Chemistry 301X Final Examination: January 24, 2006

"If you are obliged to neglect any thing, let it be
your chemistry. It is the least useful and the least amusing to a
country gentleman of all the ordinary branches of science."
Thomas Jefferson

This Final Examination is different in very few respects from the hour exams with which you are all too familiar.

However, there is choice. **PLEASE** do not do all the questions.

ANSWER QUESTIONS 9 AND 10

ANSWER ONE QUESTION FROM EACH OF GROUPS 1, 2, 3, AND 4.

ANSWER ONE OTHER QUESTION

THUS, YOU MUST DO ONLY SEVEN QUESTIONS OF THE TEN SUPPLIED

Should you ignore this instruction, we will grade ALL the questions and take an appropriate fraction of the score. We will not, **repeat not**, take the 7 best nor will we be responsive to pleas that some feeble answer should be ignored because you did not mean to have it graded. The price of choice is that you **must** be careful and clear about what you want graded and what you want ignored.

You must do Questions 9 and 10, and you must do a total of seven (7) Questions, with at least one question from each of Groups 1--->4, and both questions from Group 5.

This exam is designed to take 2 hours but you may have a full period of 3 hours. Please take some time at the end to fill out the evaluation forms, which are to be handed in with the exams themselves. We will allow 30 minutes for the evaluations, so the whole process will be over at 5 pm.

The questions are weighted equally. At the start, it is almost certainly worth some time to look over the whole exam, to sort the easy from the more challenging and the familiar from the strange. Do the easy questions first. THINK "SIMPLE."

PLEASE*:*

1. Email us your intentions regarding Chemistry 302X or write a note on the cover of your exam book. If you are taking 302X, we need your email address. PLEASE DO THIS - ***we will not return your final examination*** until we hear from you one way or the other.

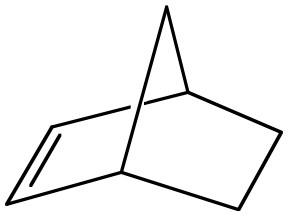
2. Fill out the evaluation forms.

3. **Show on the cover what questions are to be graded. DO THIS!** Each year people do not do this. Please do it.

4. Sign the pledge: "I pledge that I have not violated the Honour Code on this examination."

GROUP 1 - DO AT LEAST ONE OF THESE TWO QUESTIONS

1. Norbornene is compound **1**. One can imagine replacing one hydrogen of **1** to produce several possible alcohols.



1

(a) Draw each of these alcohols.

(b) All of these isomers but one (Call it **A**) show broad bands in the infrared at about 3400 cm^{-1}. Which isomer does not show that band and why?

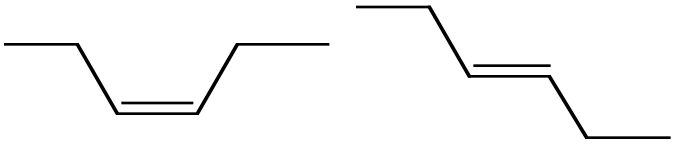
(c) Of the other isomers, only one shows no change in that broad band at ca. 3400 cm^{-1} when its concentration changes. Which is it and why does that band not change?

(d) Some of the isomers (ignore **A**) add Br_2 to give a single dibromide still showing a band in the IR at 3400^{-1}, others add Br_2 to give two different diastereomeric dibromides, each showing a band at ca. 3400 cm^{-1}. Give an example of each reaction. Show the mechanism.

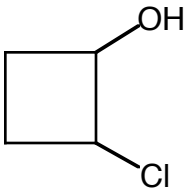
(e) One isomer, however, (ignore **A**), adds Br_2 to give a dibromide that shows a band at ca. 3400 cm^{-1} and a molecule **X**, (C_7H_9OBr) that has no band at 3400 cm^{-1}. Which isomer is it and why is that IR band missing? Show the structure of the product **X** and the mechanism of its formation.

2. Explain how would you distinguish the following sets of molecules spectroscopically (^{1}H or ^{13}C NMR or IR).

(a)



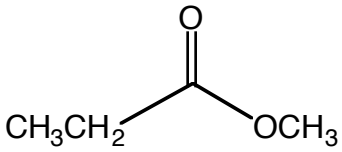
(b)

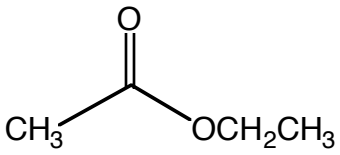


cis and trans

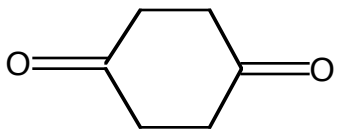
(c) CH_4 H_3C-CH_3

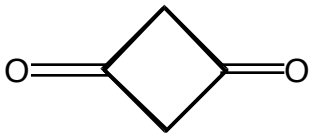
(d)





(e)





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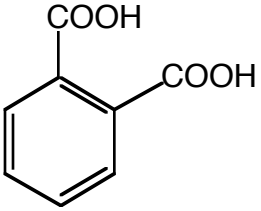
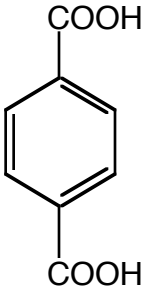
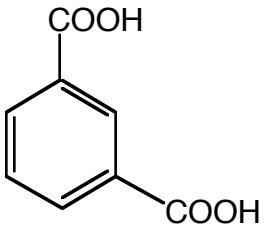


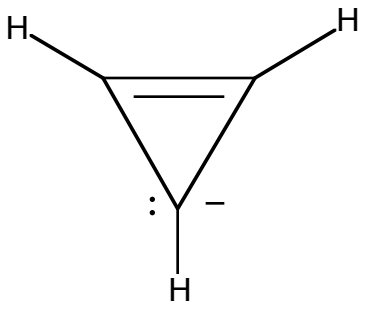




GROUP 2 - YOU MUST DO AT LEAST ONE OF THESE TWO QUESTIONS

3. Frau Dr. Prof. L. U. v. Valencebond, was asked what she thought about the stabilities of two ions, **2** and **3**. Steeped in resonance theory as she was, she did a quick analysis and said that she thought that they would both be quite stable, at least when compared to other anions and cations. She was wrong. One is very stable and the other exceptionally unstable, even for an ion.

(a) You, knowledgeable as you are about M. O. theory, can tell her why she was wrong, and tell us, with a succinct explanation, which one is relatively stable, and which is not.



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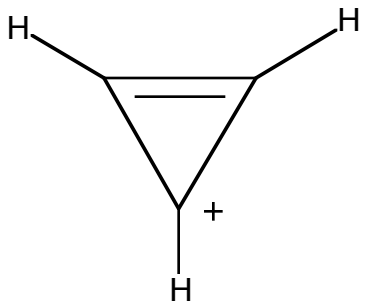
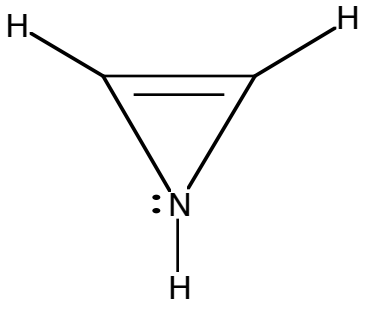
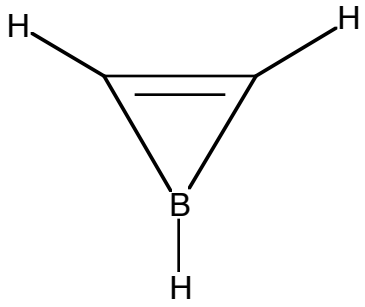


3

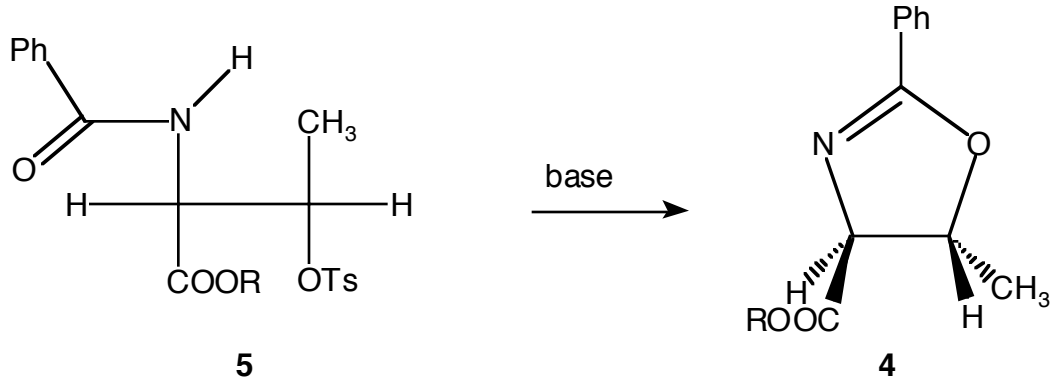
(b) Next, you can quickly tell us which of the following neutral molecules will be relatively stable and which on will not be. Explain your reasoning.





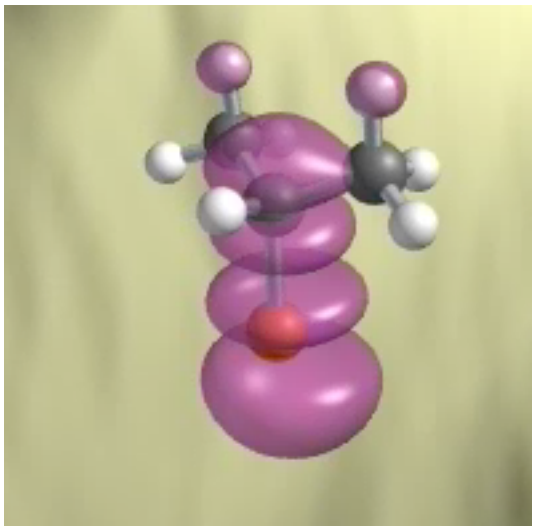
4.

(a) Compound **4** is the only product of treatment of **5** with base. Write an arrow formalism mechanism and deduce the stereochemistry of **5**.



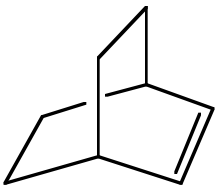
5 **4**

(b) The following picture is a screenshot from one of your animations of the S_N1 reaction. It shows the LUMO of the developing intermediate cation as the leaving group departs from isopropyl bromide. You can still see the leaving group. You can also see clearly that two of the six hydrogens of the methyl groups share in the LUMO. Explain in MO and/or resonance terms why those two hydrogens, and not the other four, are part of the LUMO.



GROUP 3 - YOU MUST DO AT LEAST ONE OF THESE TWO QUESTIONS

5. Devise syntheses of (a) ---> (e) from **6**, and of (f) ---> (j) from **7**. You may use any inorganic reagent (no carbons), solvents as needed, and the following "special" organic reagents: NBS, NBA, NRA, DNA, LSMFT, FUBAR, trifluoroperacetic acid, $Hg(OAc)_2$, $CHCl_3$, $(CH_3)_3C$-ONa, C, dimethyl sulfide, diazomethane.



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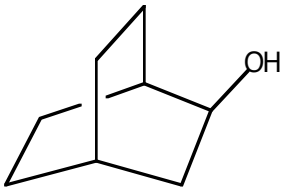
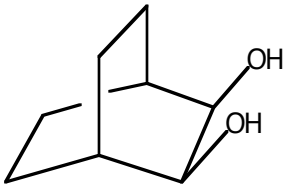
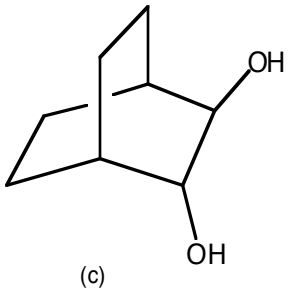


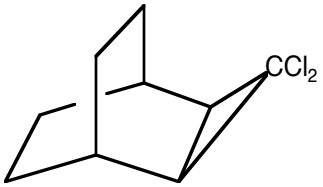
(a)



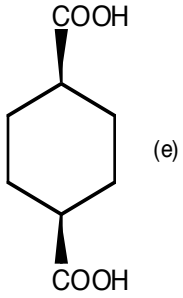
(b)



(c)

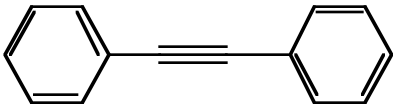


(d)



(e)

7



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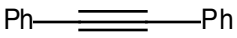

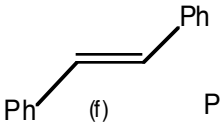

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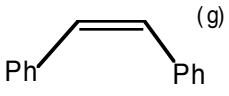

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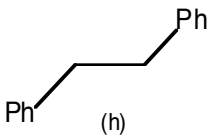
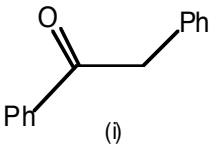
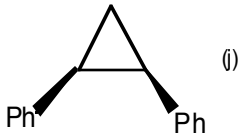


(h)

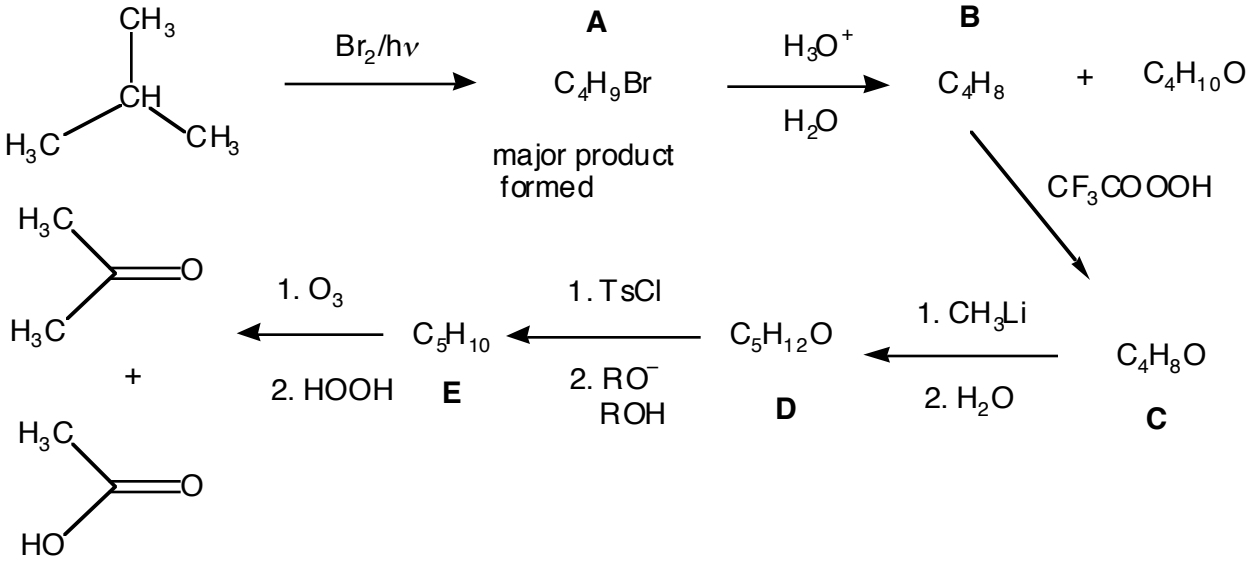


(i)

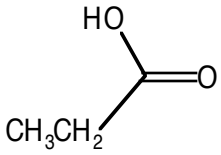


(j)

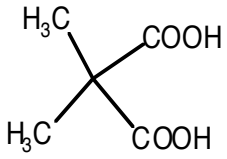
6.
(a) Provide structures for **A** ----> **E**. Mechanisms are not necessary.



(b) Draw two molecules that will produce the following products on ozonolysis/oxidation. We want two molecules for (a) and two more molecules for (b).



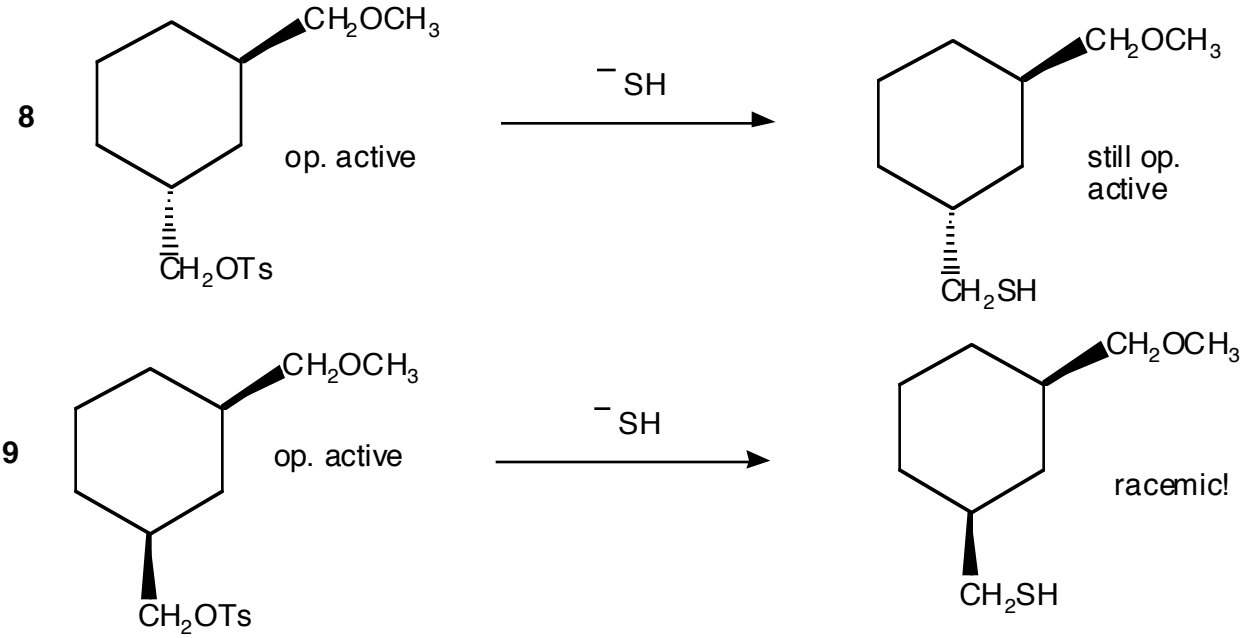
(a)



(b)

GROUP 4. YOU MUST DO AT LEAST ONE OF THESE TWO QUESTIONS

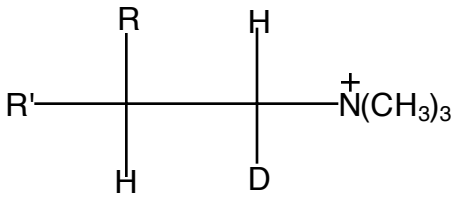
7. Optically active **8** and optically active **9** react with thiolate ($^{-}$SH) to give the corresponding mercaptans (RSH), but the product from trans compound **8** is still optically active, whereas the product from cis compound **9** is racemic. Explain mechanistically.



8.

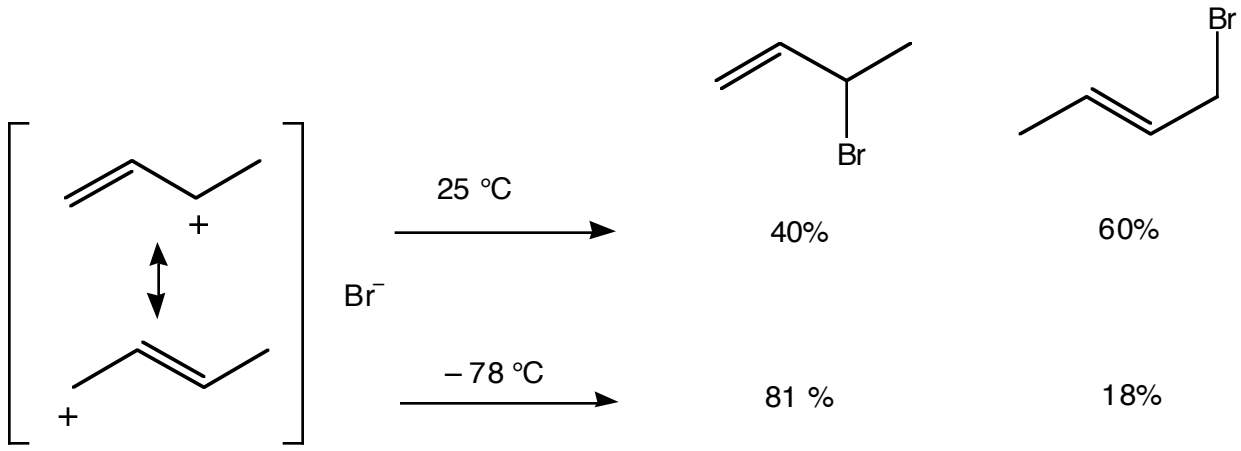
(a) Optically active *trans*-1,2-dibromocyclopentane racemizes on heating. Explain.

(b) In system **10**, shown below, the percentage of bimolecular syn elimination increases and the percentage of bimolecular anti elimination decreases as the size of R and R' increases. Explain. Newman projections are probably useful here.



GROUP 5. YOU MUST DO THESE TWO QUESTIONS

9. In Group Problems and in the book you saw the following data:

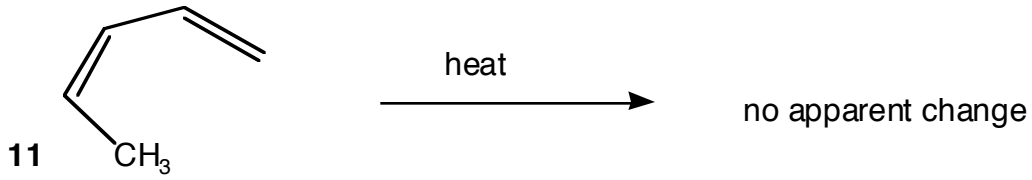


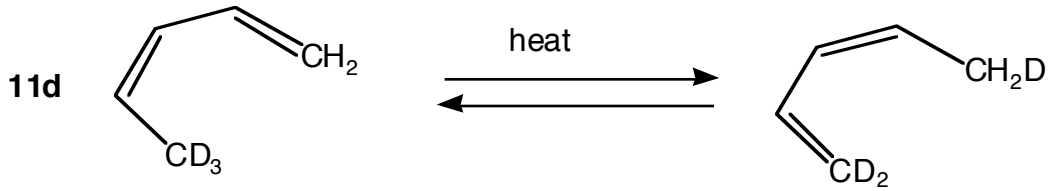
Draw a carefully labeled "Energy vs. Reaction Progress" diagram that these data demand.

10. There are reactions in chemistry in which groups go whizzing around molecules obeying seemingly weird stereochemical imperatives. Let's see if we can figure out some of what is going on in one such case.

ADMONITION-WARNING. This is not some killer question, indeed parts are very easy. But most parts do require very careful, clear drawings. DO NOT scribble and write all over the page. Organize very carefully and make it clear what you are doing. Work it out on scratch paper first if you want.

When 1,3-pentadiene (**11**) is heated, there is no apparent change. The deuterium labeling experiment shown below reveals that something is going on, however:





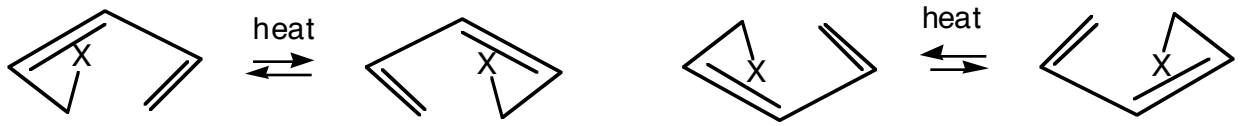
(a) There are at least two possible general mechanisms for this process, one concerted (one-step), the other non-concerted (two-step). Draw arrow formalisms for both.

A critical observation is that the rate of this reaction does *not* depend on solvent polarity. In fact, the reaction occurs in the gas phase (no solvent at all) just as well as in solution.

(b) What does this observation mean *for the nature of the transition state* in the one-step reaction? What does it mean for the nature of the intermediates in the two-step reaction? Now go back and look at your answer to (a) and revise it if necessary.

(c) Devise an experiment that will resolve the question of one-step vs. two-step. You may assume an ability to make any necessary molecule and to tell any products apart. This is neither a synthesis nor an analytical chemistry question. Hint: think about experiments that use **11** and **11d** at the same time.

OK, it turns out to be one-step. But there is much more to it. Really clever stereochemical experiments show that the migrating hydrogen (or deuterium) stays on the side it leaves from, and attaches from the same side. There is no randomness here - something controls the path the H or D takes.



X = H or D

.

(d) What might that be? Here's how to figure it out.

First, make a good orbital drawing of the breaking C-H bond before migration starts. Put in orbital phase! Second, draw that C-H bond again as it stretches in the TS for the reaction. What is happening to the C from which the H (or D) departs?

Fill in the HOMO for the carbon part of the reaction.

The answer is in your drawings - explain it to us. Remember your answer to (b).

BONUS - 5 points

WARNING - This part is hard. DO NOT try this question if there is work you can still do on the other questions on this exam.

Devise an experiment - one of those "really clever" experiments mentioned above - that will tell that **X** must leave and arrive from/on the same side of the carbon framework.

CHECK- DID YOU DO SEVEN QUESTIONS?

"I pledge that I have not violated the Honour Code on this examination."