

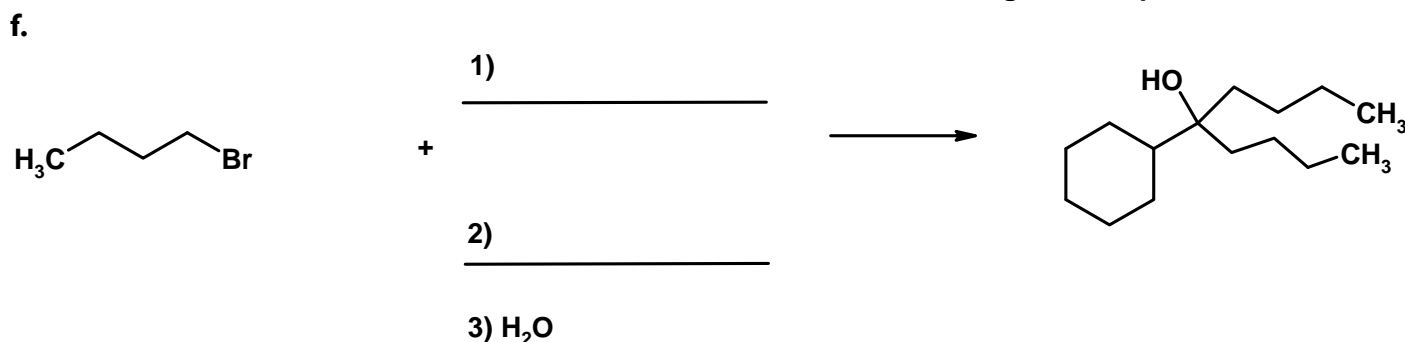
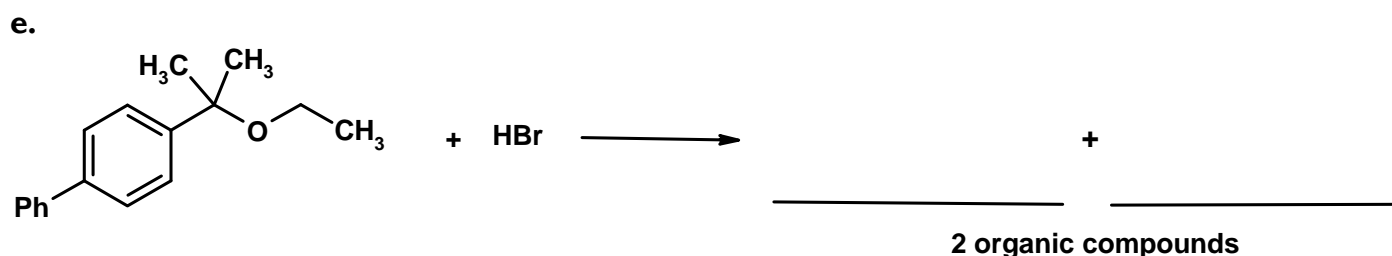
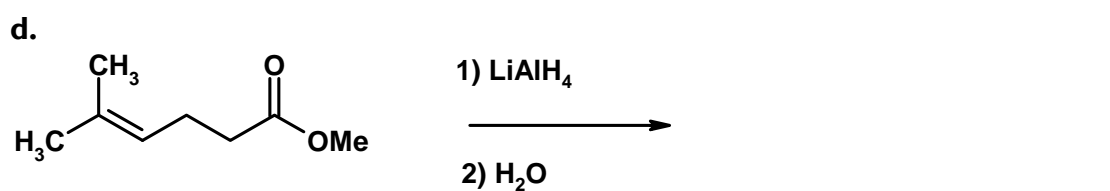
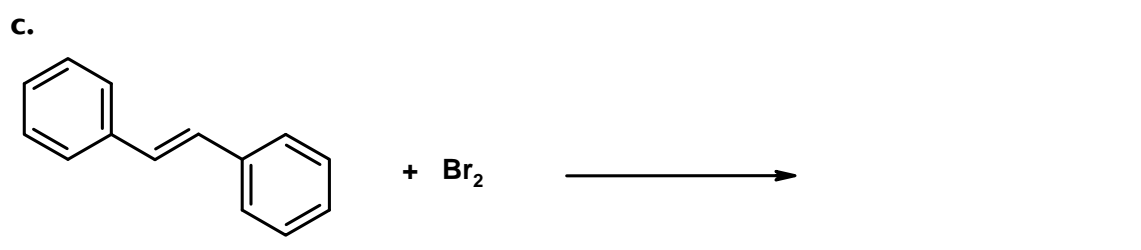
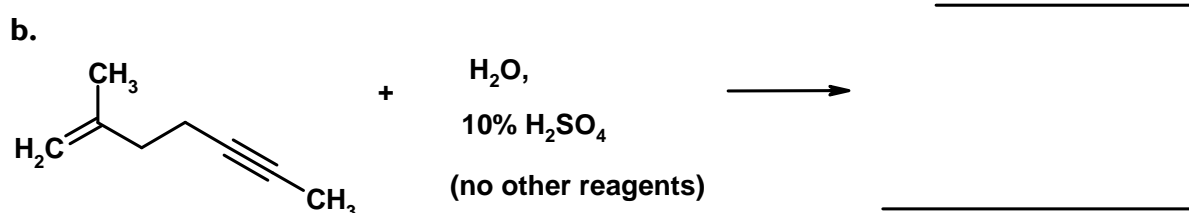
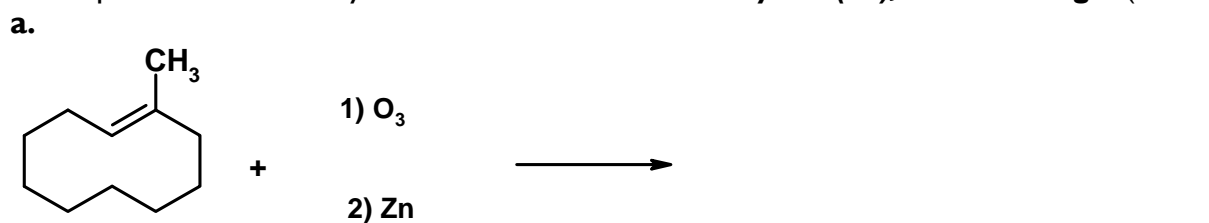
NAME \_\_\_\_\_

ID# \_\_\_\_\_

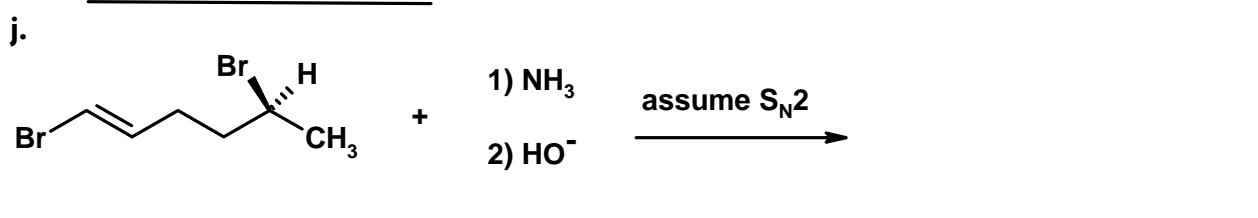
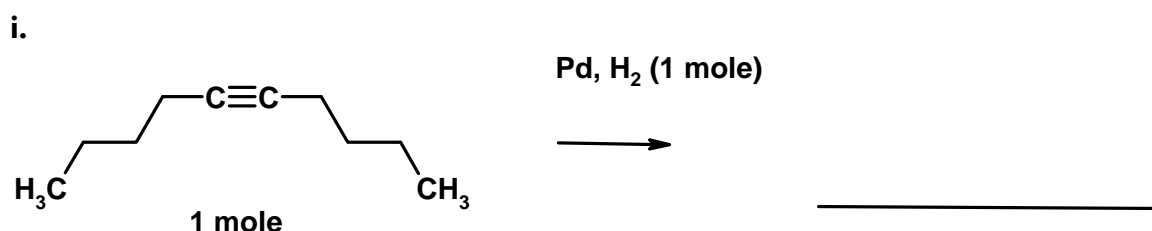
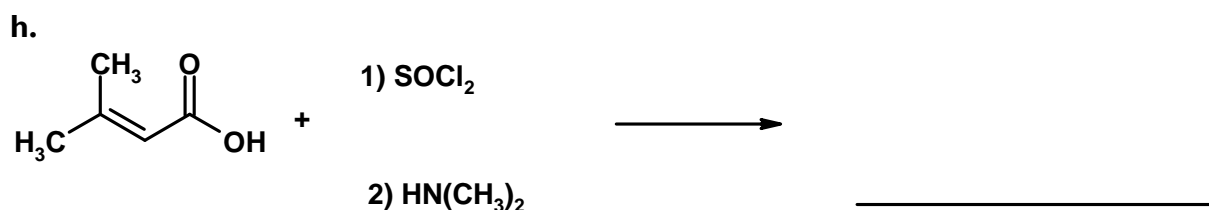
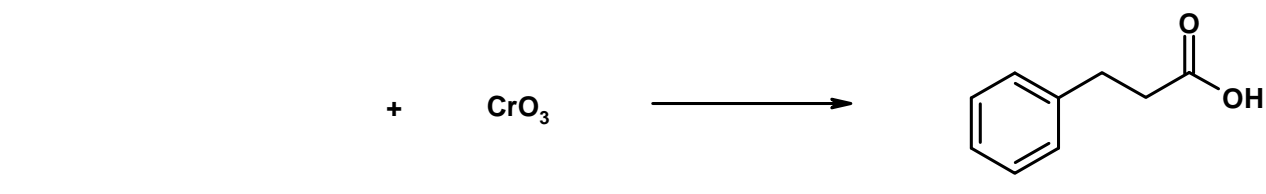
LAB SECTION (or TA name) \_\_\_\_\_

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 **150** marks on this exam.

I. Fill in the blanks with the structural formula or reagents required to complete the equation. Show any required catalysts or additional reagents over the arrow. Make sure your drawings show stereochemistry if it is important. Note: Entry "i." is worth 2 entries. **Do any ten (10), but including i. (40 marks total)**



g.



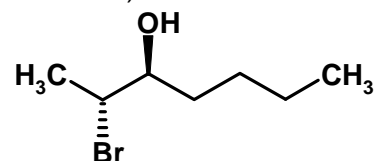
**2a. (20 marks total)** Draw the structure of *trans* 1-(hydroxy)-3-isopropylcyclohexane in its less stable chair conformation. Label the non hydrogen substituents on the cyclohexane as axial or equatorial. In terms of size, an isopropyl group is larger than a hydroxy group. (6 marks)

**b.** i) Draw the Newman projection of the following compound in its *most* stable conformation, as viewed down the C2-C3 bond. With respect to size,  $(\text{CH}_3)_3\text{C} > (\text{CH}_3)_2\text{CH} > \text{unbranched alkyl} \approx \text{CH}_3\text{CH}_2 > \text{CH}_3 > \text{OH} > \text{Br} \approx \text{Cl} \approx \text{F} > \text{H}$ . (6 marks)

ii) What is the term for the relationship between the methyl group and the OH function (I'm looking for something more detailed than staggered/eclipsed)? (2 marks)

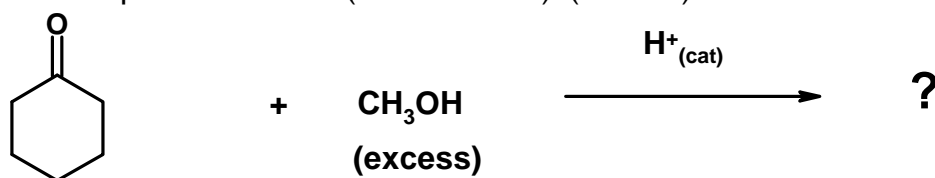
iii) What is the term for the relationship between the bromine and the OH groups? (2 marks)

iv) What is the name of this compound, including its stereochemical descriptor(s) ? (4 marks)



**3. a. (13 marks total)**

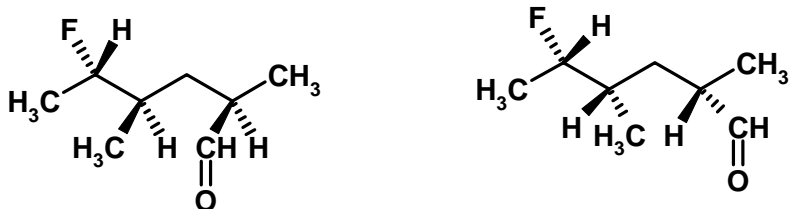
Draw the complete mechanism for the following reaction. Take the reaction to completion. Indicate which steps are reversible (or irreversible). (8 marks)



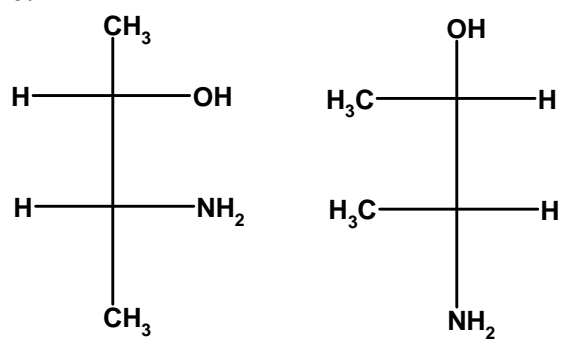
**b.** In the conversion of an acid (lets say (3S, 4S)- 3-ethyl-4-phenyloctanoic acid) to an ester (let's say it's the methyl ester (meaning  $\text{OCH}_3$ )) one never gets a successful reaction under  $\text{CH}_3\text{O}^-$  catalyzed conditions. Why is this the case (show by reaction and written explanation) (5 marks)? The complete answer will include the structure of (3S, 4S)- 3-ethyl-4-phenyloctanoic acid.

**4. (33 marks total)** Describe the relationship that exists between the following sets of compounds (i.e., enantiomer, diastereomer, geometric isomer, structural/constitutional isomer, identical). Indicate any *meso* forms (9 of the 33 marks).

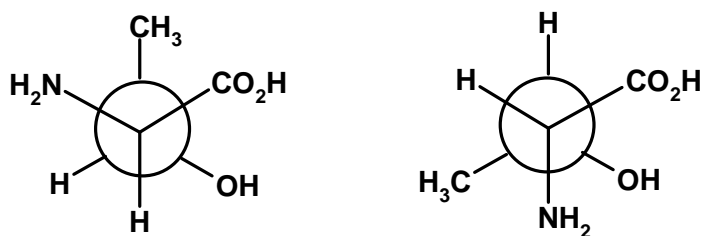
**a.**



b.



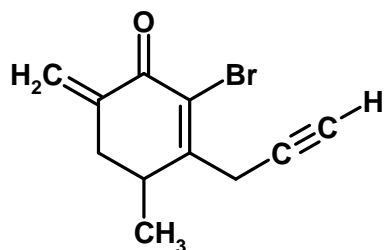
c.



Also, identify the chiral centres for the left compound in a) and b) as (R)- or (S)- (10 of 33 marks)

d. Draw the Fischer projection of (2R, 3S, 4R)-2,3-dibromo-4-fluoropentanal. (4 of the 33 marks).

e. Identify the hybridization of each carbon atom in the following molecule. (4 of the 33 marks)



f. In the above compound (in e), assign the E- or Z- stereochemical descriptor to each alkene that requires it. Show your work (6 marks)

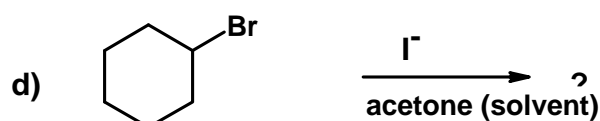
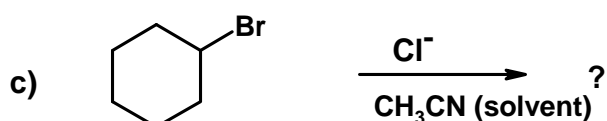
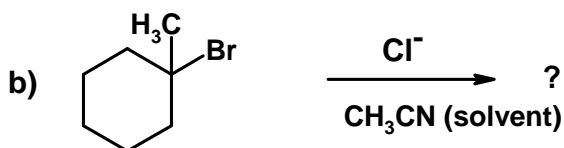
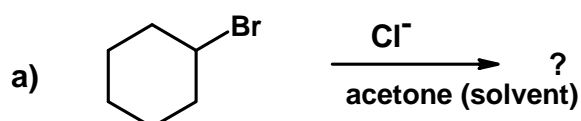
5. On the axes below, draw the energy/reaction coordinate profile for a four step reaction of A, B, and C to give D. A is consumed in the 1<sup>st</sup> step, B in the 2<sup>nd</sup> step, and C is consumed in the final step, while the 3<sup>rd</sup> step is the slowest one. Label the intermediate(s)/products.

Also, Give the rate equation for the reaction. (7 marks total)

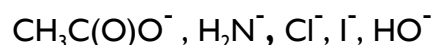


rate (v) =

6. (16 marks total) Rank the following (a-d) in terms of tendency to undergo  $S_N2$  substitution (as opposed to  $S_N1$ ). Give reasons for your ordering and the expected products. (13 of the 16 marks) Solvent dielectric constants are:  $H_2O$  (81),  $CH_3CN$  (38),  $CH_3OH$  (33),  $EtOH$  (23), acetone (23),  $Et_2O$  (4), benzene (2),  $CHCl_3$  (2),  $CCl_4$  (2).

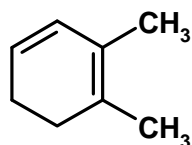


e. Rank the following from best leaving group to worst leaving group. (3 of the 16 marks)

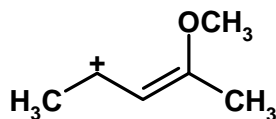


7. (10 marks) a and b Indicate all *reasonable* resonance forms of the following ions, using curved arrows to indicate electron movement. If there are *unreasonable* resonance forms, either do not draw them or label them as unreasonable. If there is a case for which there are no other resonance forms,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

a.

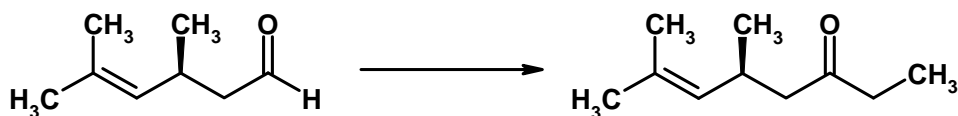


b.



**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 (8 marks). **DO one of a and b, but answer c regardless.**

a.

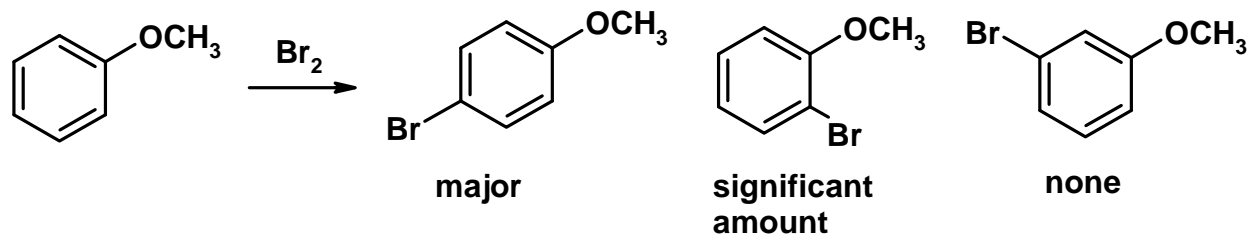


b.



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

**Bonus:** (up to +5) In benzenes, electrophilic reagents give substitution instead of addition. Can draw a mechanism for this reaction and rationalize why the indicated ones are the two major products formed?



**Another Bonus (up to +5):** I have told you that  $S_N1$  and  $S_N2$  reactions are both impossible at  $sp$  or  $sp^2$  hybridized centres, and yet the following transformation is quite common. Can you show by mechanism how this very real transformation occurs?

