

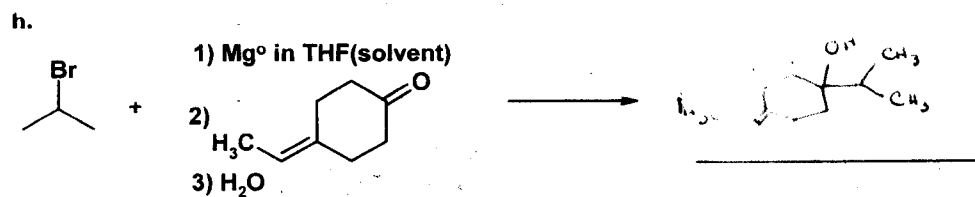
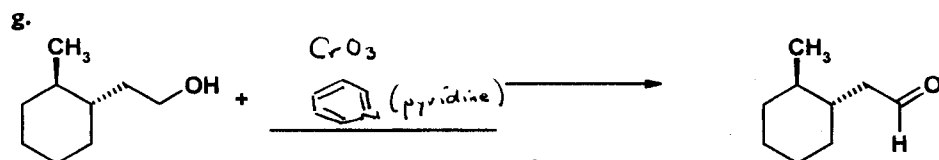
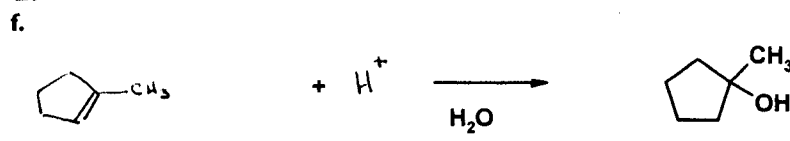
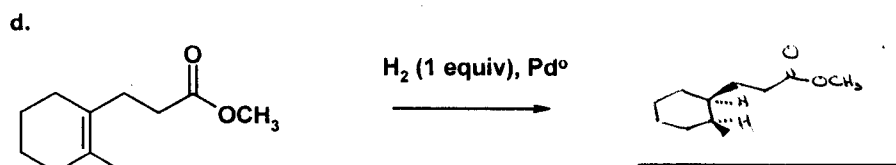
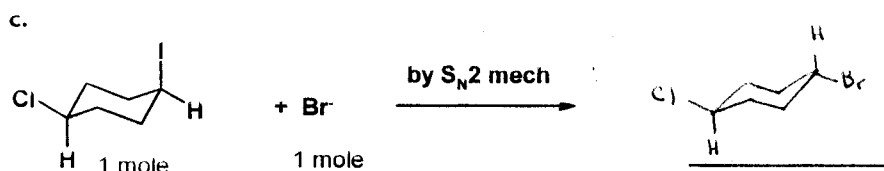
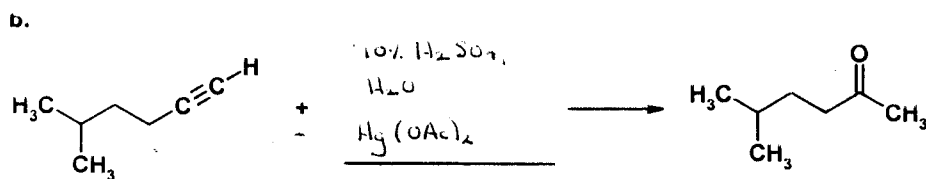
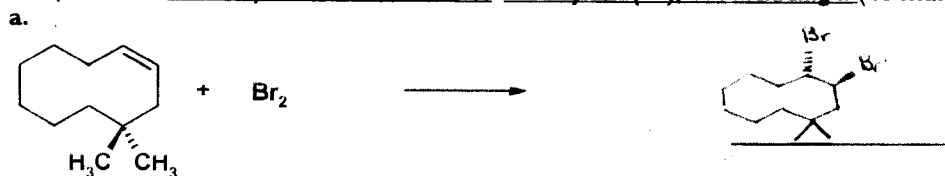
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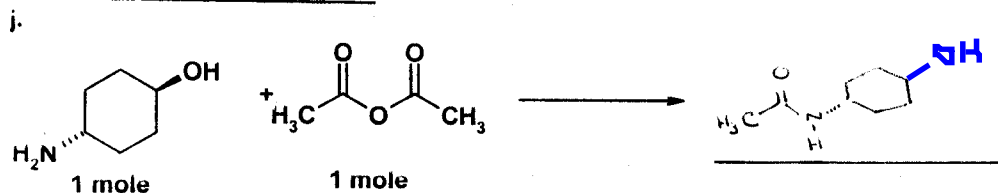
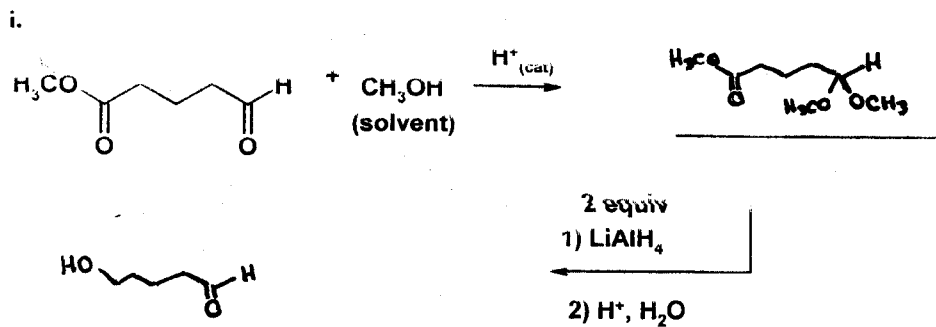
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LAB SECTION (or TA name) _____

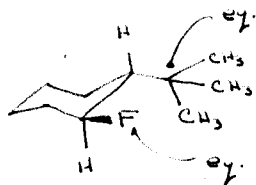
Note: Please answer on the test paper. There is an extra sheet for rough work at the back, but it will not be marked. In some questions, there is a choice of questions to answer. If all are answered, all will be marked. There are 140 marks on this exam.

1. Fill in the blanks with the structural formula or reagents required to complete the equation. Show any required catalysts 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)

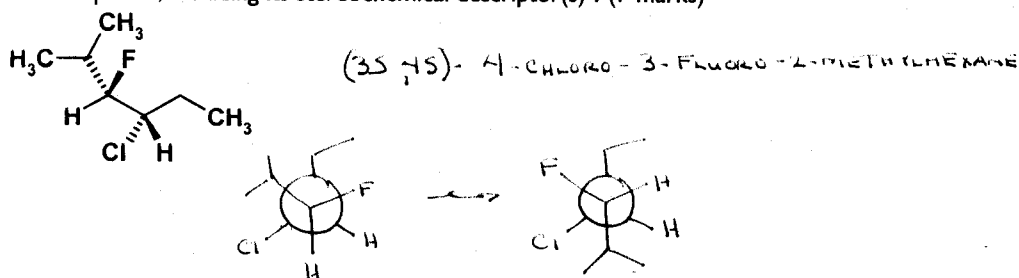




2a. (12 marks total) Draw the structure of *trans* 1-(1,1-dimethylethyl)-2-fluorocyclohexane in its most stable chair conformation. Label the non hydrogen substituents on the cyclohexane as axial or equatorial. In terms of size, a 1,1-dimethylethyl group (a.k.a tert-butyl group) is larger than a fluoro group. (5 marks)

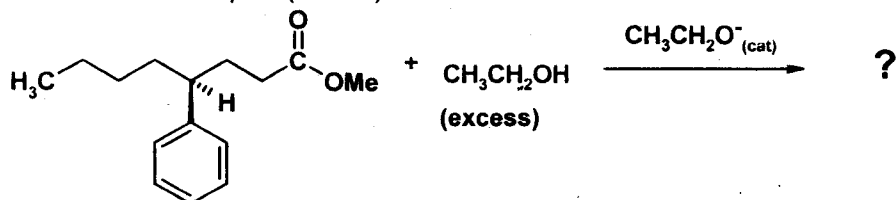


b. Draw the Newman projection of the following compound in its *most* stable conformation, as viewed down the C3-C4 bond. With respect to size, $(\text{CH}_3)_2\text{CH} > \text{CH}_3\text{CH}_2 > \text{CH}_3 > \text{Br} \approx \text{Cl} \approx \text{F} > \text{H}$. What is the name of this compound, including its stereochemical descriptor(s)? (7 marks)

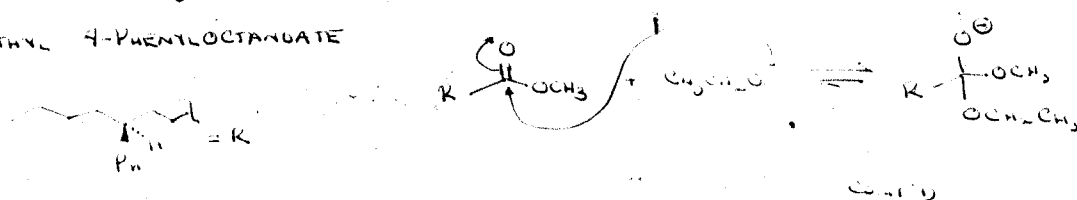


3. a. (13 marks total)

Draw the complete mechanism for the following reaction. Take the reaction to completion. Indicate which steps are reversible (or irreversible). Provide a valid IUPAC name for the starting material, including the stereochemical descriptor. (8 marks)

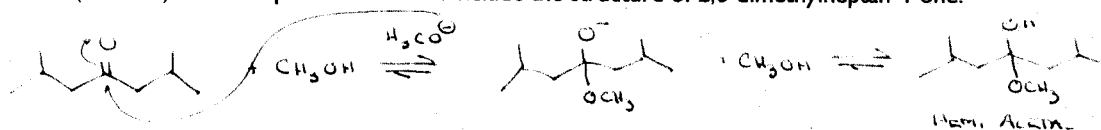


5-METHYL 4-PHENYLOCTANOATE





b. In the reaction of a ketone (lets say 2,6-dimethylheptan-4-one) with an alcohol (let's say it's CH_3OH) one never gets an acetal under base catalyzed conditions. Show by intermediates and reaction steps why is this the case (5 marks). The complete answer will include the structure of 2,6-dimethylheptan-4-one.

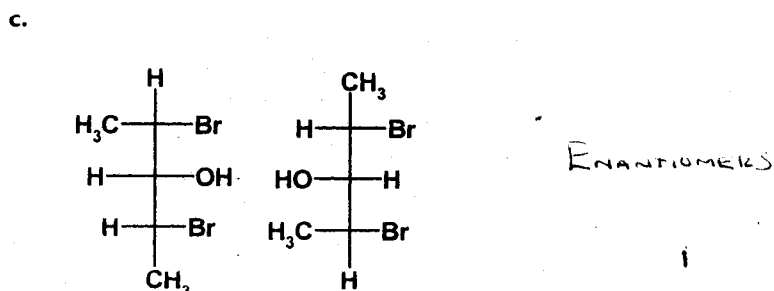
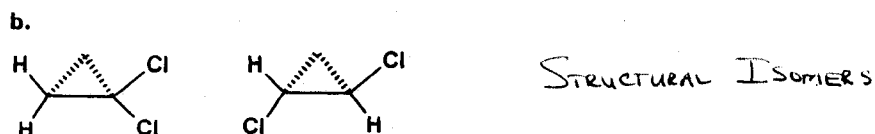
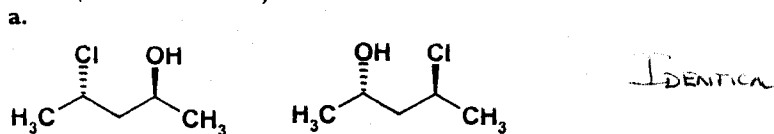


But OH^- is poor leaving group, so isn't displaced by MeO^-

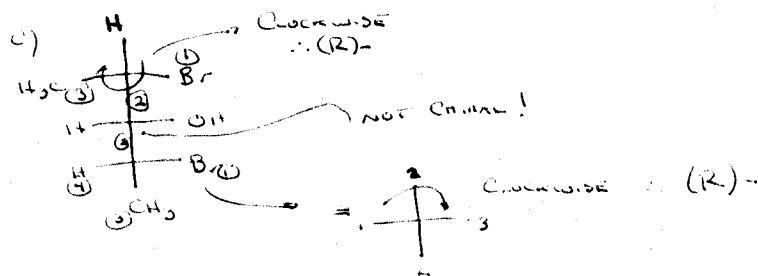
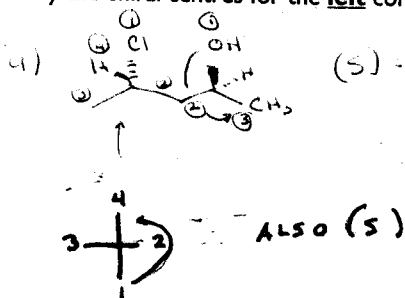
\therefore REACTION GOES NO FURTHER

AND KEYS TO HEMI ACETAL IS KEY \therefore GET KETONE BACK

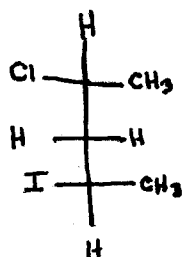
4. (33 marks total) Describe the relationship that exists between the following sets of compounds (i.e., enantiomer, diastereomer, geometric isomer, structural/constitutional isomer, identical). Indicate any meso forms (9 of the 33 marks).



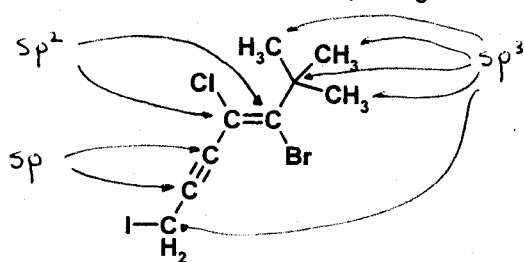
Also, identify the chiral centres for the left compound in a) and c) as (R)- or (S)- (8 of 33 marks)



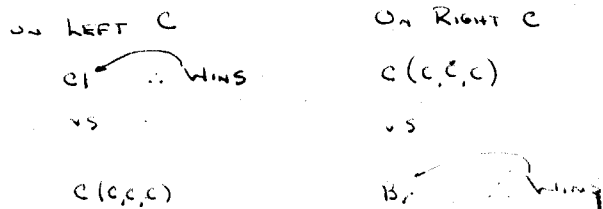
d. Draw the Fischer projection of (2S, 4R)-2-chloro-4-iodopentane. (4 of the 33 marks).



e. Identify the hybridization of each carbon atom in the following molecule. (3 of the 33 marks)



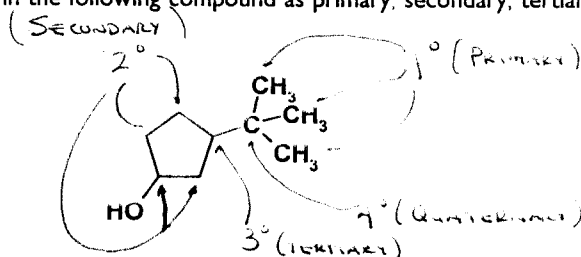
f. In the above compound (in e), assign the appropriate stereochemical descriptor to the alkene. Show your work (6 marks)



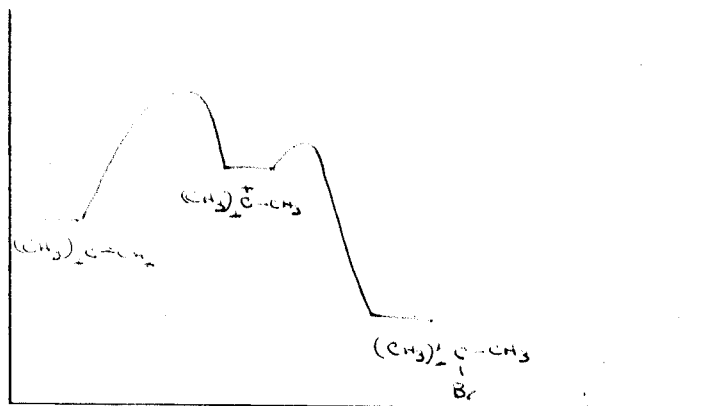
HIGHEST PRIORITY GROUPS ARE ON OPPOSITE SIDES \therefore (E)-

FIGURE MAY ALSO SHOW THAT 'MAIN CHAIN' SPANS OPPOSITE SIDES OF ALKENE
 \therefore Trans

g. Identify the carbon atoms in the following compound as primary, secondary, tertiary, or quaternary (3 of the 33 marks).

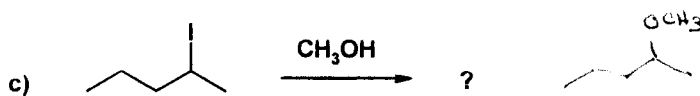
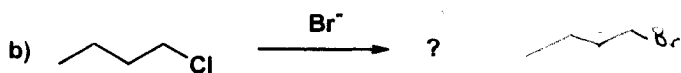
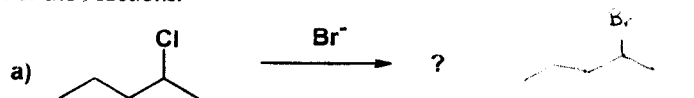


5. On the axes below, draw the energy/reaction coordinate profile for the reaction between $(\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{HBr}$ (the mechanism should be implied in the answer). Label the intermediate(s)/products. Give the rate equation for the reaction. (6 marks total)



$$\text{rate (v)} = k [(\text{CH}_3)_2\text{C}=\text{CH}_2] [\text{H}^+] \quad \text{or} \quad k [(\text{CH}_3)_2\text{C}=\text{CH}_2] [\text{HBr}]$$

6. (16 marks total) Rank the following in terms of tendency to undergo $\text{S}_{\text{N}}2$ substitution (as opposed to $\text{S}_{\text{N}}1$). Give reasons for your ordering and the expected products. (13 of the 16 marks) Assume the same solvent for each of the reactions.



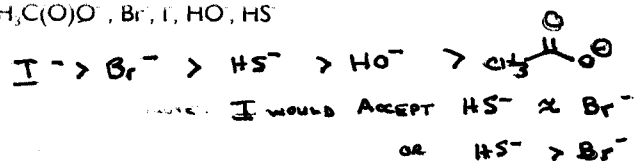
CASE a) 2° SUBSTRATE - $\text{S}_{\text{N}}1$ OR $\text{S}_{\text{N}}2$
 Cl^- LEAVING GROUP IS GOOD $\text{S}_{\text{N}}1$ OR $\text{S}_{\text{N}}2$
 Br^- NUCLEOPHILE IS V. GOOD - TOWARDS $\text{S}_{\text{N}}2$ } \therefore MIDDLE CASE

b) 1° SUBSTRATE - $\text{S}_{\text{N}}2$ ALMOST CERTAINLY
 Cl^- LEAVING GROUP IS GOOD $\text{S}_{\text{N}}1$ OR $\text{S}_{\text{N}}2$
 Br^- NUCLEOPHILE IS V. GOOD - TOWARDS $\text{S}_{\text{N}}2$ } \therefore MOST $\text{S}_{\text{N}}2$ CHARACTER

c) 2° SUBSTRATE - $\text{S}_{\text{N}}1$ OR $\text{S}_{\text{N}}2$
 I^- LEAVING GROUP IS EXCELLENT - MORE TOWARDS $\text{S}_{\text{N}}1$ THAN ABOVE CASES
 CH_3OH NUCLEOPHILE IS POOR \therefore FAVOURS $\text{S}_{\text{N}}1$ } \therefore MOST $\text{S}_{\text{N}}1$ CHARACTER

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

$\text{CH}_3\text{C}(\text{O})\text{O}^-$, Br^- , I^- , HO^- , HS^-

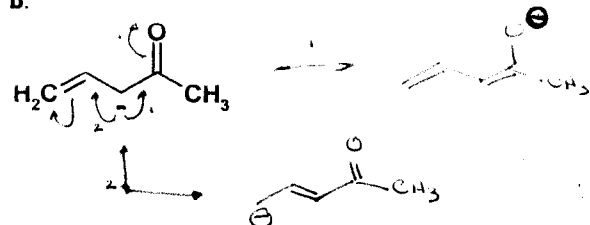


7. (9 marks) a and b Indicate all *reasonable* resonance forms of the following ions, using curved arrows to indicate electron movement. If there are *unreasonable* resonance forms, either do not draw them or label them as unreasonable. If there is a case for which there are no other resonance forms, state that fact.

a.



b.

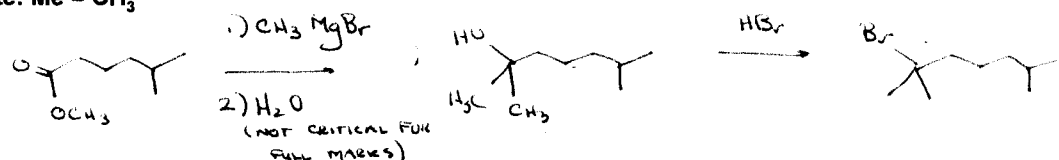


8. (11 marks total) Show by equation how you carry out the following overall transformations. Show all reagents and the structures of each reaction product. There is quite possibly more than one correct way to accomplish this overall transformation. DO one of a and b, but answer c regardless.

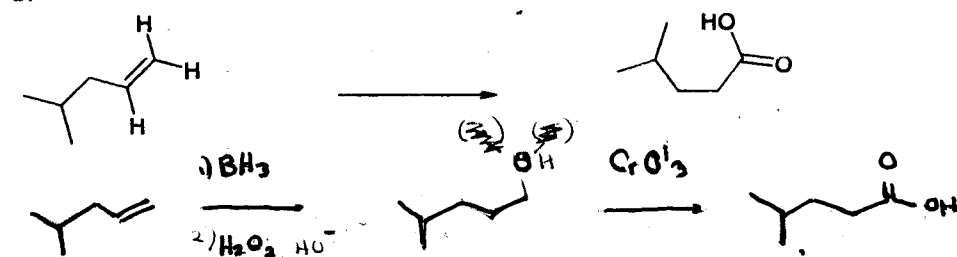
a.



Note: Me = CH_3



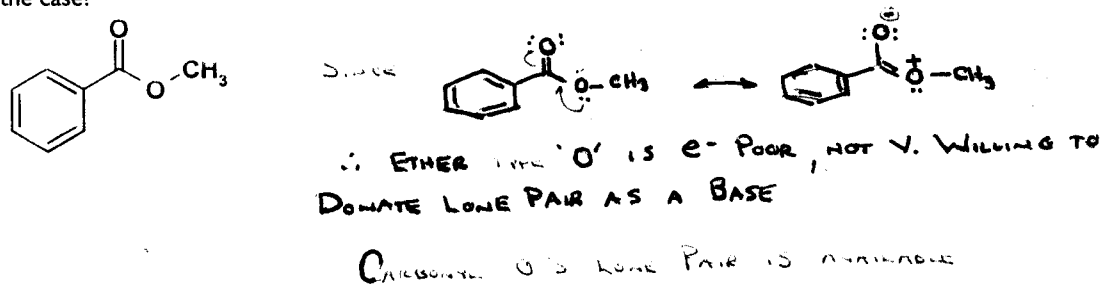
b.



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

4-METHYLPENTANOIC ACID

Bonus: (up to +3) In esters, the 'carbonyl' oxygen is the basic one, and not the 'ether type' one. Why is this the case?



Another Bonus (up to +5): An excellent way to introduce a bromine α - to (next to) a ketone function is adding Br_2 , with an acid catalyst. Can you propose a reasonable mechanism?

