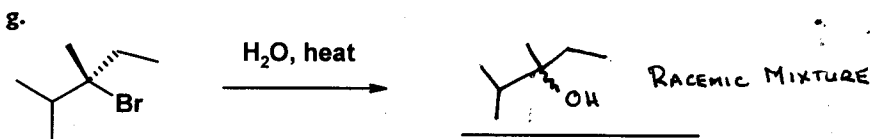
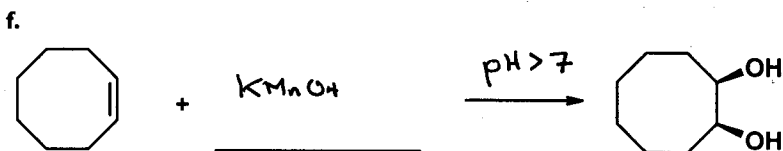
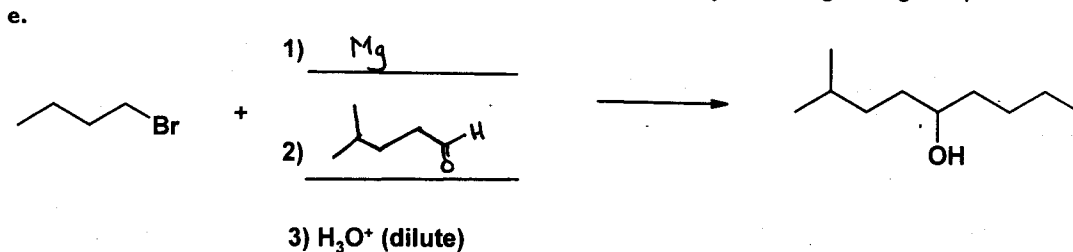
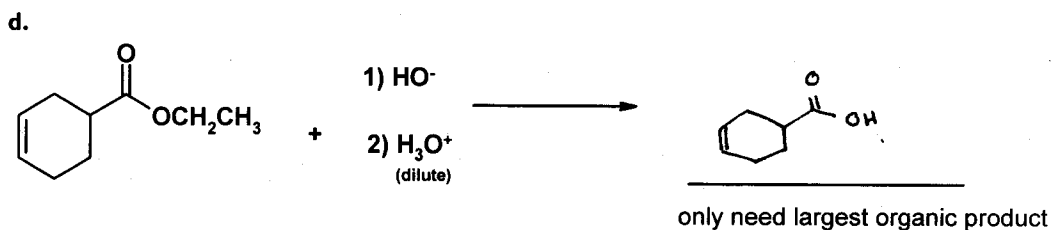
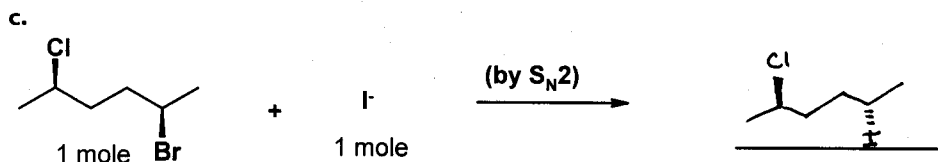
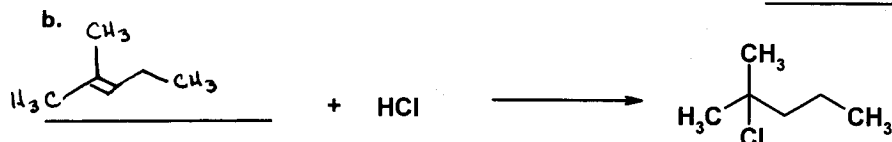
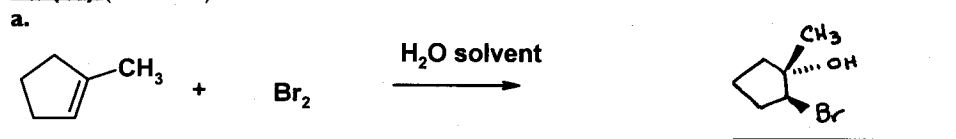


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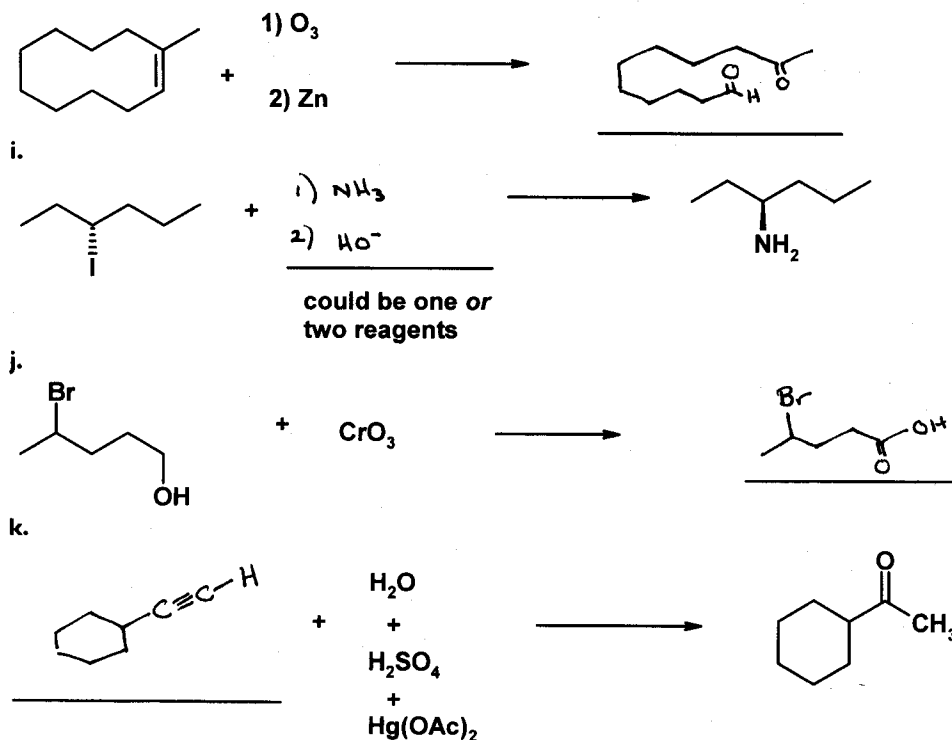
COURSE SECTION ('01' if Tues/Thurs, '02' if Mon/Wed/Fri) _____

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 130 marks on this exam.

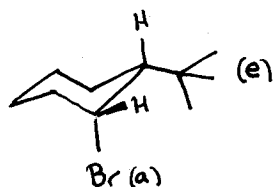
I. Fill in the blanks with the structural formula or reagents required to complete the equation. Show any required catalysts over the arrow. Make sure your drawings show stereochemistry if it is important. Do any ten (10) (40 marks)



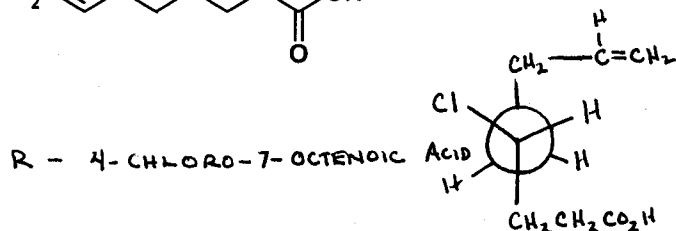
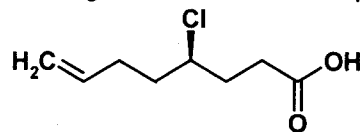
h.



2a. (12 marks total) Draw the structure of *cis* 1-bromo-2-(1,1-dimethylethyl)cyclohexane 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 (often known as a *tert*-butyl) is larger than a methyl group. (5 marks)

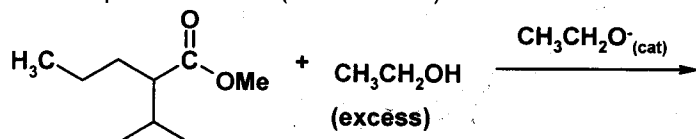


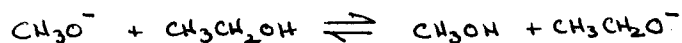
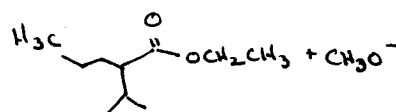
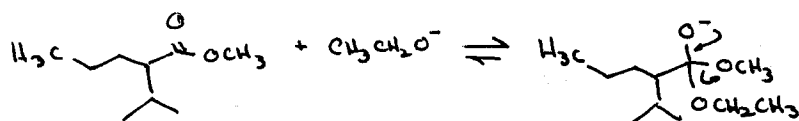
b. Draw the Newman projection of the following compound in its most stable conformation, as viewed down the C4-C5 bond. With respect to size, $\text{CH}_2\text{CH}_2\text{CO}_2\text{H} > \text{Cl} > \text{H}$. What is the name of this compound, including its stereochemical descriptor? (7 marks)



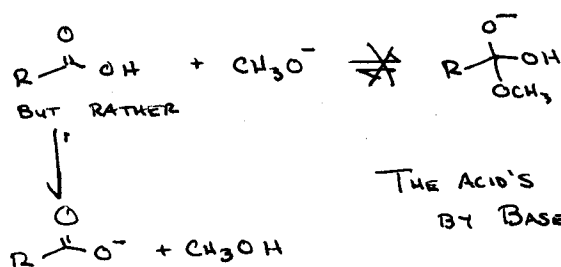
3. a. (12 marks total)

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. (9 marks)



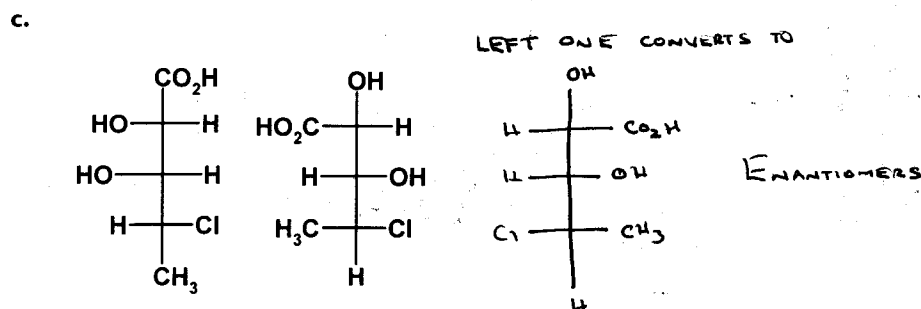
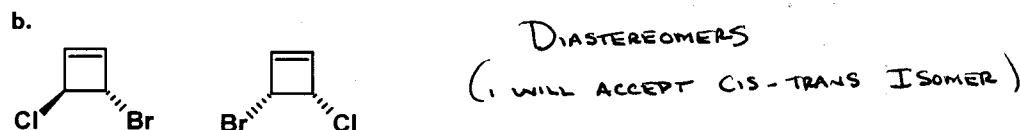
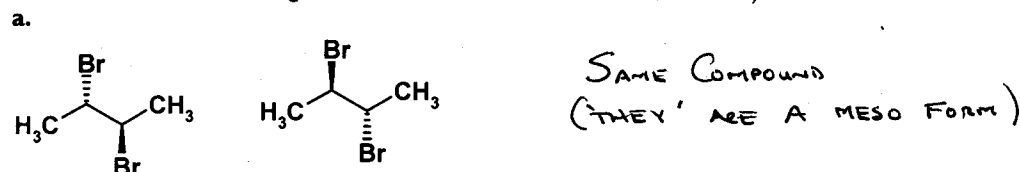


b. In the conversion of a carboxylic acid to its ester (let's say it's a methyl ester) a base catalyzed route is never employed. Show by structure and/or reaction why is this the case (3 marks).

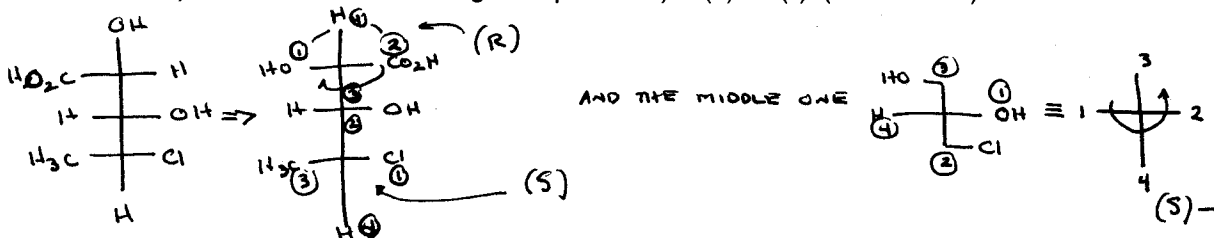


THE ACID'S OH IS ACIDIC - DEPROTONATED
BY BASE RATHER THAN ATTACKED

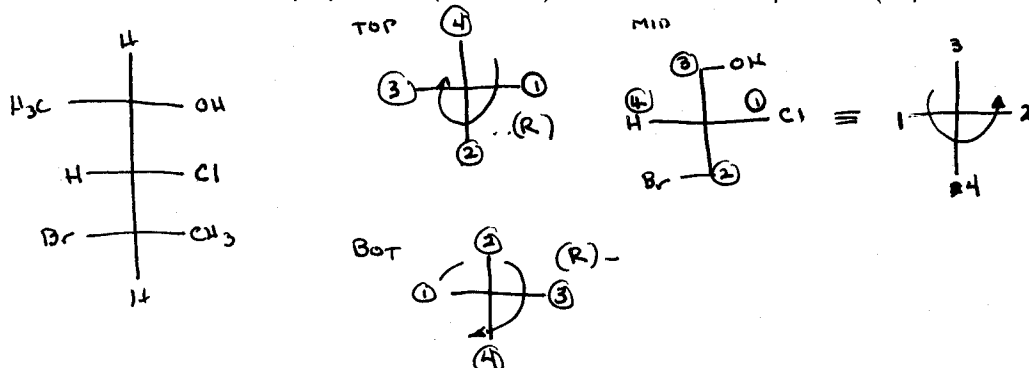
4. (18 marks total) Describe the relationship that exists between the following sets of compounds (i.e., enantiomer, diastereomer, geometric isomer, structural isomer, identical)



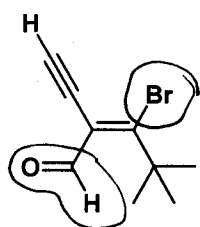
Also, identify the chiral centres for the right compound in c) as (R)- or (S)- (3 of 15 marks)



d. Draw the Fischer projection of (2R, 3S, 4R)-4-bromo-3-chloro-2-pentanol. (5 of the 15 marks).



e. Identify the following with the appropriate stereochemical descriptor. Show your work (3 marks)

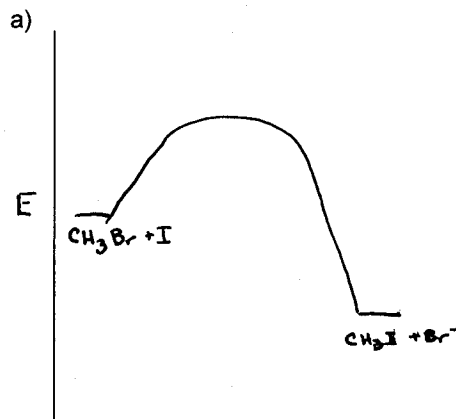


LEFT 1ST ATOM TOP C ; THEN C, C, C
 vs
 BOT C vs O, O, H + "WINS"
 RIGHT 1ST ATOM TOP Br + "WINS" (HIGHER ATOMIC #)
 vs
 BOT C
 \therefore (E)-

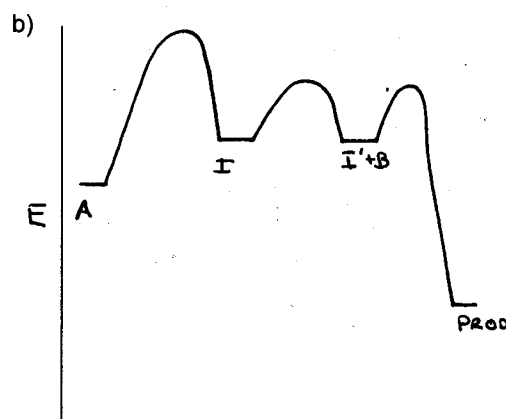
5. On the axes below, draw the energy/reaction coordinate profile for:

- The reaction between $\text{CH}_3\text{Br} + \text{I}^-$ to give $\text{CH}_3\text{I} + \text{Br}^-$ (the mechanism should be implied in the answer).
- A three step reaction between A and B, where A is involved in the 1st step and B is involved in the 3rd step. The 1st step is the slowest one.

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

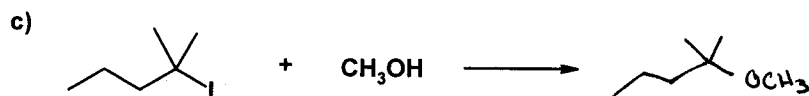
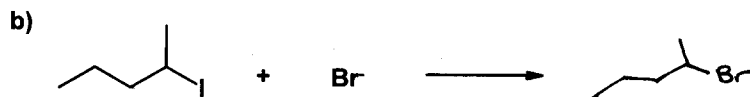
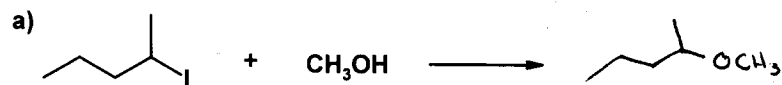


rate (v) = $k[\text{CH}_3\text{Br}][\text{I}^-]$
 THEY DON'T HAVE TO SAY $\text{S}_{\text{N}}2$,
 BUT THEY'D BETTER NOT SAY $\text{S}_{\text{N}}1$



rate (v) = $k[\text{A}]$

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



c) 3° ALKYL HALIDE - WILL ONLY REACT BY S_N1
 - POOR NUCLEOPHILE (CH₃OH) - TENDS TO FAVOUR S_N1
 ∴ MOST S_N1 CHARACTER

a) 2° ALKYL HALIDE - CAPABLE OF S_N1 OR S_N2 REACTIVITY
 - POOR NUCLEOPHILE (CH₃OH) - TENDS TO FAVOUR S_N1
 ∴ MIDDLE CASE - MORE S_N2 CHARACTER THAN ABOVE

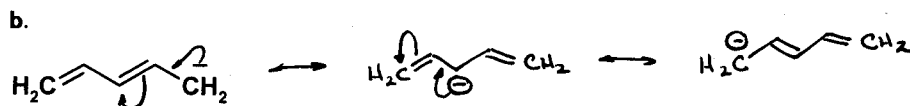
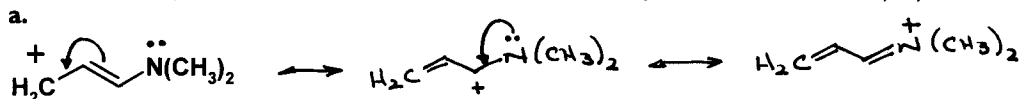
b) 2° ALKYL HALIDE - CAPABLE OF S_N1 OR S_N2 REACTIVITY
 - EXCELLENT NUCLEOPHILE (Br⁻) - TENDS TO FAVOUR S_N2
 ∴ MOST S_N2 CHARACTER

d. Rank the following from best nucleophile to worst nucleophile? (3 of the 13 marks)

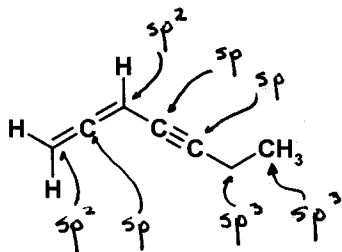
Cl⁻, Br⁻, I⁻, H₂O, CH₄



7. (11 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.

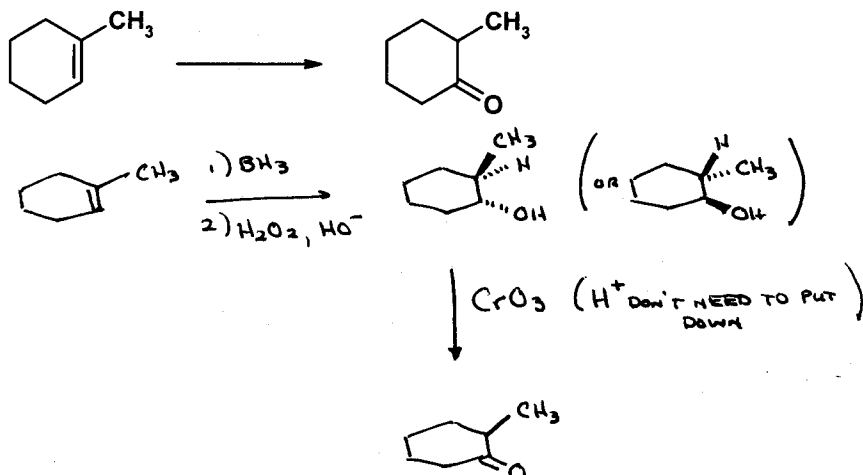


c. Indicate the hybridization of each non-hydrogen atom in the following compound

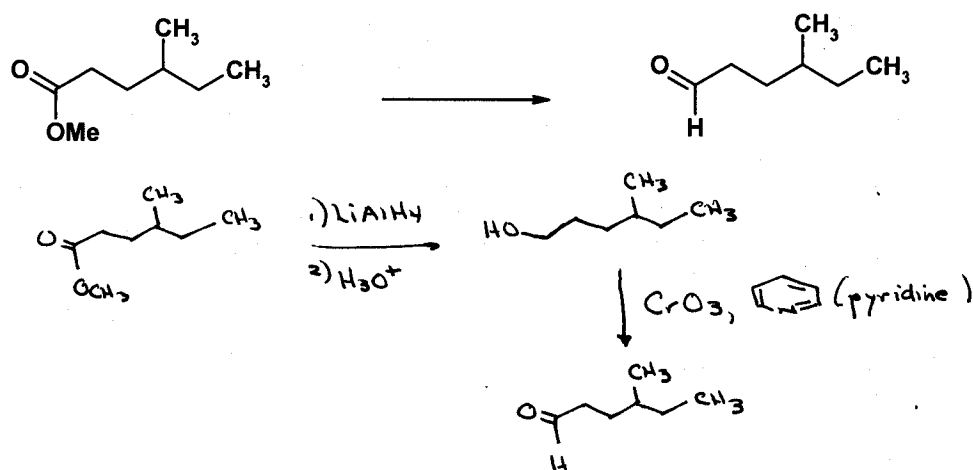


8. (11 marks total) Show by equation how you carry out the following overall transformations. Show all reagents and the structures of each reaction product. There is quite possibly more than one correct way to accomplish this overall transformation. DO one of a and b, but answer c regardless.

a.



b.



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

4-METHYLHEXANAL

Bonus: (up to +5)

The reaction of an alcohol with SOCl_2 to give a chloroalkane is a rare example of a third nucleophilic substitution mechanism, called an $\text{S}_{\text{N}}\text{i}$ mechanism. Propose a reasonable set of steps for this process.

