Department of Chemistry and Biochemistry

Chemistry 59-230/232
Time: 3 h

Final Exam
Dec. 14, 2007

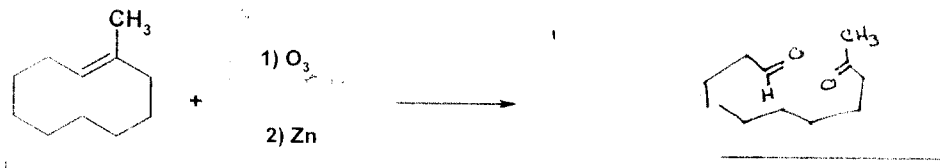
NAME _____ ID# _____

LAB SECTION (or TA name) _____

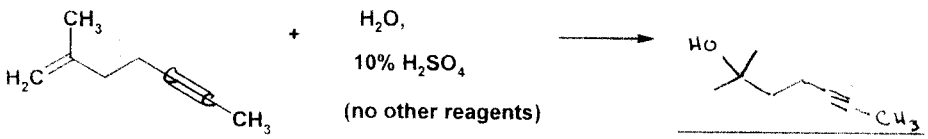
Note: **Please answer on the test paper.** There is an extra sheet for rough work at the back, but it will not be marked. In some questions, there is a choice of questions to answer. If all are answered, all will be marked. There are **150** marks on this exam.

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)

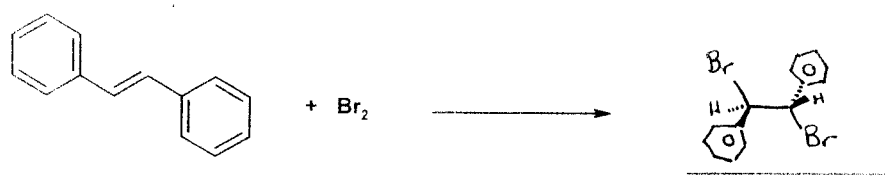
a.



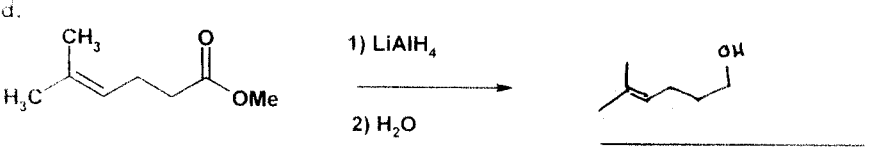
b.



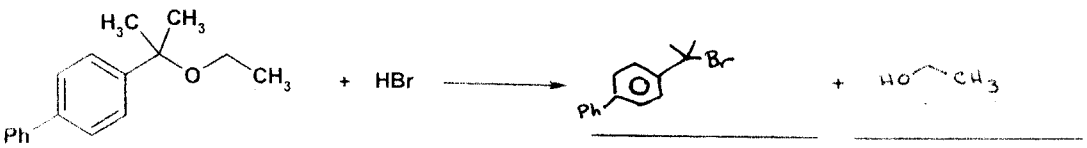
c.



d.

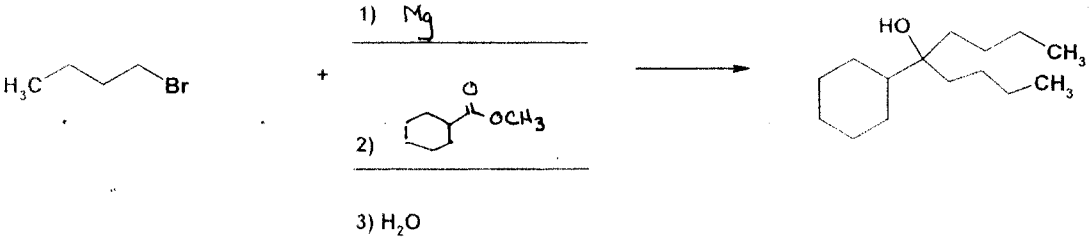


e.

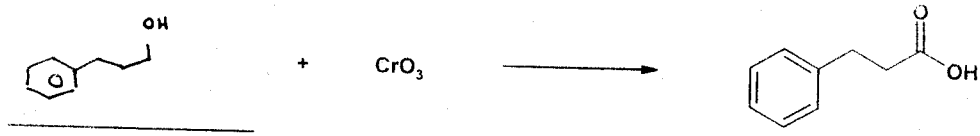


2 organic compounds

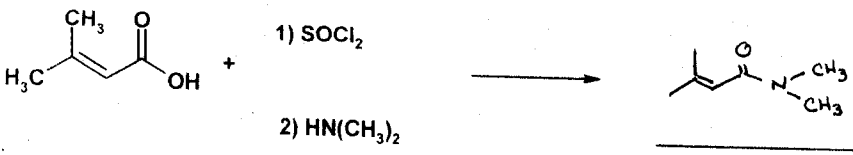
f.



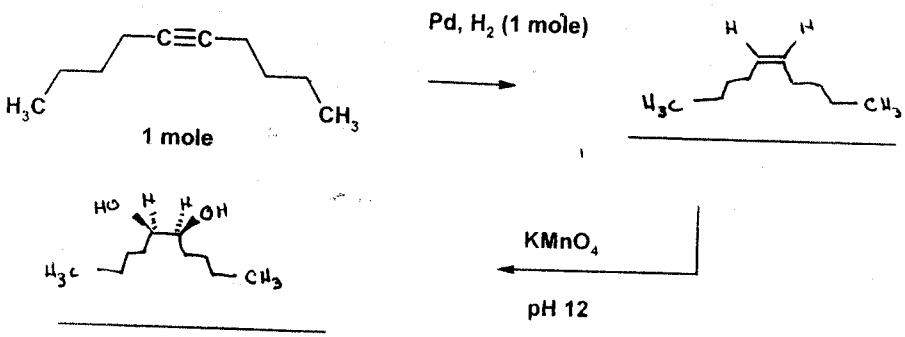
g. (on next page)



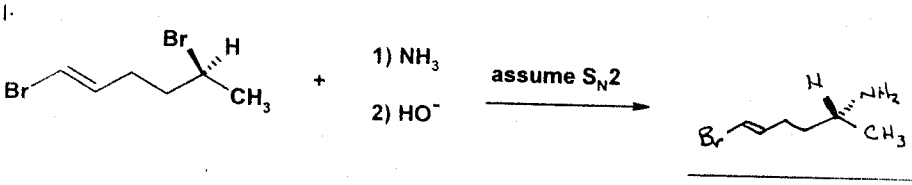
h.



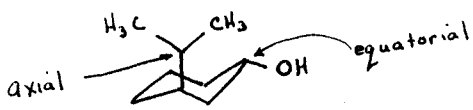
i.



j.



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)

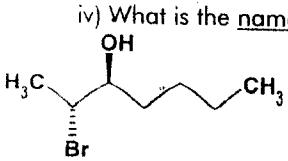


b. i)Draw the Newman projection of the following compound in its *most* stable conformation, as viewed down the C2-C3 bond. With respect to size, $(CH_3)_3C$ > $(CH_3)_2CH$ > unbranched alkyl ≈ CH_3CH_2 > CH_3 > OH > Br ≈ Cl ≈ F > H. (6 marks)

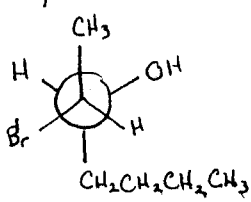
ii) What is the term for the relationship between the methyl group and the OH function (I'm looking for something more detailed than staggered/eclipsed)? (2 marks)

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)



i)



- BIGGEST GROUPS ARE ANTIPERIPLANAR
- 2ND BIGGEST GROUPS (Br, OH) ARE AS FAR AWAY AS POSSIBLE

ii) SYNCLINAL (OR GAUCHE OR SKEW)

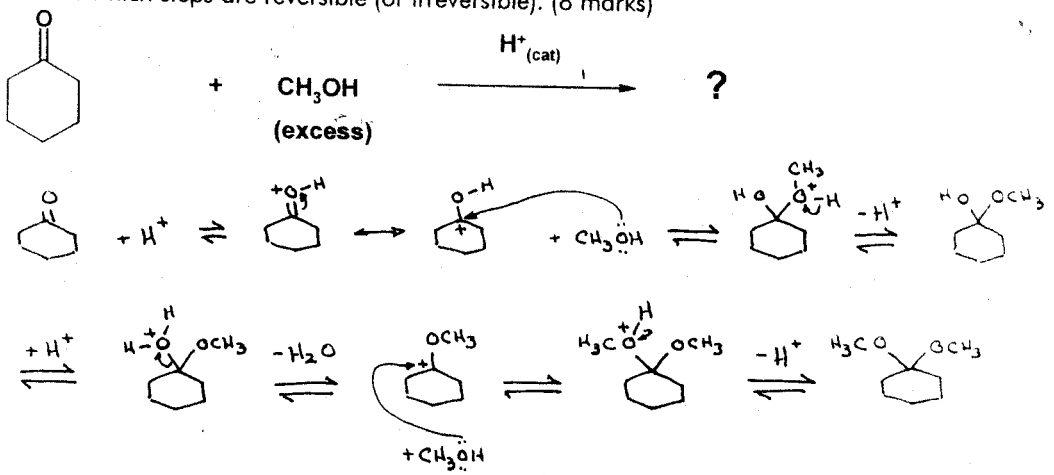
iii) ANTIPERIPLANAR

CONT'D

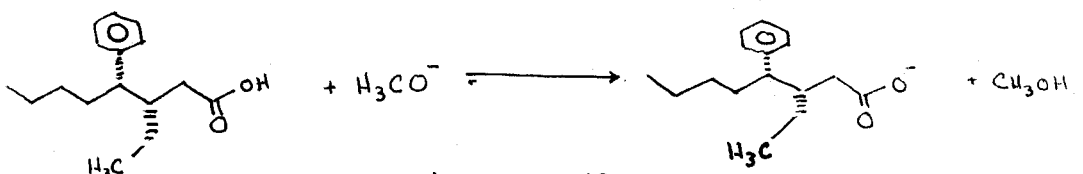
iv) (2R, 3S)- 2-BROMO-3-HEPTANOL

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)



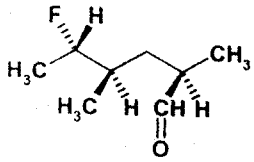
b. In the conversion of an acid (lets say (3S, 4S)- 3-ethyl-4-phenyloctanoic acid) to an ester (let's say it's the methyl ester (meaning OCH_3)) one never gets a successful reaction under CH_3O^- catalyzed conditions. Why is this the case (show by reaction and written explanation) (5 marks)? The complete answer will include the structure of (3S, 4S)- 3-ethyl-4-phenyloctanoic acid.

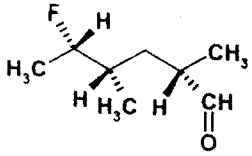


- DEPROTONATES ACID INSTEAD
- CARBOXYLATE IS ANIONIC ∴ NOT V. SUSCEPTIBLE TO NUCLEOPHILIC ATTACK

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

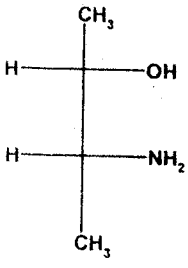
a.

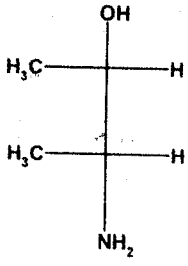




DIASTEREOMERS

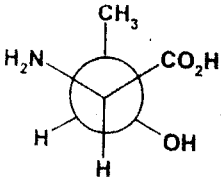
b.

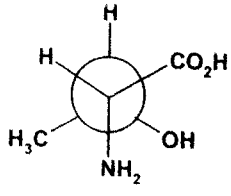




IDENTICAL

c.

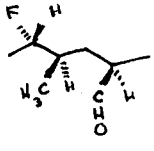


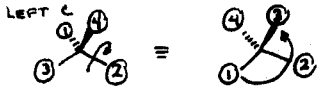


ENANTIOMERS

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

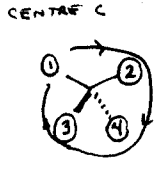
in a)





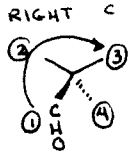
COUNTERCLOCKWISE

∴ (S)-



CLOCKWISE

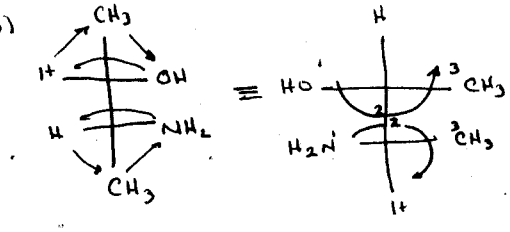
∴ (R)-



CLOCKWISE

∴ (R)-

in b)



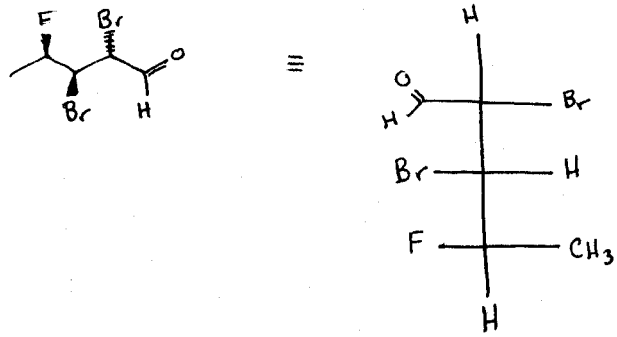
COUNTERCLOCKWISE

∴ (S)-

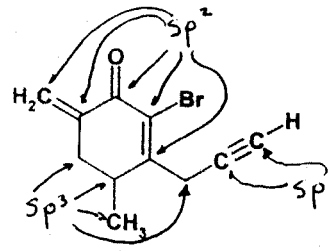
CLOCKWISE

∴ (R)-

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

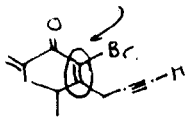


e. Identify the hybridization of each carbon atom in the following molecule. (4 of the 33 marks)



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)

ONLY ONE NEEDS IT



AT TOP

LEFT C VS RIGHT Br WINS

AT BOTTOM

LEFT C VS RIGHT C TIE

ON THAT C IS.... ON THAT C IS....

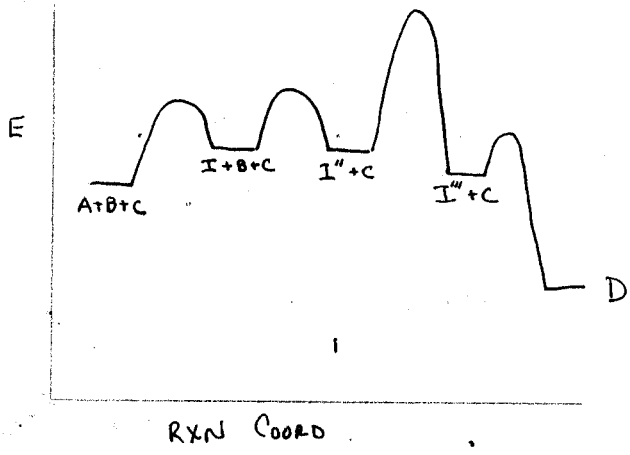
C, C, H C, H, H

WINS

OPPOSITE SIDES, ∴ (E)-

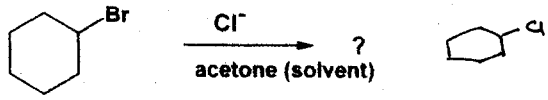
5. On the axes below, draw the energy/reaction coordinate profile for a four step reaction of A, B, and C to give D. A is consumed in the 1st step, B in the 2nd step, and C is consumed in the final step, while the 3rd step is the slowest one. Label the intermediate(s)/products.

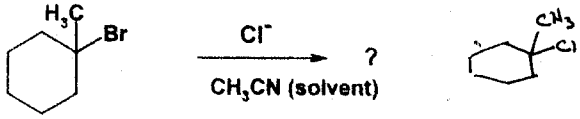
Also, Give the rate equation for the reaction. (7 marks total)

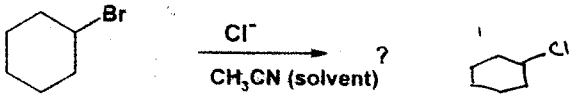


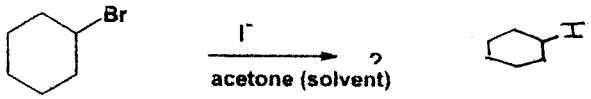
(contd from last pg) rate (v) = $k[A][B]$

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* <u>and the expected products</u>. (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).

a) 

b) 

c) 

d) 

a) SUBSTRATE 2° (S_N1 OR S_N2) NUCLEOPHILE - GOOD ∴ MORE TOWARDS S_N2
SOLVENT - NOT TOO POLAR (S_N2) ∴ SOMEWHAT TIPPED TOWARDS S_N2

b) SUBSTRATE 3° (S_N1 !) NUCLEOPHILE - GOOD ∴ MORE TOWARDS S_N1
SOLVENT - V. POLAR (S_N1) ∴ A LOT OF S_N1 CHARACTER

c) SUBSTRATE 2° (S_N1 OR S_N2) NUCLEOPHILE - GOOD ∴ MORE TOWARDS S_N2
SOLVENT - V. POLAR (S_N1) ∴ MORE S_N1 THAN CASE "a" BUT MORE S_N2 THAN "b"

d) SUSTRATE 2° (S_N1 OR S_N2) NUCLEOPHILE - EXCELLENT ∴ MUCH MORE TOWARDS S_N2
SOLVENT - NOT TOO POLAR (S_N2) ∴ MOST S_N2 CHARACTER OF ALL.

∴ FROM MOST S_N2 TO LEAST

d > a > c > b

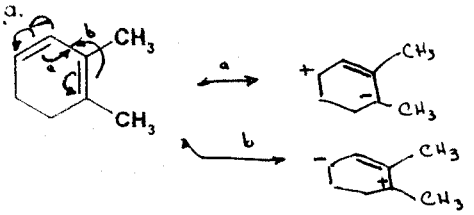
e. Rank the following from best leaving group to worst leaving group. (3 of the 16 marks)

$CH_3C(O)O^-$, H_2N^-, Cl^-, I^-, HO^-

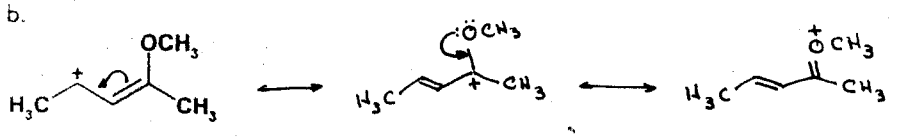
$I^- > Cl^- > CH_3C(O)O^- > HO^- > H_2N^-$

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.

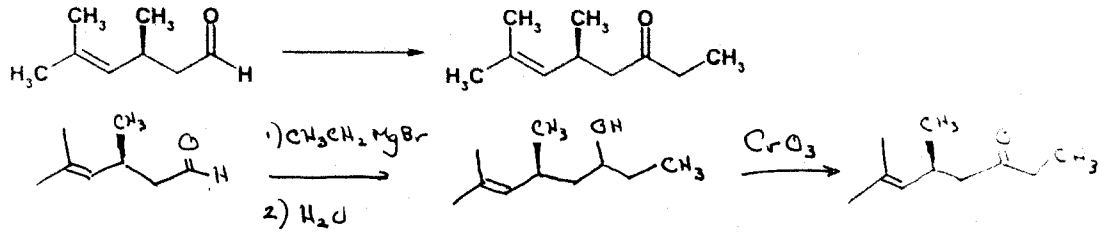


b.

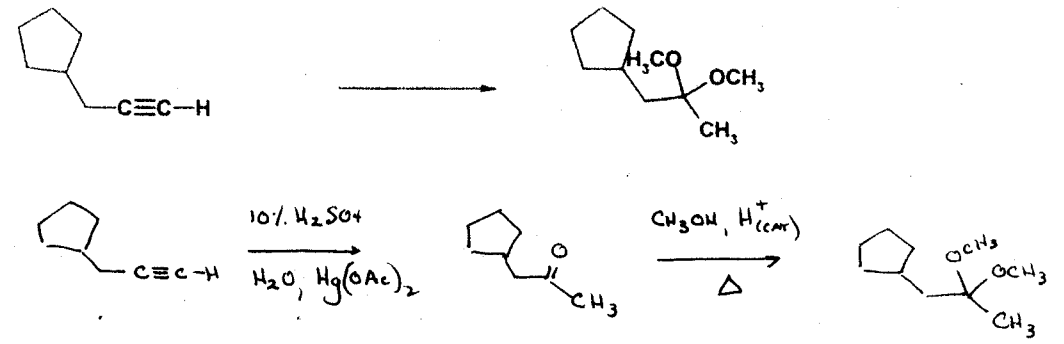


8. (11 marks total) Show by equation how you carry out the following overall transformations. Show all reagents and the structures of each reaction product. There is quite possibly more than one correct way to accomplish this overall transformation (8 marks). <u>DO one of a and b, but answer c regardless.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

a.



b.



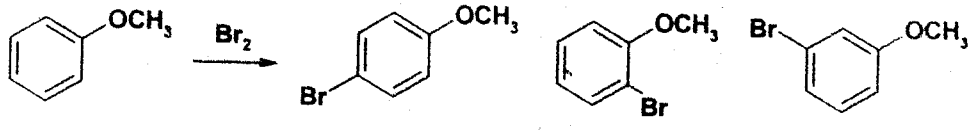
c. What is the name of the final product compound in 8a? (3 of the 11 marks)

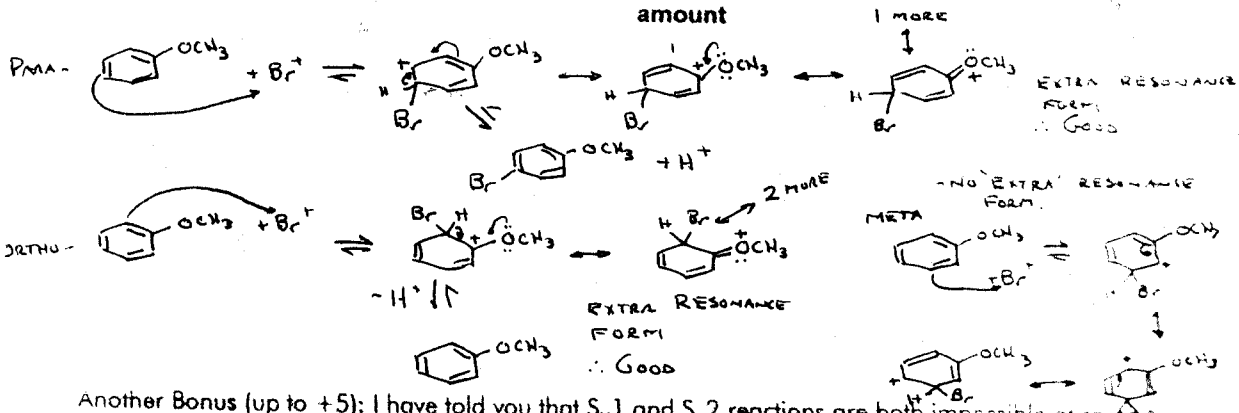
(5S)- 5,7-DIMETHYLOCT-6-EN-3-ONE

OR

(5S)- 5,7-DIMETHYL-6-OCTEN-3-ONE

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^2 hybridized centres, and yet the following transformation is quite common. Can you show by mechanism how this very real transformation occurs?