

Chem 30B Spring 2004

MIDTERM #1
(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

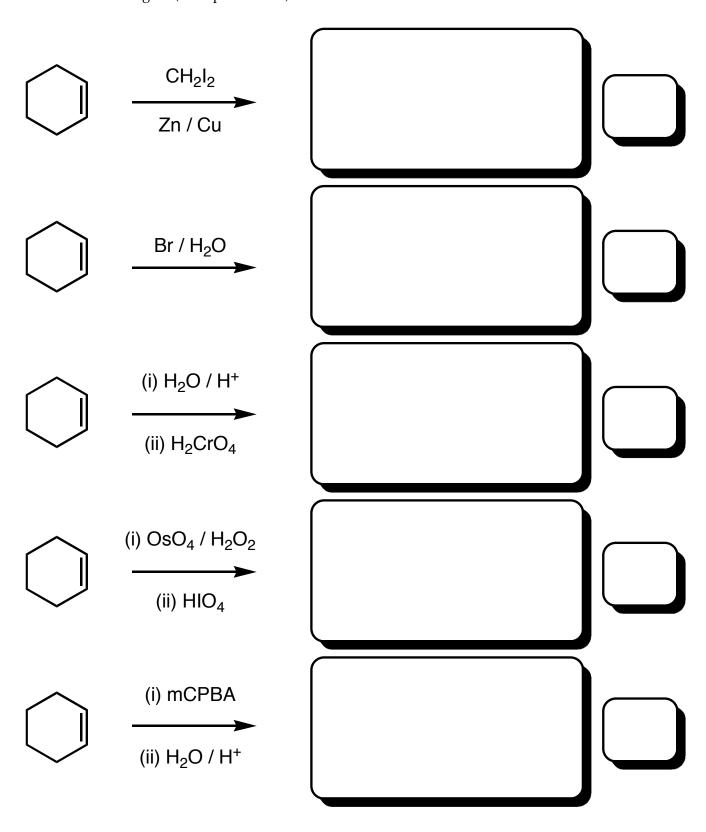
ONLY ANSWERS WRITTEN IN THE BOXES PROVIDED WILL BE GRADED

DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO

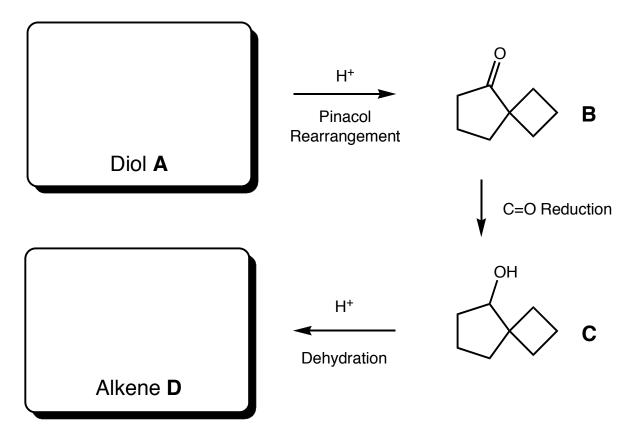
Q1	/ 25	Q4	/ 17
Q2	/ 14	Q5	/ 24
Q3	/ 20	Extra Credit	/ 15
		Total	/ 100

"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

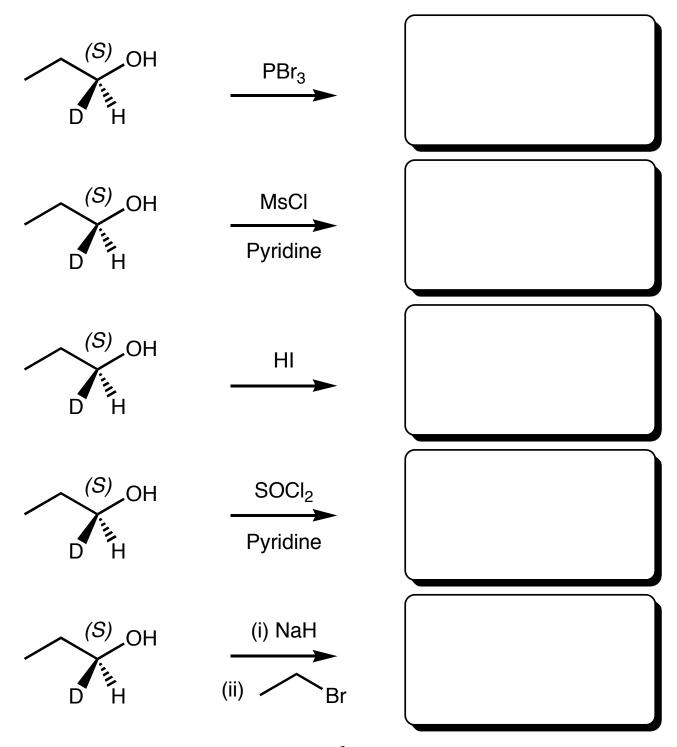
Question 1 For each of the reactions below, draw the final product and indicate clearly any relevant stereochemistry. For each reaction, indicate whether a single non-meso compound (S), a racemic mixture (R), or a meso compound (M), is formed, by writing the appropriate letter (S, R or M) in the smaller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



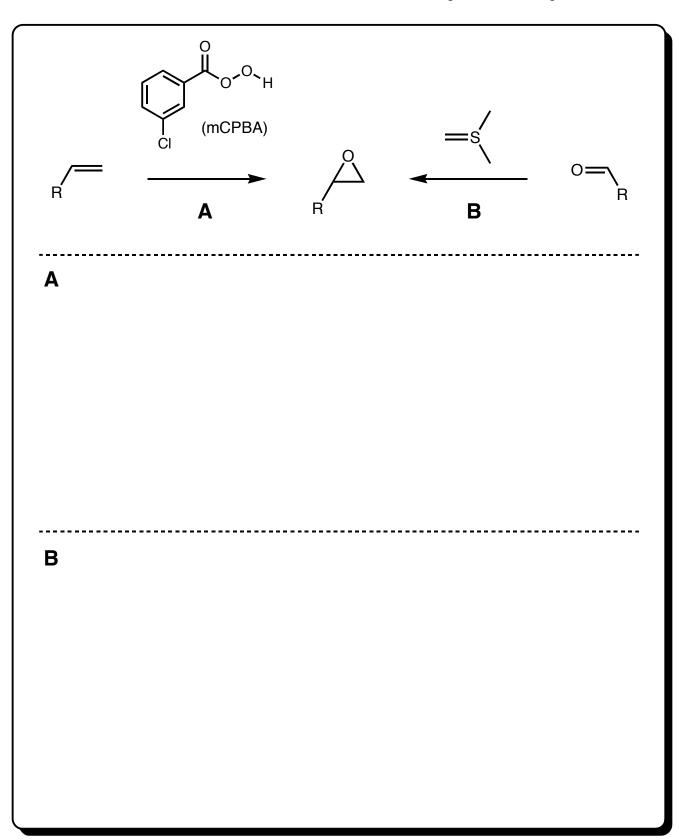
Question 2 When the 1,2-diol (**A**) undergoes an acid-catalyzed Pinacol Rearrangement, a ketone (**B**) with a spiro-4,5-ring system is formed as shown below. Reduction of the ketone to the corresponding alcohol (**C**) can be performed using many different reagents, some of which you will see later 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)



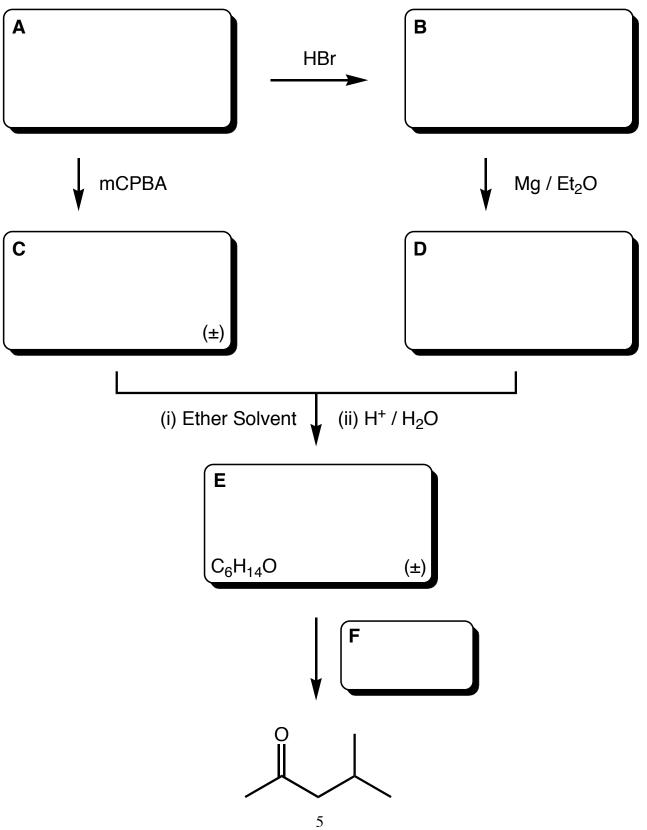
Question 3 Deuterium (D) is a heavier isotope of hydrogen (H) – its chemical properties are essentially the same, and it is just used to isotopically label organic compounds (amongst other things). (S)-1-Deutero-propanol is a chiral molecule – there are four different groups attached to the C atom next 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)



Question 4 In Chem 30B so far, you have seen how to make an epoxide from an alkene and a peroxyacid 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**)



Shown below is a short synthetic scheme. In the large boxes (A, B, C, D, E), fill in the Question 5 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)

Once more unto the breach, dear friends, once more; Or close the wall up with our English dead. In peace there's nothing so becomes a man As modest stillness and humility: But when the blast of war blows in our ears, Then imitate the action of the tiger; Stiffen the sinews, summon up the blood, Disguise fair nature with hard-favour'd rage; Then lend the eye a terrible aspect; Let pry through the portage of the head Like the brass cannon; let the brow o'erwhelm it As fearfully as doth a galled rock O'erhang and jutty his confounded base, Swill'd with the wild and wasteful ocean. Now set the teeth and stretch the nostril wide, Hold hard the breath and bend up every spirit To his full height. On, on, you noblest English. Whose blood is fet from fathers of war-proof! Fathers that, like so many Alexanders, Have in these parts from morn till even fought And sheathed their swords for lack of argument: Dishonour not your mothers; now attest That those whom you call'd fathers did beget you. Be copy now to men of grosser blood, And teach them how to war. And you, good yeoman, Whose limbs were made in England, show us here The mettle of your pasture; let us swear That you are worth your breeding; which I doubt not; For there is none of you so mean and base, That hath not noble lustre in your eyes. I see you stand like greyhounds in the slips, Straining upon the start. The game's afoot: Follow your spirit, and upon this charge Cry 'God for Harry, England, and Saint George!'

Henry V, Act III, Scene I

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