Final Examination, Chemistry 302X - 2006

> "You were almost going to condescend to marry 'M' even if he had bad skin, barbarian parents, cold calculating drives, male vanity, and an unimaginative and rather prosaic way of making love while writing out chemical formulas."
>
> Sylvia Plath

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

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.

Problems 1 and 2 are worth 14 points each; the others are each worth 12 points.

PLEASE:

1. Fill out the evaluation forms.

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

3. Take the Oath, which reads:

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

4. Follow these Instructions:

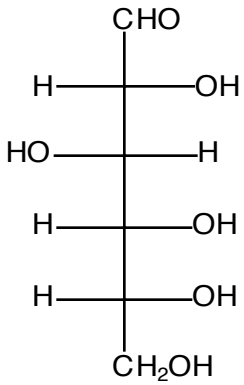
Do both questions in PART A

Do three (3) of the four (4) questions in PART B

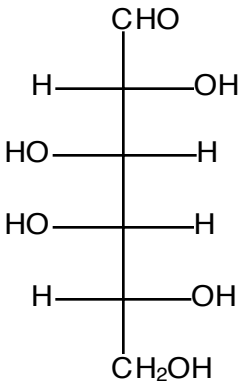
Do three (3) of the four (4) questions in PART C

PART A

1. Two D-aldohexoses, D-Glucose and D-Galactose are shown below in open, Fischer projection forms.

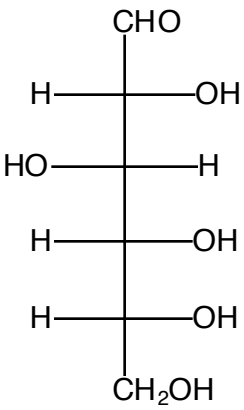


D-Glucose



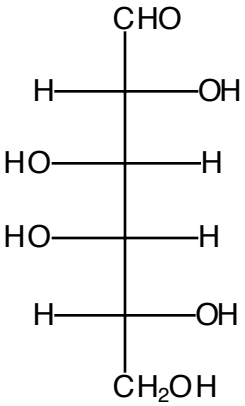
D-Galactose

Treatment of one of these two sugars with methyl alcohol and an acid catalyst leads to a mixture of α- and β-methyl pyranosides, **A**.

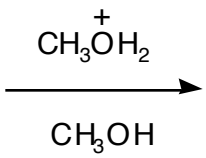


D-Glucose

or



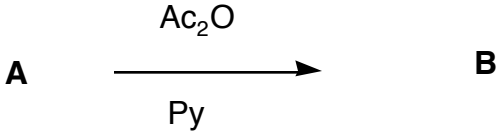
D-Galactose



A

(a) Draw a 3D picture of the chair form of this mixture **A**. Use squiggly lines to indicate any stereochemical uncertainties. Please note that you don't have to know what a methyl pyranoside is - the chemistry will lead you to the correct general structure.

Treatment of one of the four possible stereoisomers of **A** with acetic anhydride and pyridine (Ac_2O/Py) leads to a 2,3,4,6-tetraacetyl methyl pyranoside, **B**.



Problems 1(b) AND 1(c) ON NEXT PAGE

(b) Draw a 3D picture of the chair form of **B**. Use squiggly lines to indicate any stereochemical uncertainties.

(c) The following ^{1}H NMR data will allow you to resolve those stereochemical uncertainties, and to draw a good 3-D picture of **B**. You can also tell us if the original sugar was D-glucose or D-galactose. Please explain how the NMR data allow you to resolve the uncertainties.

H-1 is the old aldehyde hydrogen in the open form.

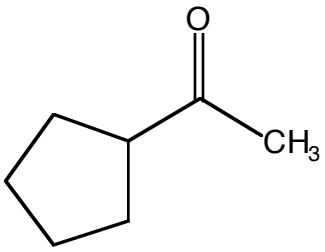
H-4 is the hydrogen originally on C-4 of the open form.

In **B**, H-1 appears as a broad doublet with $J = 3.7$ Hz.

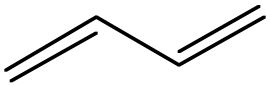
In **B**, H-4 appears as a doublet of doublets with $J = 10.2$ and 9.4 Hz.

2. Devise syntheses of the following molecules from the indicated starting materials. You may also use any inorganic reagent, alcohols containing no more than two carbons, and gusto.

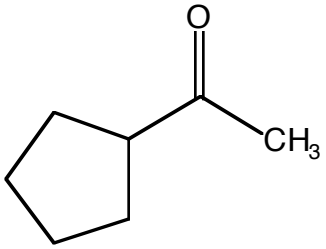
(a)



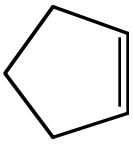
from acetic acid and



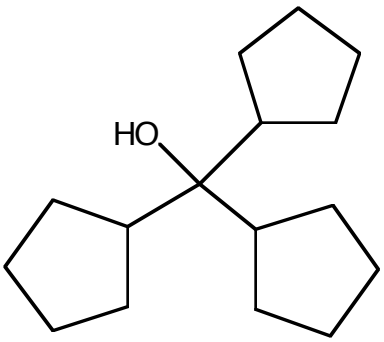
(b)



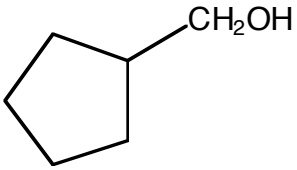
from acetic acid and



(c)

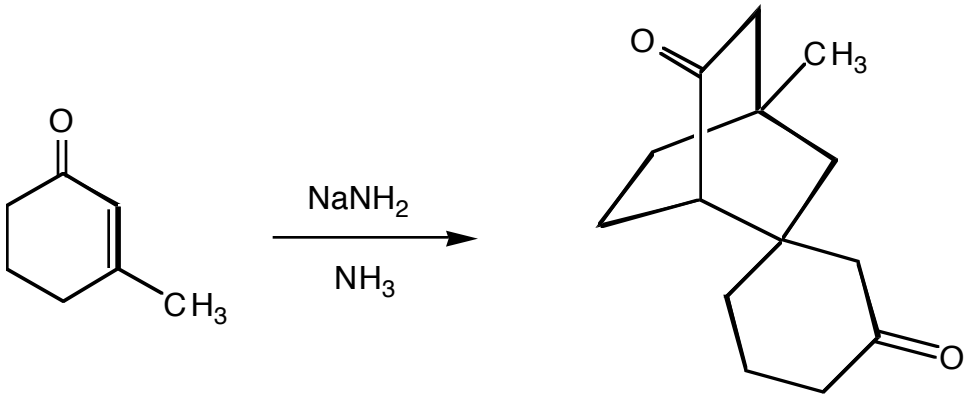


from



PART B - DO ONLY THREE (3) QUESTIONS

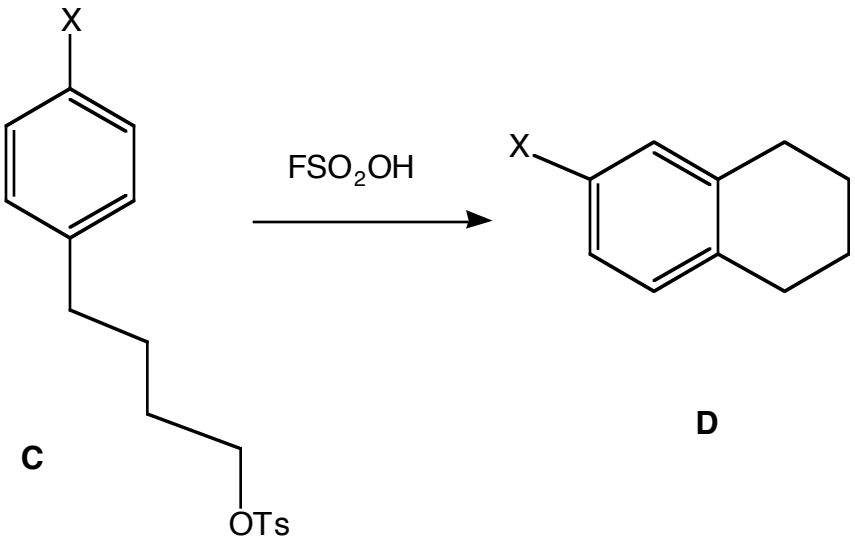
3. Provide a nice mechanism for the following change. Analysis is the key to success in this problem.



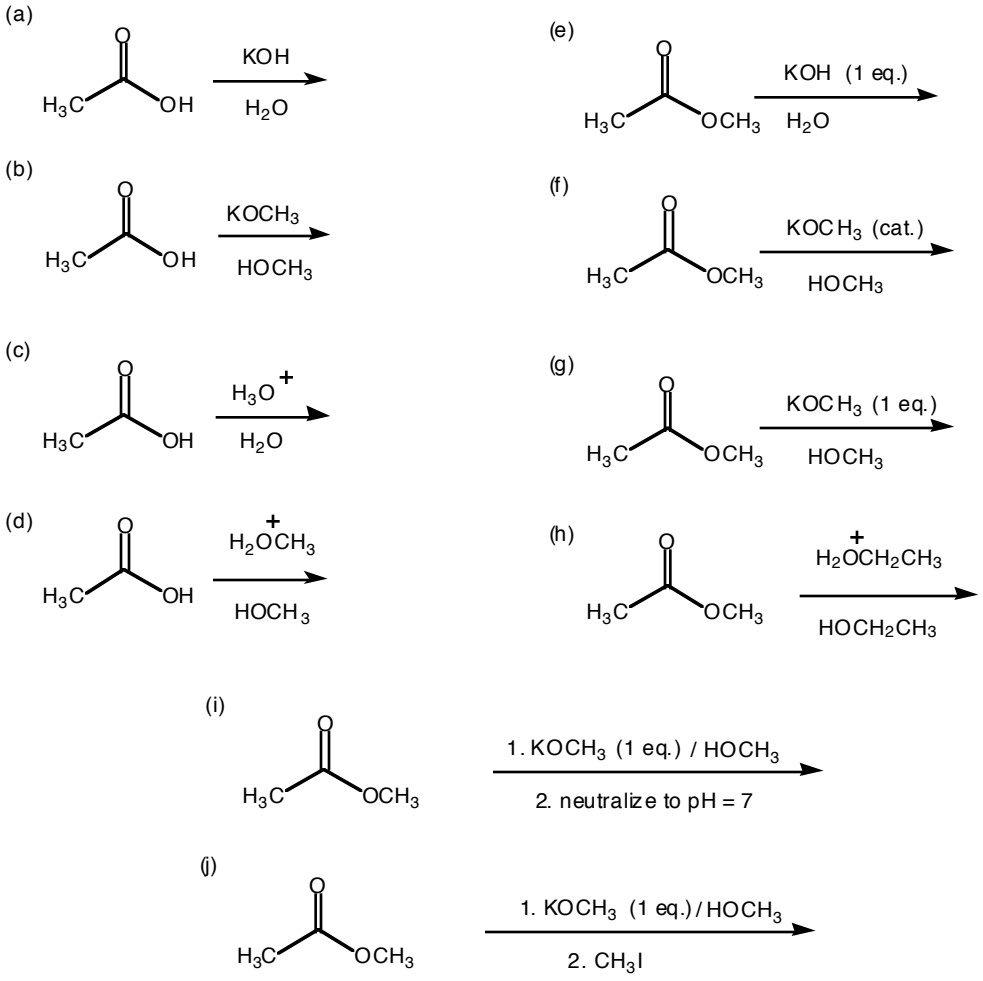
4. Find two related, but different mechanisms that lead from **C** to **D** in a highly polar, but non-nucleophilic medium.

When X = methyl, one mechanism is favored, but when X = nitro, it is the other that "wins."

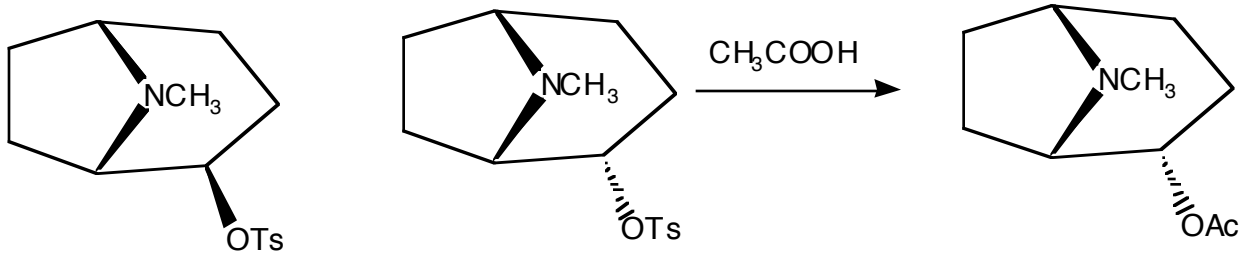
Which group favors which mechanism? Explain.



5. Acids and esters do lots of different things under different conditions. Write the ***major*** products of the following reactions. Mechanisms are **not** necessary.



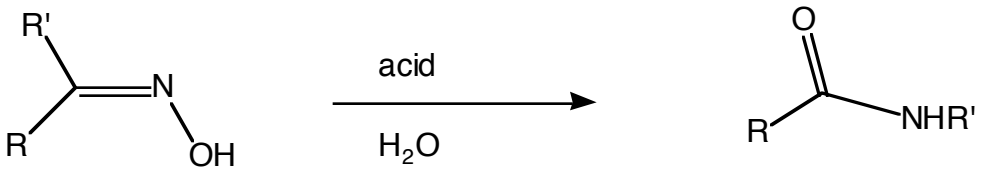
6. (a) Optically active molecule **I** reacts several times faster than its epimer **J**, and gives racemic acetate **K**. Provide a mechanism that explains the stereochemical and rate data.



J optically active **I** racemic **K**

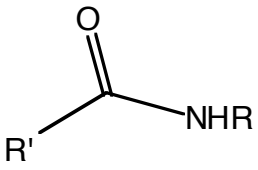
PROBLEM 6b ON THE NEXT PAGE

(b) Here is the Beckmann rearrangement, a reaction we visited in Group Problems.

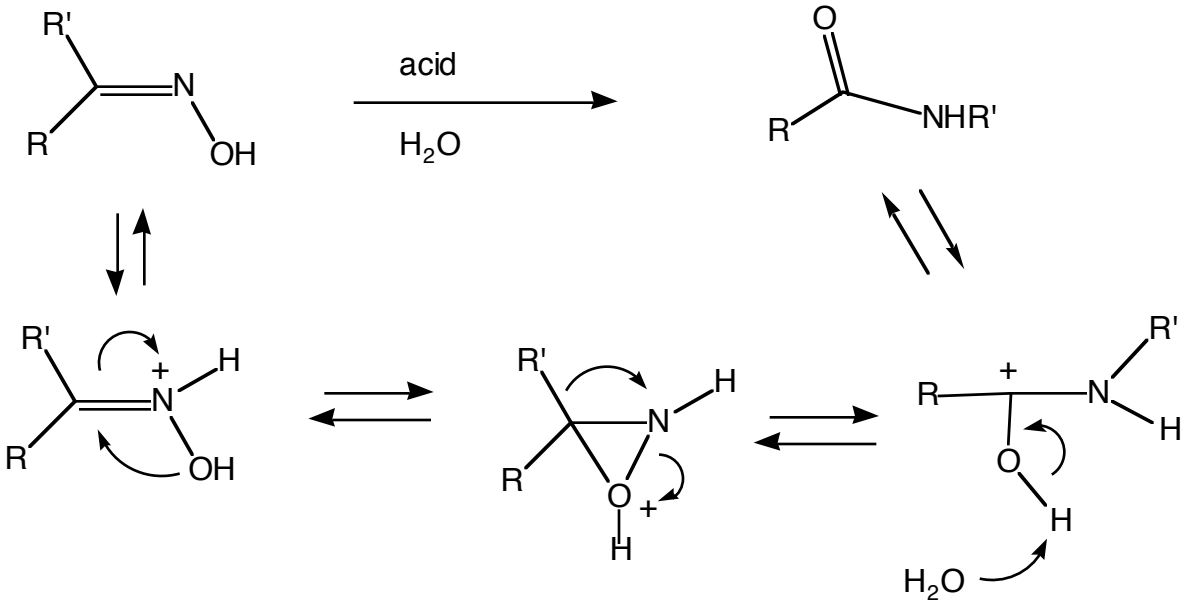


1. In the Beckmann rearrangement, if R' is optically active, optical activity is found in the product.

2. In the Beckmann rearrangement shown above the product is never:



Is the following mechanism consistent with observations 1 and 2? Why or why not?

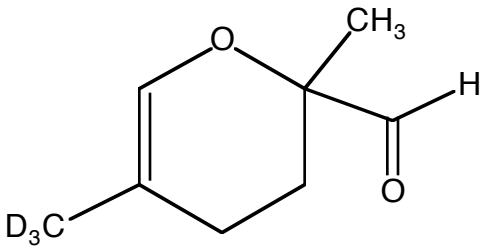


Sketch the mechanism of the Beckmann rearrangement - if you are unhappy with the one above.

THIS IS THE END OF PART B

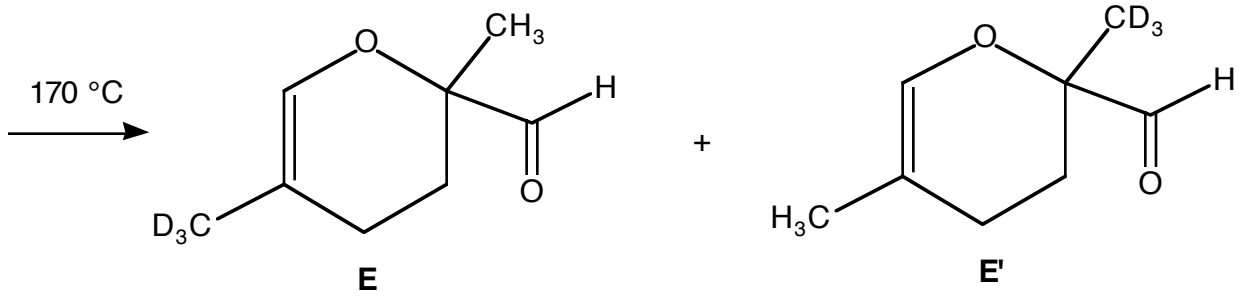
PART C - DO THREE (3) OF THE FOLLOWING QUESTIONS.

7. (a) Molecule **E** was required for a labeling experiment.



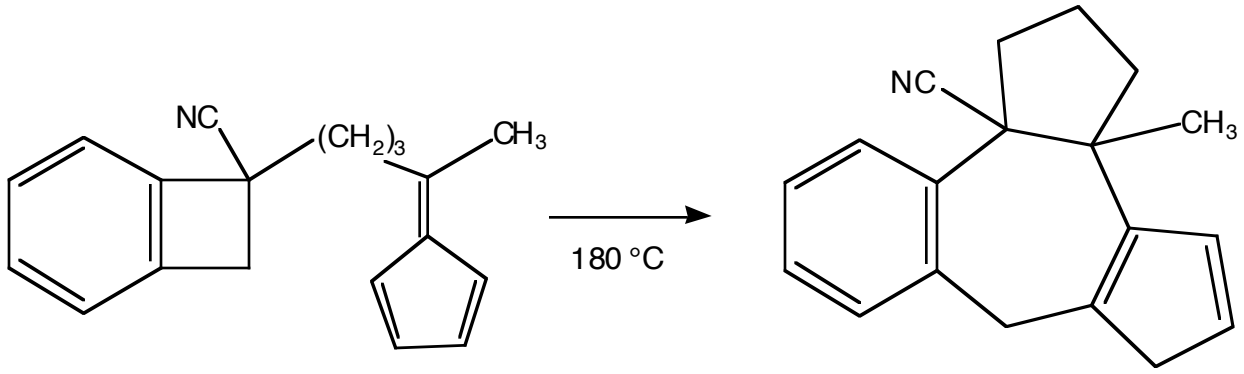
E

A clever route was devised that required a final step at 170 °C. The people who did that final reaction at 170 °C were shocked, shocked do you hear, to discover that the deuterium label was equally distributed as shown. Explain what is happening.



E **E'**

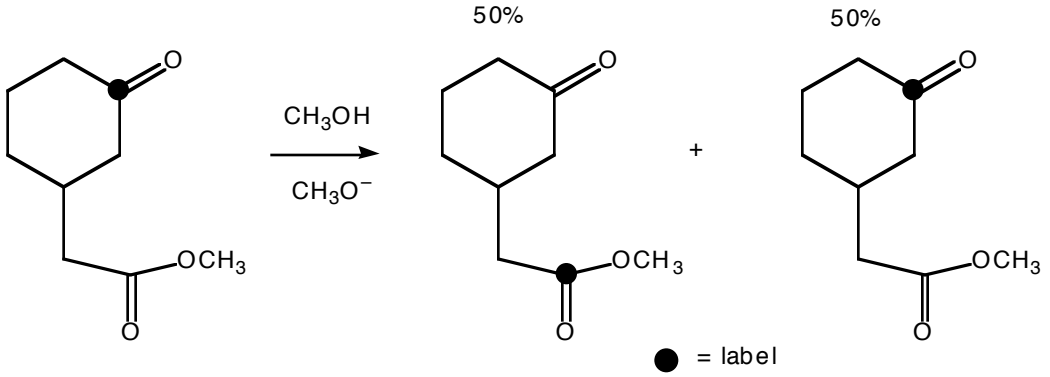
(b) Provide a mechanism for the following change:



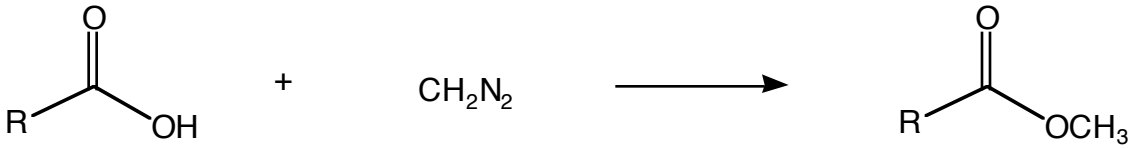
8. The following problem comes from an analysis of one particularly clever step in the synthesis of Kaurene. It may or may not actually have been done, but it has to work. Either:

(a) Draw us Kaurene in all its spectacular glory (no partial credit), or:

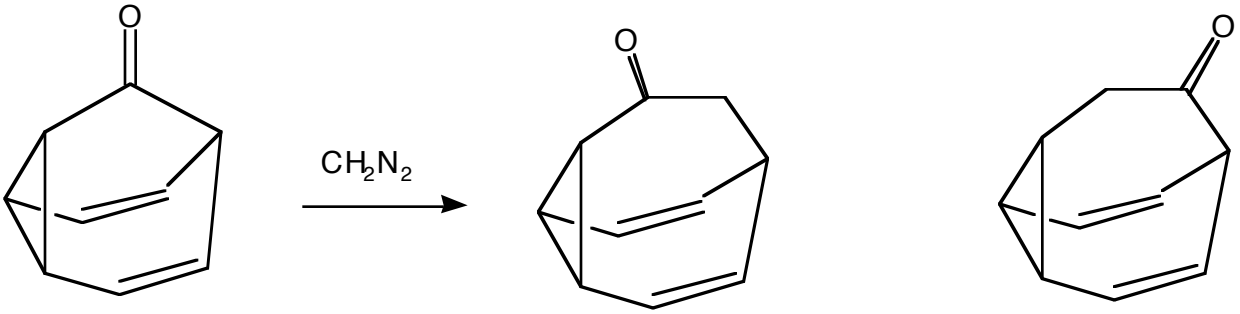
(b) Give us a detailed mechanistic explanation of the following base-induced switch-a-rama:



9. a) We told you that diazomethane (CH_2N_2) reacted with carboxylic acids to give methyl esters. We are not sure we ever told you how this useful reaction happens, so please provide a mechanism for this process. You should start with a good Lewis dot structure for diazomethane.



(b). A critical step in the synthesis of "bullvalone" (**F**) from "Barbaralone" (**G**) involved reaction with diazomethane. Write a mechanism.



G **F** **H**

(c) Oops - why were we not worried about the mechanism of part (b) giving **H**?

10. Provide structures for compounds **A** – **E**. Pay attention to the formulae - they frequently give valuable information. If you get stuck, try working backward. Mechanisms are not necessary.