Chemistry 301A-301X Final Examination: January 12, 2005

"Why, for example, should a group of simple, stable compounds of carbon, oxygen, and nitrogen struggle for billions of years to organize themselves into a professor of chemistry? What is the motive?"

Robert Pirsig

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 1 AND 2 AND ONLY FIVE (5) OF THE REMAINING SEVEN (7) QUESTIONS**. Should you ignore this simple 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 (It is amazing, but some of you will not do this).

You must do Questions 1 and 2, and you must do a total of seven (7) Questions.

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 noon.

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."

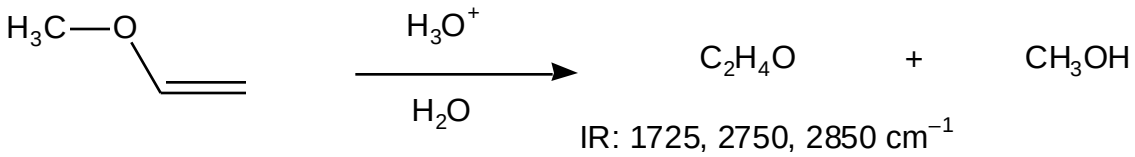
PLEASE:

1. Fill out the evaluation forms.

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

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

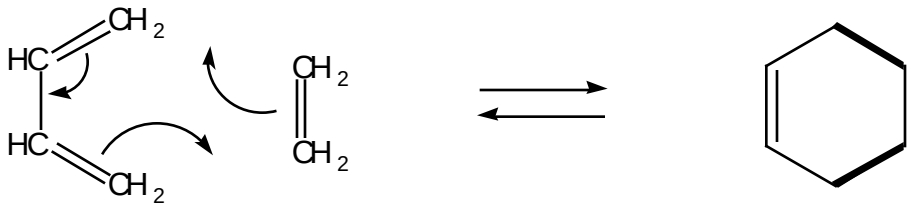
1. Write a perfect arrow formalism mechanism for the following reaction that should be very familiar to you. The figure below does not give full Lewis structures, but you should provide them for all structures in this problem. Show *all* lone pairs throughout.



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

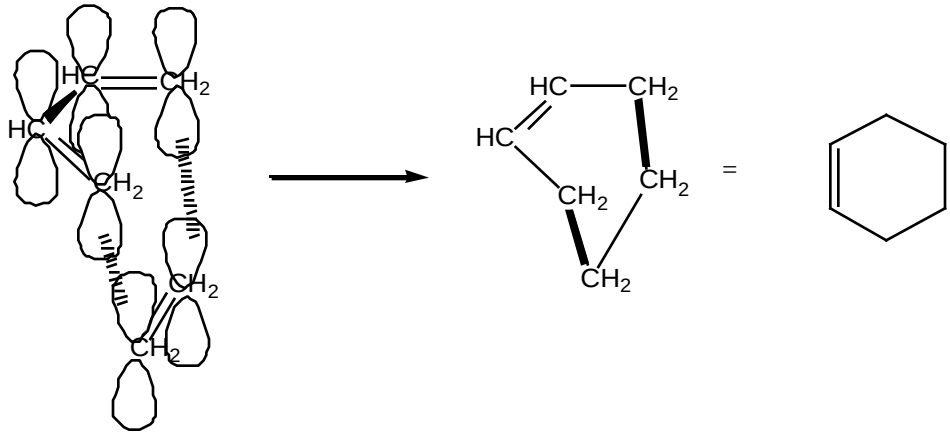
2. When 1,3-butadiene (**1**) and ethene are heated together, cyclohexene (**2**) is formed as shown in reaction (a).

(a)



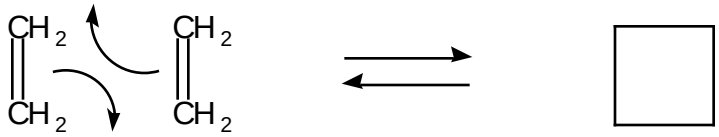
1 **2**

Here it is in three dimensions - note the 2*p* orbitals overlap end-on, not side-to-side:



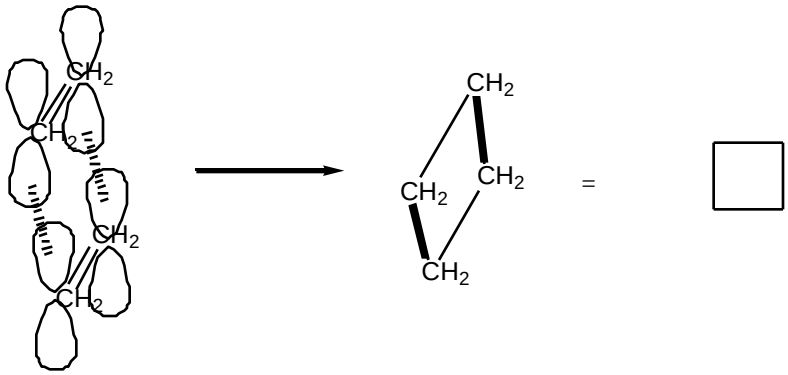
A similar reaction (b) might be imagined in which two ethenes combine to form cyclobutane (**3**). The little arrows in the figures above and below just track the making and breaking of bonds.

(b)



3

Here is reaction (b) in three-dimensions:



(a) Estimate quantitatively the exothermicity or endothermicity (ΔH) of each of these reactions. Yes, we want numbers, but if you can't come up with numbers, an answer that tells us the end result (exo- or endothermic) and why is far better than nothing.

(b) Reaction (a) is exceptionally well-known - it happens all the time. Reaction (b), however, is not. It is essentially unknown. Your task is to figure out why and explain your reasoning to us. Here's how to do that:

You only need make the assumption that filled-empty interactions between Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied Molecular orbitals (LUMO) control reactivity.

Sketch out the π molecular orbitals for the molecules involved in reactions (a) and (b), determine the HOMOs and LUMOs, and then explain why (a) succeeds and (b) fails.

Do Only Five (5) of the Following Seven (7) Questions. Please note on the cover which ones we are to grade.

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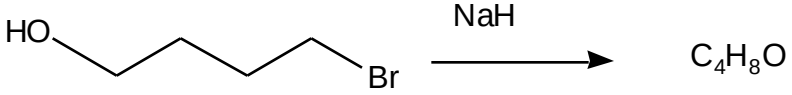
3. In each case predict the product. A mechanism is not necessary, but a mechanistic analysis may help you make your prediction. Then, for each case briefly tell how you would use ^{1}H NMR *and* ^{13}C NMR *and* IR (three different answers for each part) to tell the indicated product = P [in (b) you do not have to consider $H_2C{=}O$] from starting material = SM. Be pithy.

(a)

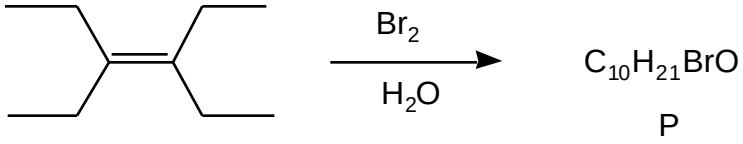


SM P

(b)

SM P

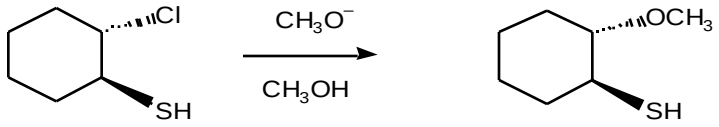
(c)



SM P

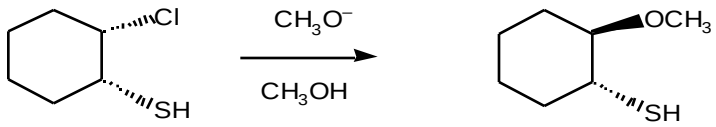
4. The two optically active diastereomers **4** and **5** react very differently when treated with methoxide in methyl alcohol. Give a mechanistic explanation for the products formed, and be *very* careful to account for the stereochemical details.

4



racemic product

5



optically active product

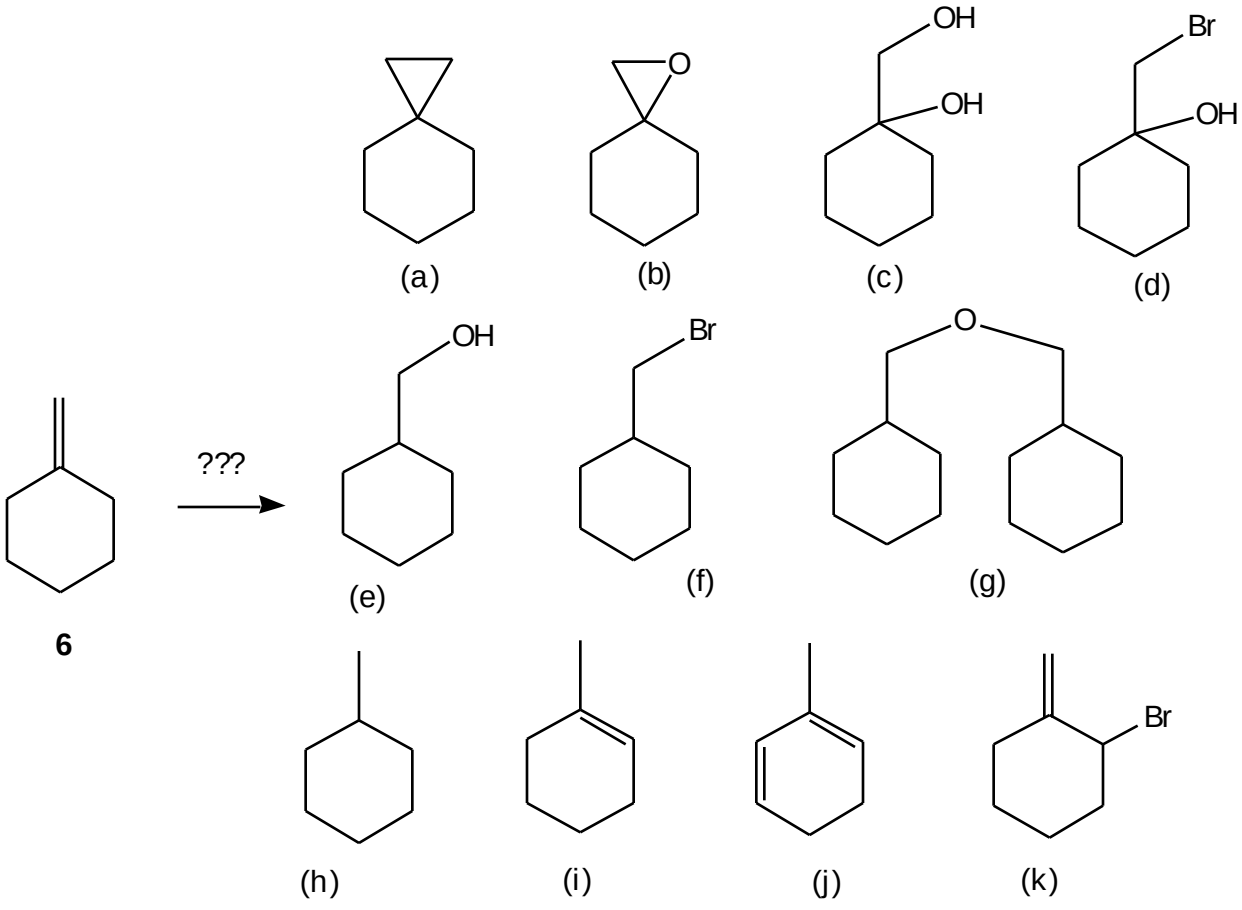
5. Provide syntheses for the following products. You may start from methylenecyclohexane (**6**), inorganic reagents of your choice (no carbons) and sodium hydride (NaH), diazomethane, *tert*-butyl alcohol, carbon tetrachloride, *N*-bromosuccinimide (NBS), chloroform, chlorophyll, clorox, chlordane, chlordane, chloramphetamines, dimethyl sulfide, trifluoroperacetic acid, and a single frog's toe. Be careful how you write these answers. "A" means "Add clorox and a frog's toe to X *all at once*." "B" means, "First add clorox to X, then, *in a second step*, add a frog's toe."

A

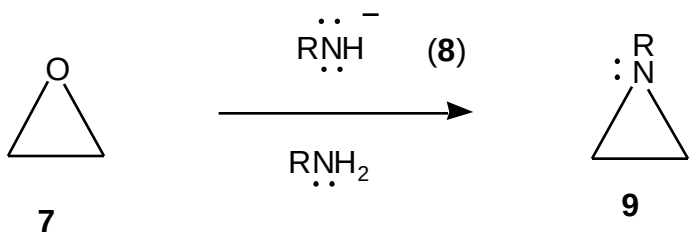
X $\xrightarrow[\text{frog's toe}]{\text{clorox}}$

B

X $\xrightarrow[\text{2. frog's toe}]{\text{1. clorox}}$

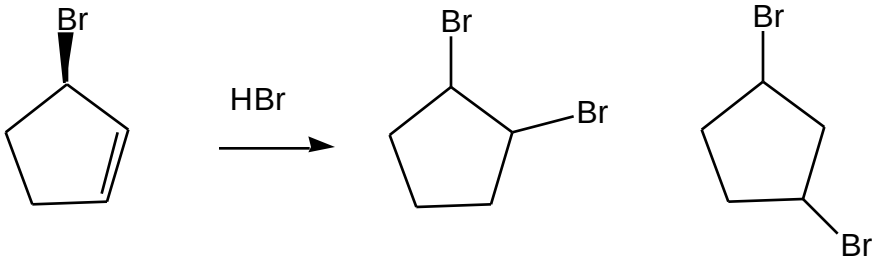


6. When ethene oxide (**7**) is treated with amide ion **8,** aziridine **9** is formed. Devise a mechanism that clearly predicts the stereochemistry of the product when (*R,R*)- *trans*-2-butene epoxide is used instead of **7**.



7 **9**

7. When (*R*)-3-bromocyclopentene (**10**) is treated with HBr, *trans*-1,2-dibromocyclopentane (**11**) and *cis*- and *trans*-1,3-dibromocyclopentane (**12**) are formed.



10 **11** **12**

Develop a mechanism that accounts for the following observations. Explicitly explain how your mechanism rationalizes each of the following four observations.

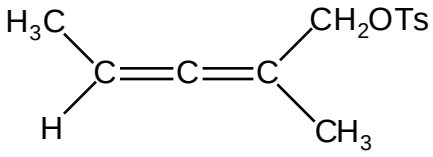
The *cis*-1,3-dibromocyclopentane formed is optically inactive.

The *trans*-1,3-dibromocyclopentane formed is optically active.

The *trans*-1,2-dibromocyclopentane is formed as a racemic mixture.

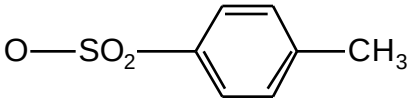
There is no *cis*-1,2-dibromocyclopentane formed.

8. Consider the allene **13**.



13

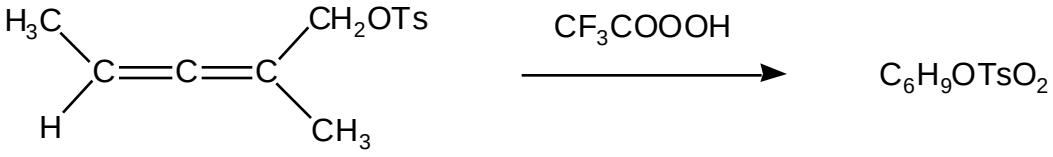
(C_6H_9OTs)

OTs = 

(a) Draw **13** in gloriously three-dimensional detail. Indicate the hybridization of each carbon (you can ignore the OTs part).

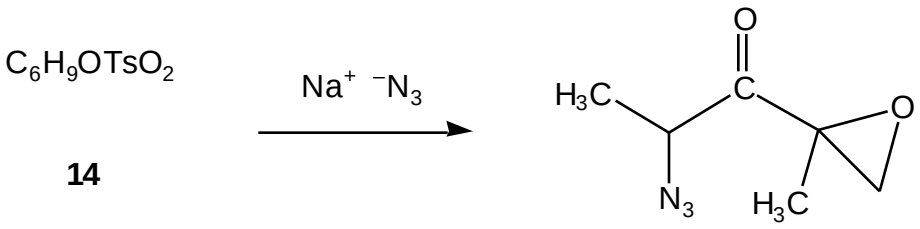
(b) Is this molecule chiral? Explain your yes/no answer briefly.

(c) When **13** is treated with excess trifluoroperacetic acid (CF_3COOOH), a new compound $C_6H_9OTsO_2$ (**14**) is formed. Draw a three-dimensional structure for any diastereomer of this product.



13 **14**

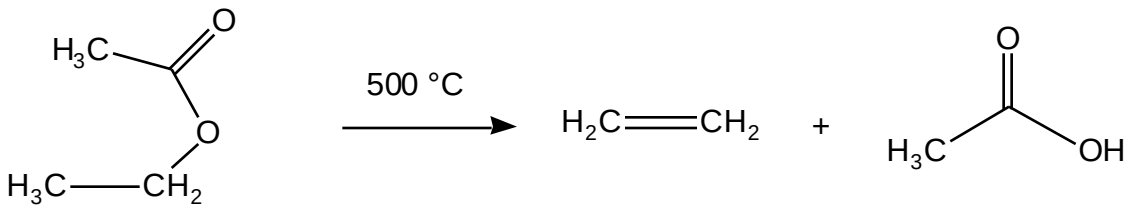
(d) When compound **14** is treated with sodium azide ($Na^+ {}^-N_3$) compound **15** is formed. Provide an arrow formalism mechanism. You may ignore stereochemistry in this part.



14 **15**

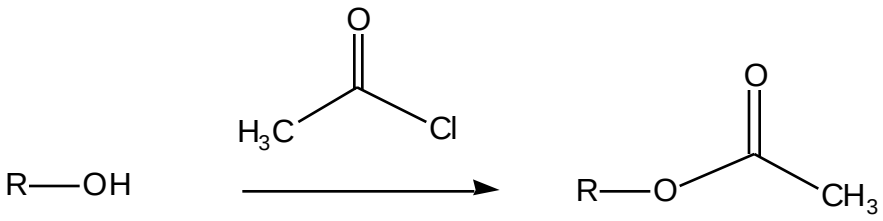
9. Here is a reaction you have never seen (probably). It is *not* some killer impossible reaction, but a quite ordinary process.

(a) Draw a mechanism for the following change that takes place when compounds such as **16** are heated to about 500 °C. Please note that this unimolecular reaction takes place without any intermediates.



16

(b) First some information: Alcohols can be made into **16**-like compounds by treatment with acetyl chloride, CH_3COCl. You do ***not*** have to write a mechanism for this change (though it is not very hard to do so).

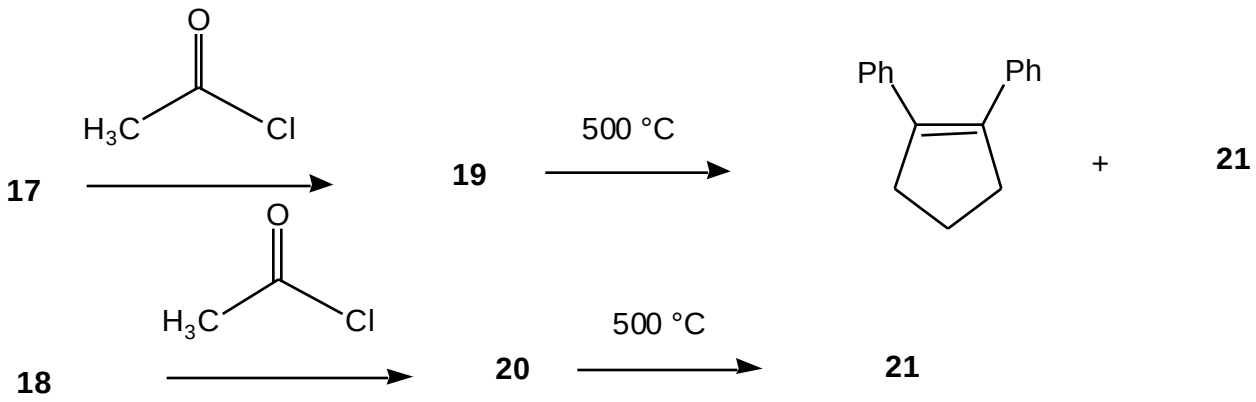


1,2-Diphenylcyclopentene reacts in acidic water to give a pair of diastereotopic alcohols, **17** and **18**. (Phenyl = Ph)

Draw three dimensional structures for **17** and **18** and sketch an arrow formalism for their formations.

Compounds **17** and **18** react with acetyl chloride, CH_3COCl, to give two new compounds **19** and **20**.

Compound **19** gives 1,2-diphenylcyclopentene back when it is heated to 500 °C, along with an isomeric cyclopentene **21**, but compound **20** gives only **21**. Give structures for **17**, **18, 19, 20** and **21**, arrow formalisms for the reactions described above and an explanation for why **19** and **20** react differently at 500 °C.



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