

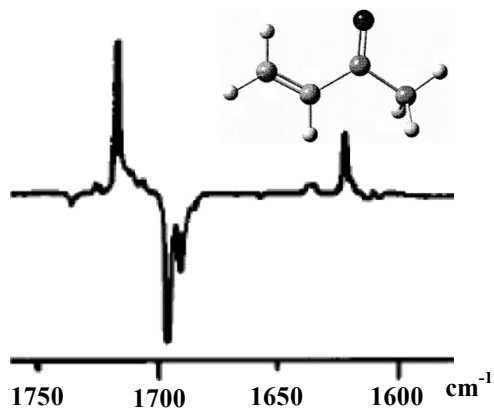
Chemistry 125 Seventh Examination
April 5, 2010

Name _____

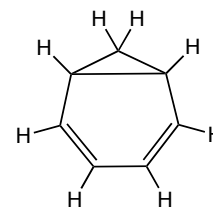
The exam budgets 50 minutes, but you may have 60 minutes to finish it. Good answers can fit in the space provided. Question values correspond to allotted time. Don't waste too much time on cheap questions.

1. (3 min) **Explain** which electronic transition should be easier to achieve by interaction with light of the appropriate wavelength: $1s$ to $2s$ or $1s$ to $2p$.

2. (5 min) The following *difference* IR spectrum was obtained after irradiating a sample of methylvinylketone at 308 nm for 2.5 hrs. at 15K. **Describe the normal modes** corresponding to the three largest peaks (2 positive, 1 negative).



3. (5 min) **Explain how a chemical reaction was used** to assign (erroneously) the “cyclopropane diene” structure shown below, **AND how NMR proved** that the molecule had a different structure.



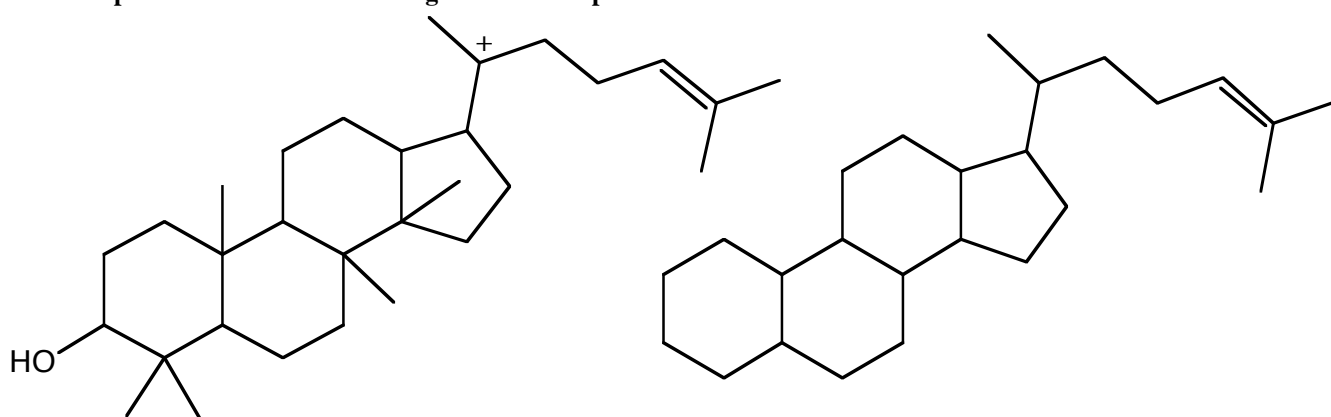
4. (5 min) **Explain three different ways** in which 2,4-dinitrofluorobenzene is perfectly suited for the purpose to which Frederick Sanger applied it (winning Nobel prize). [It would help to draw the reaction intermediate and product.]

5. (4 min) Give an example of a Friedel-Crafts alkylation with Lewis-acid catalysis that proceeds with *o,p*-orientation and rearrangement.

6. (4 min) Define a “90° pulse”, and tell why is it required to make protons “sing out” their precession frequency.

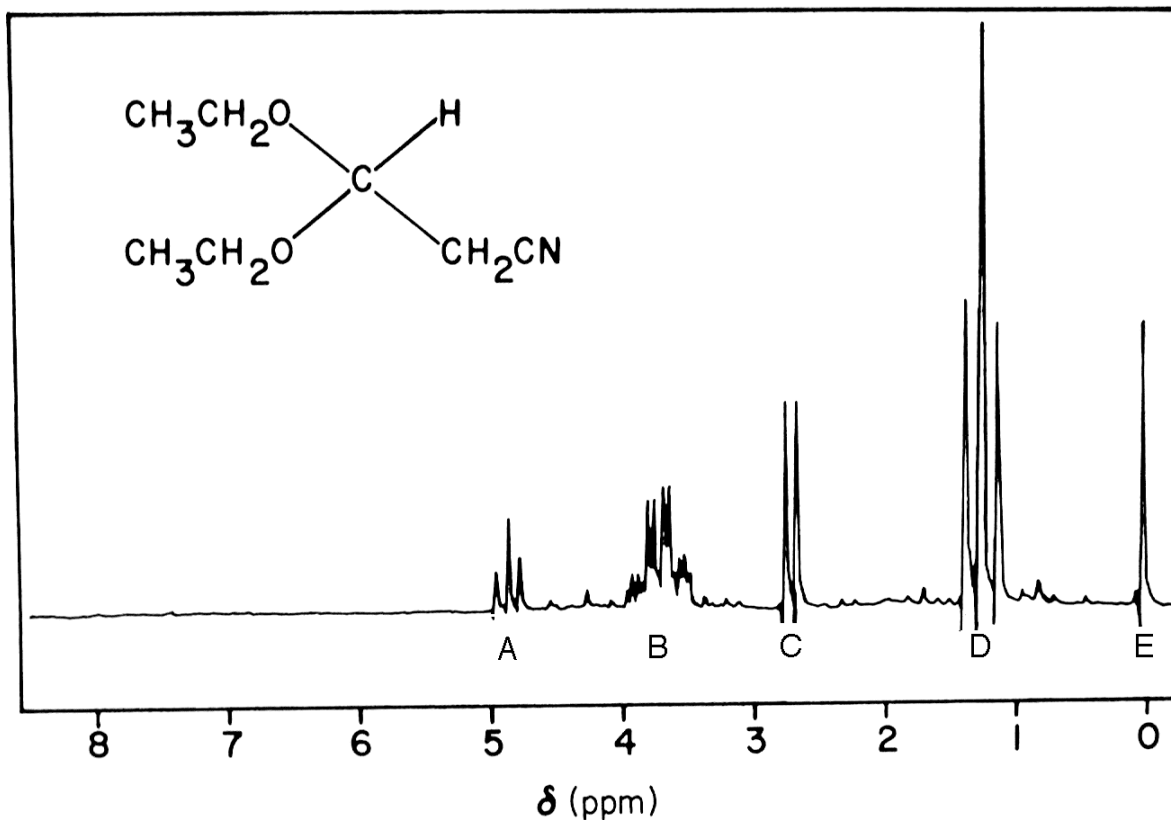
7. (6 min) This cation below left is an intermediate in the synthesis of lanosterol from isopentenyl pyrophosphate.

A) Elaborate the diagram (include curved arrows) to show the multistage rearrangement that happens next, and complete the structure on the right to show its product.



B) Describe briefly how an experiment involving NMR was conducted to provide strong confirmation of your mechanism.

8. Here is one of the most embarrassing NMR spectra of all time. It was published in 1982 in a paper whose author list included a Chemistry Nobel Laureate (who may not have played a very big role in writing the paper). The spectrum was captioned "Figure 1. Proton magnetic resonance spectrum of 3,3-diethoxypropanenitrile showing the existence of the two conformers." The **paper contended** that unexpected doubling of certain peaks in the spectrum showed that the molecule existed as a mixture of **two different conformational isomers**.



- A) (8 min) Each significant signal in the spectrum is labeled with a letter. **Write the appropriate letter above each proton** (or group of protons) in the structural diagram.

In a few words explain the **size, position, and multiplicity** of each of these signals:

A

B

C

D

E

- B)** (1 min) Which of the five patterns has the **“unexpected doubling”** that suggested the existence of two conformers to the authors?
- C)** (2 min) The spectrum was measured at room temperature with a 60 MHz spectrometer. What is the **approximate magnitude** of the “unexpected” doubling **in Hz**?
- D)** (5 min) If the authors were correct, what could one say about the **rate of interconversion** of the two proposed conformational isomers from having observed this doubling, and what would this say about the **barrier** (kcal/mole) to interconversion? **How large would you guess** such a conformational barrier should be?
- E)** (2 min) Suggest a more probable interpretation of the doubling based on **stereotopicity** relationship between the two protons within each of this compound’s methylene groups.