Department of Chemistry and Biochemistry

Chemistry 59-230/232 **Final Exam**
Time: 3 h **Dec. 12, 2009**

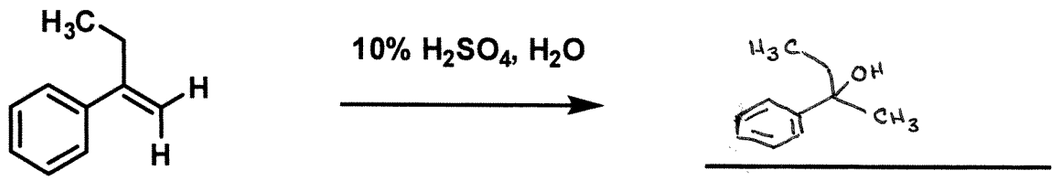
NAME _____ **ID#** _____

LAB SECTION (or TA name) _____

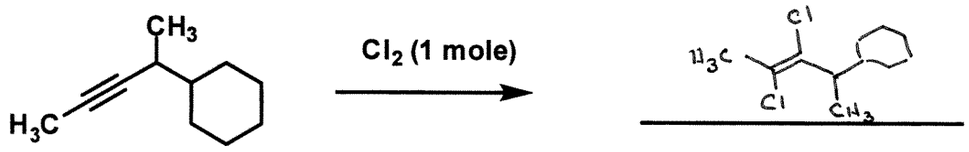
Note: **Please answer on the test paper.** There is an extra sheet for rough work at the back, but it will not be marked. In some questions (1 and 8), there is a choice of questions to answer. If all are answered, all will be marked. There are **150** marks on this exam.

1. Fill in the blanks with the structural formula or reagents required to complete the equation. A single blank could indicate more that one compound. 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 all of i.*** **(40 marks total)**

a.

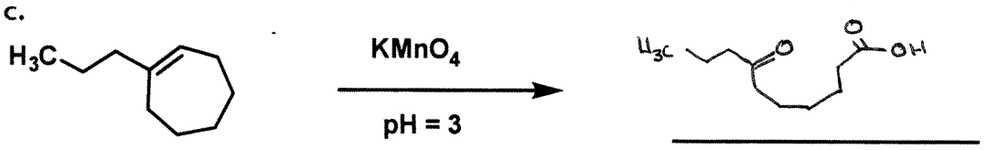


b.

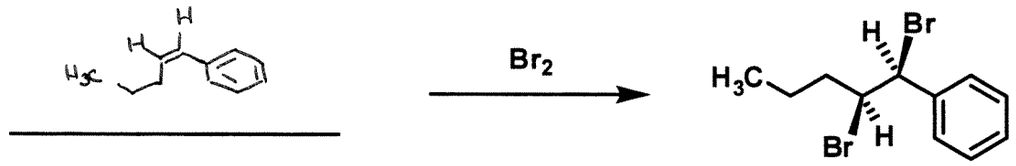


(1 mole)

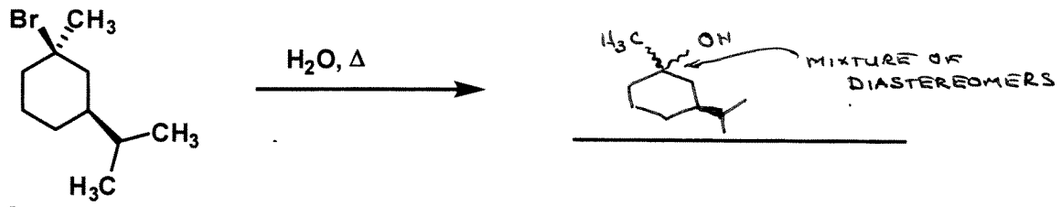
c.



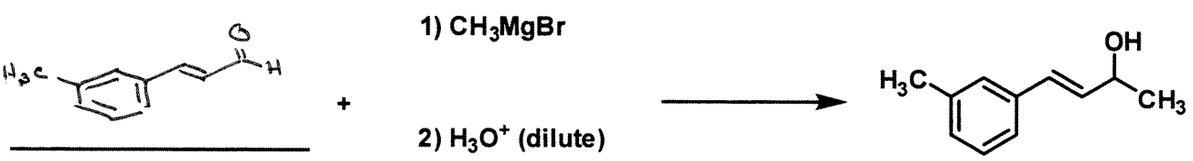
d.



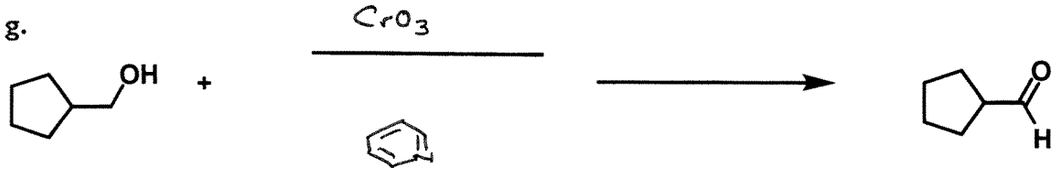
e.



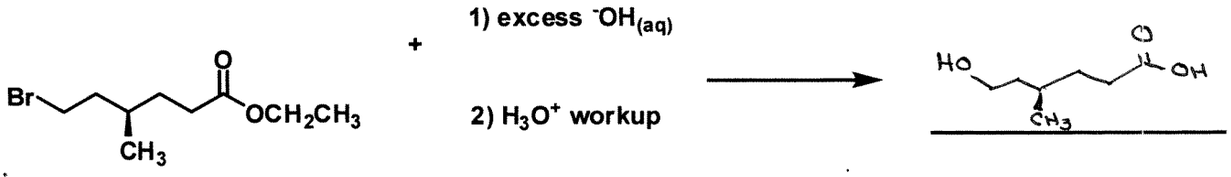
f.



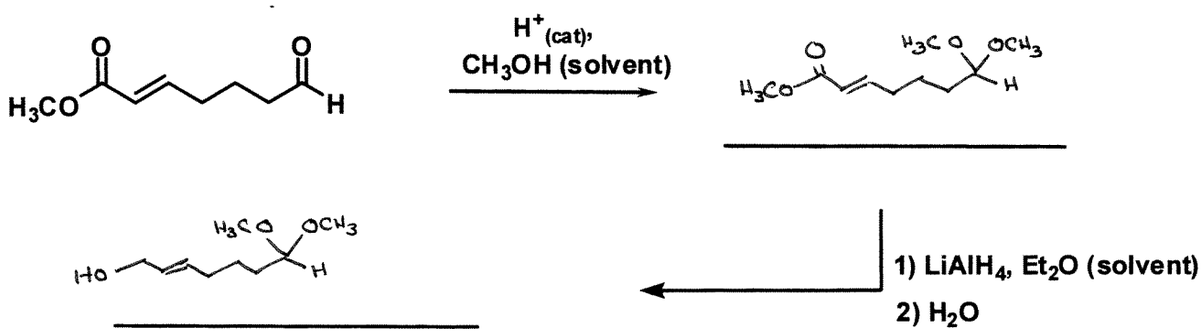
g.



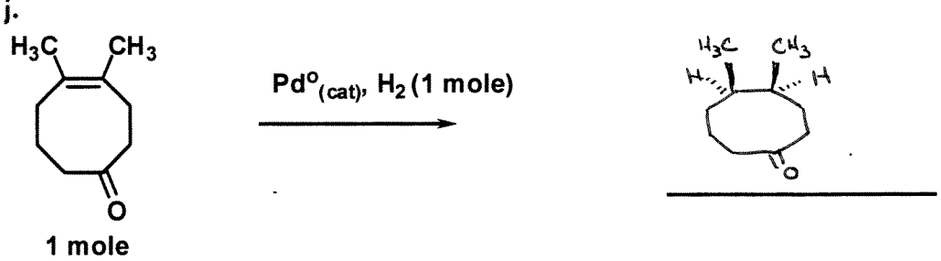
h.



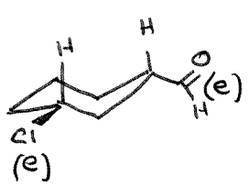
i.



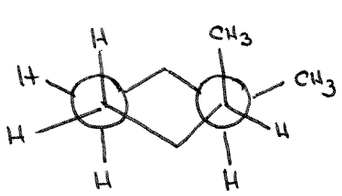
j.



2a. (20 marks total) Draw the structure of *cis* 3-chlorocyclohexanecarbaldehyde in its *most* stable chair conformation. Label the non-hydrogen substituents on the cyclohexane as axial or equatorial. In terms of size, an aldehyde group is larger than a chloro group. (6 marks)



b. i) Draw the Newman projection of *cis*-1,2-dimethylcyclohexane (4 marks).



ii) Is this the most stable possible isomer of 1,2-dimethylcyclohexane (yes/no)? (2 marks)

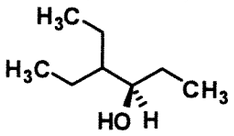
NO

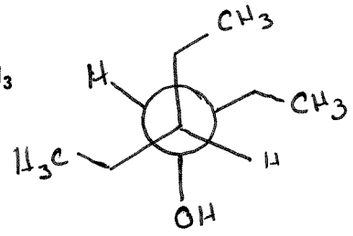
iii) What is the name for the relationship between the two methyl groups in *cis* 1,2-dimethylcyclohexane? I am looking for something more detailed that eclipsed or staggered. (2 marks)

SYNCLINAL (OR GAUCHE OR SKEW)

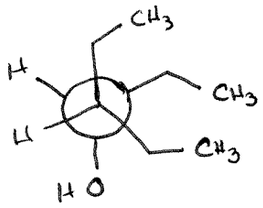
c. Draw the Newman projection of the following compound (next page) in its most stable conformation of all **and** in its *least* stable staggered conformation, as viewed down the C3-C4 bond..

With respect to size, $(CH_3)_3C$ > $(CH_3)_2CH$ > unbranched alkyl ≈ CH_3CH_2 > CH_3 > OH > Br ≈ Cl ≈ F > H. (6 marks)





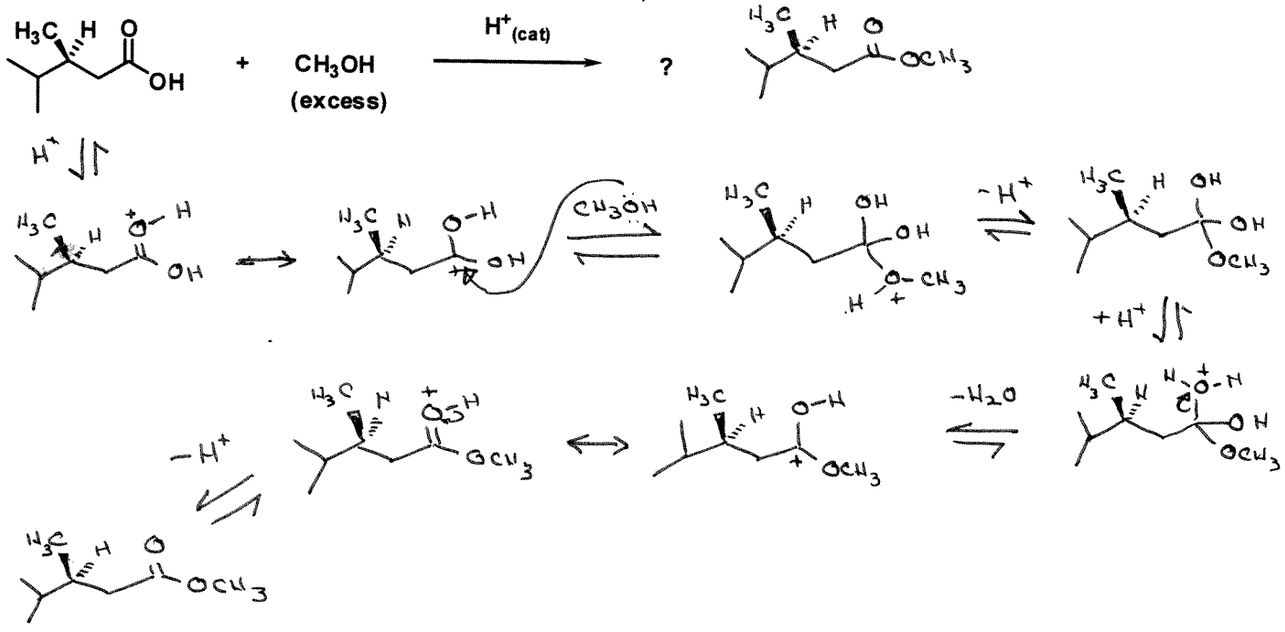
BEST OF ALL



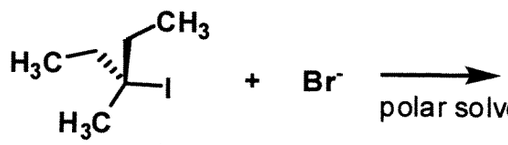
WORST STAGGERED

3. a. (15 marks total)

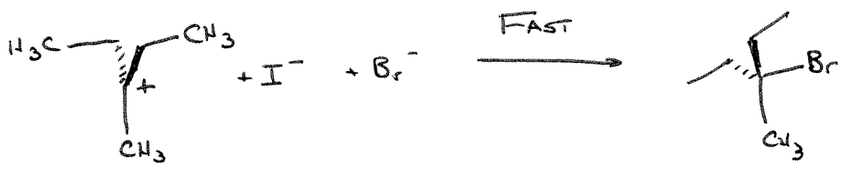
Draw the complete mechanism for the following reaction. Take the reaction to completion. Indicate which steps are reversible (or irreversible). (10 marks)



b. Show the complete mechanism for the reaction of the following compound with bromide ion (let's say KBr). If there is more than one step in the process, indicate which step is the rate determining (slow) one. What is the name for the mechanism involved? (5 marks)



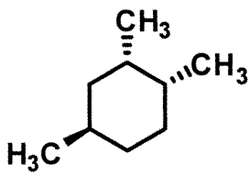
SLOW STEP

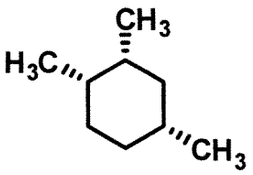


S_N1 MECHANISM

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

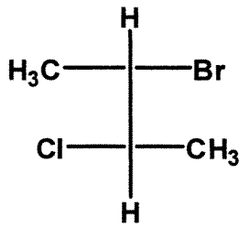
a.

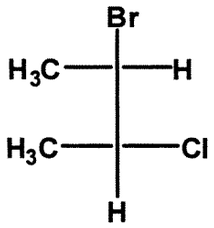




DIASTEREOMERS

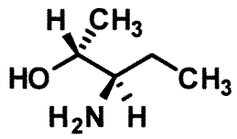
b.

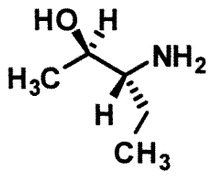




ENANTIOMERS

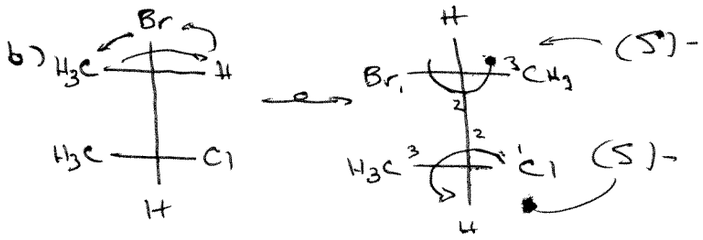
c.

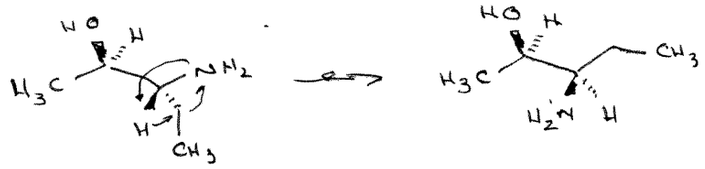


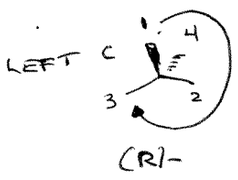


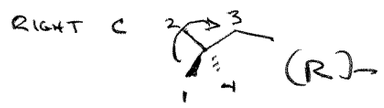
IDENTICAL
(WELL, DIFFERENT CONFORMATIONS)

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

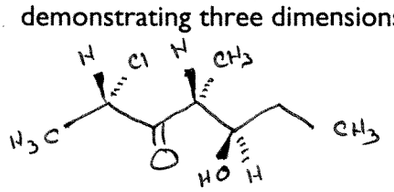




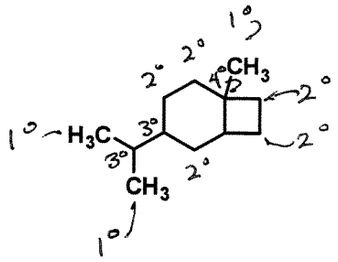




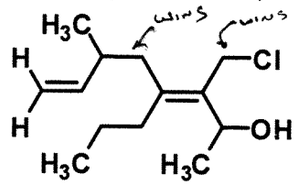
d. Draw of (2S,4R,5R)- 2-chloro-5-hydroxy-4-methyl-3-heptanone in any convincing structure demonstrating three dimensions. (6 *of the* 33 marks).



e. Identify each of the carbon atoms as primary, secondary, tertiary, or quaternary. (4 of the 33 marks)



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



LEFT SIDE Top C on it C, H, N on it C, C, N wins

vs

Bot. C on it C, N, H on it C, H, H

TIE TIE

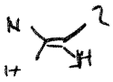
RIGHT SIDE Top C on it Cl, H, H wins

vs

Bot C on it O, C, H

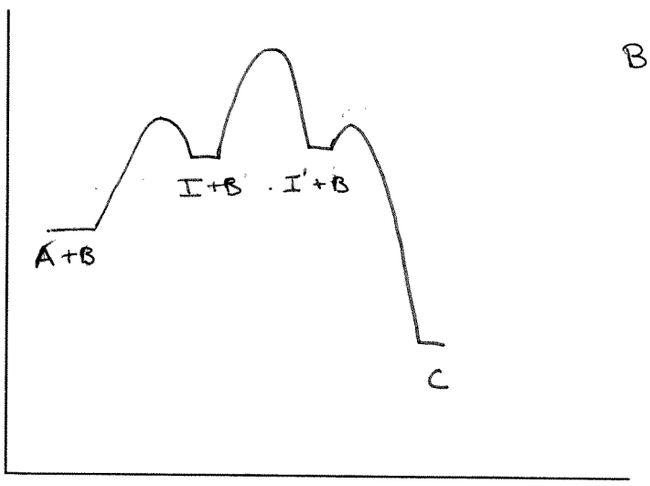
TIE

HIGHEST PRIORITY GROUP ON SAME SIDE ∴ (Z)-

THE OTHER C=C  NEEDS NO DESCRIPTOR

5. On the axes below, draw the energy/reaction coordinate profile for a three step reaction of A, and B to give C. A is consumed in the 1st step, while B is consumed in the 3rd step. The first and third transition states are lower than the second. Label the intermediate(s)/products.

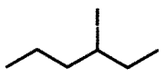
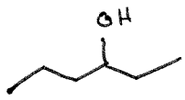
Also, Give the rate equation for the reaction. (7 marks total)

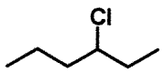
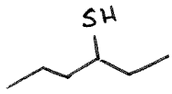


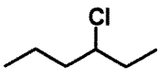
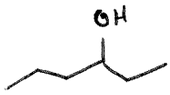
B NOT CONSUMED UNTIL AFTER THE SLOW STEP

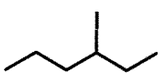
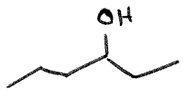
rate (v) = $k[A]$

6. (**14 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. (11 of the 14 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).

a)  HO^-, H_2O solvent → ? 

b)  HS^-, acetone solvent → ? 

c)  HO^-, acetone solvent → ? 

d)  H_2O, Δ, H_2O solvent → ? 

a) NUCLEOPHILE V. GOOD ∴ TOWARDS S_N2

SUBSTRATE 2° - ALL SAME - S_N1 OR S_N2

LEAVING GROUP - EXCELLENT - MORE S_N1 TENDENCY THAN Cl

SOLVENT - VERY POLAR - MORE S_N1 TENDENCY

b) SUBSTRATE 2° - SAME AS ABOVE

NUCLEOPHILE EXCELLENT - TENDS TOWARDS S_N2

LEAVING GROUP - GOOD NOT GREAT - MORE S_N2 TENDENCY

SOLVENT - MODERATE POLARITY - TENDS TOWARDS S_N2

c) SUBSTRATE 2° - SAME AS ABOVE

NUCLEOPHILE - V. GOOD ∴ TOWARDS S_N2, NOT QUITE LIKE b)

LEAVING GROUP - GOOD NOT GREAT - MORE S_N2 TENDENCY

SOLVENT - MODERATE POLARITY - TENDS TOWARDS S_N2

b) MOST S_N2 > c) close 2ND for S_N2 > a) 3RD for S_N2 >> d) MOST S_N1

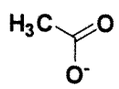
d) SUBSTRATE - 2° - SAME

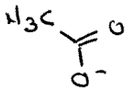
NUCLEOPHILE - POOR - TEND TOWARDS S_N1

LEAVING GROUP - EXCELLEN MORE S_N1

SOLVENT - VERY POLAR - MORE S_N1

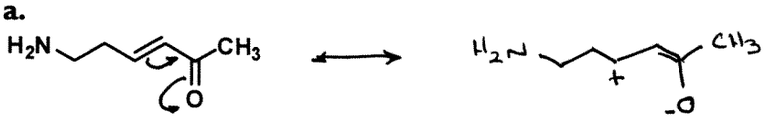
e. Rank the following from best nucleophile to worst nucleophile. (3 *of the* 14 marks)

 HS^- Br^- HO^- Cl^-

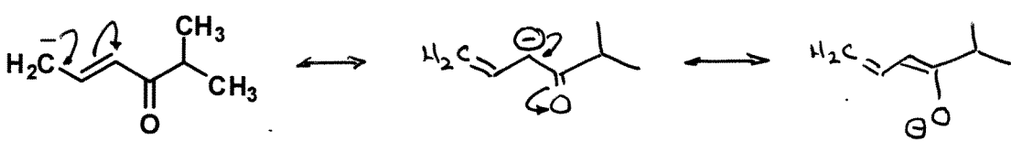
$HS^- \approx Br^-$ (SIMILAR) > $HO^- \approx Cl^-$ (SIMILAR) > 

7. (**10 marks**) a and b Indicate all *reasonable* resonance forms of the following species, using curved arrows to indicate electron movement. If there are *unreasonable* resonance forms, <u>either</u> 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.

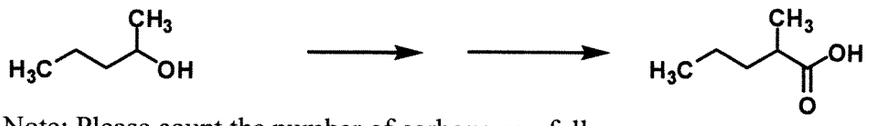


b.

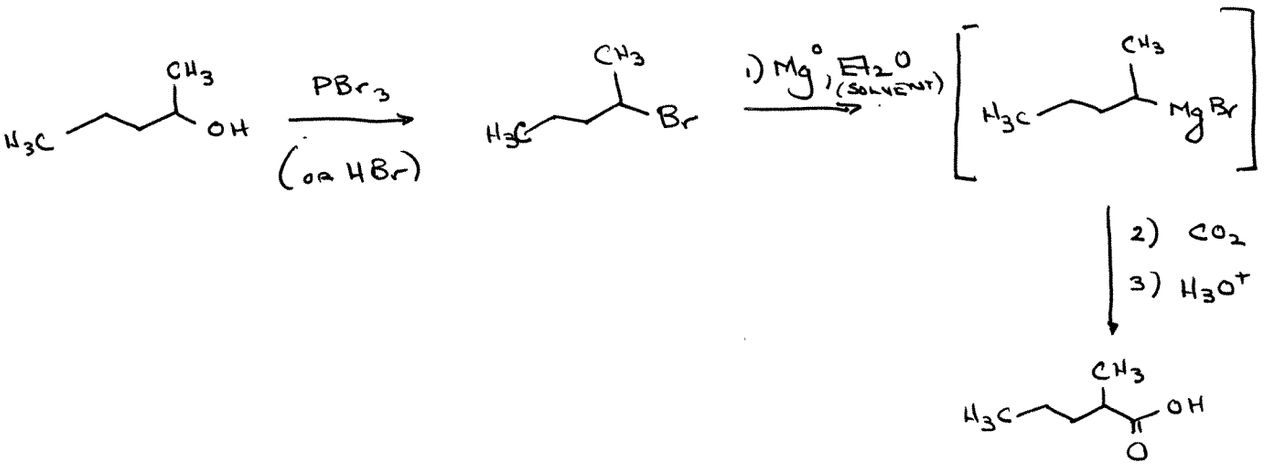


8. (**11 marks total**) Show by equation how you carry out the following overall transformations. Show all reagents and the structures of each reaction product. There is quite possibly more than one correct way to accomplish this overall transformation (8 marks). ***DO one of a and b, but answer c regardless.***

a.

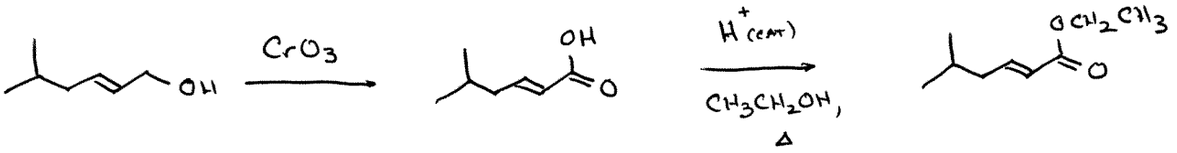


Note: Please count the number of carbons carefully.



b.

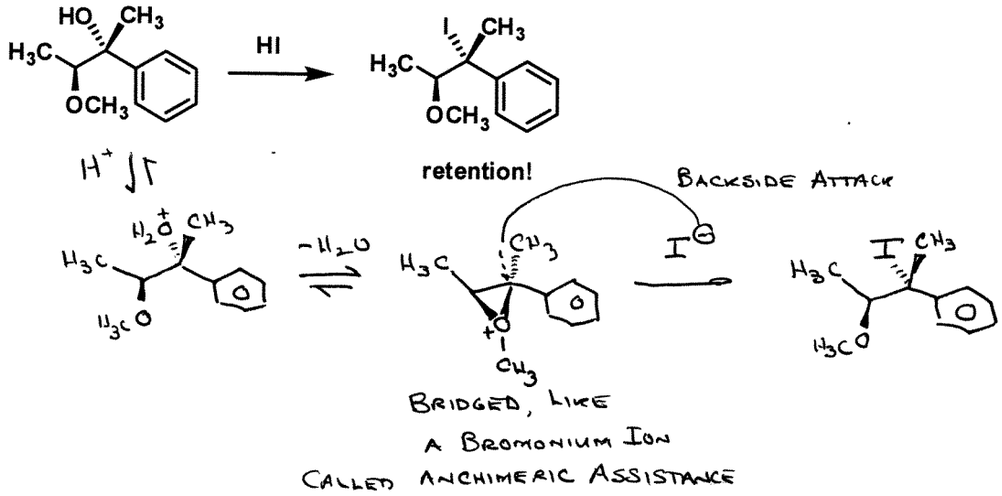
Note: This C=C is not electron rich



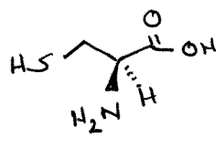
c. What is the name of the final product compound in **8b**? Include any stereochemical descriptors. (3 of the 11 marks)

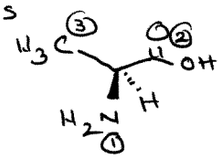
(E)- ETHYL 5-METHYL-2-HEXENOATE

Bonus: (up to +5) The following substitution reaction does not go with inversion of configuration, and also does not racemize at the reacting centre. Instead it gives retention of configuration. Can you explain mechanistically why this is the case?



Another Bonus (up to +5)**:** I have told you that of the 20 essential amino acids, 19 are chiral and 18 exist as the (S)- enantiomers. Which is the one that exists as the (R)- enantiomer and why is different?

CYSTEINE  IS (R)-. WITH EVERY OTHER AMINO ACID EXCEPT GLYCINE (WHICH IS ACHIRAL), N IS HIGHEST PRIORITY CO_2N IS 2ND HIGHEST R IS 3RD HIGHEST

FOR EXAMPLE, PROLINE IS  (S)-

DUE TO THE SULPHUR ATOM 'R' (CH_2SH) IS 2ND HIGHEST PRIORITY CO_2N IS 3RD HIGHEST

I.E., REVERSED.