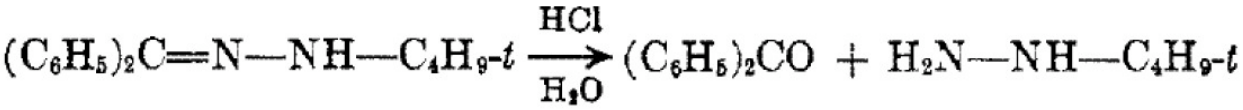
Chemistry 125 Seventh Examination Name _____

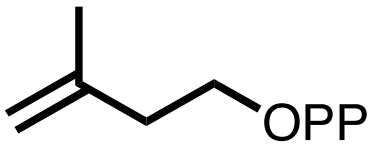
April 8, 2009

The exam budgets 50 minutes, but you may have 60 minutes to finish it. Good answers can fit in the space provided.

1. (2 min) Jo-David Fine had fits trying to prepare t-butylhydrazine by repeating the following reaction from the chemical literature. Show what actually happened instead. Use **curved arrows** (**two steps will suffice**).

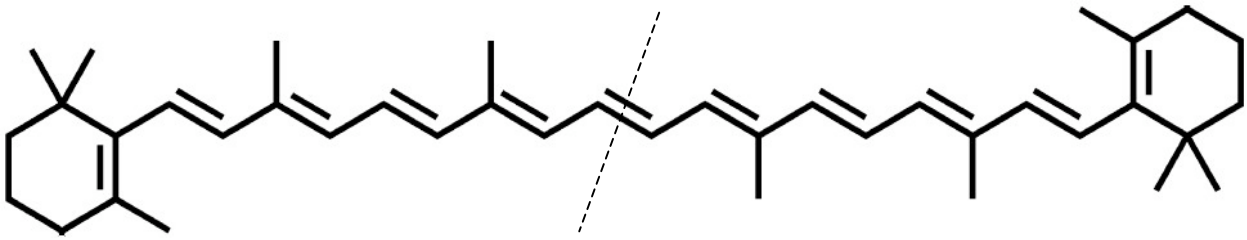


2. The structure below is β-carotene. A dashed line is drawn in the structure to show that the molecule was assembled by head-to-head dimerization of units that were assembled from isopentenyl pyrophosphates (IPP, show on the right).



A. (2 min) Label every carbon of IPP with its oxidation state number.

B. (3 min) Draw **additional dashed lines** to divide the ***left half*** of β-carotene into units from different IPP molecules, Then **label each** unit to show whether overall it was oxidized (O), reduced (R), or neither (N) relative to IPP.



C. (1.5 min) Not surprisingly β-carotene is in the family of "carotenoids". It is also a "tetraterpene". Briefly explain the meaning of the term "tetraterpene".

3. The following pairs of numbers are relevant for distinguishing spectroscopically between certain (Z) and (E) alkenes:

967 *vs.* 710 cm^{-1} **0-12 *vs.* 12-18 Hz**

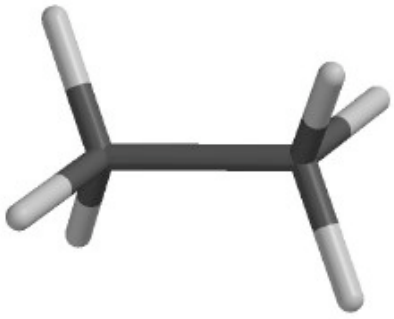
A. (2 min) In each pair circle the member that indicates a (Z) alkene.

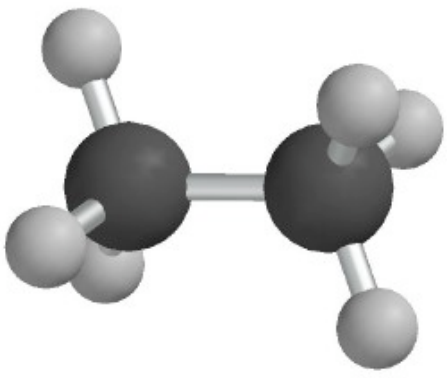
B. (6 min) Choose **ONE** of the pairs of numbers and explain in detail **WHY** the isomers differ in this direction.

4. Consider the vibrational normal modes of ethane.

A. (2 min) How many such normal modes should the molecule possess? _____

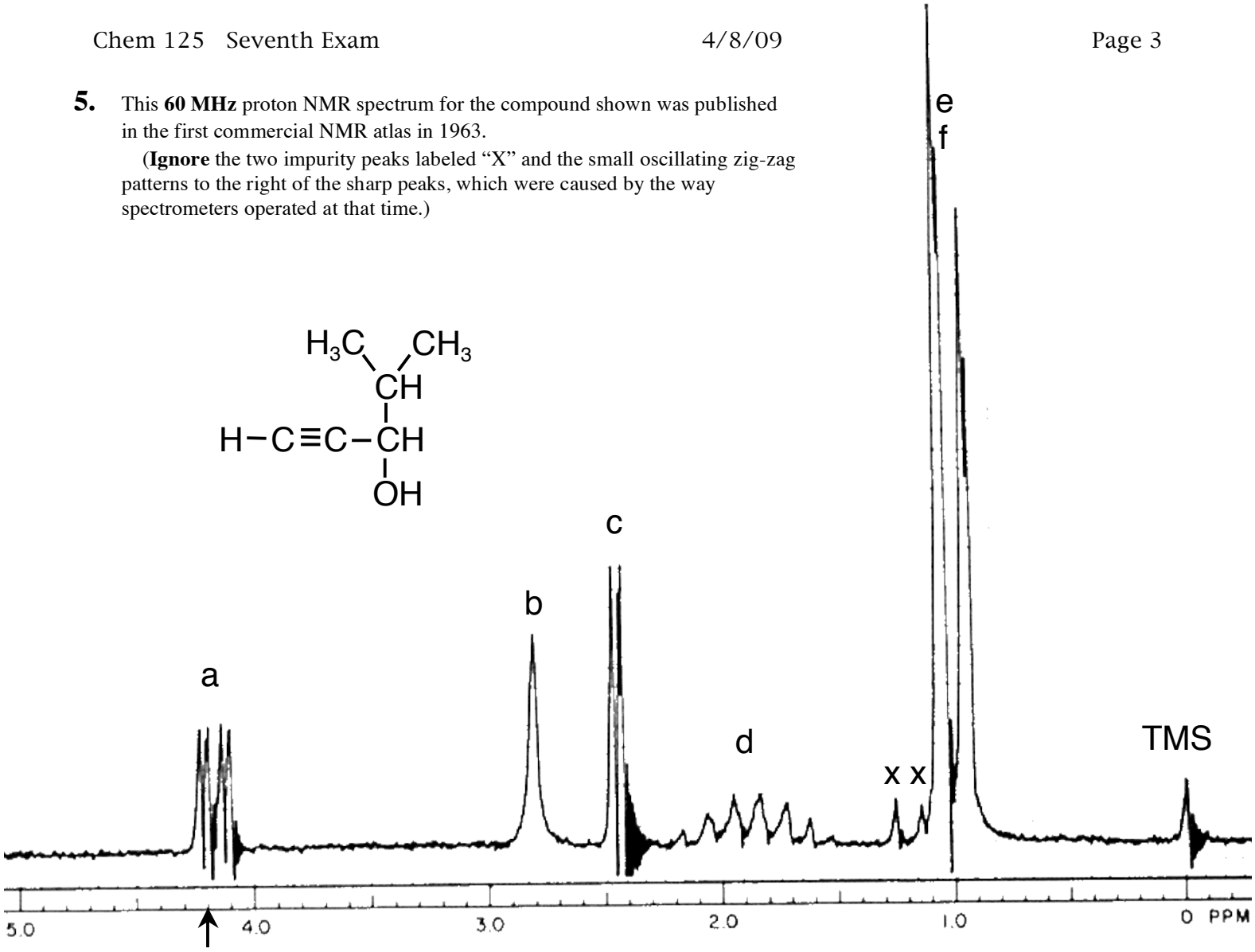
B. (3 min) **Draw arrows** on appropriate H and/or C atoms or bonds in the structure below (use either or both) to show the directions in which they might be moving at a particular instant in a **normal mode** that absorbs IR light ~3000 cm^{-1}.





5. This **60 MHz** proton NMR spectrum for the compound shown was published in the first commercial NMR atlas in 1963.

(**Ignore** the two impurity peaks labeled "X" and the small oscillating zig-zag patterns to the right of the sharp peaks, which were caused by the way spectrometers operated at that time.)



A. (1 min) **Draw a second arrow** beneath the ppm scale that is **7 Hz** from the arrow at 4.2 ppm.

B. (5 min) **Label** the protons in the **chemical formula** with the letters **a-f** to correspond to the labeled groups of peaks.

C. (3 min) Explain why the **chemical shift** of the peak labeled "**b**" is strongly **dependent on concentration** and **temperature**.

(Continued on next page)

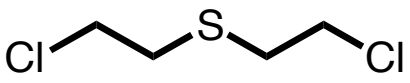
Question 5 (cont)

D. (3 min) Explain the **spin-spin splitting** of the proton at "**a**".

E. (3 min) **Describe TWO** competing factors that determine the **chemical shift** of the peak labeled "**c**".

6. (2.5 min) Explain why the magnetic fields used for medical MRI must be very different from those used for chemical NMR. (Don't worry about their physical size.)

7. In 1886 German chemist Viktor Meyer reacted 1,5-dihydroxy-3-thiapentane with PCl_3 to form 1,5-dichloro-3-thiapentane, which ultimately became known as "mustard gas", one of the most notorious chemical warfare agents.



It was used first at Ypres in July 1917 against British soldiers. Although outlawed internationally in 1925, it was used by Iraq against Iran in the 1980s and perhaps by the Sudanese army in the 1990s. Mustard gas functions by dissolving readily in body lipids and then alkylating biological nucleophiles such as R_2NH or ROH, deactivating them and releasing HCl.

A. (1.5 min) Draw a mechanism with curved arrows to show how PCl_3 converts an alcohol to an alkyl chloride.

B. (6 min) Give three fundamental reasons to explain why mustard gas is a much faster in alkylating a nucleophile like ROH than 1,5-dichloropentane is.

8. (3.5 min) Explain briefly why dilute ^{13}C double labeling NMR experiments are useful for biosynthetic studies.

(Answer on back of this page)