Department of Chemistry and Biochemistry

Chemistry 59-230/232 **Final Exam**
Time: 3 h **Dec. 16, 2005**

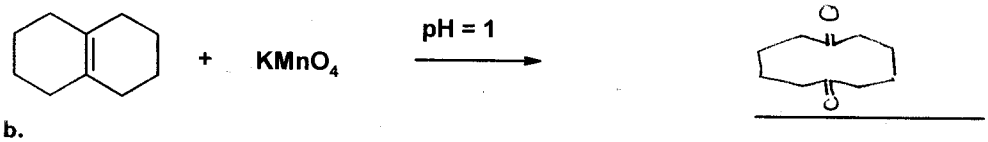
NAME _____ **ID#** _____

COURSE SECTION (*'01' if Tues/Thurs, '02' if Mon/Wed/Fri*) _____

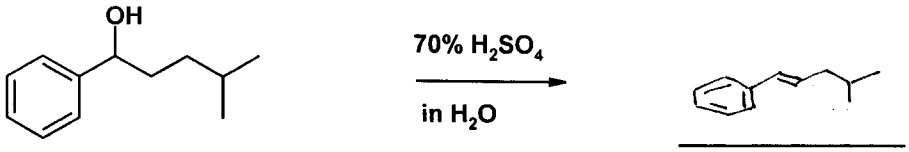
Note: **Please answer on the test paper.** There is an extra sheet for rough work at the back, but it will not be marked. In some questions, there is a choice of questions to answer. If all are answered, all will be marked. There are **140** marks on this exam.

1. Fill in the blanks with the structural formula or reagents required to complete the equation. Show any required catalysts over the arrow. Make sure your drawings show stereochemistry if it is important. ***Do any ten (10)*** (40 marks)

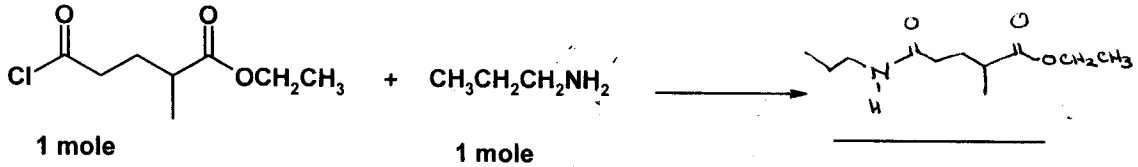
a.



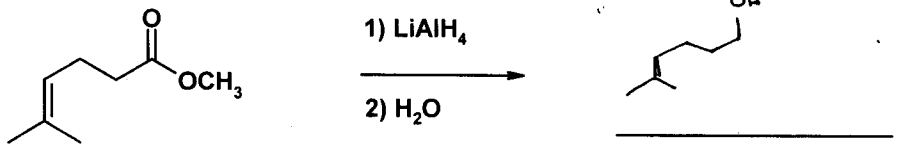
b.



c.

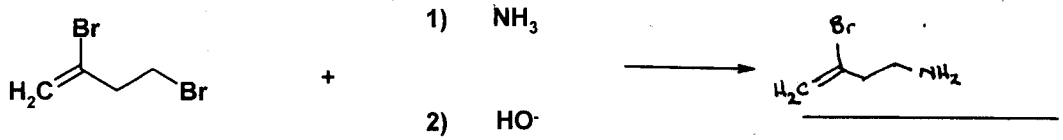


d.

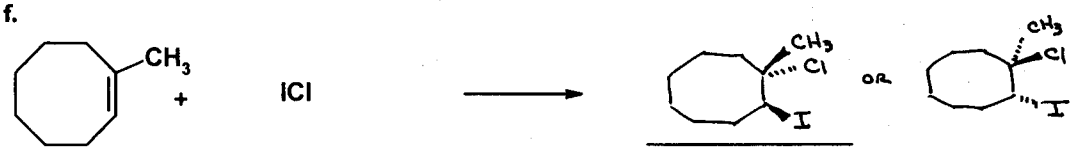


only need largest organic product

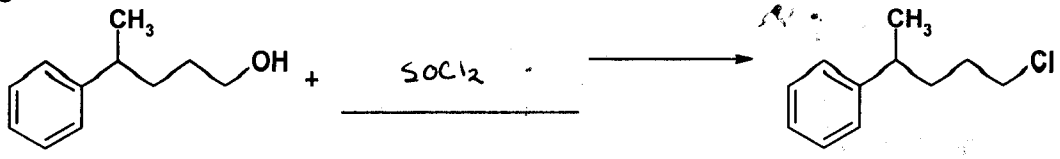
e.



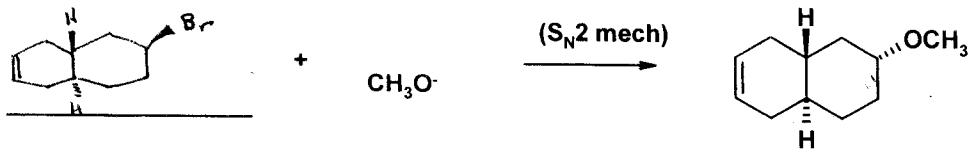
f.



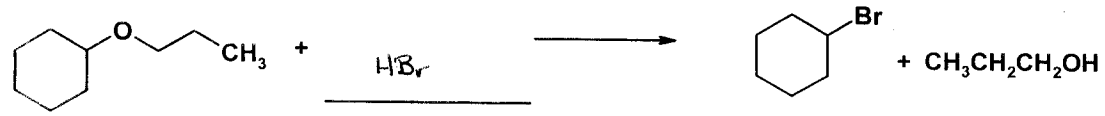
g.



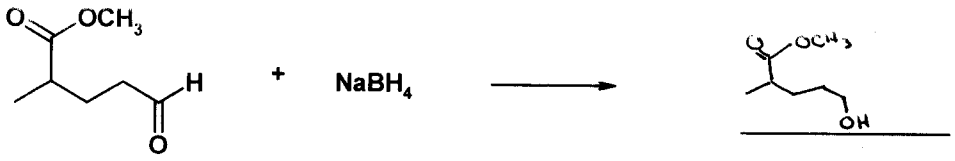
h.



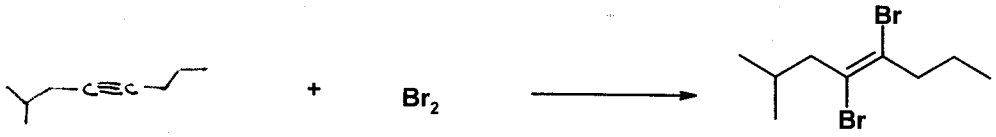
i.



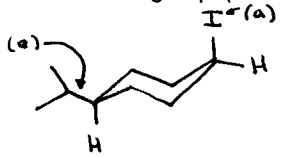
j.



k.

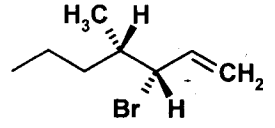


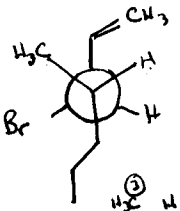
2a. (12 marks total) Draw the structure of *cis* 1-iodo-4-(isopropyl)cyclohexane is its most stable chair conformation. Label the non hydrogen substituents on the cyclohexane as axial or equatorial. In terms of size, an isopropyl is larger than an iodo group. (5 marks)



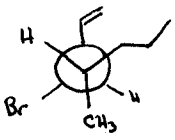
C3 - C4 bond

b. Draw the Newman projection of the following compound in its *least* stable staggered conformation, as viewed down the C2-C3 bond. With respect to size, $CH_2CH_2CH_3 > CH_3 > C(H)=CH_2 > Br > H$. What is the name of this compound, including its stereochemical descriptor ? (7 marks)

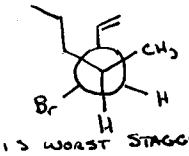




2ND IS BEST STAGGERED

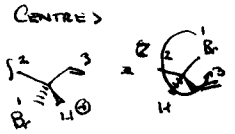


IS BEST

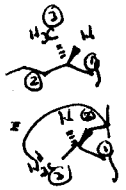


IS WORST STAGGERED

CHIRAL CENTRES



(S) -

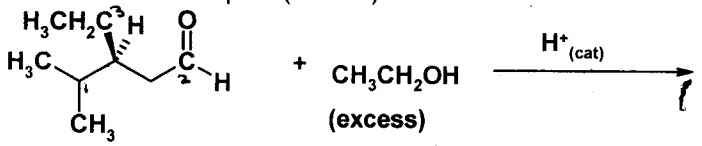


(S) -

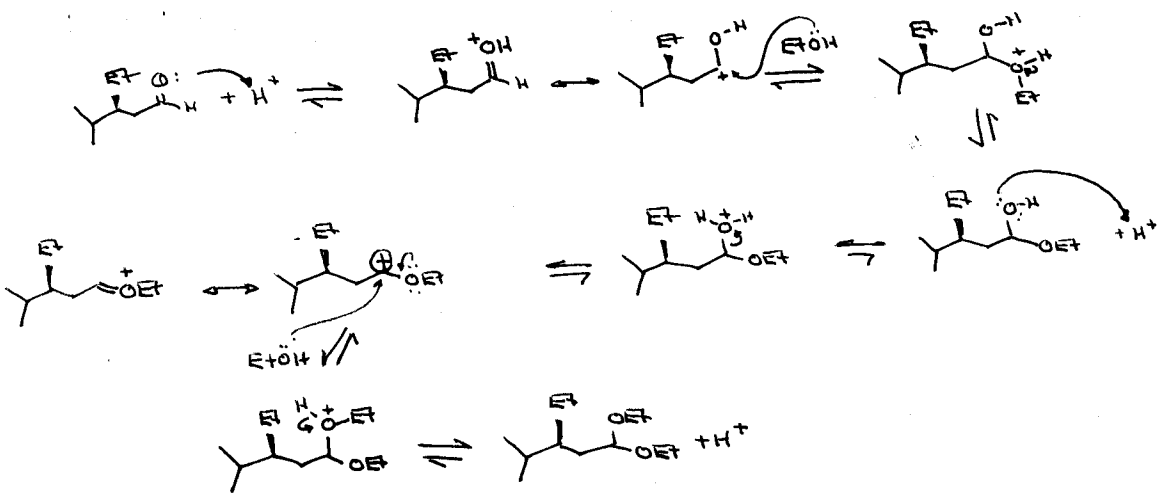
∴ (3S, 4S) - 3-BROMO-4-METHYL-1-HEPTENE

3. a. (14 marks total)

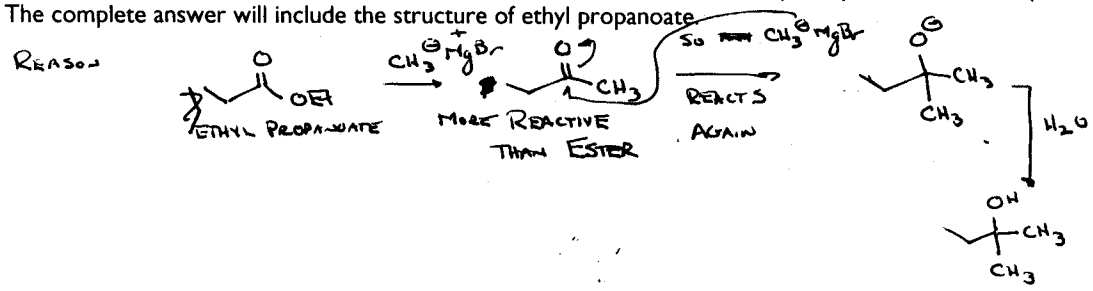
Draw the complete mechanism for the following reaction. Take the reaction to completion. Indicate which steps are reversible (or irreversible). Provide a valid IUPAC name for the starting material, including the stereochemical descriptor. (9 marks)



(S) - 3-ETHYL-4-METHYLPENTANAL

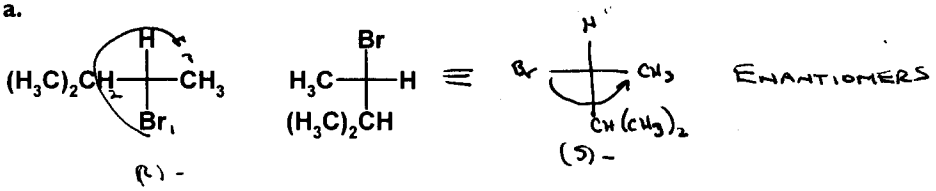


b. In the reaction of an ester (lets say ethyl propanoate) with a Grignard reagents (let's say it's CH_3MgBr) one never gets a ketone as a product. Show by intermediates and reaction steps why is this the case (5 marks). The complete answer will include the structure of ethyl propanoate.

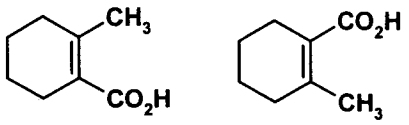


4. (**27 marks total**) Describe the relationship that exists between the following sets of compounds (i.e., enantiomer, diastereomer, geometric isomer, structural isomer, identical). Indicate any *meso* forms.

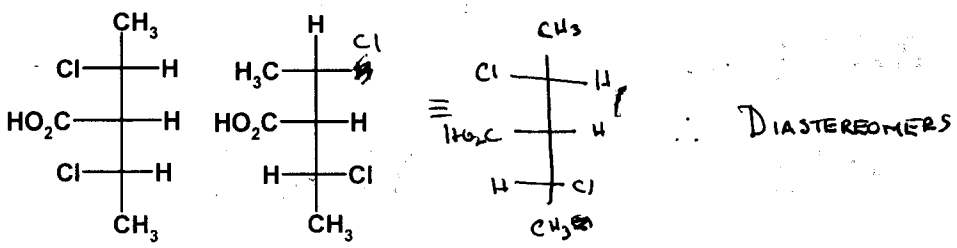
a.



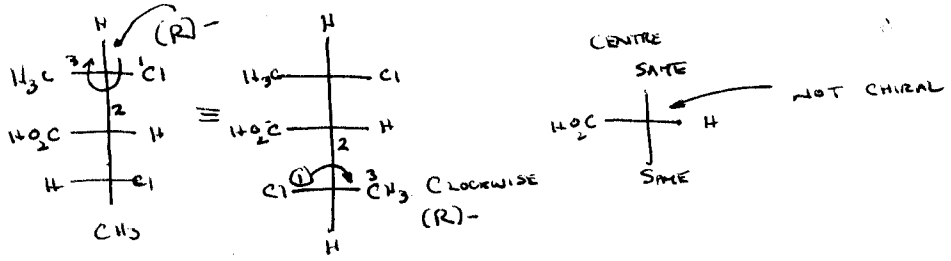
b.



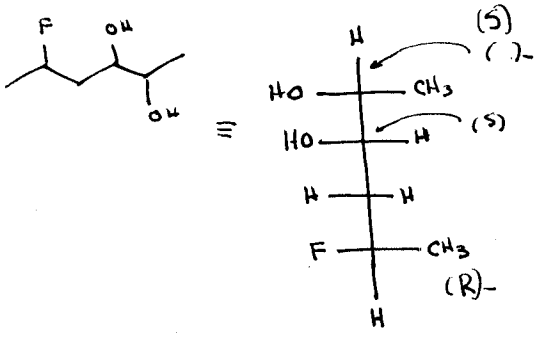
c.



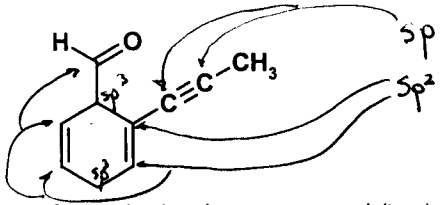
Also, identify the chiral centres for the right compound in c) as (R)- or (S)- (3 of 27 marks)



d. Draw the Fischer projection of (2S, 3S, 5R)-5-fluoro-2,3-hexanediol. (5 *of the* 27 marks).



e. Identify each carbon atom of the following with its hybridization. (3 marks)



f. In the above compound (in e), assign the appropriate stereochemical descriptor to each alkene. Show your work (6 marks)

RIGHT SIDE WINS (-C≡C-CH₃)

RIGHT ALKENE — TOP — C vs C AND C,C,C vs C,C,H

BOTTOM — C vs H — LEFT SIDE WINS ∴ (E)-

LEFT ALKENE — TOP — H vs C — LEFT WINS

BOTTOM — H vs C — LEFT WINS ∴ (Z)-

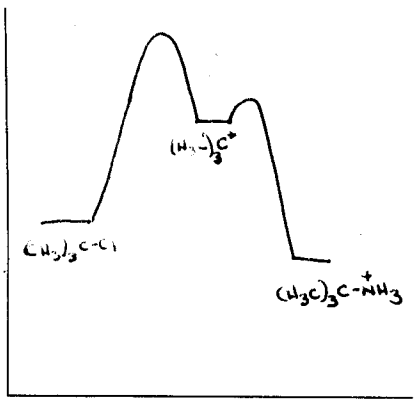
5. On the axes below, draw the energy/reaction coordinate profile for:

a. The reaction between $(CH_3)_3C\text{-}Cl + NH_3$ to give $(CH_3)_3C\text{-}N^+H_3$ (the mechanism should be implied in the answer).

b. A four step reaction between A and B, where A is consumed in the 1st step and B is involved in the 2nd step. The 3rd step is the slowest one.

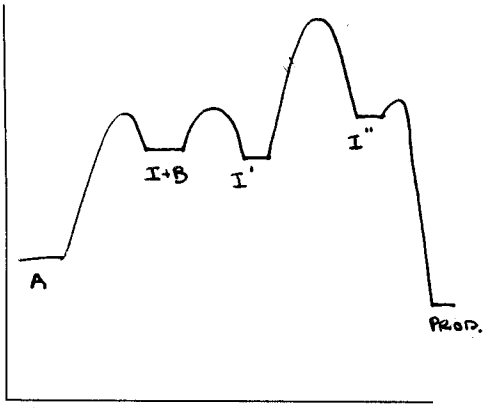
In each of these cases, give the rate equation for the reaction. (10 marks total)

a)



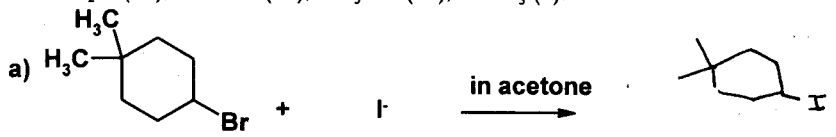
rate (v) = $k\,[(CH_3)_3C-Cl]$

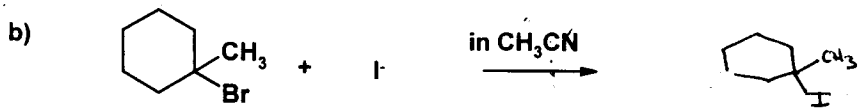
b)

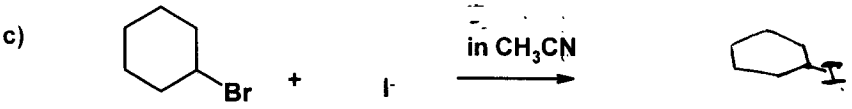


rate (v) = $k\,[A]\,[B]$

6. (**16 marks** total) Rank the following in terms of tendency to undergo S_N1 substitution (as opposed to S_N2). Give reasons for your ordering and the expected products. (13 of the 16 marks) Note the following dielectric constants: H_2O (81); acetone (23); CH_3CN (38); $CHCl_3$ (2).

a) 

b) 

c) 

1ST CASE 2° HALIDE - DOESN'T FAVOUR S_N1 OR S_N2
GOOD NÜ - FAVOURS S_N2, BUT WOULD DO S_N1
NOT TOO POLAR A SOLVENT FAVOURS S_N2 HERE
LOOKS LIKE S_N2 MOSTLY TO ME

2ND CASE 3° HALIDE - S_N1 ! ONLY!
GOOD NÜ - FAVOURS S_N2, BUT WILL DO S_N1
SOLVENT - POLAR - WOULD HELP S_N1 - NOT HELP S_N2
VERDICT - MOST S_N1 OF ALL

3RD CASE 2° HALIDE - S_N1 OR S_N2 - SAME AS 1ST CASE
GOOD NÜ - FAVOURS S_N2 BUT WILL DO S_N1
SOLVENT - POLAR - WOULD HELP S_N1
∴ MIDDLE CASE - MORE S_N1 THAN 1ST CASE, LESS THAN 2ND

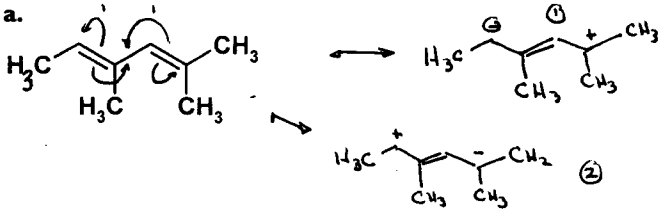
d. Rank the following from best nucleophile to worst leaving group ? (3 *of the* 16 marks)

Cl^-, Br^-, I^-, HO^-, HS^-

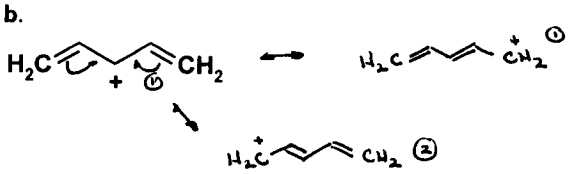
$I^- > Br^- > Cl^- > HS^- > HO^-$

7. (**10 marks**) a and b Indicate all *reasonable* resonance forms of the following ions, using curved arrows to indicate electron movement. If there are *unreasonable* resonance forms, either do not draw them or label them as unreasonable. If there is a case for which there are no other resonance forms, state that fact.

a.

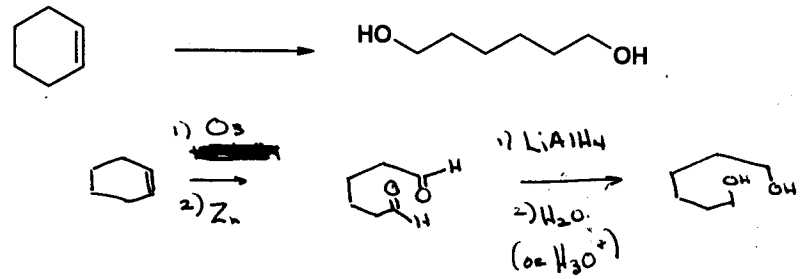


b.

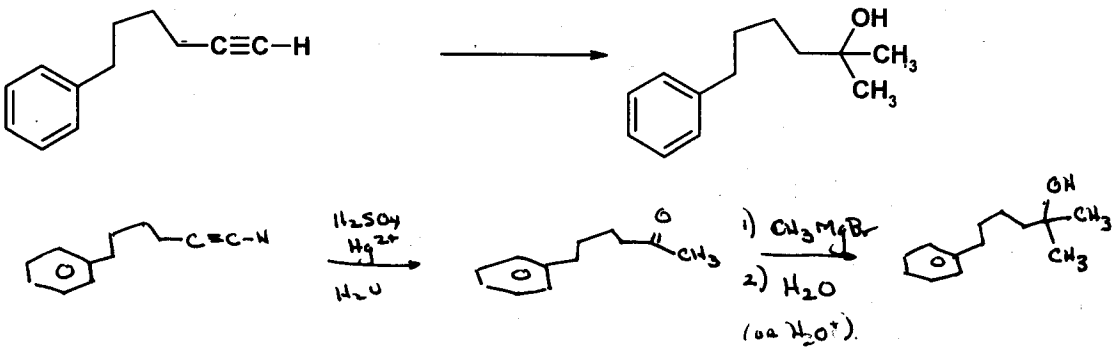


8. (**11 marks total**) Show by equation how you carry out the following overall transformations. Show all reagents and the structures of each reaction product. There is quite possibly more than one correct way to accomplish this overall transformation. ***DO one of a and b, but answer c regardless.***

a.



b.



c. What is the name of the final product compound in **8b**? (3 of the 11 marks)

2-METHYL-6-PHENYL-2-HEXANOL

Bonus: (up to +5)
The reaction of ketones in the presence of hydroxide ion often gives 3-hydroxy ketones in a well known reaction called the aldol condensation. Could you suggest a plausible mechanism for this reaction?