Final Examination, Chemistry 302X-302A, 2005

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

However, there is substantial choice. There is a total of 10 questions, but **PLEASE** do not do all the questions.

ANSWER ONLY EIGHT (8) QUESTIONS, AS DIRECTED

Question 1 is worth 9 points; all others are 13 points

Should you ignore these instructions we will grade all the questions you answer and take an appropriate fraction of the score. We will not, repeat not, take the best nor will we be responsive to pleas that we should ignore some feeble answer 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 the full examination period of 3.5 hours. 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 be sure to fill out the two evaluation forms.

PLEASE:

1. Fill out the evaluation forms.

2. Put “X” or “A” on the cover.

3. Show on the cover which questions are **NOT** to be graded (PLEASE DO THIS!).

4. Sign the pledge, which reads:

"I pledge that I have not violated the honour code on this examination.”

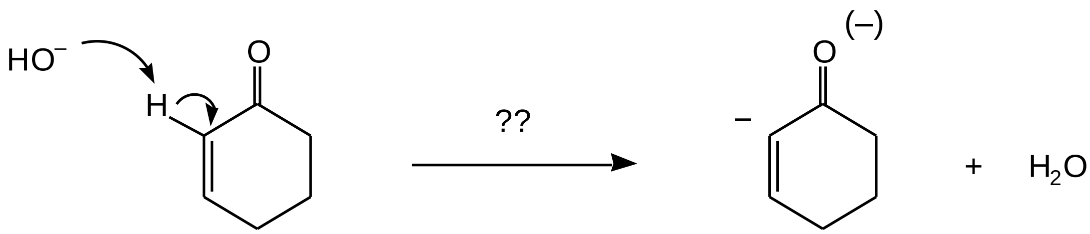
“An answer is always a form of death.”

John Fowles, “The Magus”

YOU MUST DO QUESTION 1

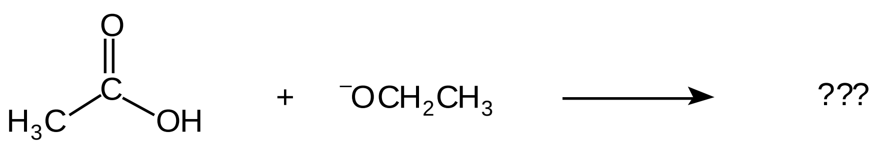
1. Answer the following three questions:

(a) Is compound **1** acidic at the position shown? Why or why not?



1

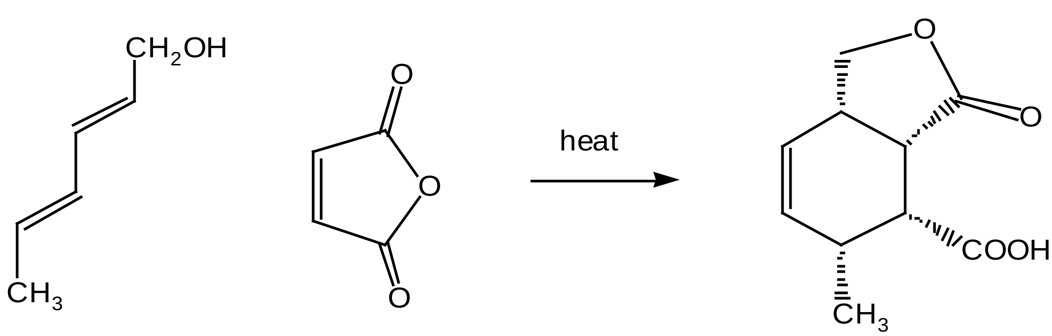
(b) Is there a reaction between acetic acid and sodium ethoxide? If so, what is it? If not, just write “no reaction.”



(c) Draw a perfect Lewis dot structure of the hydronium ion, H_3O^+.

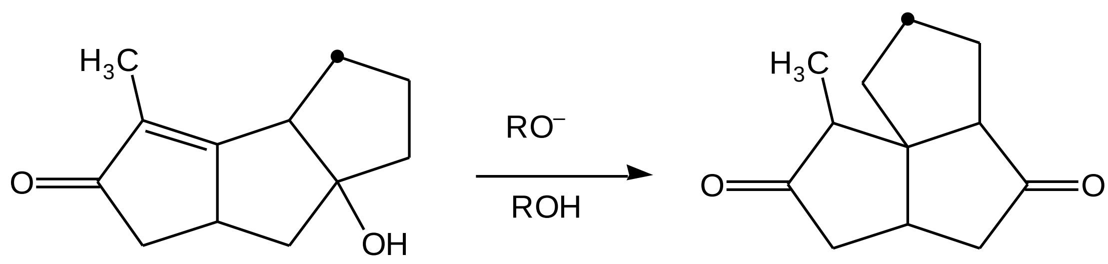
DO SEVEN OF THE FOLLOWING NINE QUESTIONS

2. Write a mechanism for the following transformation. Be sure to use careful - repeat, careful - repeat, very careful, <u>legible</u> drawings that account for the observed stereochemistry.



(racemic)

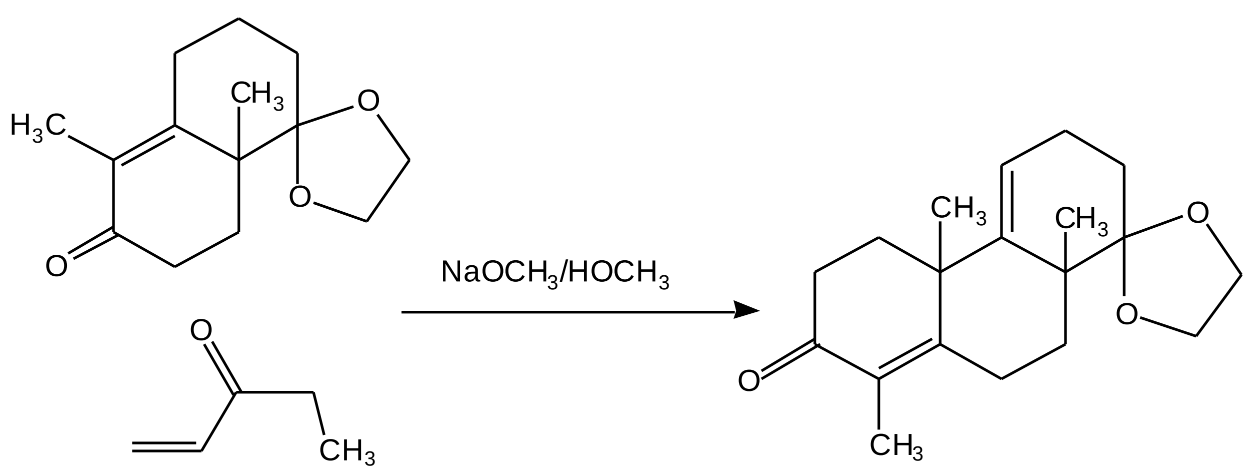
3. Provide a mechanism for the following transformation. Note the position of the label.



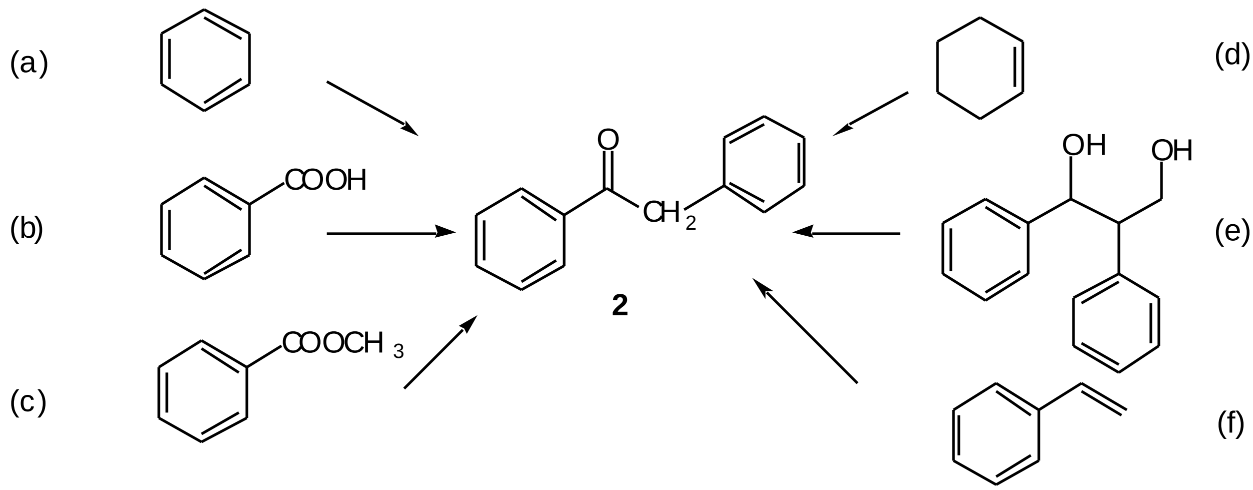
4. The synthesis of Germanicol depended upon this early transformation. For full points **either**:

(a) Draw a perfect three-dimensional structure for Germanicol in all its glorious stereochemical detail (no partial credit) **or**,

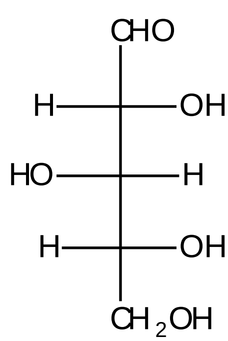
(b) Provide us with a nice mechanism for the following change:



5. Devise syntheses of benzyl phenyl ketone (**2**) from each of the following starting materials. You may also use alcohols containing no more than four carbons and one OH, $PhCH_2OH$, $PhCH_2CH_2OH$, and anything inorganic.



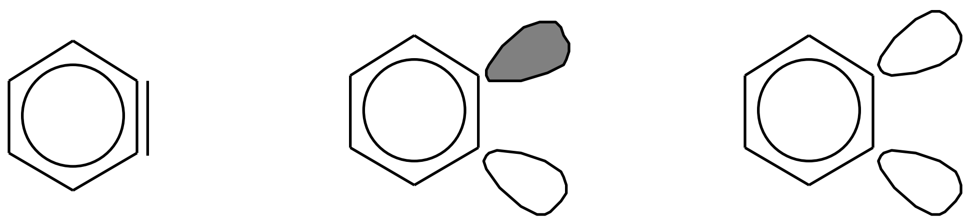
6. It is 1875 in a small town in Germany. You are in possession of four bottles, each containing one of the four D-aldopentoses. Unfortunately, the labels have fallen off three of the bottles. Only D-xylose retains it's label, which also shows the structure in Fischer projection.



D-xylose

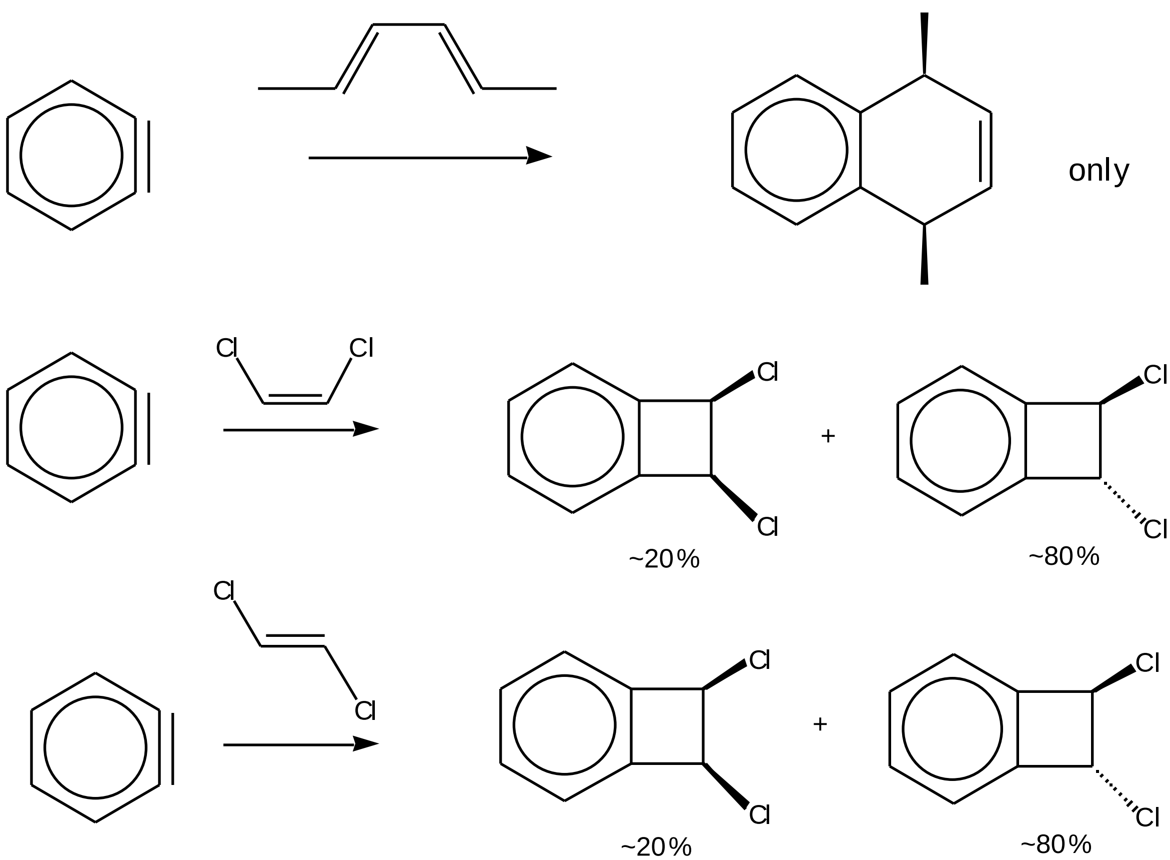
You have only two pieces of equipment in your primitive lab, a melting point apparatus and a polarimeter. You also have supplies of phenylhydrazine, sodium borohydride, and nitric acid in your pitifully equipped lab. Moreover, the local Graf has cut the budget for libraries and there are no books. Explain to us how you would determine the structures - not the names - of the other three sugars.

7. Some years ago, there was a controversy over the symmetry of the HOMO and LUMO of the “extra” double bond in benzyne. It doesn’t matter what the (crazed) reasoning was that led to the thought that the HOMO might be **A** and the LUMO **B**, but there were those who claimed that such was the case.

For: 

HOMO = **A** LUMO = **B**

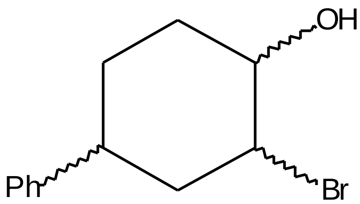
Of course, others set out to test that assertion. Here is a set of data from one such test:



Your job is to use an orbital analysis to explain in detail how the data were interpreted. What was the point of the experiment, and what did the results tell those who ran the experiment?

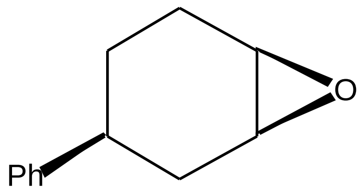
8. There are four diastereomers of **A**, each with an interconverting chair form (thus a total of eight diastereomers). Note that we are not considering optical activity here - each of those chair forms has an enantiomer that you do not need to consider.

Separate treatment of two of the four pairs of interconverting chairs with base leads to **B** in one case (faster) and **C** in the other (slower).

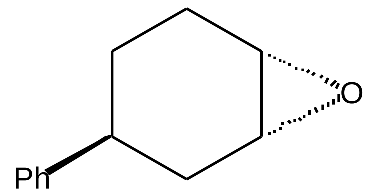


A

(squiggle means no stereochemistry specified)



B



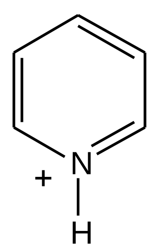
C

Your task is to determine which diastereomer of **A** leads to **B** and which to **C**, as well as to explain briefly why and how they are formed from the specific isomers. You also should explain why the formation of **B** is faster than that of **C**.

9.

(a) The pyridinium ion (**B**) can be substituted by an “E^+” reagent. Will that substitution be ortho/para or meta to the nitrogen? Explain. Will substitution be faster or slower than substitution of benzene with the same “E^+” reagent--(there is a factor of 10^{24} involved here, so this one is not a close call!)?

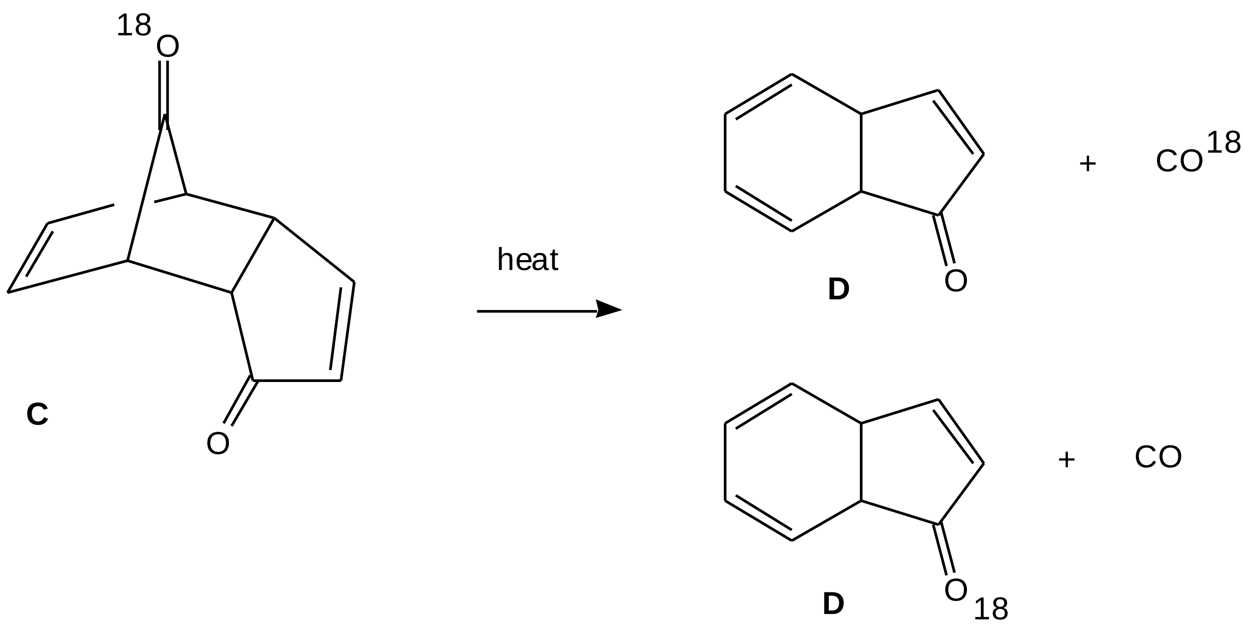
B



(b) The ^{1}H NMR spectrum of benzene in the presence of strong acids such as HF is very different at – 134 °C and – 80 °C. At one temperature, the spectrum consists of signals at δ = 5.86 (2H), 8.4 (2H), 9.2 (1H), and 9.4 (2H). At the other temperature the spectrum is a single line at δ 8.19. You have forgotten which spectrum goes with which temperature. Fortunately it is easy to figure it out. Tell us which goes with which, and explain why the spectrum changes. Benzene itself has a signal at δ 7.3, so it is not involved in the spectra tabulated above.

10.

(a) Heating of **C** leads to **D** and carbon monoxide in what must seem like a mindlessly simple reaction. However, at high temperature, a labeling experiment shows that an ^{18}O label appears in both the residual C=O group in **D** and in carbon monoxide. Explain.



(b) Provide a mechanism for the following weird-looking transformation: