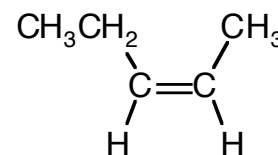
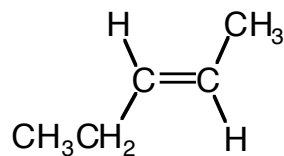
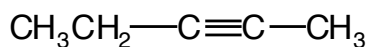
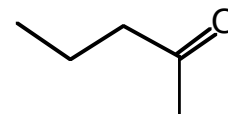
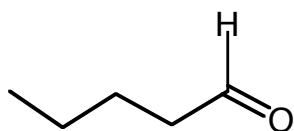


Chemistry 125 Sixth Examination
March 3, 2003

Name _____

1. (8 min) Show how one may transform 2-pentyne in the center of the following diagram into each of the four molecules in the corners of the diagram in high yield. Just give reagents, not mechanisms, but if more than one reaction is necessary, show the structure of stable intermediate molecule(s).

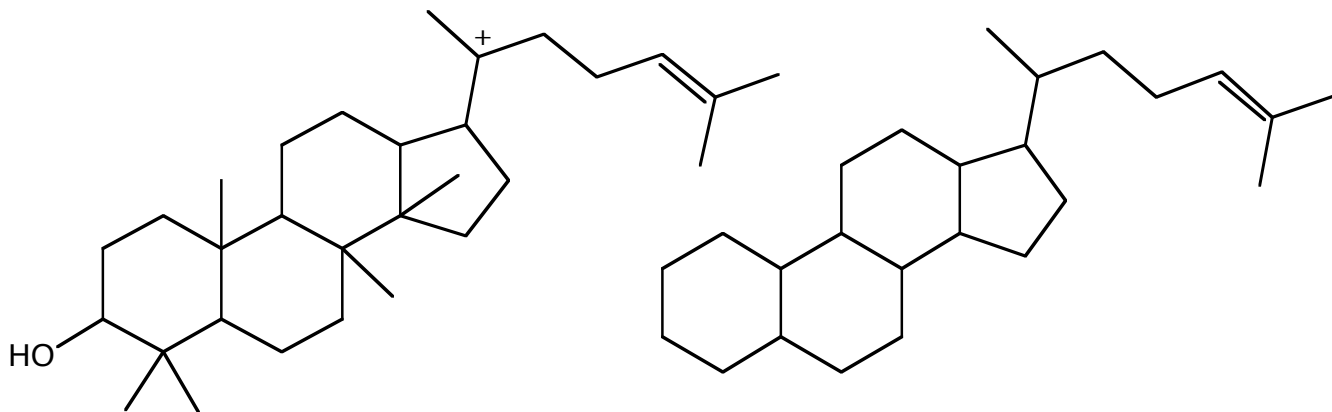


2. (3 min) Explain how you would use **BOTH PMR and CMR** spectroscopies to distinguish between the isomeric **alkenes** at the bottom of the diagram in Question 1. Don't explain the entire spectra, just mention one feature in each spectrum that allows reliable discrimination between the molecules.

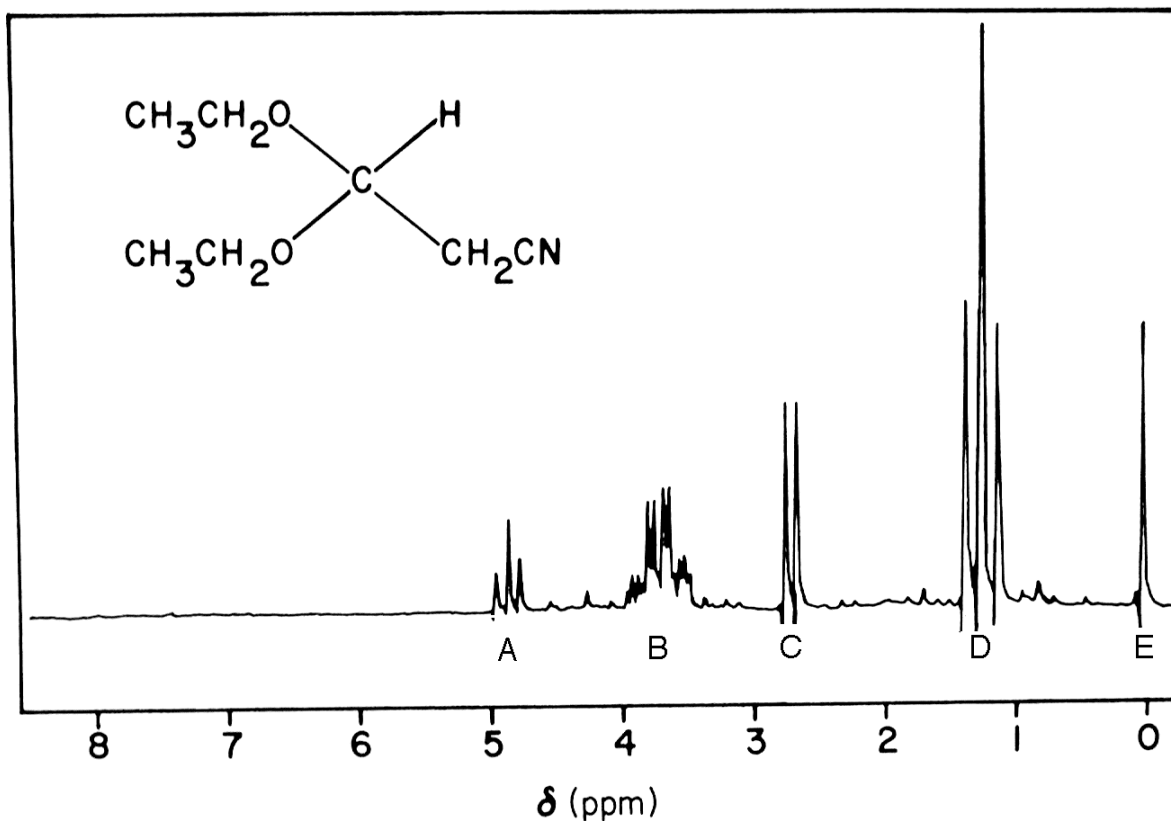
NOT 2010

6. (5 min) Draw the multistep mechanism for **ONE** of the following two processes:
Hydrogenation of an alkene with Pt catalysis **OR** Cyclopropanation of an alkene with CH_2I_2 and $\text{Zn}(\text{Cu})$

7. (5 min) This cation below left is an intermediate in the synthesis of lanosterol from isopentenyl pyrophosphate. **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**. Mention in a couple sentences experimental evidence consistent with your mechanism.



8. The following 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 some of the 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)** (4 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?
- E)** (2 min, Hard question for little credit) Suggest a more probable interpretation of the doubling based on **stereotopicity** relationship between the two protons within each of this compound’s methylene groups.