Final Examination, Chemistry 301X, January 24, 2007

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

However, there is choice. **DO ONLY EIGHT (8) QUESTIONS**

PLEASE do not do all the questions.

YOU MUST ANSWER QUESTION 1

THUS, YOU MUST DO ONLY 7 QUESTIONS OF THE REMAINING 8

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 8 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.

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 12:30 pm.

Question 1 is worth 16 points. The others are worth 12 points each. 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 AND 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. Take the Oath: "I pledge that I have not violated the Honour Code on this examination."

“Although we often hear that data speak for themselves, their voices can be soft and sly.”

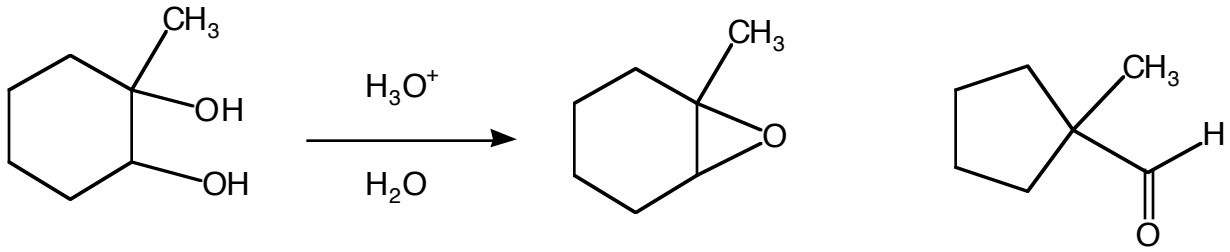
Frederick Mosteller, Stephen E. Feinberg, and Robert E. K. Rourke, Beginning Statistics with Data Analysis,

(stolen from E. R. Tufte, Visual and Statistical Thinking)

YOU MUST DO THIS QUESTION

1. We haven't yet beaten this one to death. It comes back here because we want to revisit the details of the mechanisms, and to look at some stereochemical points. It makes a good "big and small" question. Here it is. Pay attention to detail!

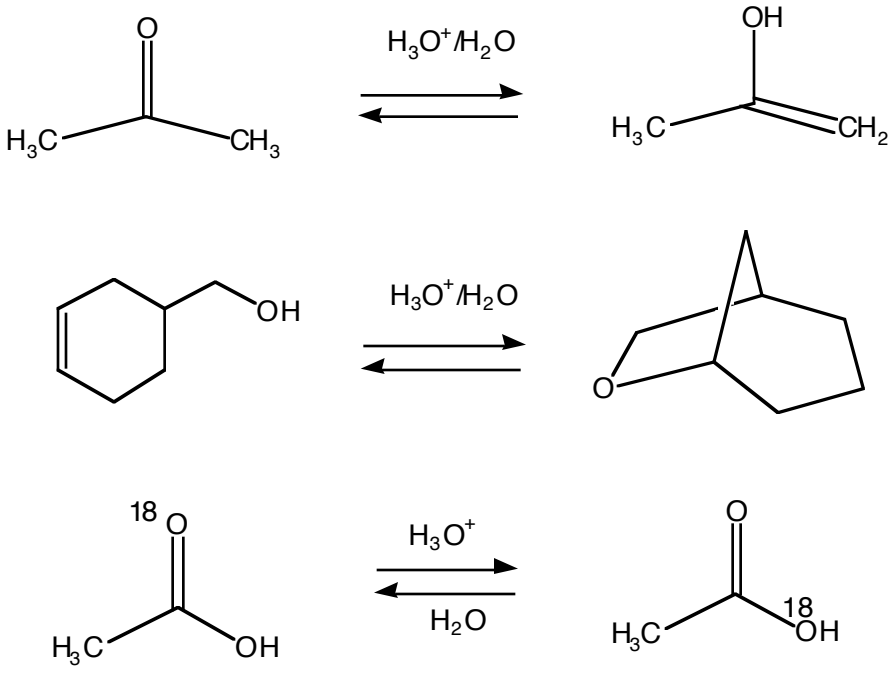
Each racemic diastereomer of **1** leads to **2** and/or **3**. Write us two perfect mechanisms, one in which **2** and **3** are formed from either diastereomer of **1**, and another in which one diastereomer leads only to **2** and the other only to **3**.



1 **2** **3**

DO ONLY 7 OF THE FOLLOWING 8 QUESTIONS

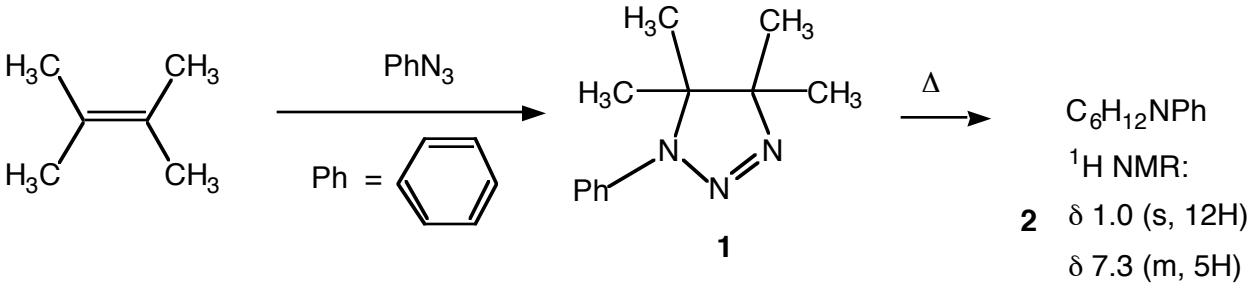
2. Provide arrow formalism mechanisms for the following three reactions:



3. Azides (R-N_3 = R—NNN) react with alkenes to give products called triazolines (**1**).

(a) Write a straightforward arrow formalism for this reaction. You will need a perfect Lewis structure for the azide.

When triazolines are heated or irradiated they often lose N_2 (**2**). An example is outlined below:



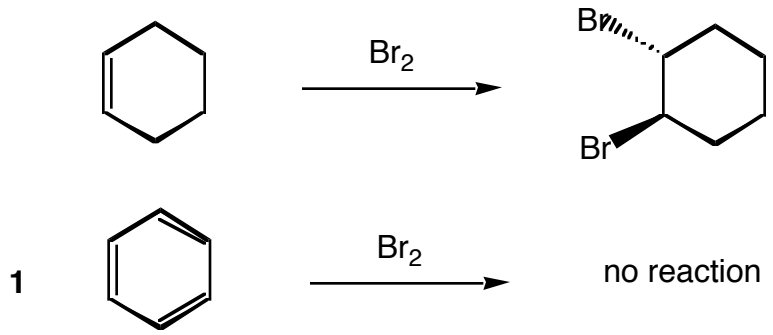
1

2

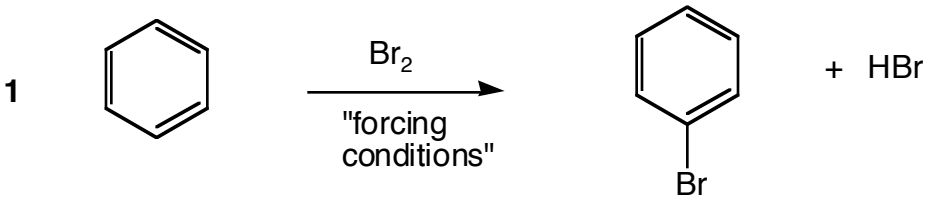
(b) Provide arrow formalisms for both reactions above and a structure for **2**.

(c) Modify the starting material to devise an experimental test to determine whether the formation of **2** takes place in one step or two.

4. Although cyclohexene undergoes the normal addition reaction with bromine, benzene (**1**) does not.

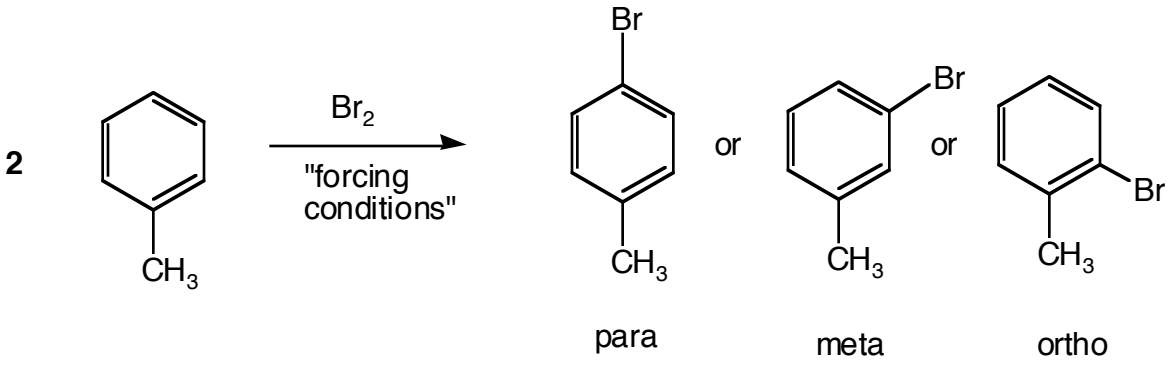


Under forcing conditions, benzene will react, but the product does not come from the addition reaction, but from a substitution. The rate of the reaction depends on solvent polarity, *so it is still an ionic (not radical) reaction*.

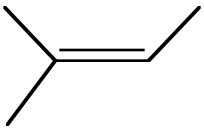


(a) Your job is NOT to explain why benzene fails to do the normal addition reaction, but simply to craft a decently detailed arrow formalism mechanism for the substitution reaction.

(b)Toluene (**2**) could, in principle, form any or all of the three products shown. Use your mechanism to predict whether para or meta will be preferred, and explain why. We are NOT asking you to make any predictions about ortho.



5. In each part of this question, the spectroscopic information allows you to identify the missing reagent or reagents in the box. Please do so, give a structure for the product or products, and explain your reasoning briefly.

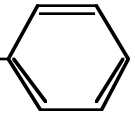
(a) 

1. O_3

2. ??

X IR 1719 cm^{-1}

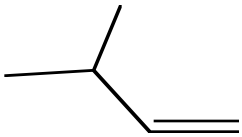
Y IR, 1725, 2850, 2750 cm^{-1}

(b) $(CH_3)_3C-C\equiv C-$ 

$(C_{12}H_{14})$

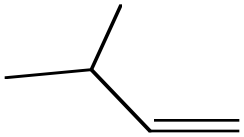
?? → $C_{12}H_{16}$

^{1}H NMR shows two 1H signals, at about δ 6, J = 8 Hz

(c) 

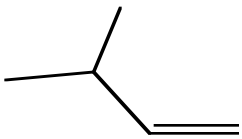
?? → $C_5H_{12}O$ IR ~ 3400 cm^{-1}

^{1}H NMR shows a 2H triplet at δ 4.5

(d) 

?? → $C_5H_{12}O$ IR ~ 3400 cm^{-1}

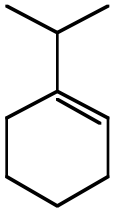
^{1}H NMR shows a 1H multiplet at δ 4.5

(e) 

?? → $C_5H_{12}O$ IR ~ 3400 cm^{-1}

^{1}H NMR shows no signal at δ 4.5

[There will be some of the product from (d) as well.]

(f) 

C_9H_{16}

?? → $C_9H_{17}Br$

two products, one major, one minor, each $C_9H_{17}Br$

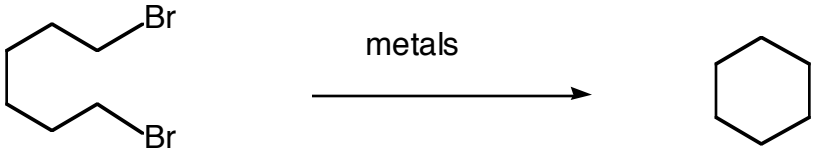
The ^{1}H NMR spectrum of each product shows two 3H doublets

6. Construct the molecular orbitals (MOs) for linear H-N-H from H_2 and N. We suggest the following protocol:

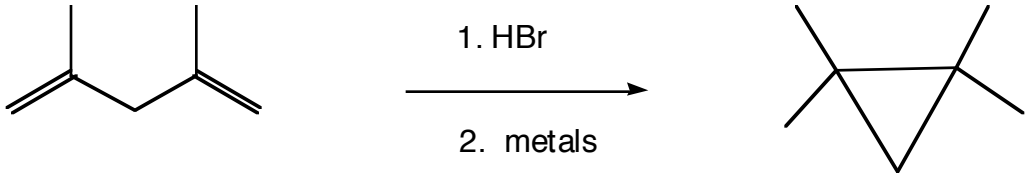
(a) how many MOs will there be?
(b) show the orbitals of H_2 and N that you will use in your construction.
(c) construct the proper MOs for linear NH_2.
(d) order the bonding and nonbonding MOs in energy.

There is a machine, called an EPR spectrometer, that can detect ("see") unpaired electron spin. Would the EPR spectrometer see unpaired spin in: neutral linear NH_2? $^+NH_2$? $^-NH_2$? Explain.

7. Background. Dibromides can sometimes be used to make ring compounds by eliminating the two bromine atoms. You don't need to worry about the mechanism(s) involved, but you will have to use reactions of the type:

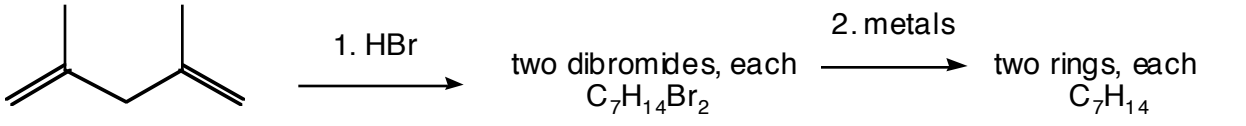


When compound **1** is treated with HBr, the results seem to vary depending on whether it is done in Russia or Sweden. In Russia, where everyone knows that the chemicals are very pure, a single dibromide is produced that reacts with metals to give 1,1,2,2-tetramethyl-cyclopropane (**2**). Explain.



1 **2**

In Sweden where the HBr is polluted with all sorts of hideous things like peroxides, the results are completely different. First of all, compound **1** yields two dibromides (one a meso compound, the other a racemic mixture), not one. When the ring-closing reaction initiated by metals is attempted, two diastereomeric cyclopentanes are produced. Show structures for both dibromides and the two rings, and explain what is happening in Sweden.



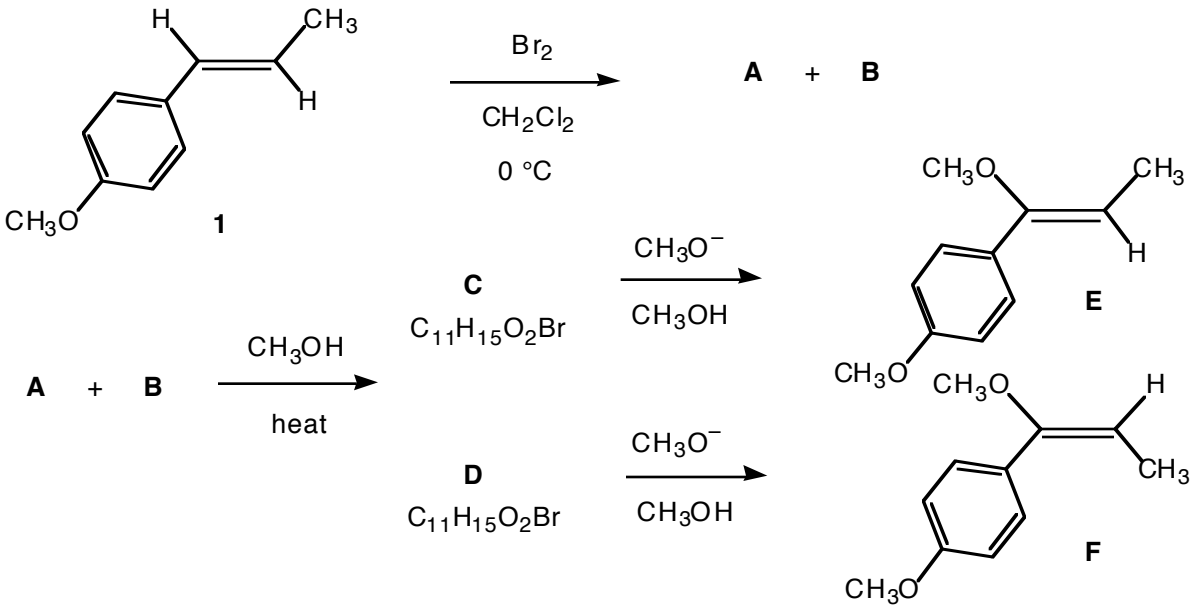
1

one meso, the other a racemic mixture

one meso, the other a racemic mixture

8. When achiral compound **1** is brominated with Br_2 formed from $PyHBr_3$ (recall lab experiment) at 0 °C, a mixture of diastereomers - that is, two pairs of enantiomers, racemic **A** and racemic **B -** is produced. Treatment of a mixture of **A** and **B** with methyl alcohol/heat leads to racemic **C** and racemic **D**, also diastereomers. Finally, treatment of **C** alone with methoxide leads to **E**, whereas similar treatment of **D** alone gives **F**.

Give the structures shared by **A** and **B** (these data do not allow you to say which is which). and structures for **C** and **D**. Please also provide mechanisms for the reactions shown below.

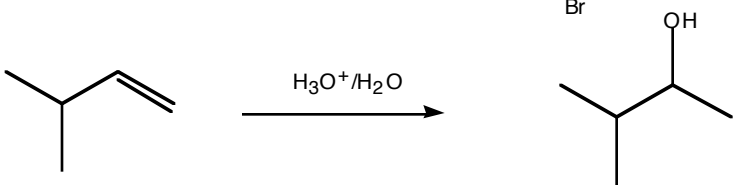


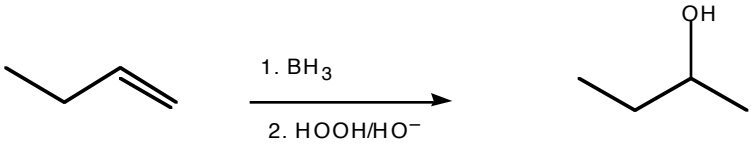
9. In each of the synthetic schemes on the next page (supplied, no doubt, by Amos Alonzo Stagg) there is at least one problem - that is, the product would not be the one shown. In each case, explain what is wrong and tell us what the real product would be.

In examples (b), (c) and (i), modify the reagents so that the reaction would work as shown.

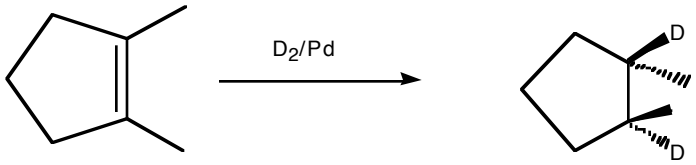
In examples (g) and (h), modify the starting material so that the reaction would work as shown. You just have to show us what to do, you don't have to devise a synthetic scheme to do it.

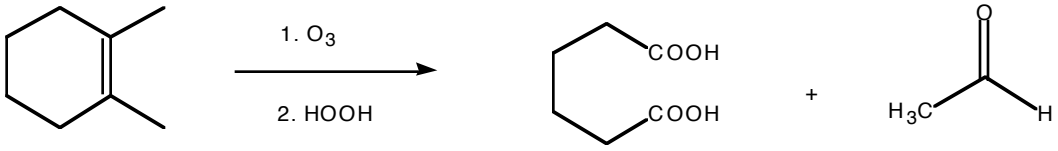
(a) 

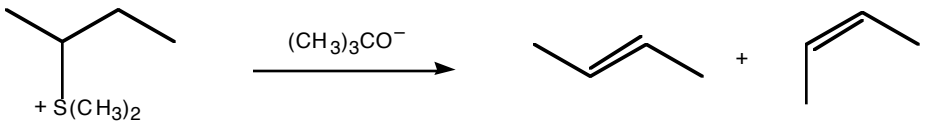
(b) 

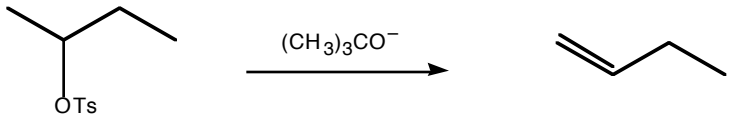
(c) 

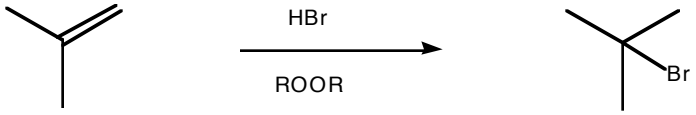
(d) 

(e) 

(f) 

(g) 

(h) 

(i) 

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