

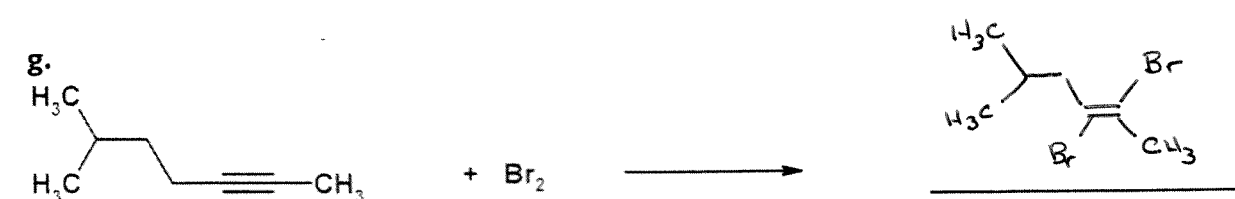
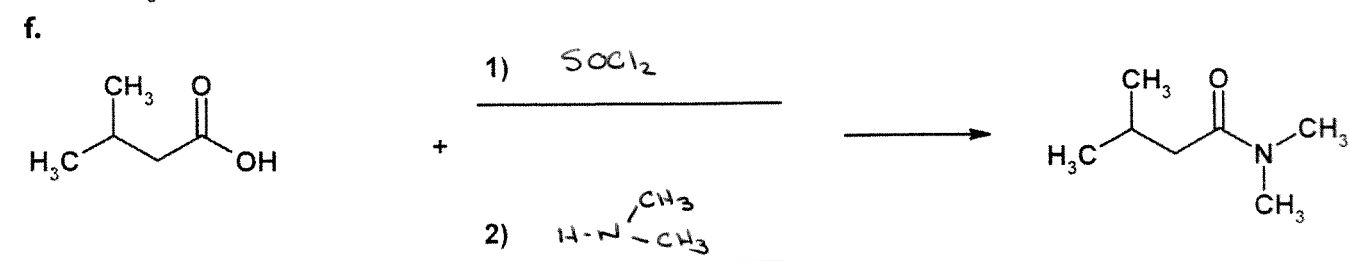
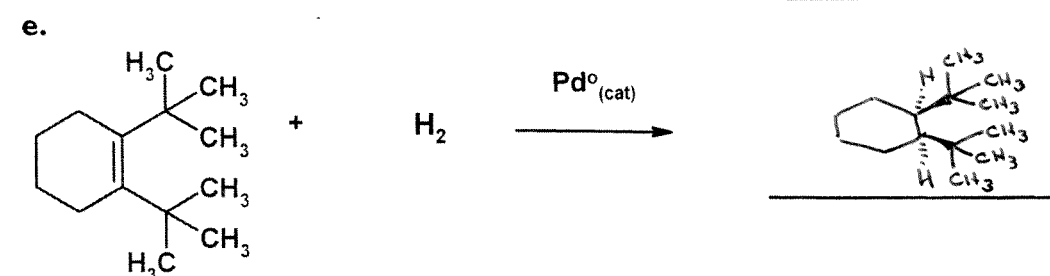
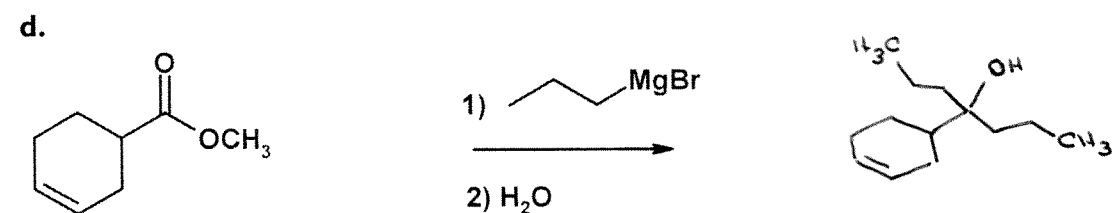
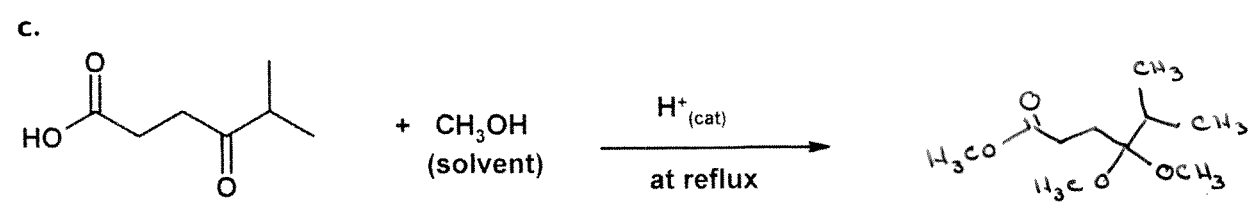
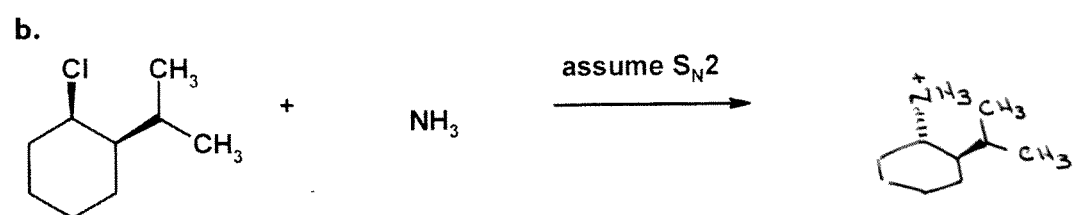
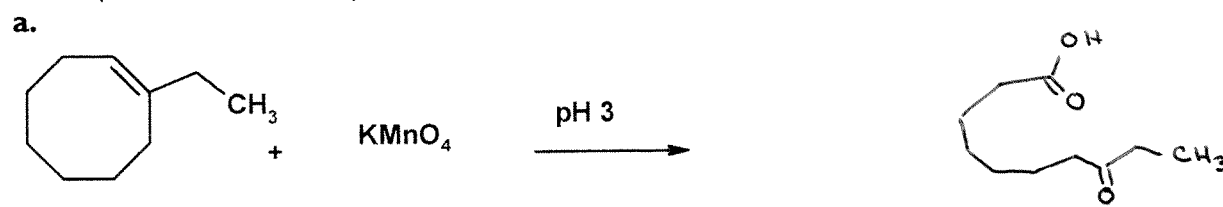
NAME _____

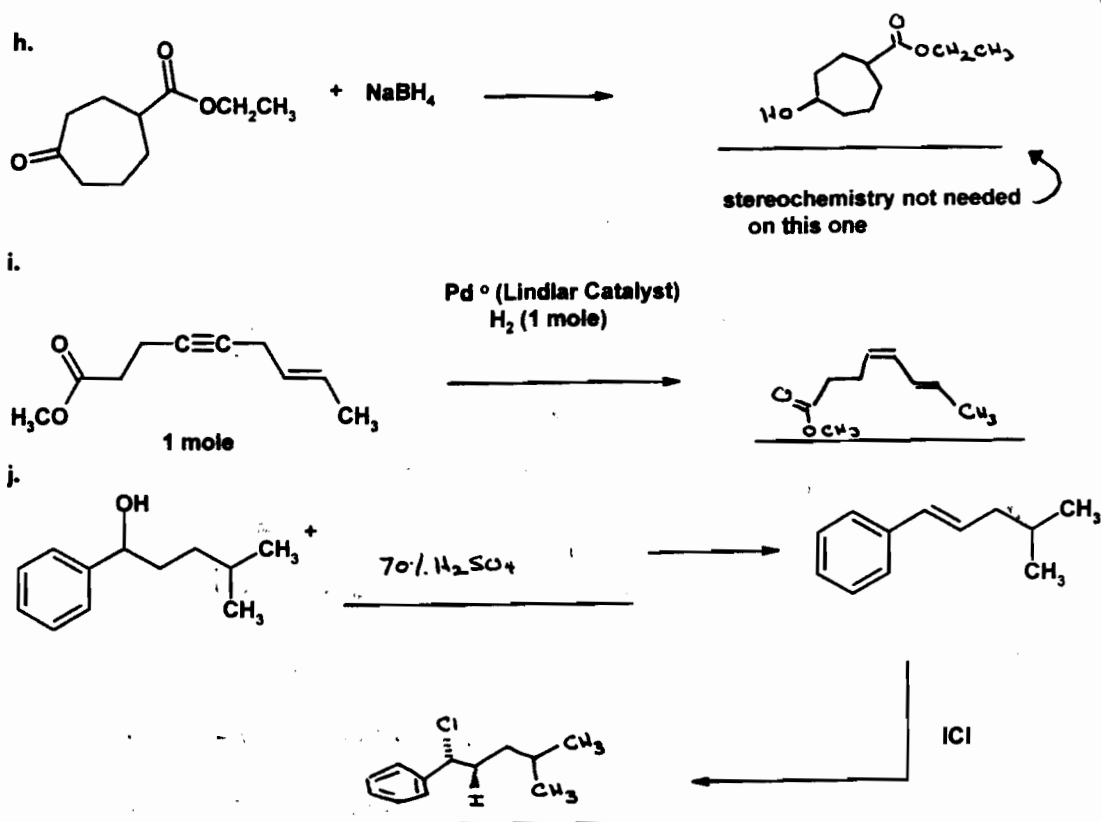
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LAB SECTION (or TA name) _____

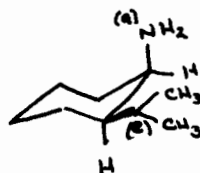
Note: **Please answer on the test paper.** There is an extra sheet for rough work at the back, but it will not be marked. In some questions, there is a choice of questions to answer. If all are answered, all will be marked. There are **150** marks on this exam.

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 "j." is worth 2 entries. **Do any ten (10), but including j. (40 marks total)**





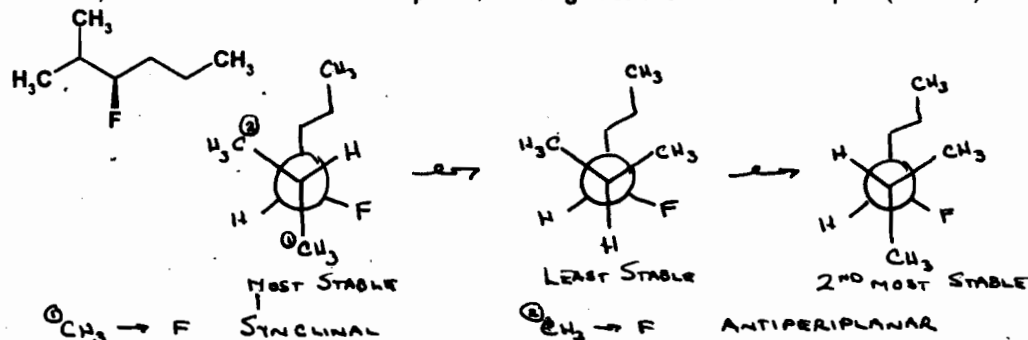
2a. (20 marks total) Draw the structure of *cis* 1-(amino)-2-isopropylcyclohexane in its most stable chair conformation. Label the non hydrogen substituents on the cyclohexane as axial or equatorial. In terms of size, an isopropyl group is larger than an amino group. (6 marks)



b. i) Draw the Newman projection of the following compound in all of its staggered conformations, as viewed down the C2-C3 bond. Rank them in terms of stability. With respect to size, (CH₃)₃C > (CH₃)₂CH > unbranched alkyl ≈ CH₃CH₂ > CH₃ > OH > Br ≈ Cl ≈ F > H. (9 marks)

ii) In the best of these what is the term for the relationship between the methyl groups and the F function (I'm looking for something more detailed than staggered/eclipsed)? (2 marks)

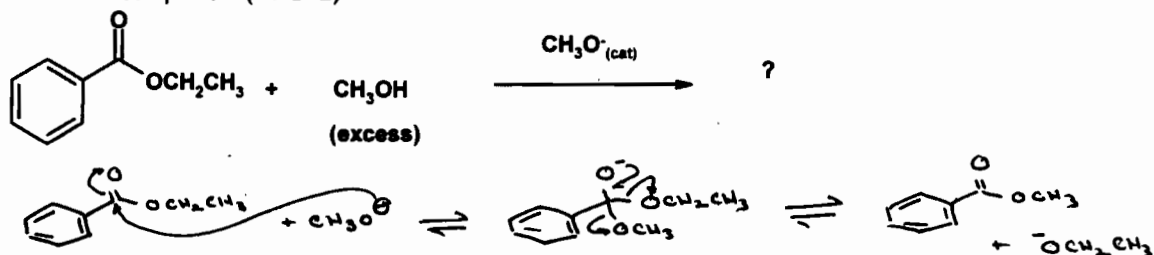
iii) What is the name of this compound, including its stereochemical descriptor (3 marks)



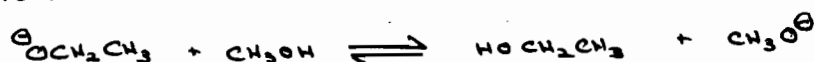
(R)- 3-FLUORO-2-METHYLHEXANE

3. (14 marks total)

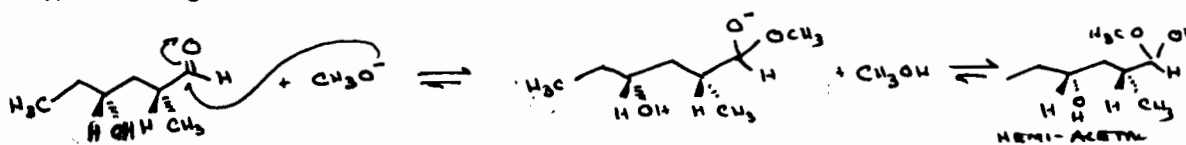
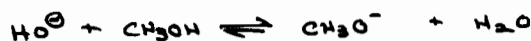
a. Draw the complete mechanism for the base catalyzed transesterification of ethyl benzoate. Take the reaction to completion. (7 marks)



TO ABSOLUTELY FINISH THE MECHANISM

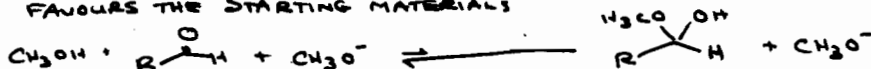


b. In the conversion of an aldehyde (lets say (2R,4R)- 4-hydroxy-2-methylhexanal) to an acetal (let's say it's the dimethyl acetal) one never gets an amount of intended product under base (HO^-) catalyzed conditions. Why is this the case (show by reaction and written explanation) (7 marks)? The complete answer will include the structure of (2R,4R)- 4-hydroxy-2-methylhexanal, but a complete mechanism of acetal formation is not needed.



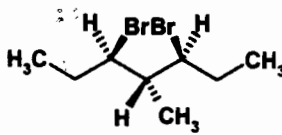
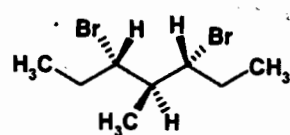
BUT. REACTION CAN GO NO FURTHER THAN HEMI-ACETAL, BECAUSE HO^- ISN'T A GOOD LEAVING GROUP, AND....

THE EQUILIBRIUM BETWEEN THE HEMI-ACETAL AND THE STARTING MATERIALS FAVOURS THE STARTING MATERIALS



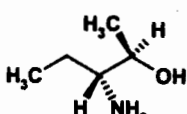
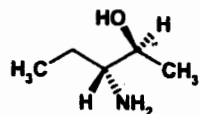
4. (31 marks total) Describe the relationship that exists between the following sets of compounds (i.e., enantiomer, diastereomer, geometric isomer, structural/constitutional isomer, identical). Indicate any meso forms (11 of the 31 marks).

a.



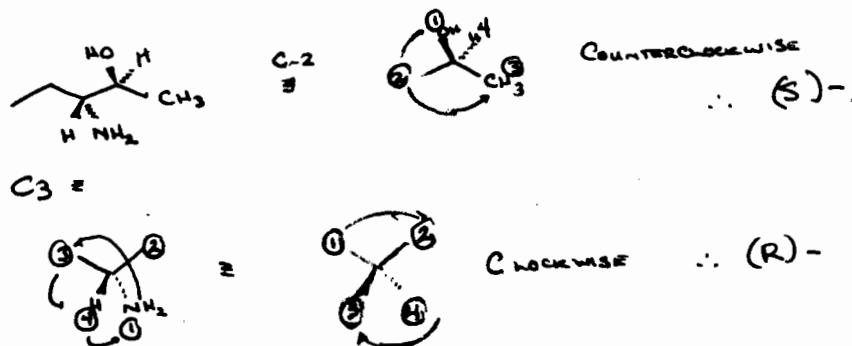
IDENTICAL
BOTH ARE THE SAME
MESO FORM

b.

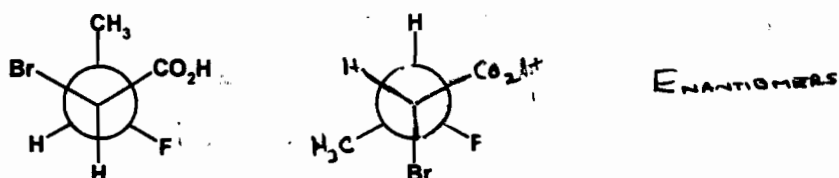


DIASTEREOMERS

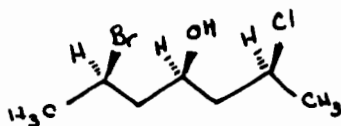
Also, identify the chiral centres for the left compound in b) as (R)- or (S)-. Show how you arrived at your conclusion. (6 of 31 marks)



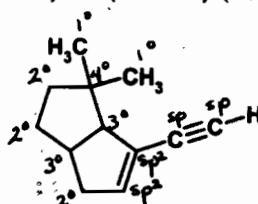
c.



d. Draw (2R,4S,6S)-2-bromo-6-chloro-4-heptanol in any convincing structure showing three dimensions. (4 of the 31 marks).



e. In the following compound, label the hybridization of the carbons that are not sp^3 . For the sp^3 hybridized C's label them as primary, secondary, tertiary, or quaternary (1° , 2° , 3° , 4°) (4 marks of the 31).



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)

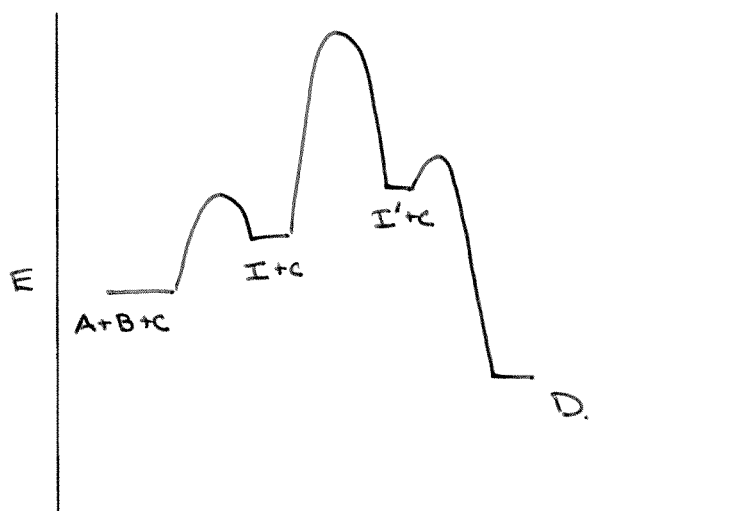
AT TOP	LEFT	vs	RIGHT
	C		C
ON THAT C	C, C, H	vs	C, C, C (BY DISSECTING) C=C
			WINS.

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

ON BOTTOM	LEFT	vs	RIGHT
	C		H
	WINS		

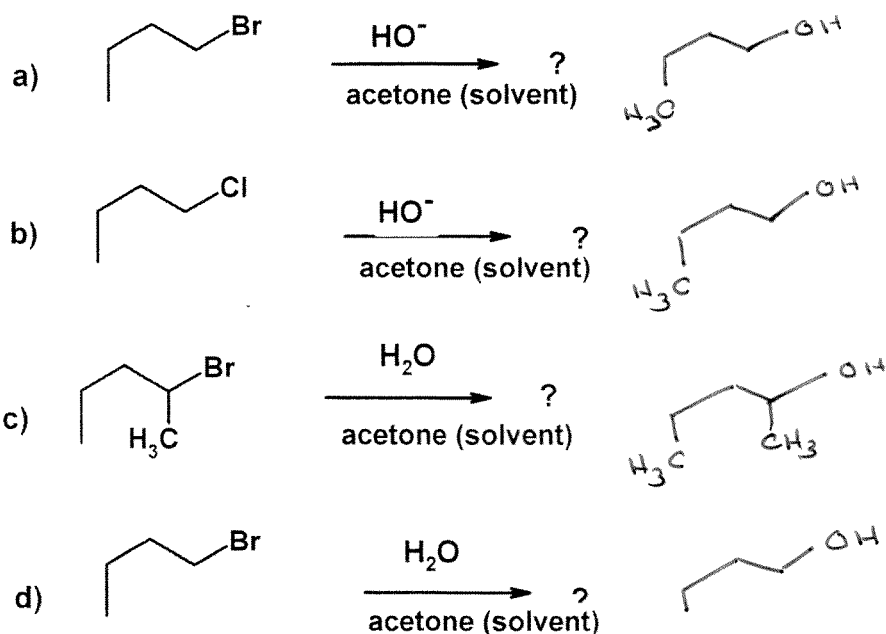
5. On the axes below, draw the energy/reaction coordinate profile for a three step reaction of A, B, and C to give D. A and B are consumed in the 1st step, and C is consumed in the final step, while the 2nd step is the slowest one. Label the intermediate(s)/products.

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



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

6. (15 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. (12 of the 15 marks) Acetone is a moderate polarity solvent (dielectric constant = 23).



CASE a) 1° ALKYL HALIDE ∴ TENDS TOWARDS S_N2
 HO⁻ EXCELLENT NUCLEOPHILE ∴ TENDS TOWARDS S_N2
 Br⁻ EXCELLENT LEAVING GROUP ∴ VIABLE IN S_N1 OR S_N2
 ∴ 2ND MOST S_N2 CHARACTER

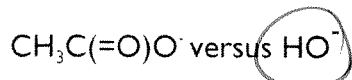
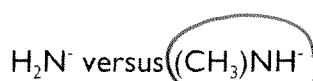
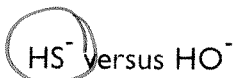
b) 1° ALKYL HALIDE ∴ TENDS TOWARDS S_N2
 HO⁻ EXCELLENT NUCLEOPHILE ∴ TENDS TOWARDS S_N2
 Cl⁻ GOOD LEAVING GROUP ∴ MORE TOWARDS S_N2 THAN a)
 ∴ MOST S_N2 CHARACTER

c) 2° ALKYL HALIDE ∴ COULD BE S_N1 OR S_N2
 H₂O POOR NUCLEOPHILE ∴ TENDS TOWARDS S_N1
 Br⁻ EXCELLENT LEAVING GROUP ∴ VIABLE IN S_N1 OR S_N2
 ∴ MOST S_N1 CHARACTER

d) ON NEXT PAGE.

d) 1° ALKYL HALIDE ∴ TENDS TOWARDS S_N2
 H₂O POOR NUCLEOPHILE ∴ TENDS TOWARDS S_N1
 Br⁻ EXCELLENT LEAVING GROUP ∴ VIABLE IN S_N1 OR S_N2
 ∴ 2ND LEAST S_N2 CHARACTER

e. In each of the following pairs, pick the better of the two nucleophiles. (3 of the 15 marks)

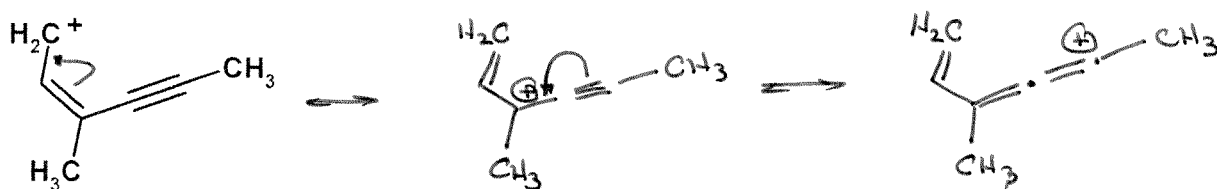


7. (12 marks) a and b Indicate all *reasonable* resonance forms of the following ions, using curved arrows to indicate electron movement. If there are *unreasonable* resonance forms, either do not draw them or label them as unreasonable. If there is a case for which there are no other resonance forms, state that fact.

a.

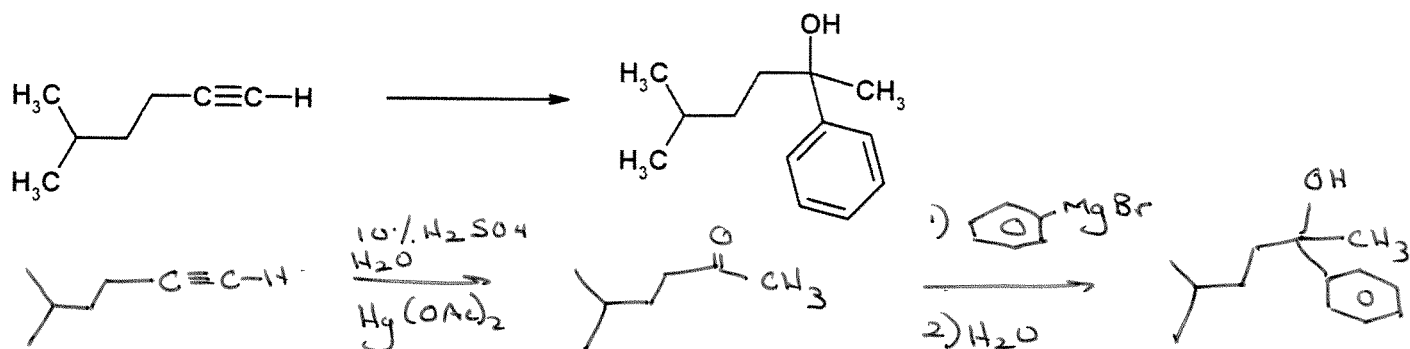


b.

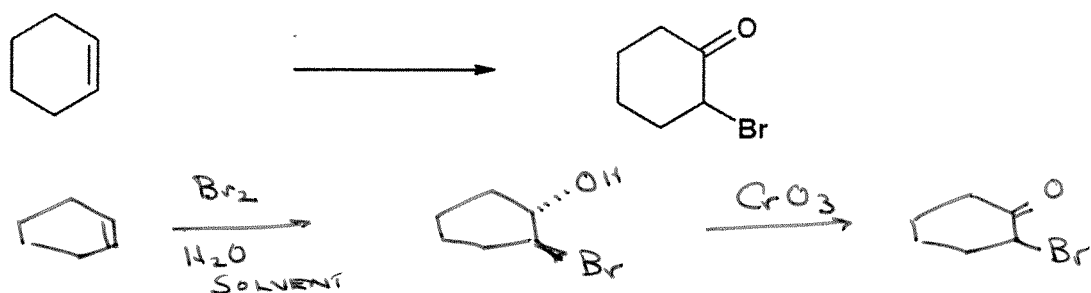


8. (11 marks total) Show by equation how you carry out the following overall transformations. Show all reagents and the structures of each reaction product. Show any stereochemistry within your intermediates or reaction products. There is quite possibly more than one correct way to accomplish this overall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

a.



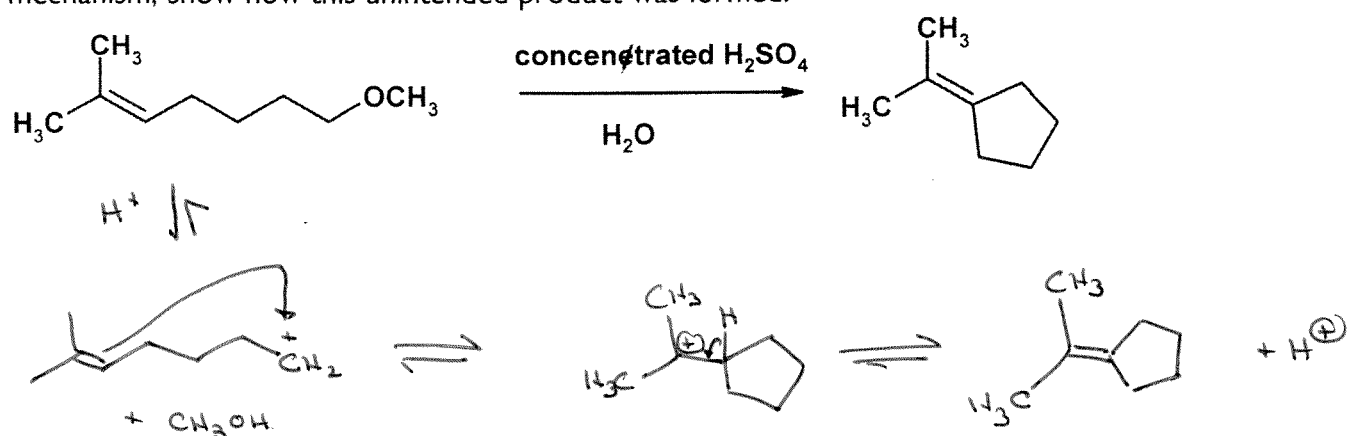
b.



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

2-Bromocyclohexanone

Bonus: (up to +5) In an attempt to convert an ether into its corresponding alcohol, a beginning chemists accidentally isolated a significant amount of a cyclic alkene, shown below. By way of step-by-step mechanism, show how this unintended product was formed.



Another Bonus (up to +5): A budding chemist attempted to get access to (S)-valine by the base induced hydrolysis of its corresponding enantiomerically pure methyl ester. Unfortunately, once the valine itself was isolated, it showed no optical activity whatsoever. Show by mechanism what happened to cause this compound to become racemic.

