

Last Name	First Name	MI
Student ID Number:		Total Score
Circle the name of your TA: MIKE ROB		115
Discussion Section – Day: Time:		/ 100

Chem 30B Spring 2004

MIDTERM #1 KEY (50 Min)

Weds April 28th

*INTERPRETATION OF THE QUESTIONS IS PART OF THE EXAM –
DO NOT ASK FOR THE QUESTIONS TO BE EXPLAINED TO YOU*

ONLY ANSWERS WRITTEN IN THE BOXES PROVIDED WILL BE GRADED

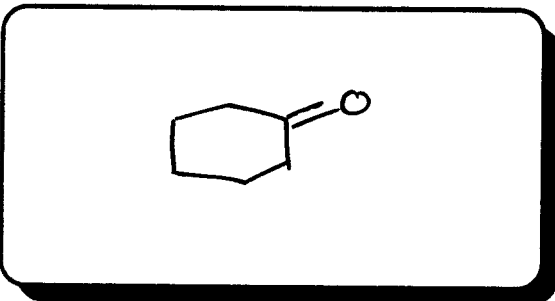
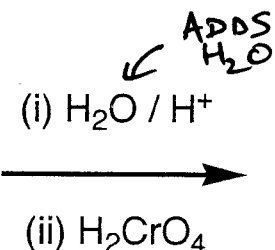
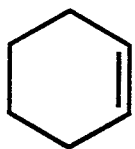
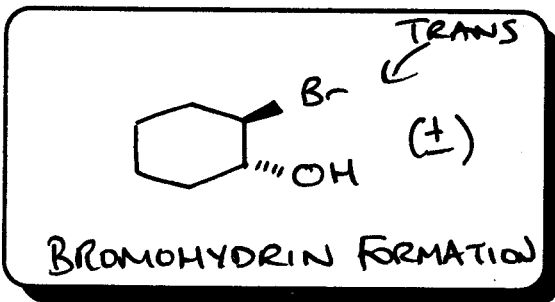
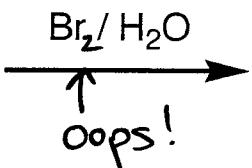
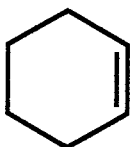
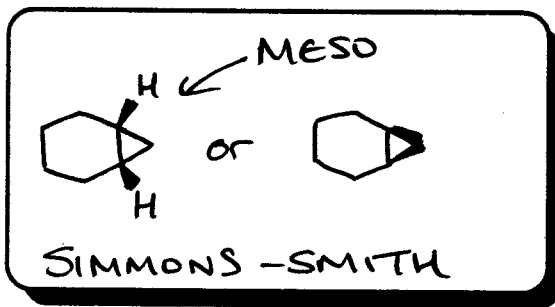
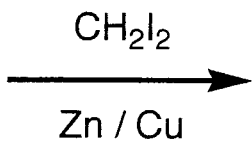
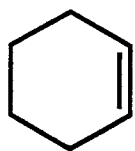
****DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO****

Q1	25 / 25	Q4	17 / 17
Q2	14 / 14	Q5	24 / 24
Q3	20 / 20	Extra Credit	15 / 15
		Total	115 / 100

"This is not the end. It is not the beginning of the end. But it is perhaps the end of the beginning" - Sir Winston Churchill

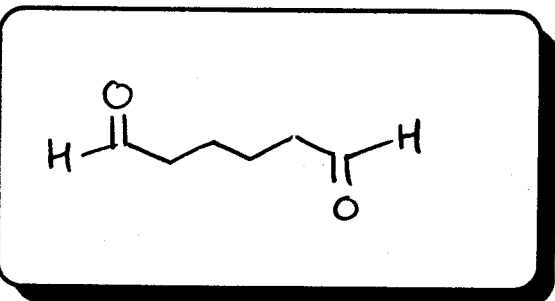
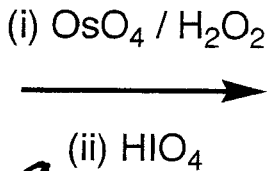
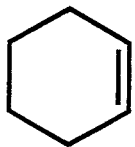
KEY

Question 1 For each of the reactions below, draw the final product and indicate clearly any relevant stereochemistry. For each reaction, indicate whether a single non-meso compound (S), a racemic mixture (R), or a meso compound (M), is formed, by writing the appropriate letter (S, R or M) in the smaller box to the right. (4 + 1 points each)

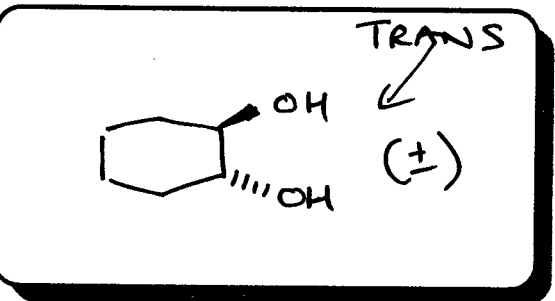
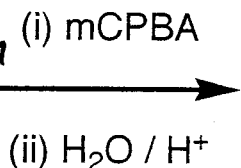
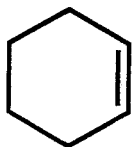


DIHYDROXYLATION

↑ OXIDIZES TO KETONE



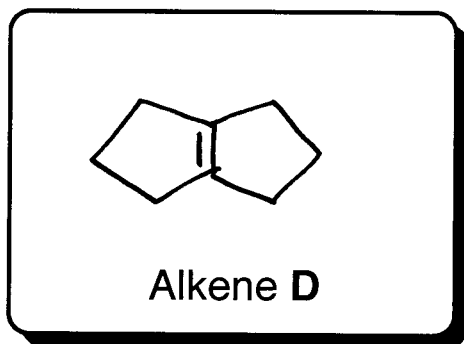
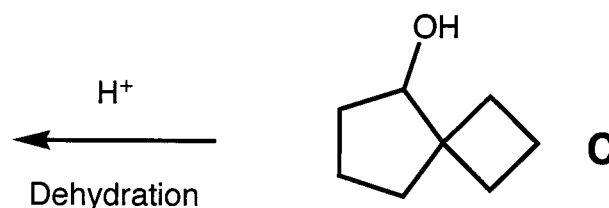
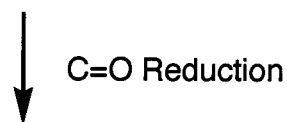
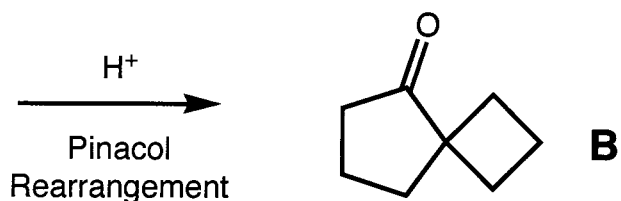
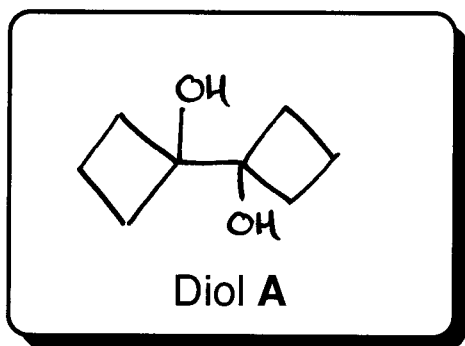
1,2 DIOL CLEAVAGE BY PERIODATE



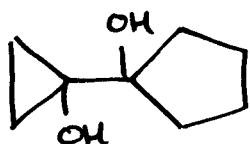
MAKES EPOXIDE

↑ OPENS EPOXIDE

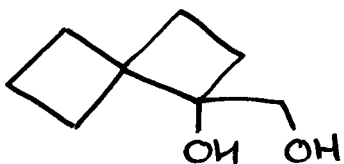
Question 2 When the 1,2-diol (A) undergoes an acid-catalyzed Pinacol Rearrangement, a ketone (B) with a spiro-4,5-ring system is formed as shown below. Reduction of the ketone to the corresponding alcohol (C) can be performed using many different reagents, some of which you will see later on in Chem 30B. Once formed, this alcohol can undergo an acid-catalyzed dehydration reaction to form an alkene (D) – with a structure that DOES NOT CONTAIN ANY 4-MEMBERED RINGS. What are the structures of compounds A and D? Note – if you get the structures wrong, partial credit MAY be given based on any notes written below. (7 points each)



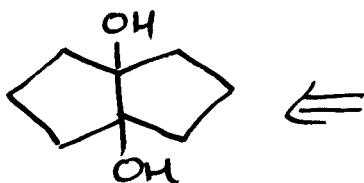
NOTE:



\Leftarrow THIS WOULD ALSO WORK



\Leftarrow THIS MAY WORK

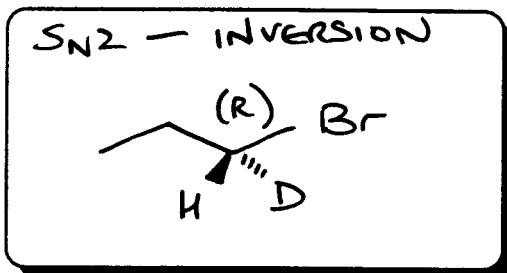
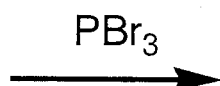
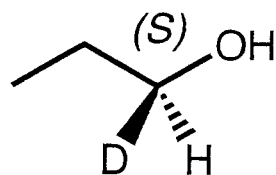


\Leftarrow WOULD NOT WORK, REQUIRES RING CONTRACTION OF A STABLE 5-MEMBERED RING TO A STRAINED 4-MEMBERED RING

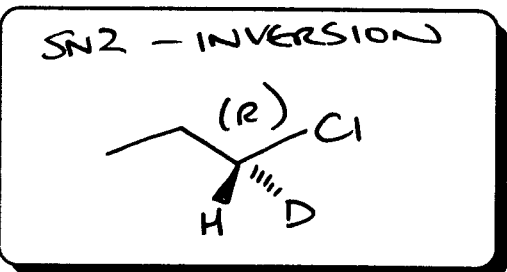
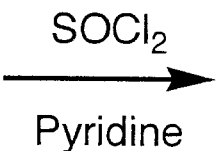
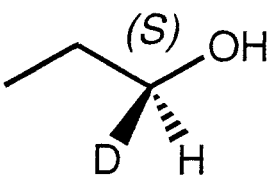
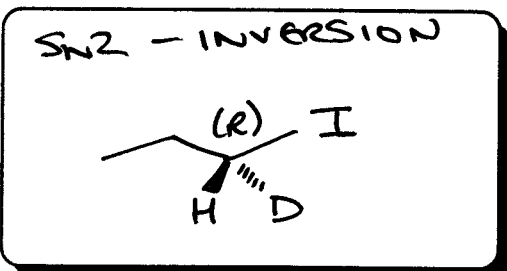
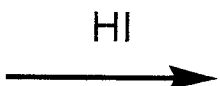
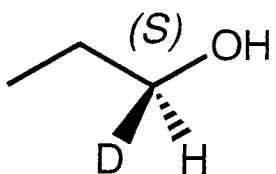
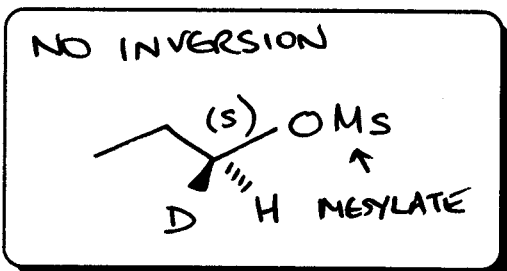
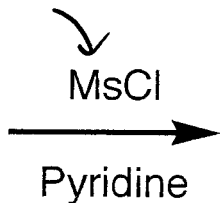
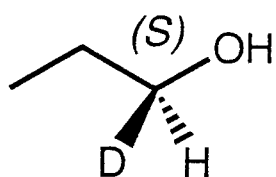
2

(THERE MAY BE OTHERS I MISSED)

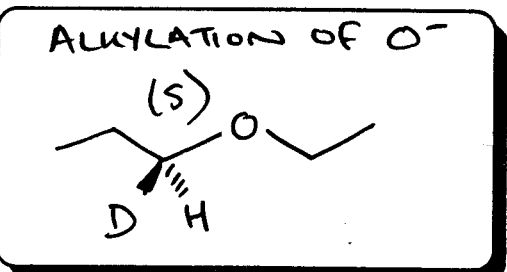
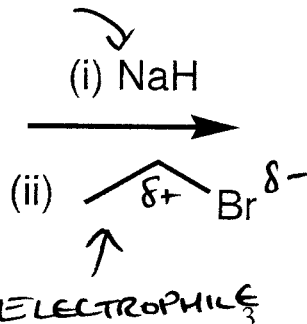
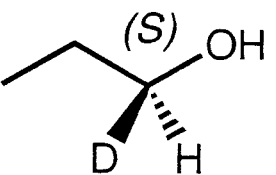
Question 3 Deuterium (D) is a heavier isotope of hydrogen (H) – its chemical properties are essentially the same, and it is just used to isotopically label organic compounds (amongst other things). (S)-1-Deutero-propanol is a chiral molecule – there are four different groups attached to the C atom next to the O atom. The assignment of (S) stereochemistry is done using the usual priority rules, in which D with its greater mass than H receives a slightly higher priority. In each of the reactions below, draw what you expect to be the MAJOR product of the reaction, carefully drawing any stereochemistry and indicating your assignment by writing “R”, “S”, (or “RS” if racemization occurs) next to any chiral centers in your products. (3 + 1 points each)



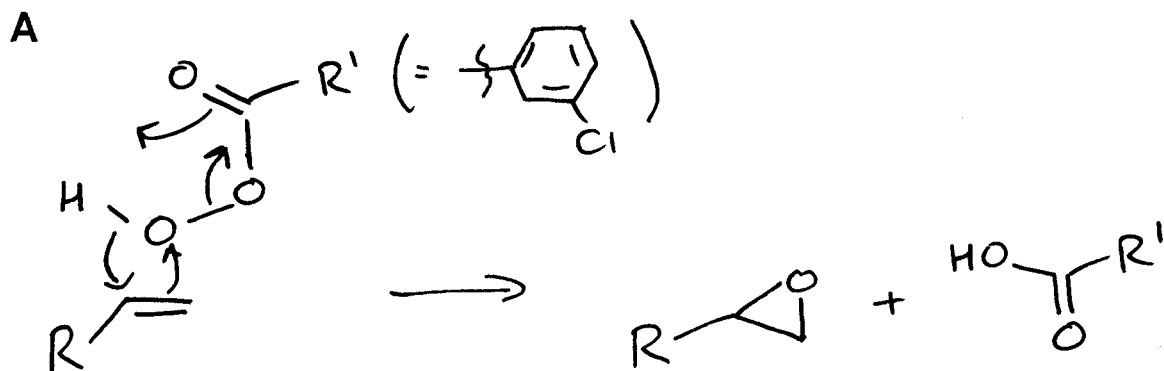
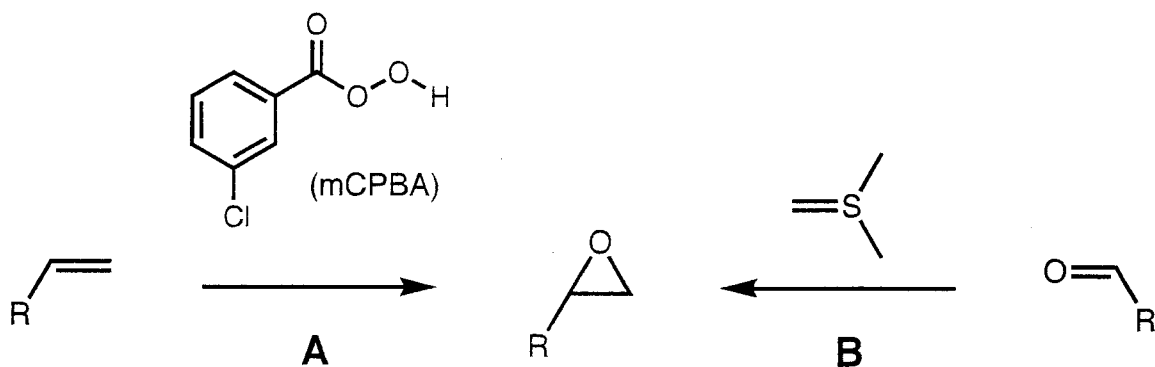
MESYL CHLORIDE



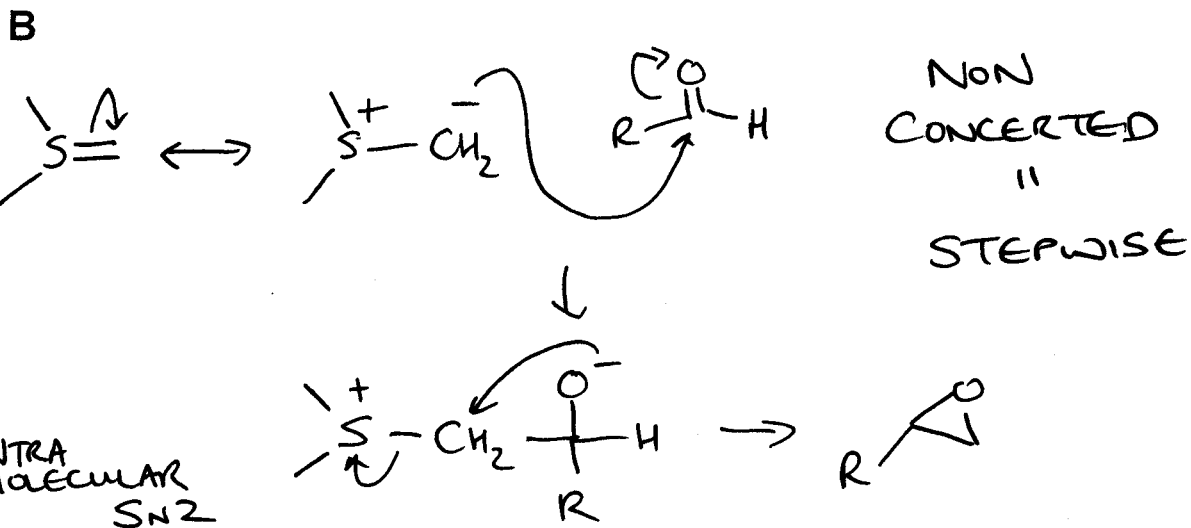
FORMS ALKOXIDE



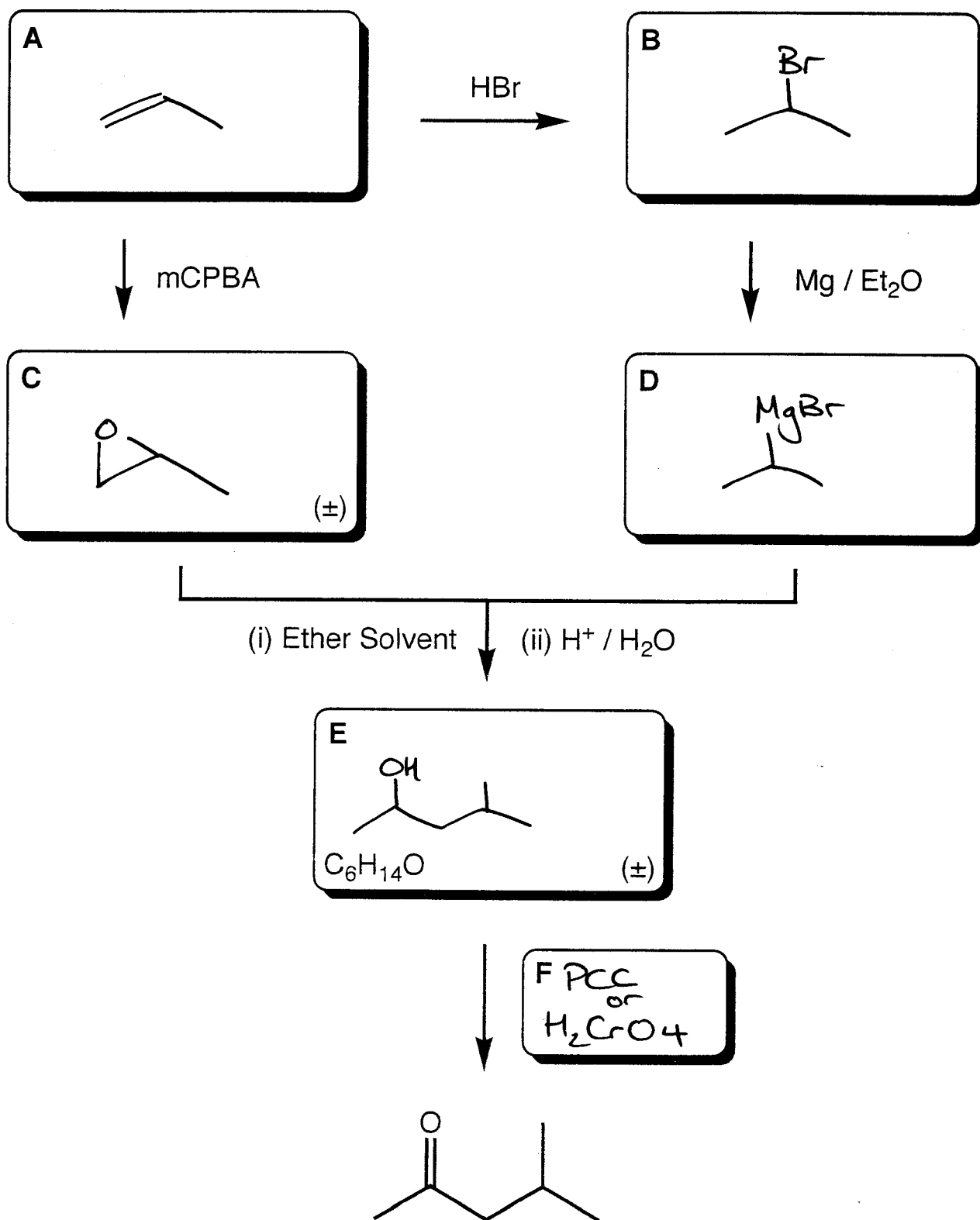
Question 4 In Chem 30B so far, you have seen how to make an epoxide from an alkene and a peroxy-acid such as mCPBA (route A), and also from an aldehyde and a sulfur ylid (route B). What are the reaction mechanisms for each of these routes – SHOW ALL STEPS. (7 points for A, 10 points for B)



CONCERTED = ALL HAPPENS AT ONCE



Question 5 Shown below is a short synthetic scheme. In the large boxes (A, B, C, D, E), fill in the structures of plausible intermediate compounds – ONLY ONE STRUCTURE PER BOX. In the small box (F), fill in the reagent necessary to achieve the transformation of E (molecular formula $C_6H_{14}O$) into the final ketone product. Note: compounds C and E are formed as racemic mixtures. (4 points per box)



Extra Credit Question The di-ene-yne compound shown below undergoes an alkyne-relayed ring-closing alkene metathesis reaction (when treated with the ruthenium catalyst) to give compound **A** which has a structure that contains 2 five-membered rings. What is the structure of **A**, and what is the mechanism of the reaction? Note: you may abbreviate the whole catalyst structure to $[Ru]=$ for the purposes of drawing the mechanism. (5 points for structure, 10 points for mechanism)

