compound is more stable? (1) H I

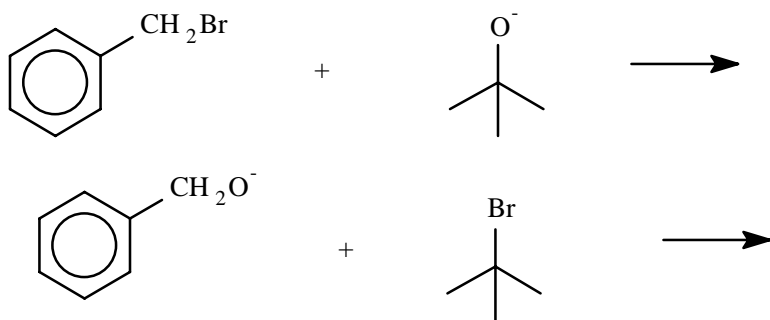
This reaction is best described as a { regioselective / stereoselective } { syn / anti } addition. (2)

### Question 5. (13 Marks)

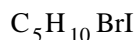
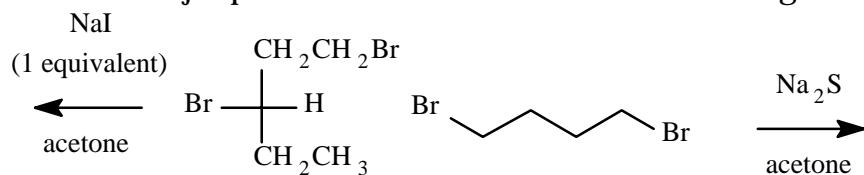
a) Using structural formulas and reaction arrows, including the use of "electron arrows", clearly show the steps of a reasonable mechanism for the following transformation. (5)



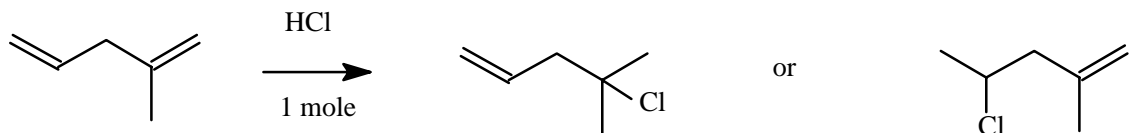
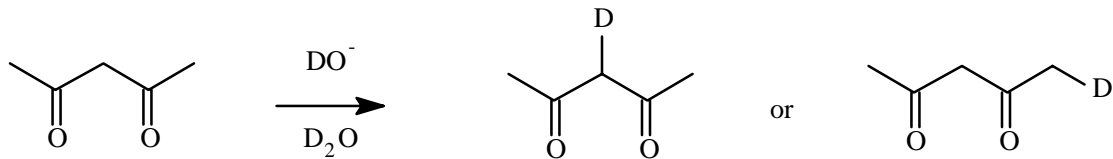
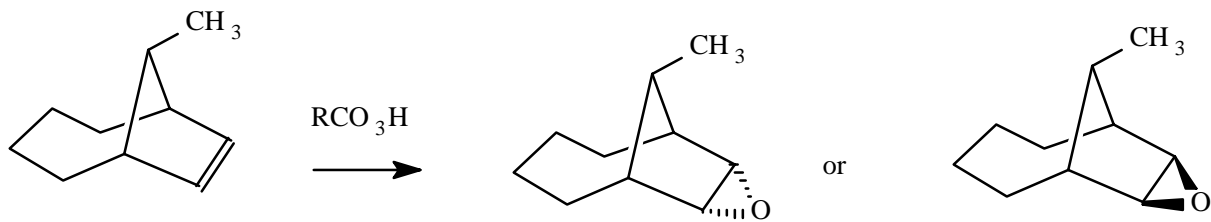
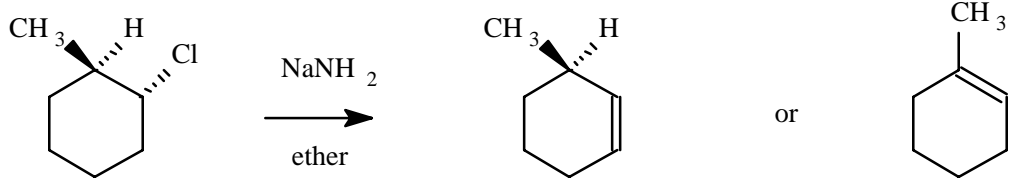
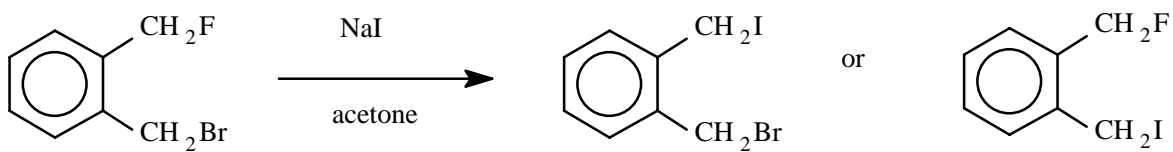
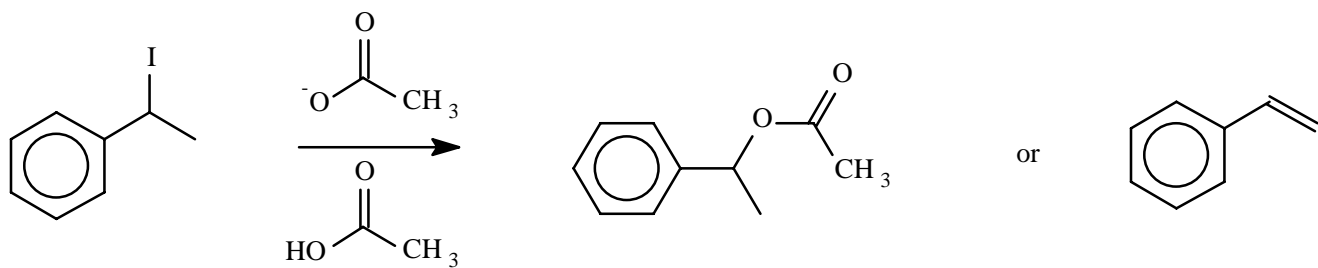
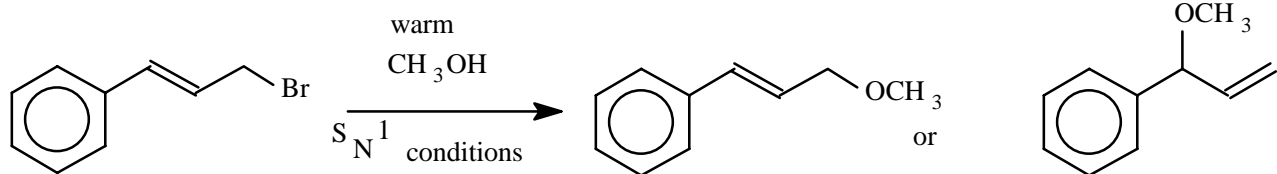
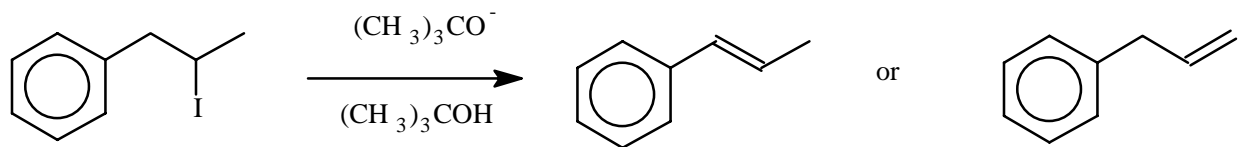
b) Clever Calvin, that renowned CHEM 2320 graduate, set out to prepare benzyl t-butyl ether. He tried the following two methods; but unfortunately, only one of them gave good yields of the desired product. Indicate which process would give the best yield (giving the structure of the benzyl t-butyl ether), and for the other one, give the structure of the major product(s) which would have been isolated instead. (4)



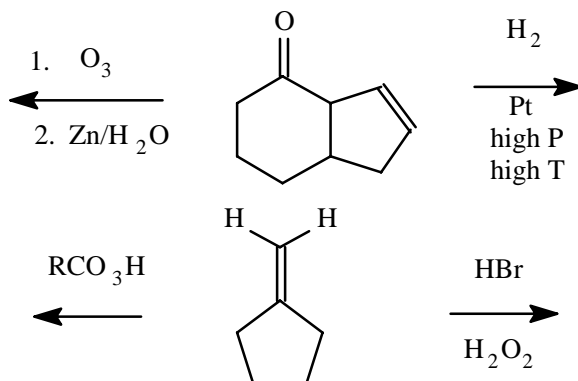
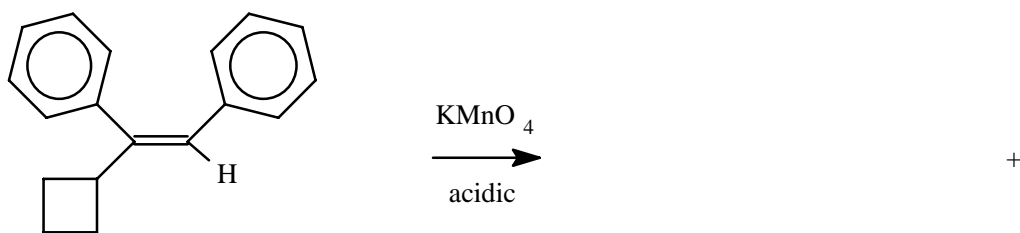
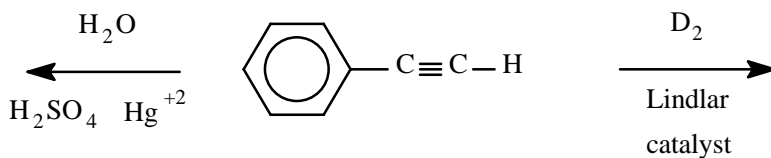
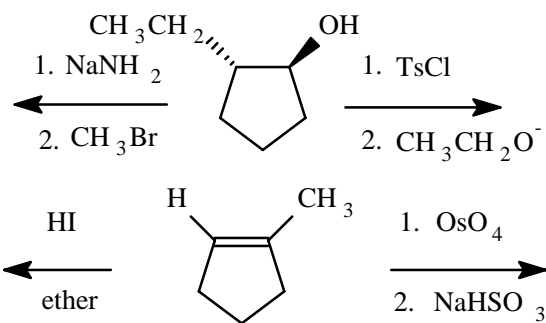
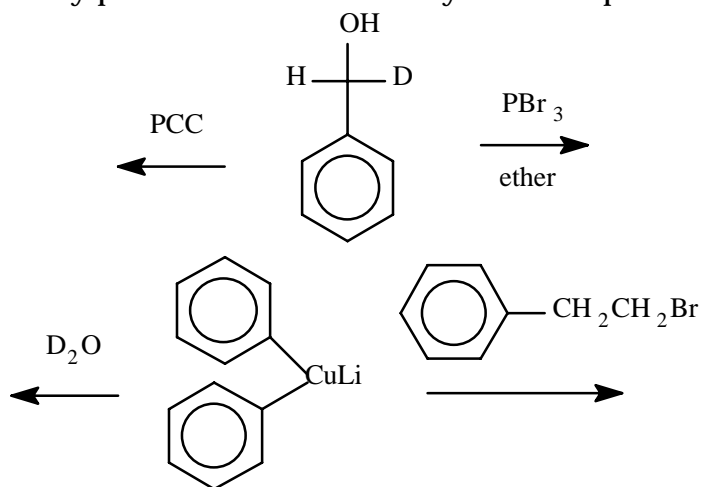
c) Propose a structure for the major product formed in each of the following reactions. (4)



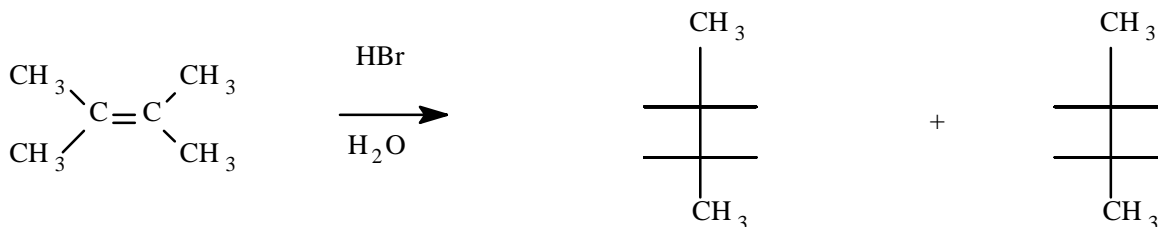
**Question 6. (16 Marks)** In many reactions where more than one product **MIGHT** be formed, it is quite often found that one compound may be formed to a greater extent than others. For each of the following reactions, circle the compound that would be the major product.



**Question 7. (24 Marks)** Provide the structure of the major product expected in each of the following reactions. Include any pertinent stereochemistry where important.

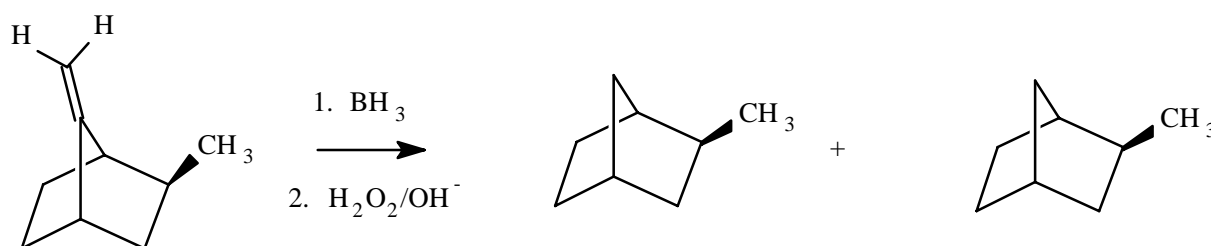


**Question 8. (20 Marks)** Each of the following reactions produces **two major products**. Complete the structure of each product (clearly showing any pertinent stereochemistry) and indicate the relationship between the two compounds; i.e., **enantiomers, diastereomers, positional isomers, tautomers, not isomers, etc .....** . Provide the **name of the type of reactive intermediate** involved in the process (if there isn't any, put **none**).



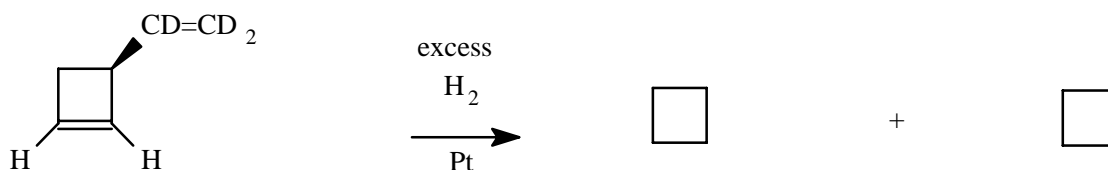
intermediate: \_\_\_\_\_

relationship: \_\_\_\_\_



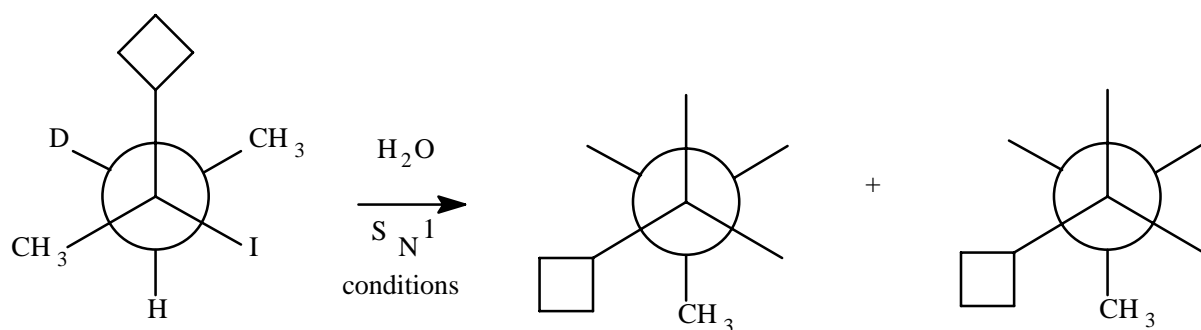
intermediate: \_\_\_\_\_

relationship: \_\_\_\_\_



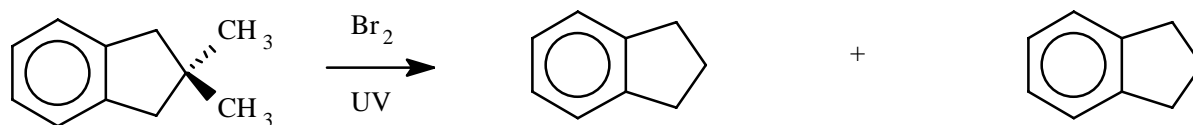
intermediate: \_\_\_\_\_

relationship: \_\_\_\_\_



intermediate: \_\_\_\_\_

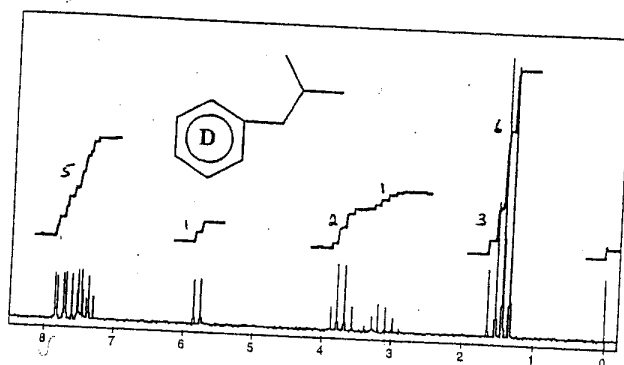
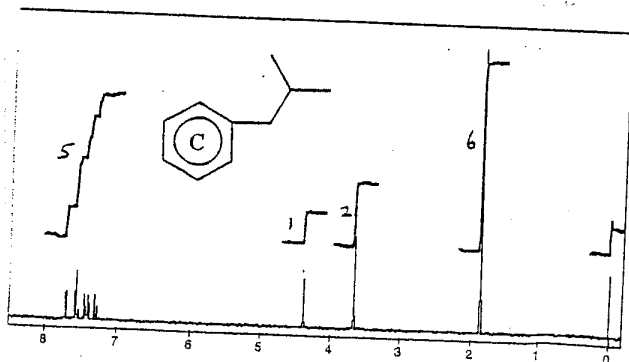
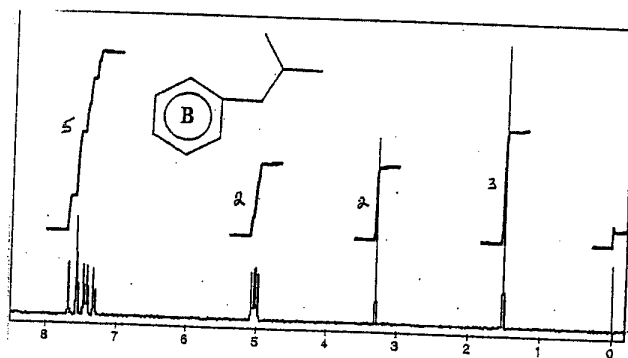
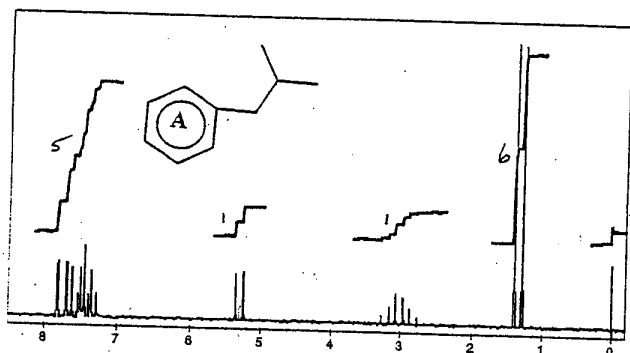
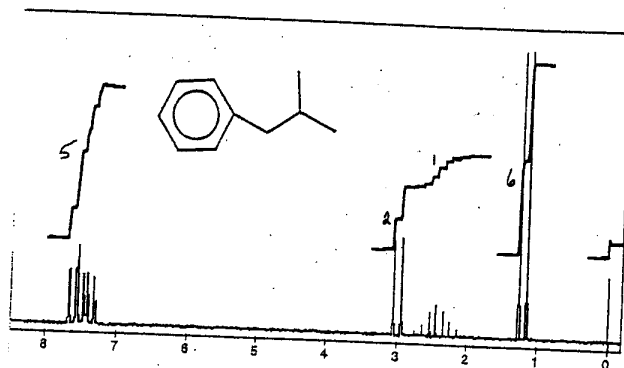
relationship: \_\_\_\_\_



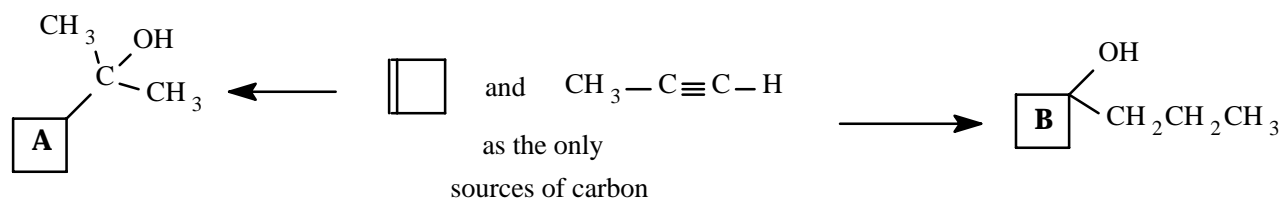
intermediate: \_\_\_\_\_

relationship: \_\_\_\_\_

**Question 9. (14 Marks)** Sidney Smart is having a really bad day at ACME Chemicals. He has treated isobutyl benzene with  $\text{Cl}_2$  in the presence of UV radiation and then boiled a portion of the resulting mixture of monochloride products in a mixture of ethanol and water. After isolating several compounds, he arranged to have their  $^1\text{H}$  NMR spectra taken. As you can guess, he has forgotten everything he once knew about chemical shifts, splitting patterns etc ... Help out poor Sidney by assigning the portions of the molecule responsible for the signals in the  $^1\text{H}$  NMR spectrum of isobutylbenzene ( $\text{C}_{10}\text{H}_{14}$ ), and then complete the structures of the compounds **A** ( $\text{C}_{10}\text{H}_{13}\text{Cl}$ ), **B** ( $\text{C}_{10}\text{H}_{12}$ ), **C** ( $\text{C}_{10}\text{H}_{14}\text{O}$ ) and **D** ( $\text{C}_{12}\text{H}_{18}\text{O}$ ).



**Question 10. (10 Marks)** Clever Calvin needs your help again, this time with a synthetic problem. He has a rush order for the two alcohols A and B below (constitutional isomers of each other). Propose suitable sequences of reactions (including the necessary reagents/solvents etc..) to prepare each of the two alcohols. 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.**



**Question 11. (15 Marks)** The optically pure compound A ( $C_6H_{14}O$ ) had a strong band in the IR around  $3400\text{ cm}^{-1}$ , and could be converted to the optically pure compound B ( $C_6H_{12}O$ ) with PCC. Compound B had a strong band in the IR around  $1700\text{ cm}^{-1}$ . Treatment of compound B with  $H_2/Pt$  at high temperature and high pressure reformed compound A as a mixture of two diastereomers. Treatment of optically pure compound A (or the mixture of diastereomers) with concentrated  $H_2SO_4$  lead to the formation of the achiral diastereomers C and D (both  $C_6H_{12}$ ) as major products. Treatment of compound C or D with dilute acid produced the same achiral compound E ( $C_6H_{14}O$ ) which had a strong band in the IR around  $3400\text{ cm}^{-1}$ . Compound E gave no reaction with PCC. Propose complete structures for compounds A  $\rightarrow$  E in the boxes below. Make certain that any pertinent stereochemistry is clearly shown.

A	B	C
D	E	