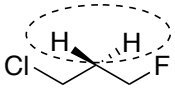
Section: A-Hudson B-Katz Name_____

CH241 Exam 3

Question 1. If the molecular ion peak for a compound is an odd number, it suggests that the compound contains what?

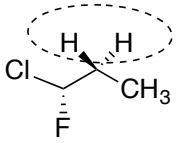
The compound contains at least one nitrogen atom (1, 3, 5, or any odd number of N's)

Question 2. For each compound below, identify whether the circled hydrogen atoms are homotopic, enantiotopic, or diastereotopic.

a) 

Answer:

enantiotopic

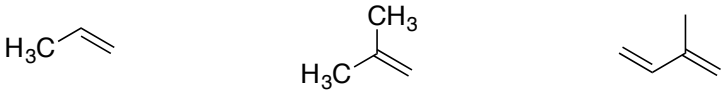
b) 

Answer:

diasteriotopic

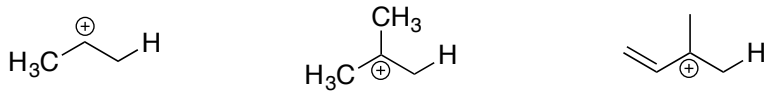
Question 3. Addition of HBr to the following olefins occurs at very different rates. Give a clear and concise explanation for the relative rate trend shown below. *You may include chemical structures to enhance your answer.*

Slowest ⟶ *Fastest*



Your explanation:

The rate of protonation correlates with the stability of the carbocation intermediate that is generated:



least stable ⟶ *most stable*

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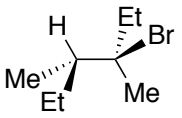
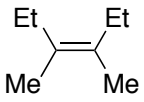
Question 4. Identify the major product(s) of the following reactions. In the small box, identify the reaction type (S_N2, S_N1, E2, E1, olefin Addition). Be sure to pay close attention to stereochemistry where appropriate.



$NaOC(CH_3)_3$

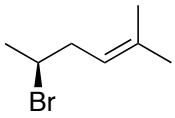
$HOC(CH_3)_3$

Product:



reaction type:

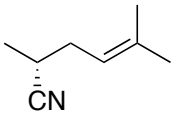
E2



NaCN

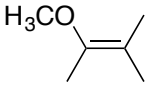
acetone

Product:



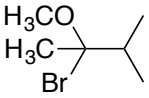
reaction type:

S_N2



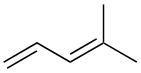
HBr

Product:



reaction type:

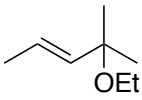
Addition



H^+

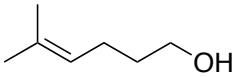
EtOH

Product (Formula = $C_8H_{16}O$):



reaction type:

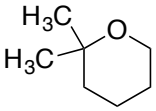
Addition



H^+

EtOH

Product (Formula = $C_7H_{14}O$):



reaction type:

Addition

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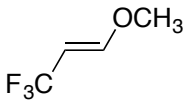
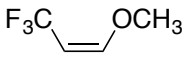
Question 5. What information from a ^{1}H NMR spectrum could be used to easily distinguish the two olefin isomers shown below? *Circle your answer and provide an explanation.*

A) Chemical Shift
B) Multiplicity
C) Coupling Constants
D) Integration

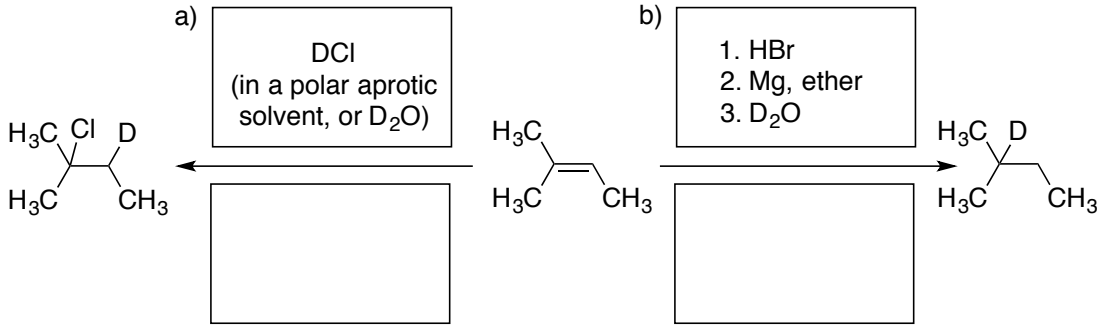




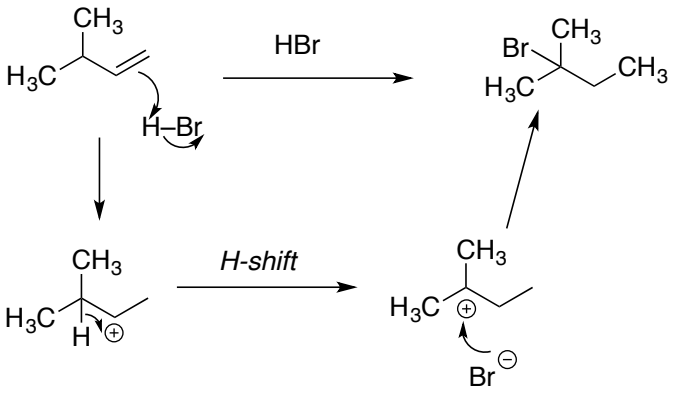
Explain your answer:

The coupling constant for the olefinic hydrogens will be in the 6-12 Hz range for the cis-olefin and 12-18 Hz for the trans-olefin.

Question 6. Suggest a synthetic route from 2-methyl-2-butene to the deuterium-labeled compounds shown below. *Multiple steps may be needed – leave unused boxes blank.*



Question 7. Provide a complete mechanism for the following transformation, and make sure to include all relevant intermediates.



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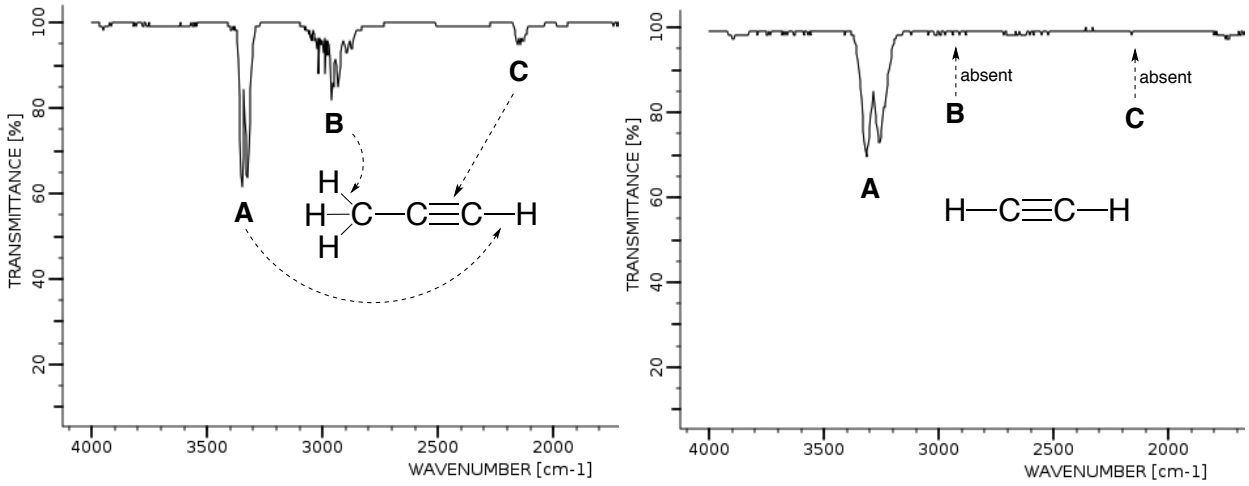
Question 8. Below are portions of the IR spectra for 1-propyne (left) and acetylene (right).

a) On the left spectrum, draw arrows connecting the absorbances marked **A**, **B**, and **C** and the functional group(s) on 1-propyne that cause those absorbances.



b) Why is absorbance **B** absent in the second spectrum?

There are no C_{sp3}-H bonds in actetylene.

c) Why is absorbance **C** absent in the second spectrum?

There is no dipole change for the alkyne stretching vibration in actetylene.

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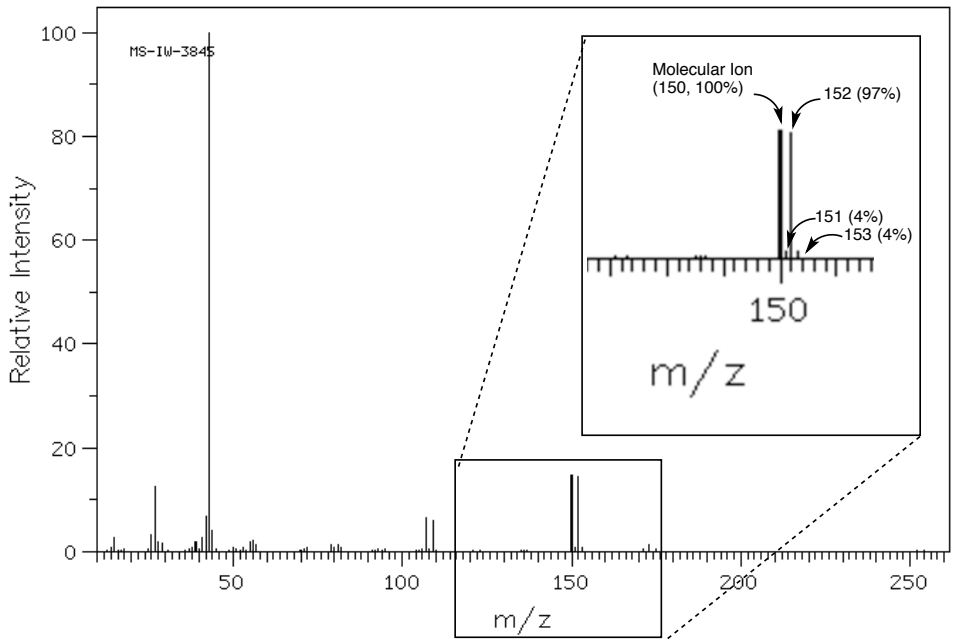
Question 9. Pages 5-7 of the exam contain MS, ^{1}H NMR, ^{13}C NMR, and IR spectra for a single unknown compound. First answer the questions related to the individual spectra and then solve the complete structure.

MS



a) The nearly identical intensity of the signal at 152 m/z to the signal at 150 m/z on the mass spectrum indicates the presence of what?

One bromine atom

b) The relative intensity of the signal at 151 m/z (relative to the signal at 150 m/z) can be used to estimate what?

The number of carbon atoms (due to ^{13}C isotope abundance)

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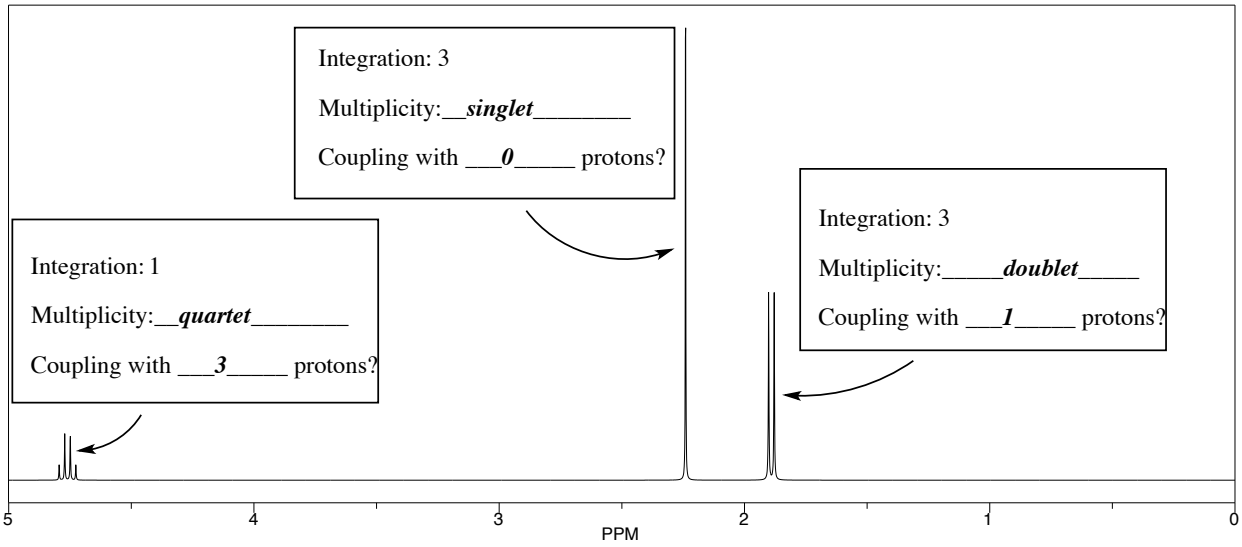
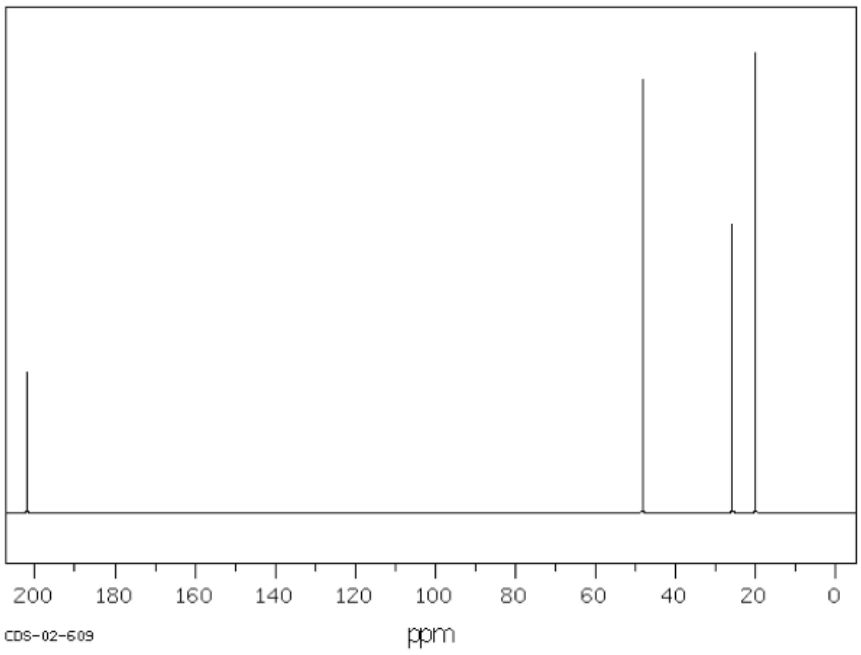


^{1}H NMR

c) In the box next to each peak on the ^{1}H NMR spectrum above, indicate the multiplicity and the number of protons coupling to that signal.

d) How many distinct proton environments are in the compound? _____***3***_____

^{13}C NMR



e) How many distinct carbon environments does the compound have? _____***4***_____

f) The peak at 200 ppm suggests the presence of what? ***A ketone or aldehyde (carbonyl)***

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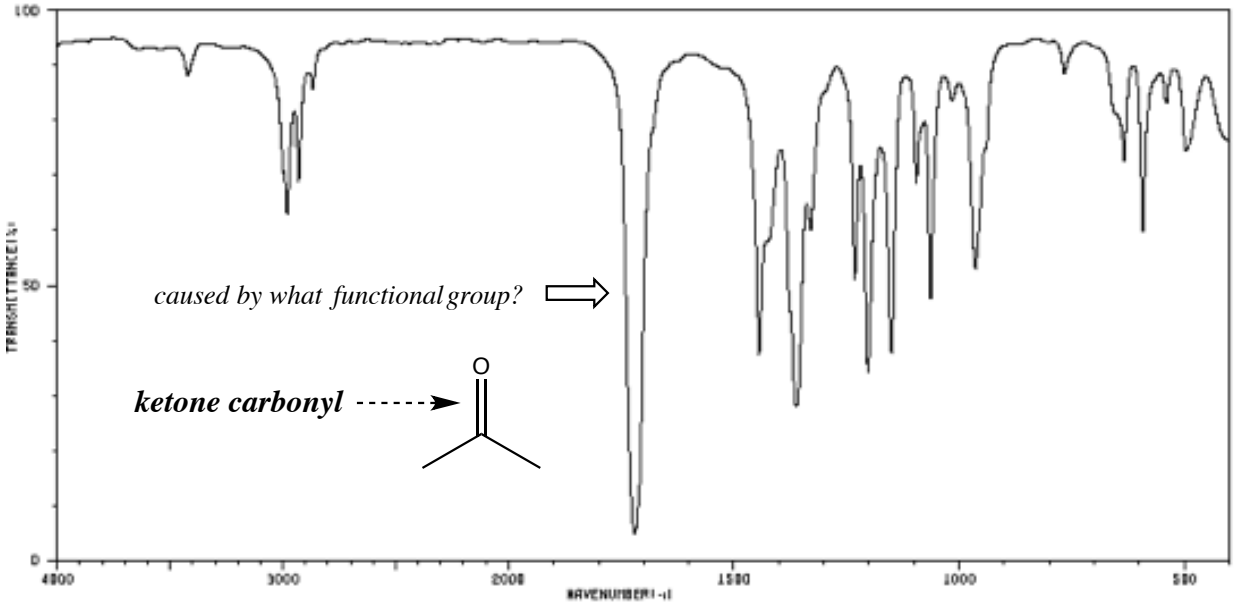
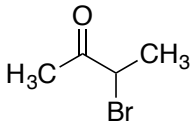
IR



g) Draw the structure of the unknown compound below. On the IR spectrum (above), draw the functional group that causes the IR absorption at 1720 cm^{-1} (marked with the arrow).



3-bromo-2-butanone

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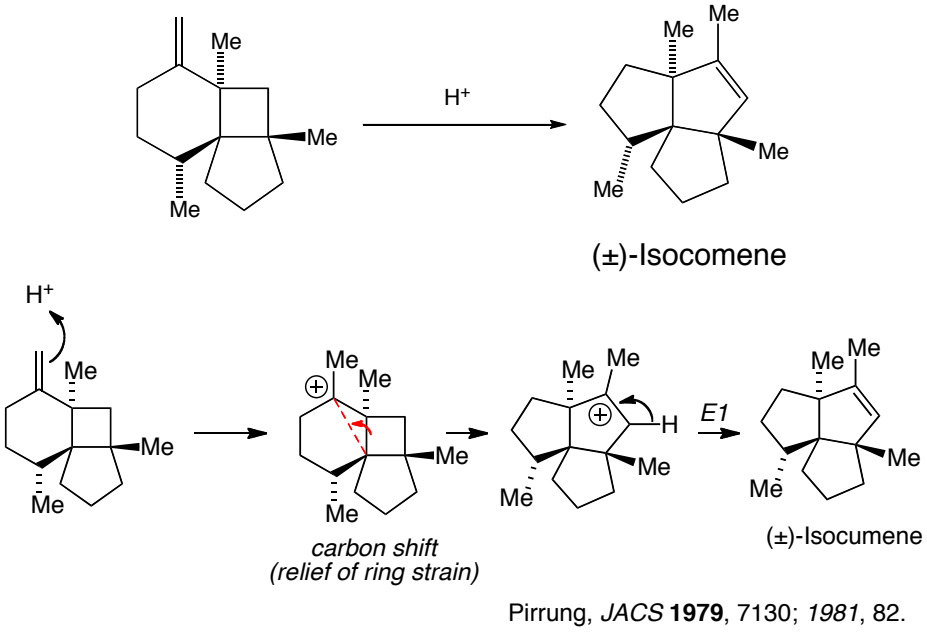
Extra credit. Isocomene is a naturally occurring toxin found in the plant goldenrod that was synthesized by Michael Pirrung at UC Berkeley in 1979. Provide a complete mechanism for the (very clever!) key transformation in the synthesis, which is shown below.



Pirrung, *JACS* **1979**, 7130; *1981*, 82.