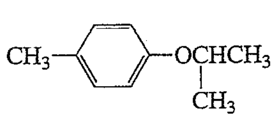
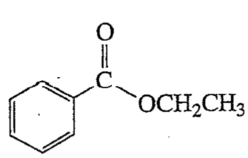
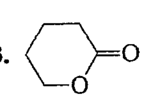
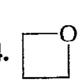
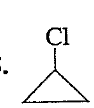
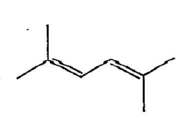
SOME IMPORTANT THINGS TO REMEMBER

- **NMR spectroscopy** identifies the carbon–hydrogen framework of an organic compound.
- Each set of chemically equivalent protons produces a signal, so the number of signals in an ^{1}H NMR spectrum indicates the number of different kinds of protons in a compound.
- The **chemical shift** (δ), which is independent of the operating frequency of the spectrometer, is a measure of how far the signal is from the reference TMS signal.
- The larger the magnetic field sensed by the proton, the higher the frequency of its signal.
- The electron density of the environment in which the proton is located **shields** the proton from the applied magnetic field. Therefore, a proton in an electron-dense environment shows a signal at a lower frequency than a proton near electron-withdrawing groups.
- Low-frequency signals have small δ (ppm) values; high-frequency signals have large δ values. Thus, the position of a signal indicates the kind of proton(s) responsible for the signal and the kinds of neighboring substituents.
- In a similar environment, the chemical shift of a methine proton is at a higher frequency than that of methylene protons, which is at a higher frequency than that of methyl protons.
- **Integration** tells us the relative number of protons that produce each signal.
- **Diamagnetic anisotropy** causes unusual chemical shifts for hydrogens bonded to carbons that form π bonds.
- The **multiplicity** of a signal indicates the number of protons bonded to adjacent carbons. Multiplicity is described by the **$N+1$ rule,** where N is the number of equivalent protons bonded to an adjacent carbon.
- Coupled protons split each other's signal.
- A **splitting diagram** describes the splitting pattern obtained when a signal is split by more than one set of protons.
- The **coupling constant** (J), which is independent of the operating frequency of the spectrometer, is the distance between two adjacent peaks of a split NMR signal. Coupled protons have the same coupling constant.
- The coupling constant for trans alkene protons is greater than that for cis alkene protons.
- When two different sets of protons split a signal, the multiplicity of the signal is determined by using the $N+1$ rule separately $(N_a+1)(N_b+1)$ for each set of protons when the coupling constants for the two sets are different. When the coupling constants are similar, the $N+1$ rule is applied to both sets at the same time.
- The chemical shift of a proton bonded to an O or to an N depends on the extent to which the proton is hydrogen bonded.
- In the presence of trace amounts of acid or base, protons bonded to oxygen undergo **proton exchange.** In that case, the signal for a proton bonded to an O is not split and does not split the signal of adjacent protons.
- The number of signals in a ^{13}C NMR spectrum corresponds to the number of different kinds of carbons in the compound. Carbons in electron-rich environments produce low-frequency signals, whereas carbons close to electron-withdrawing groups produce high-frequency signals.
- ^{13}C NMR signals are not split by attached protons unless the spectrometer is run in a proton-coupled mode.
- A DEPT ^{13}C NMR spectrum tells whether a signal is produced by CH_3, CH_2, CH, or C.
- NMR (known in medical applications as **MRI**) is an important tool in medical diagnosis because it allows internal structures to be examined without surgery or harmful X-rays.
- **2-D NMR** and **X-ray crystallography** are techniques that can be used to determine the structures of large molecules.

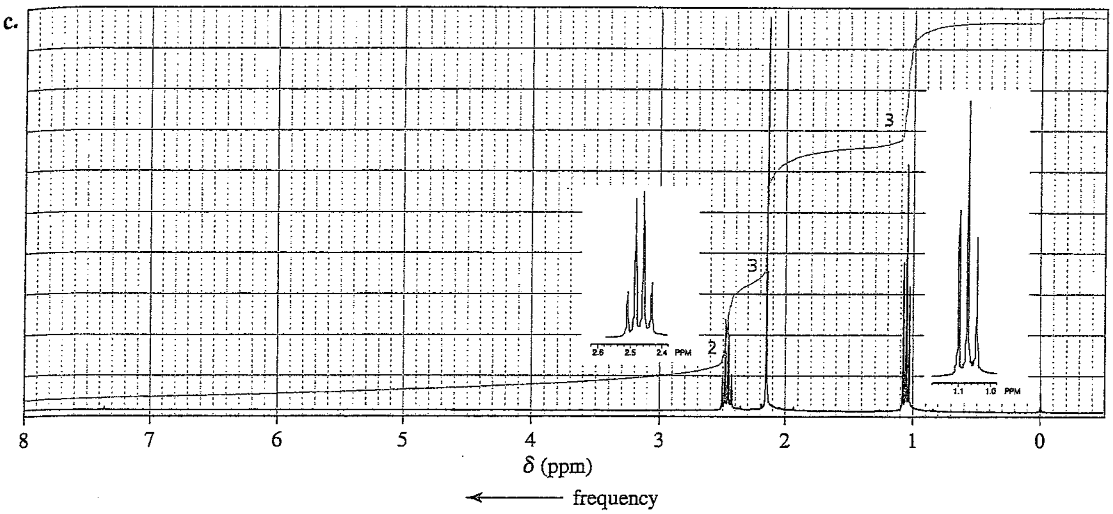
PROBLEMS

46. How many signals are produced by each of the following compounds in its

a. ^{1}H NMR spectrum? b. ^{13}C NMR spectrum?

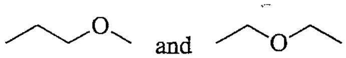
1. 
2. 
3. 
4. 
5. 
6. 

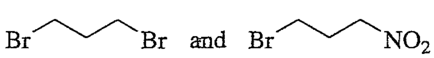
c.

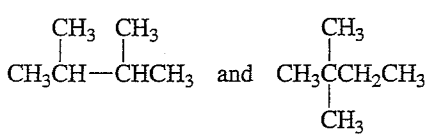


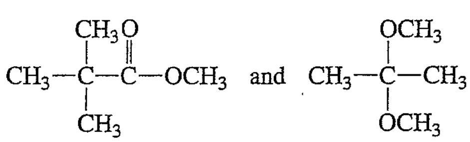
50. Determine the ratios of the chemically nonequivalent protons in a compound if the steps of the integration curves measure 40.5, 27, 13, and 118 mm, from left to right across the spectrum. Draw the structure of a compound whose ^{1}H NMR spectrum would show these integrals in the observed order.

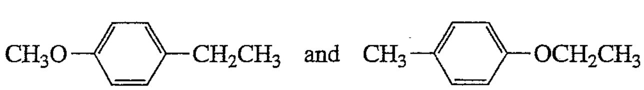
51. How could ^{1}H NMR distinguish between the compounds in each of the following pairs?

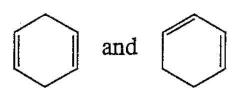
a. 

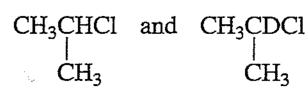
b. 

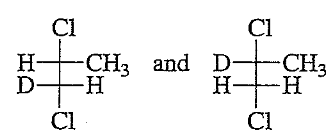
c. 

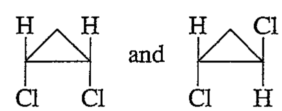
d. 

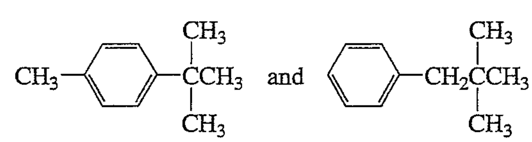
e. 

f. 

g. 

h. 

i. 

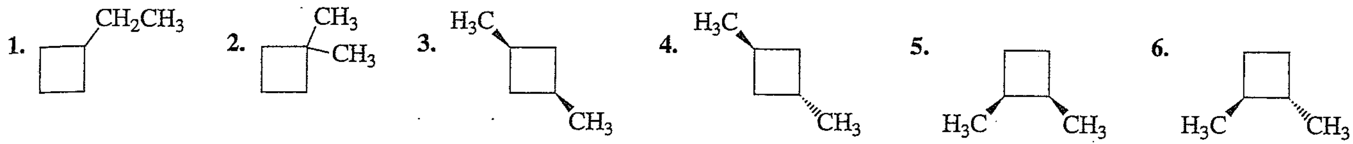
j. 

52. Answer the following questions:

a. What is the relationship between chemical shift in ppm and operating frequency?
b. What is the relationship between chemical shift in hertz and operating frequency?
c. What is the relationship between coupling constant in hertz and operating frequency?
d. How does the operating frequency in NMR spectroscopy compare with the operating frequency in IR and UV/Vis spectroscopy?

54. How many signals are produced by each of the following compounds in its

a. ^{1}H NMR spectrum? b. ^{13}C NMR spectrum?



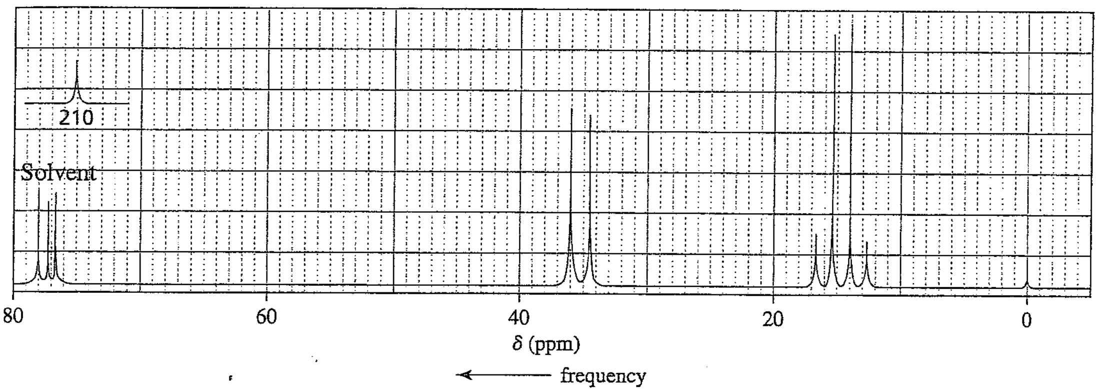
55. Identify each of the following compounds from the ^{1}H NMR data and molecular formula. The number of hydrogens responsible for each signal is shown in parentheses.

a. $C_4H_8Br_2$ 1.97 ppm (6) singlet
3.89 ppm (2) singlet

b. C_8H_9Br 2.01 ppm (3) doublet
5.14 ppm (1) quartet
7.35 ppm (5) broad singlet

c. $C_5H_{10}O_2$ 1.15 ppm (3) triplet
1.25 ppm (3) triplet
2.33 ppm (2) quartet
4.13 ppm (2) quartet

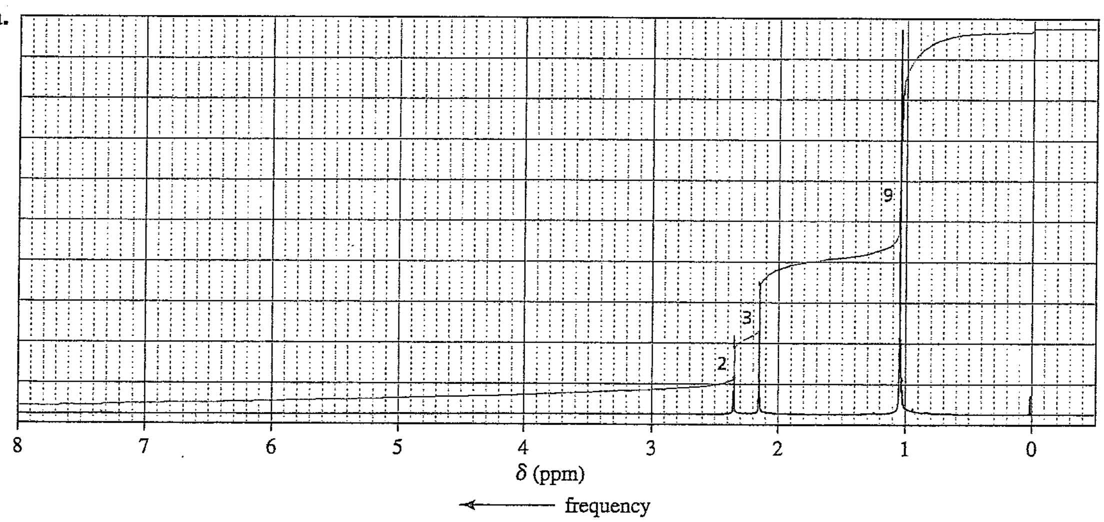
56. Identify the compound with molecular formula $C_7H_{14}O$ that gives the following proton-coupled ^{13}C NMR spectrum:



57. Compound **A**, with molecular formula C_4H_9Cl, shows two signals in its ^{13}C NMR spectrum. Compound **B**, an isomer of compound **A**, shows four signals, and in the proton-coupled mode, the signal farthest downfield is a doublet. Identify compounds **A** and **B**.

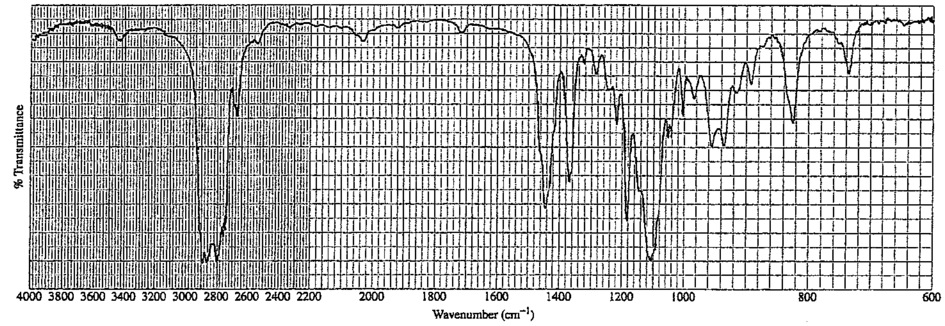
58. The ^{1}H NMR spectra of three isomers with molecular formula $C_7H_{14}O$ are shown here. Which isomer produces which spectrum?

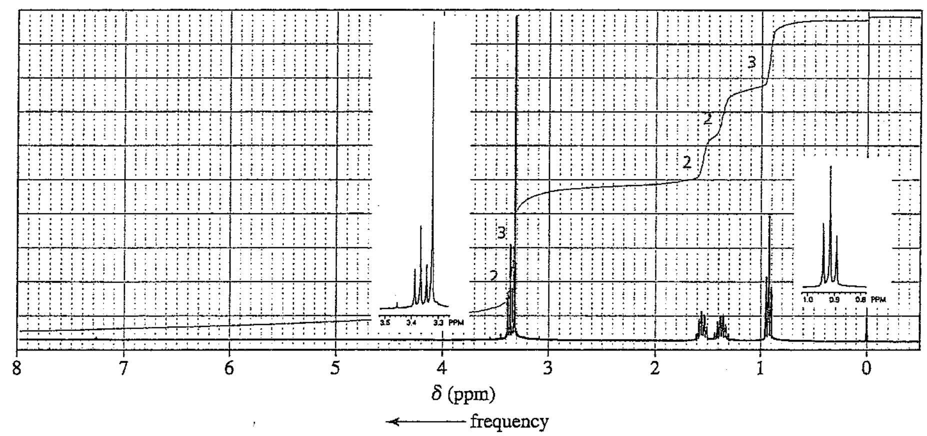
a.



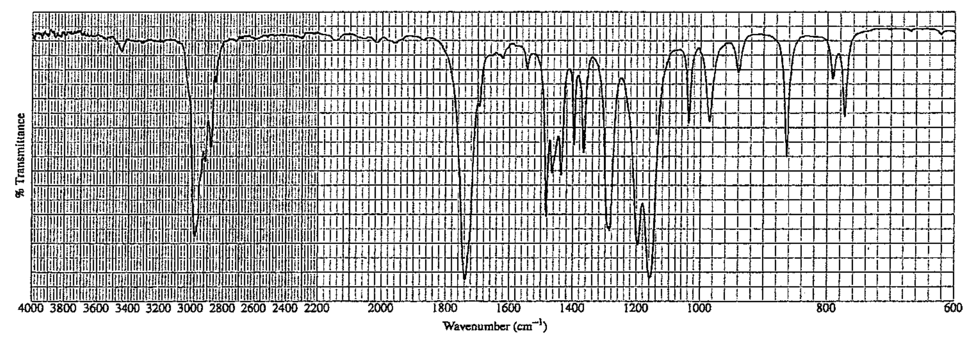
62. Determine the structure of each of the following unknown compounds based on its molecular formula and its IR and ^1H NMR spectra.

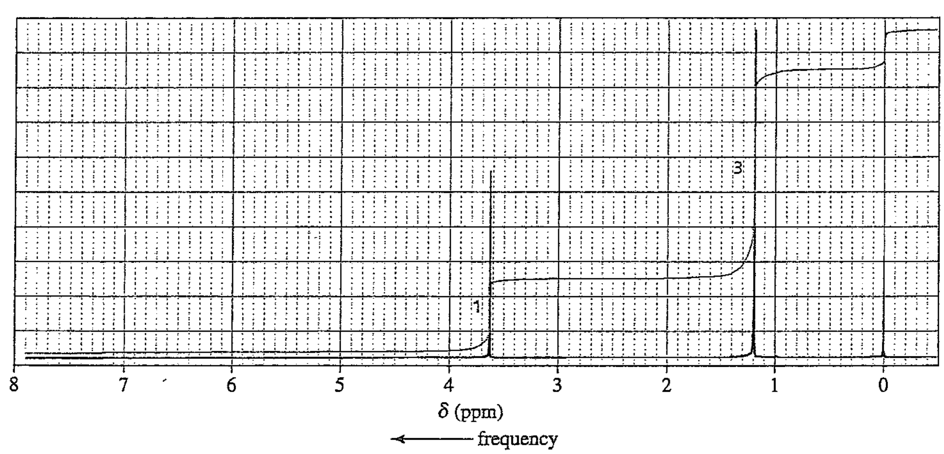
a. $C_5H_{12}O$





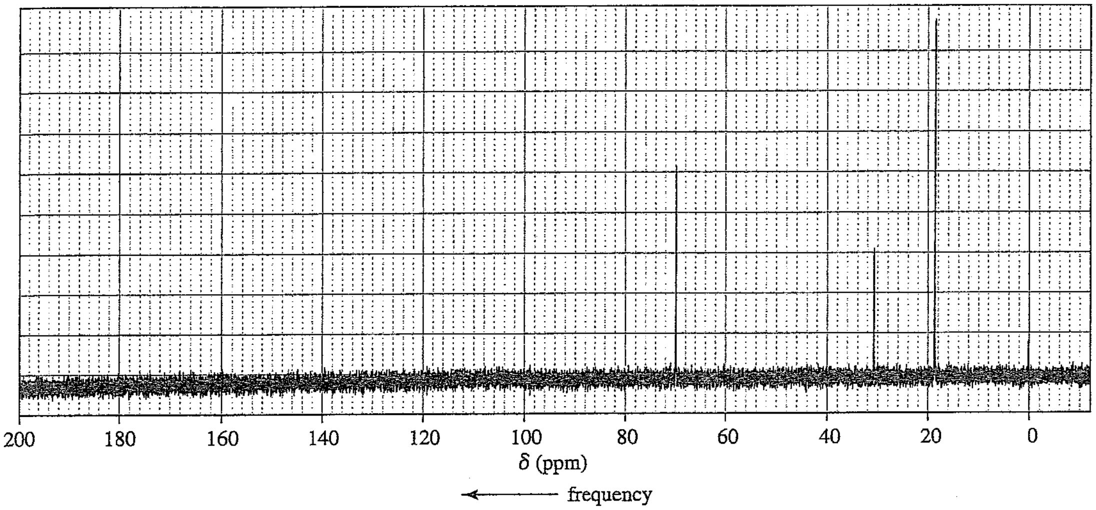
b. $C_6H_{12}O_2$



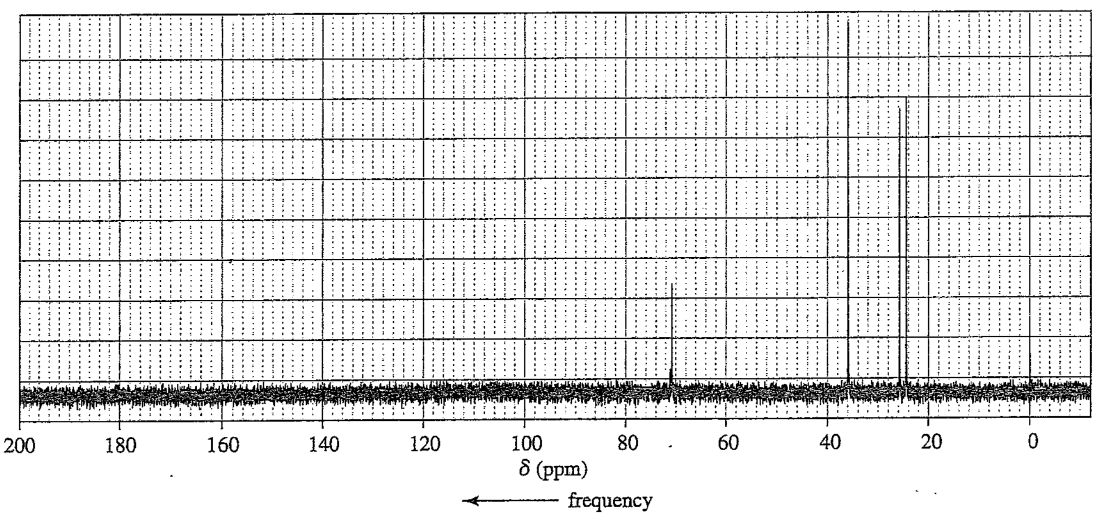


63. Determine the structure of each of the following compounds based on its molecular formula and its ^{13}C NMR spectrum:

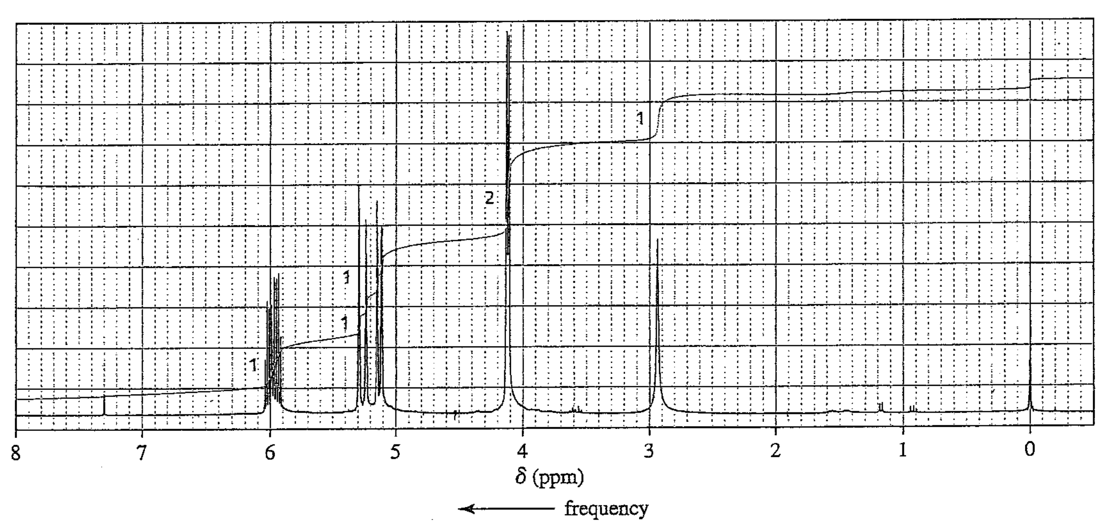
a. $C_4H_{10}O$



b. $C_6H_{12}O$



64. The ^1H NMR spectrum of 2-propen-1-ol is shown here. Indicate the protons in the molecule that give rise to each of the signals in the spectrum.



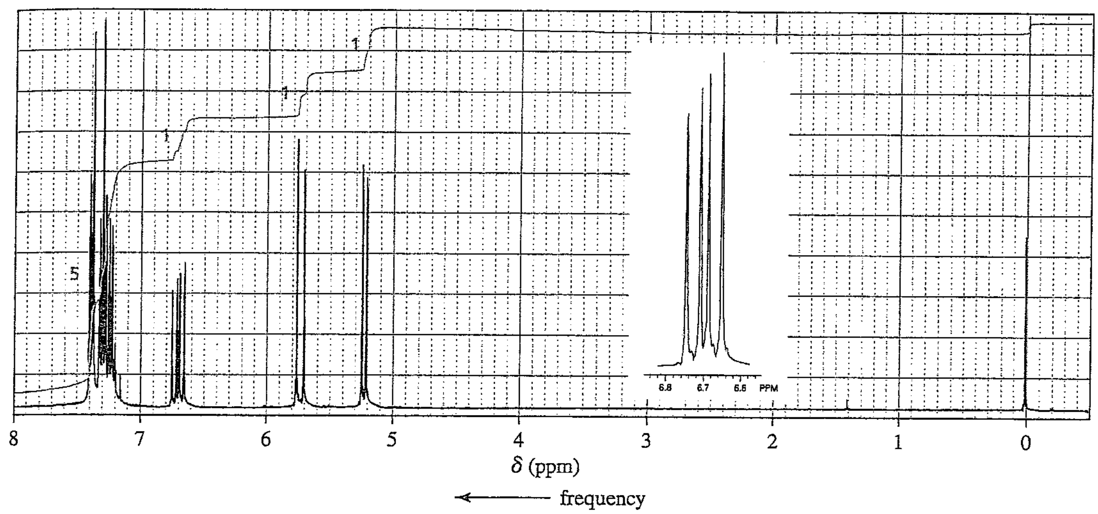
68. Sketch the following spectra that would be obtained for 2-chloroethanol:

a. The ^{1}H NMR spectrum for an anhydrous sample of the alcohol.
b. The ^{1}H NMR spectrum for a sample of the alcohol that contains a trace amount of acid.
c. The ^{13}C NMR spectrum.
d. The proton-coupled ^{13}C NMR spectrum.
e. The four parts of a DEPT ^{13}C NMR spectrum.

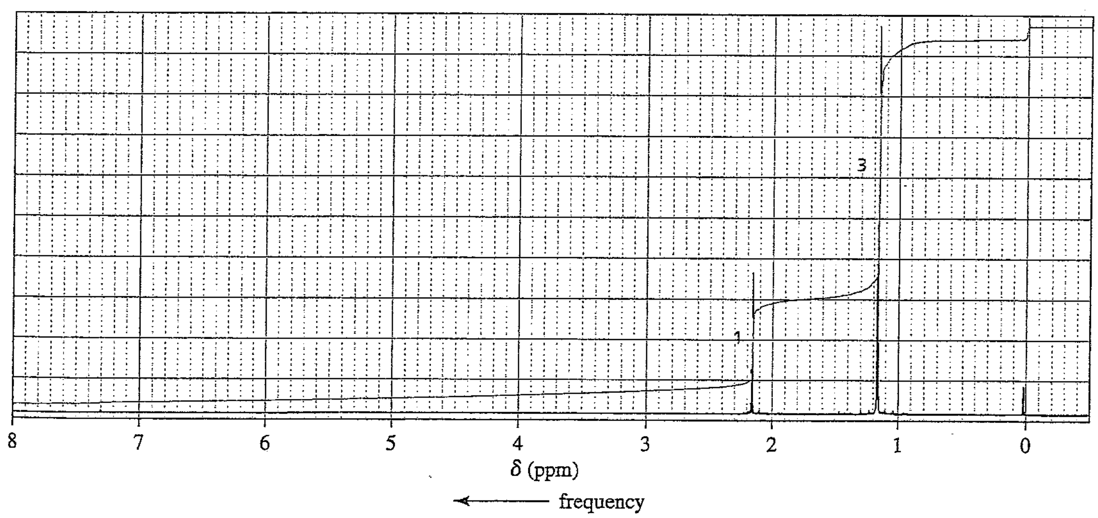
69. How can ^{1}H NMR be used to prove that the addition of HBr to propene follows the rule that says that the electrophile adds to the sp^2 carbon bonded to the greater number of hydrogens?

70. Identify each of the following compounds from its molecular formula and its ^{1}H NMR spectrum:

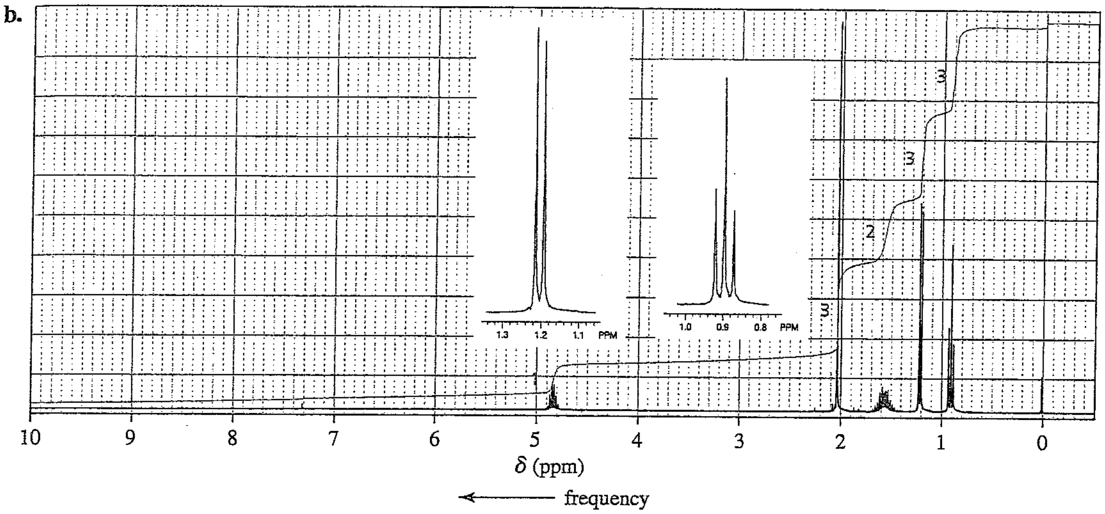
a. C_8H_8



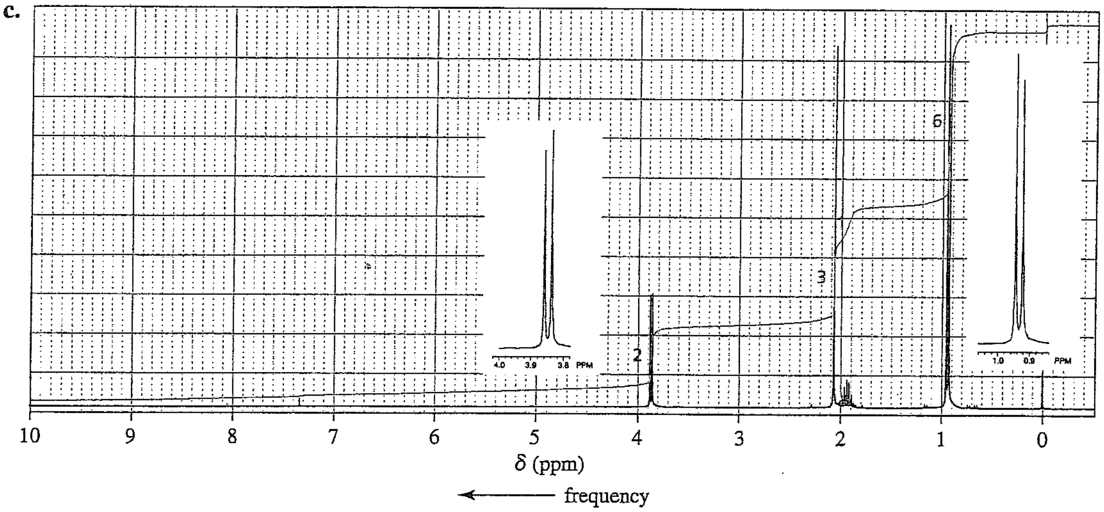
b. $C_6H_{12}O$



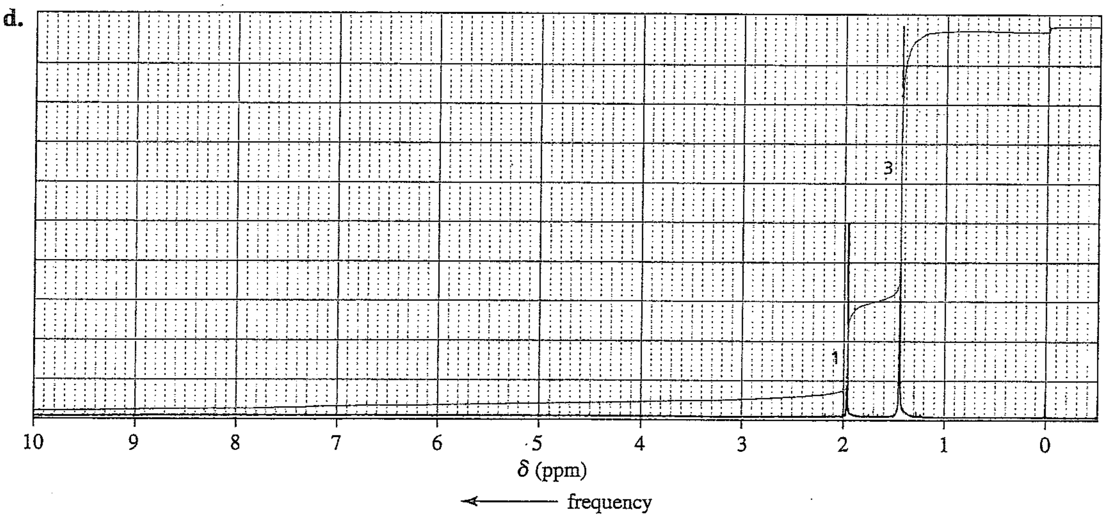
b.



c.

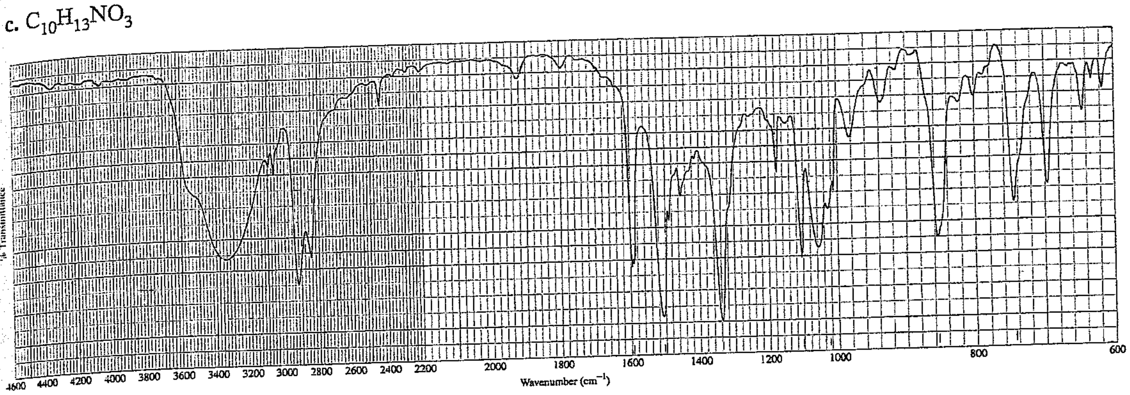


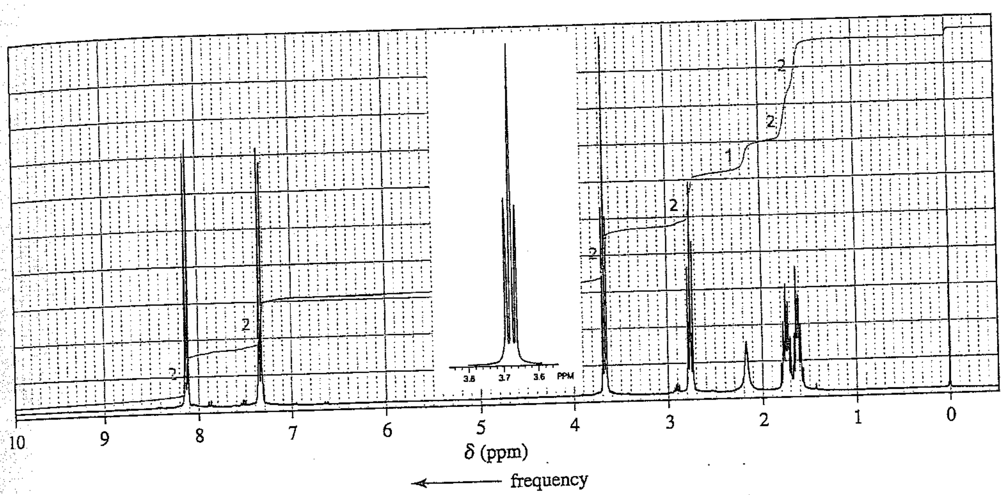
d.



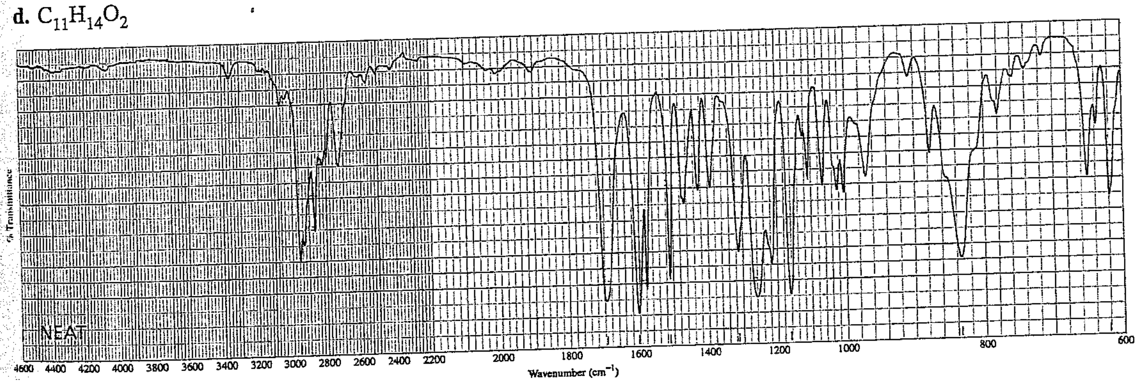
74. When compound **A** ($C_5H_{12}O$) is treated with HBr, it forms compound **B** ($C_5H_{11}Br$). The ^1H NMR spectrum of compound **A** has one singlet (1), two doublets (3, 6), and two multiplets (both 1). (The relative areas of the signals are indicated in parentheses.) The ^1H NMR spectrum of compound **B** has a singlet (6), a triplet (3), and a quartet (2). Identify compounds **A** and **B**.

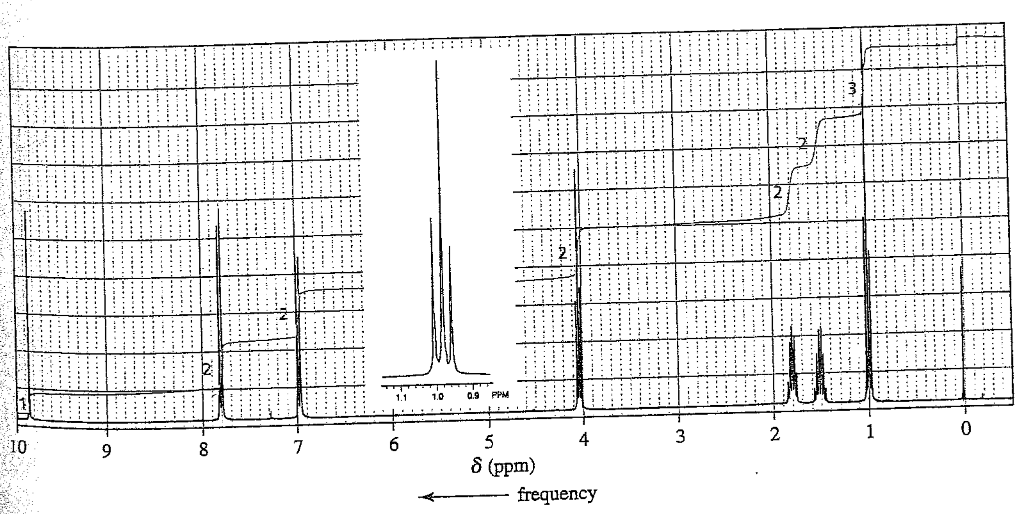
c. $C_{10}H_{13}NO_3$



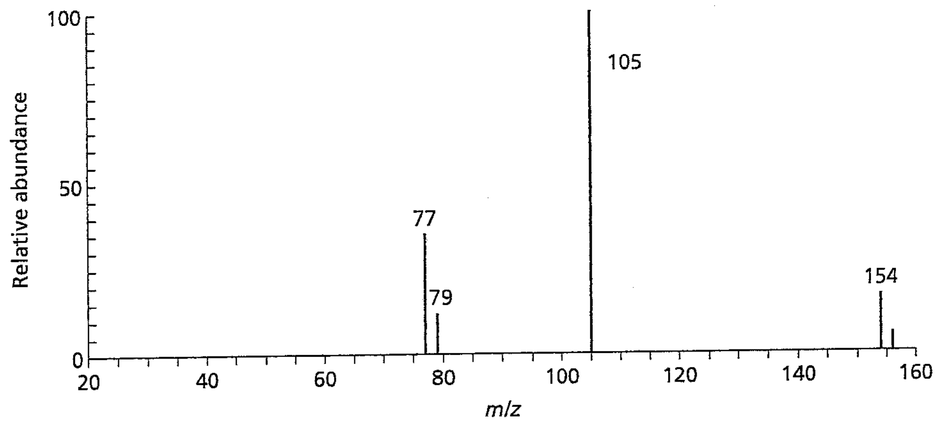


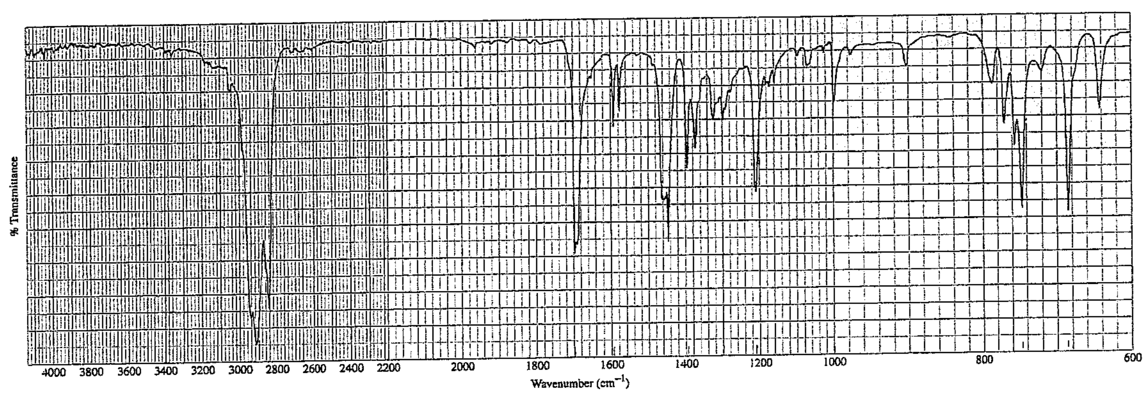
d. $C_{11}H_{14}O_2$

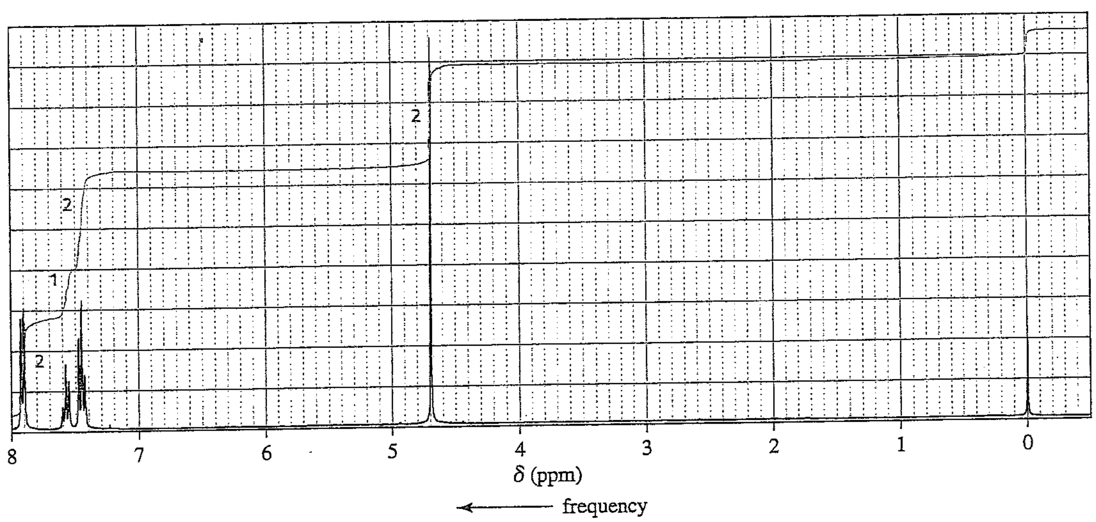




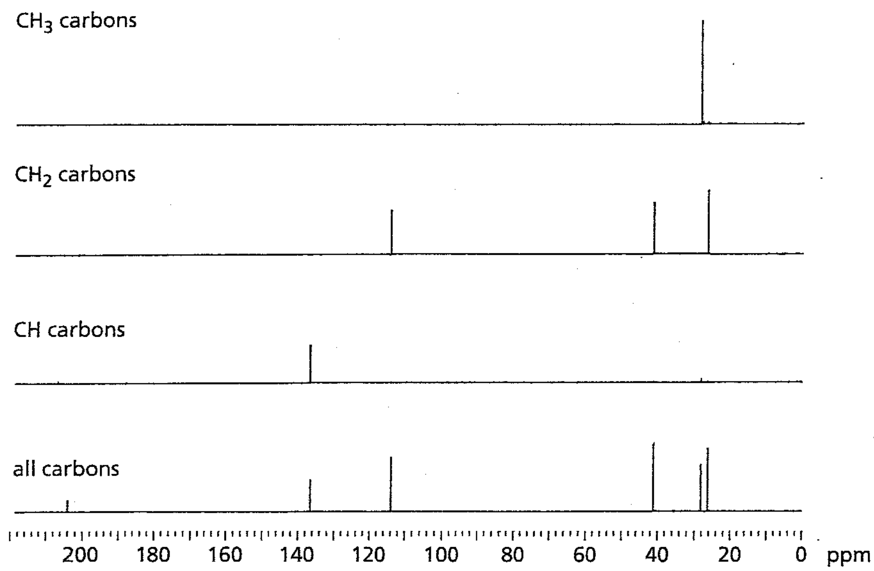
b.


100
50
0
Relative abundance
105
77
79
154
20
40
60
80
100
120
140
160
m/z

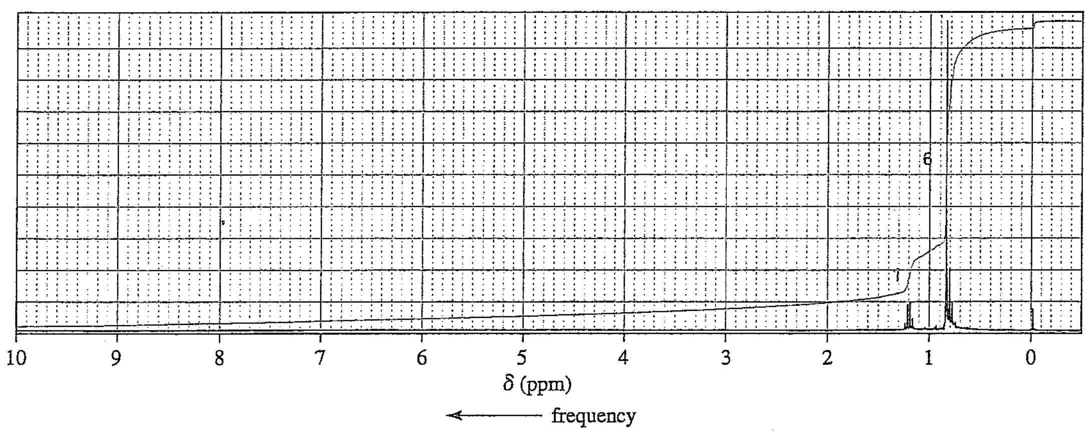

% Transmittance
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600
Wavenumber (cm⁻¹)


2
2
1
2
8 7 6 5 4 3 2 1 0
δ (ppm)
frequency

77. Identify the compound with molecular formula $C_6H_{10}O$ that is responsible for the following DEPT ^{13}C NMR spectrum:

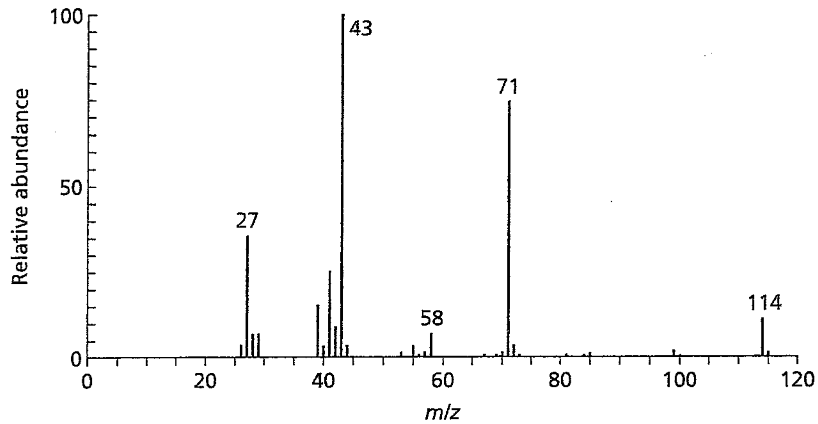


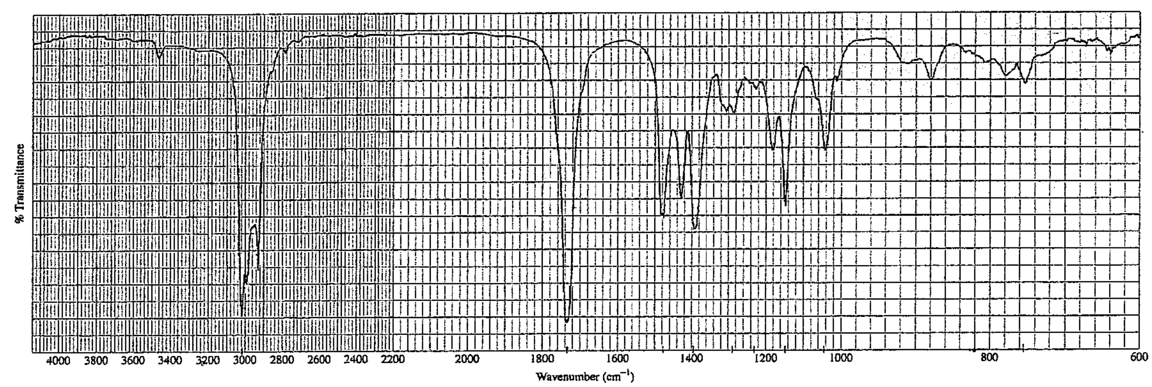
78. Identify the compound with molecular formula C_6H_{14} that is responsible for the following ^1H NMR spectrum:

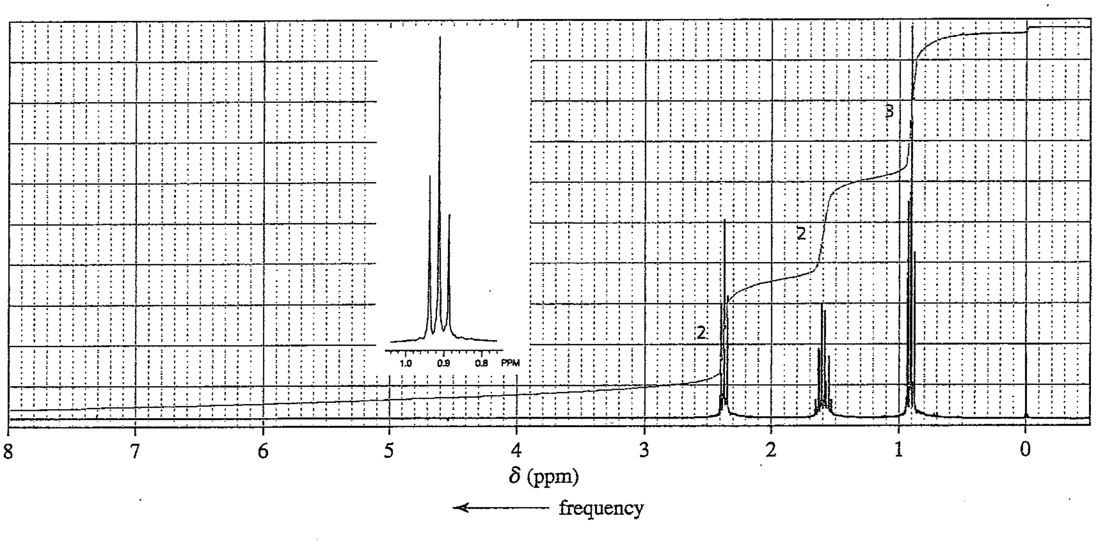


76. Determine the structure of each of the following compounds, based on the compound's mass spectrum, IR spectrum, and ^{1}H NMR spectrum:

a.

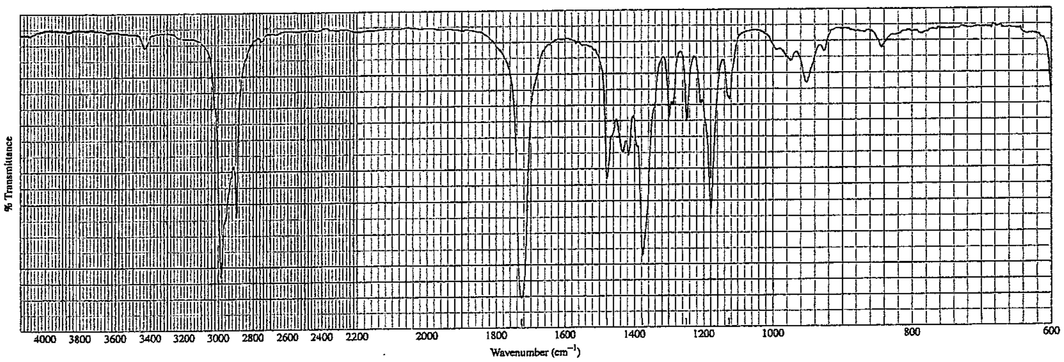


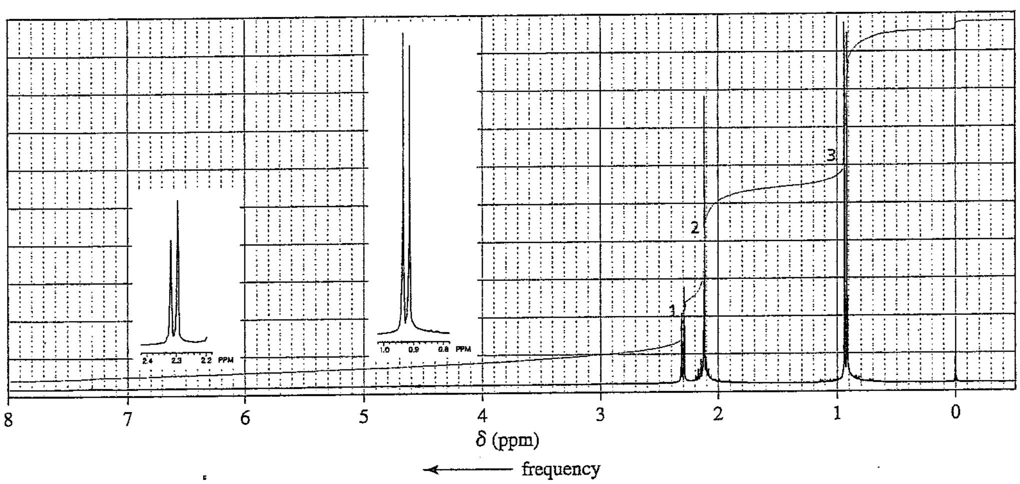




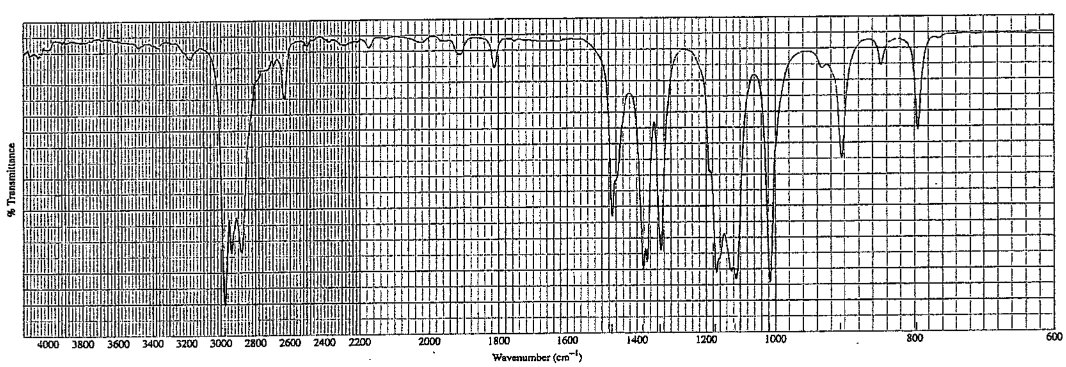
75. Determine the structure of each of the following compounds, based on its molecular formula and its IR and ^{1}H NMR spectra:

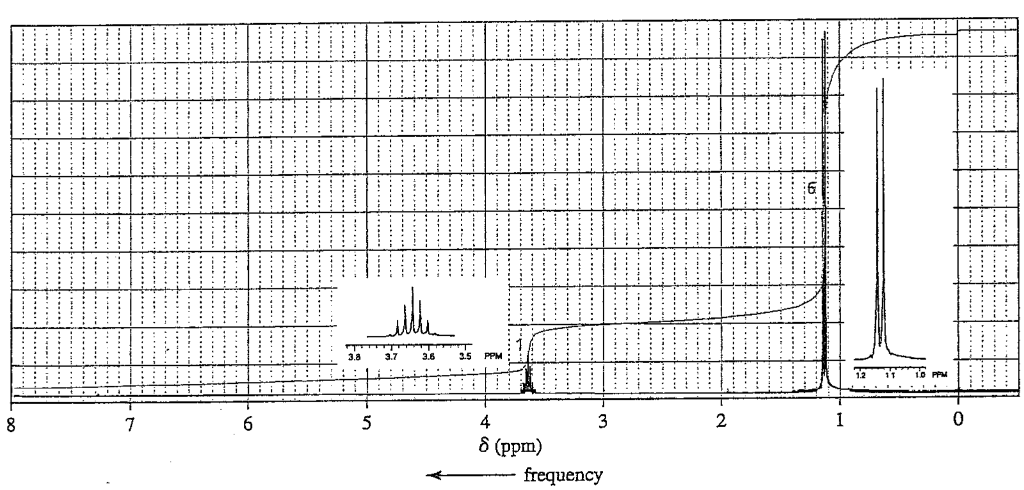
a. $C_6H_{12}O$



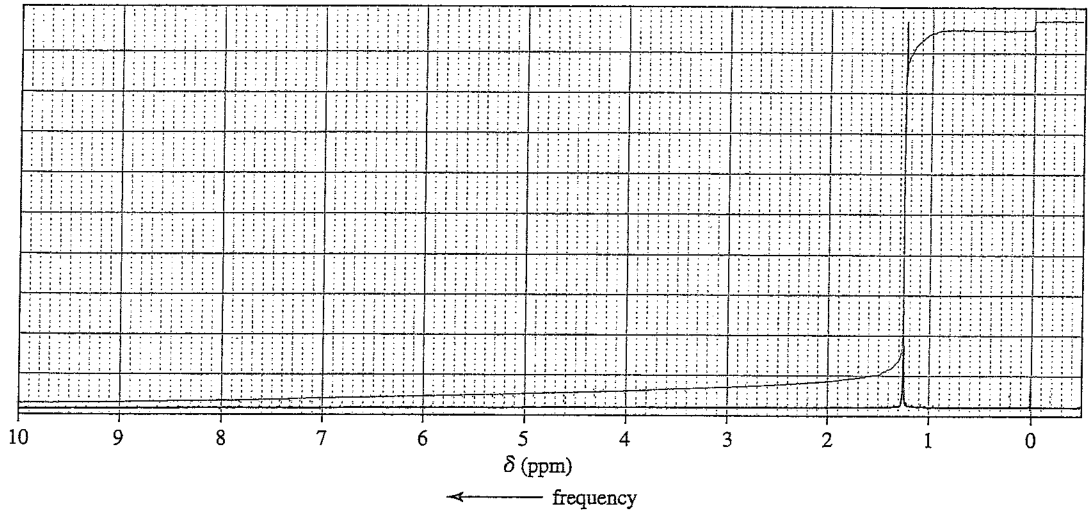


b. $C_6H_{14}O$

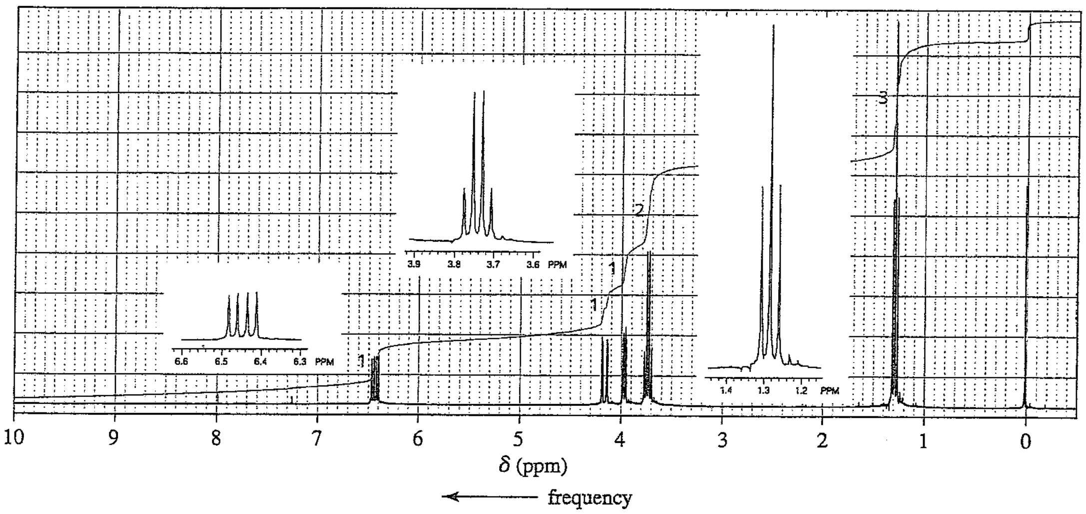




c. $C_9H_{18}O$



d. C_4H_8O

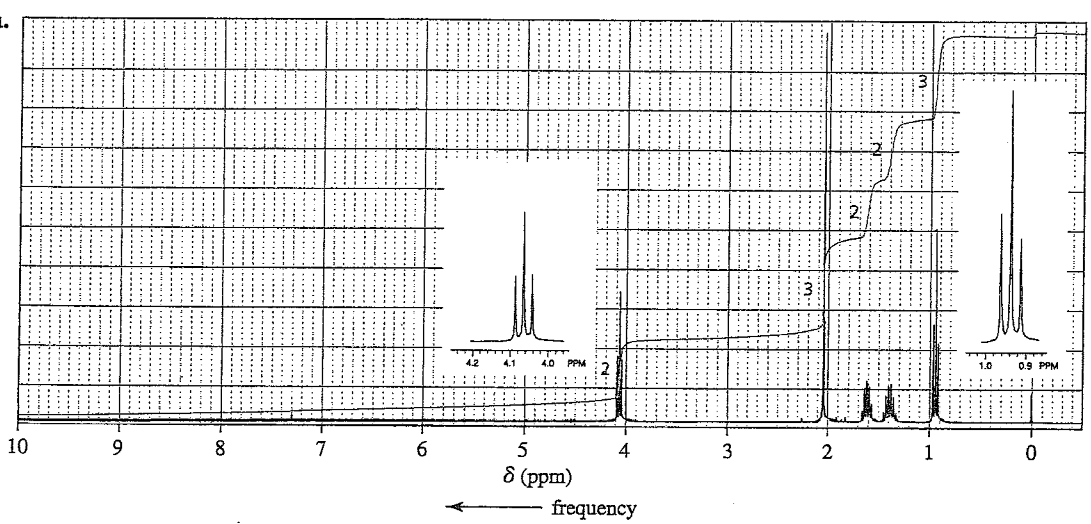


71. Dr. N. M. Arr was called in to help analyze the ^1H NMR spectrum of a mixture of compounds known to contain only C, H, and Br. The mixture showed two singlets—one at 1.8 ppm and the other at 2.7 ppm—with relative integrals of 1 : 6, respectively. Dr. Arr determined that the spectrum was that of a mixture of bromomethane and 2-bromo-2-methylpropane. What was the ratio of bromomethane to 2-bromo-2-methylpropane in the mixture?

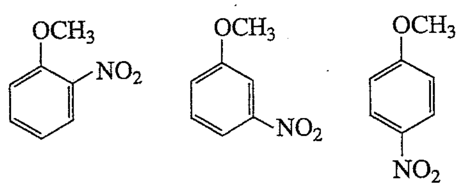
72. Calculate the amount of energy (in calories) required to flip an ^1H nucleus in an NMR spectrometer that operates at 300 MHz.

73. The following ^1H NMR spectra are for four compounds, each with molecular formula of $C_6H_{12}O_2$. Identify the compounds.

a.

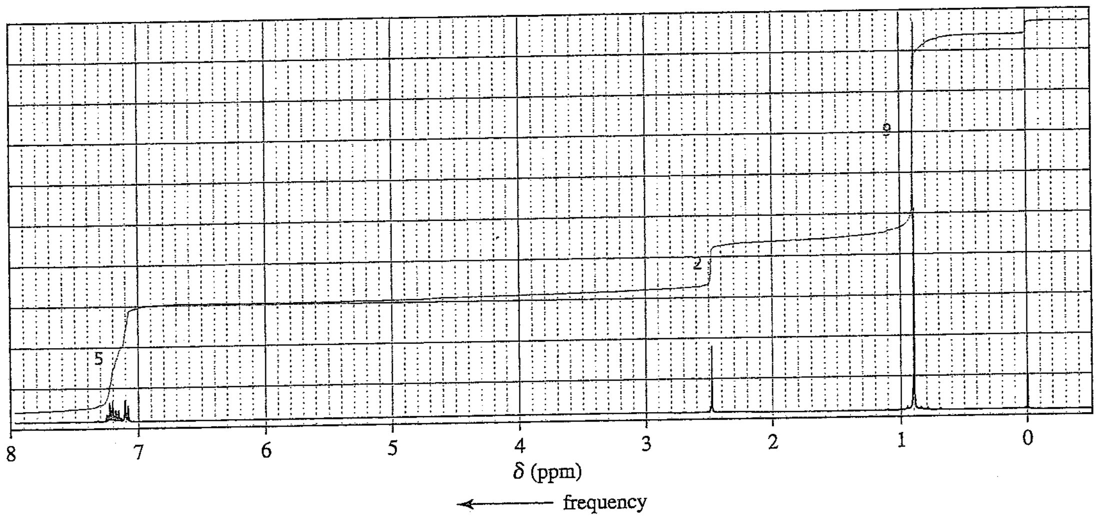


65. How can the signals in the 6.5 to 8.1 ppm region of their ^{1}H NMR spectra distinguish the following compounds?

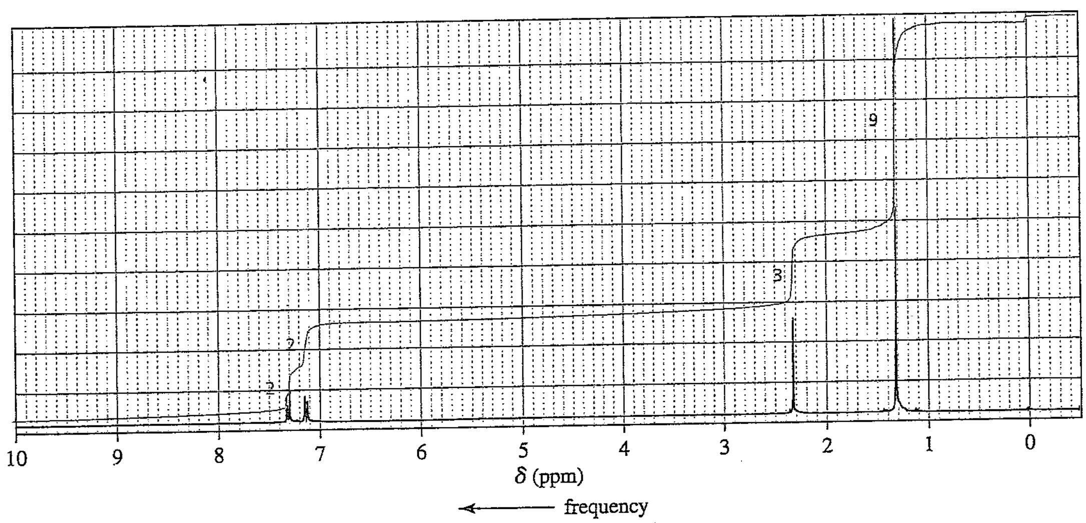


66. The ^{1}H NMR spectra of two compounds, each with molecular formula $C_{11}H_{16}$, are shown here. Identify the compounds.

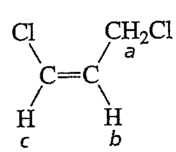
a.



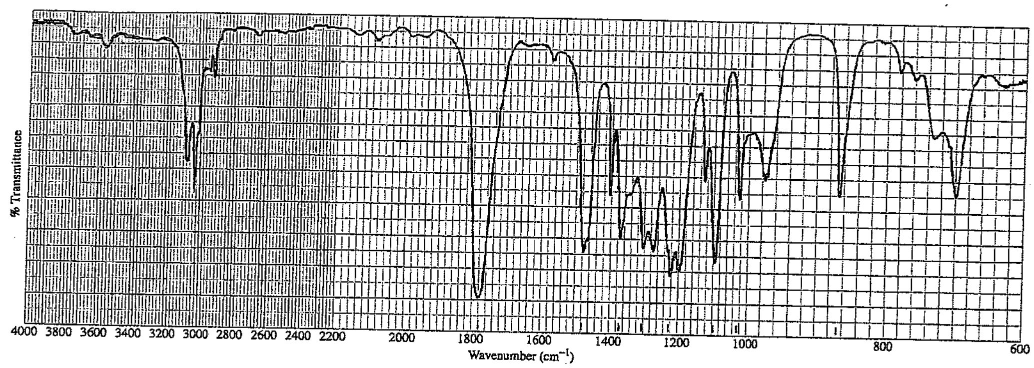
b.

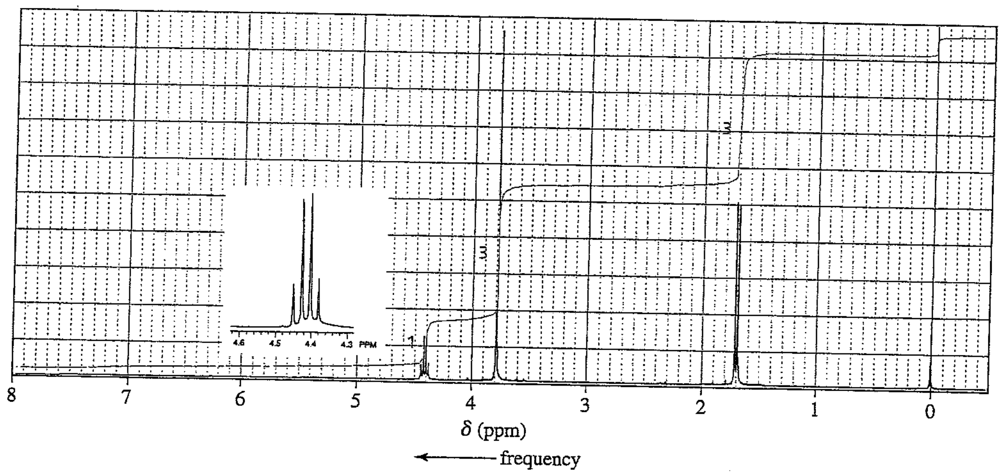


67. Draw a splitting diagram for the H_b proton if $J_{bc} = 10$ and $J_{ba} = 5$.

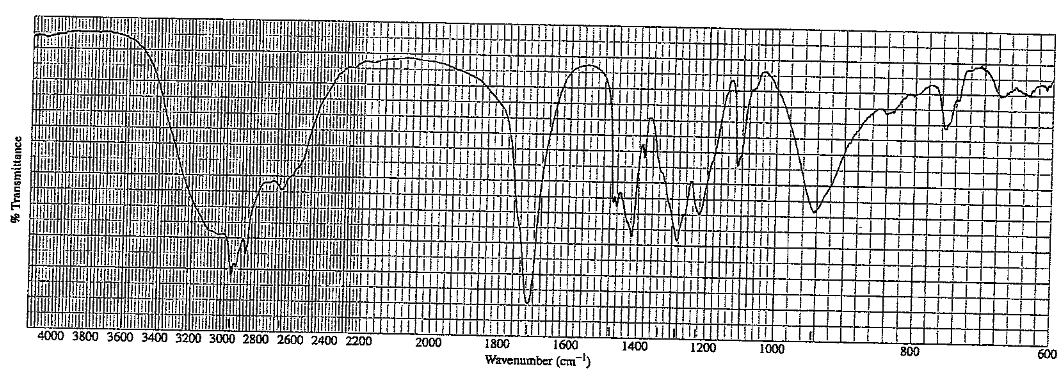


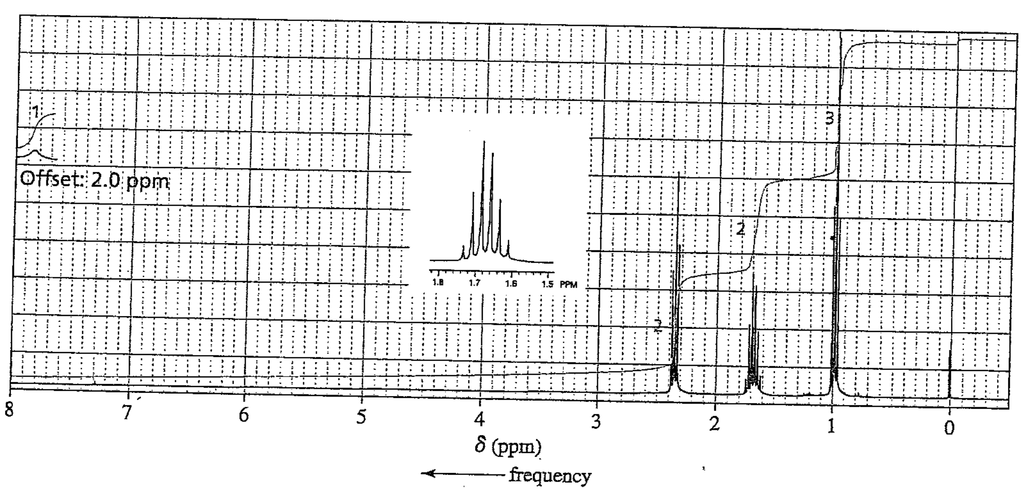
c. $C_4H_7ClO_2$



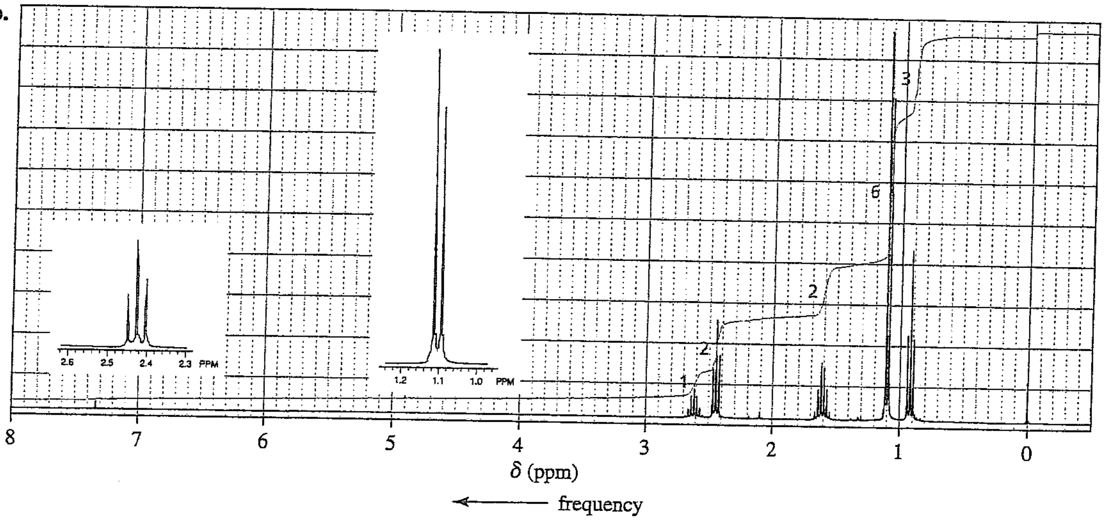


d. $C_4H_8O_2$

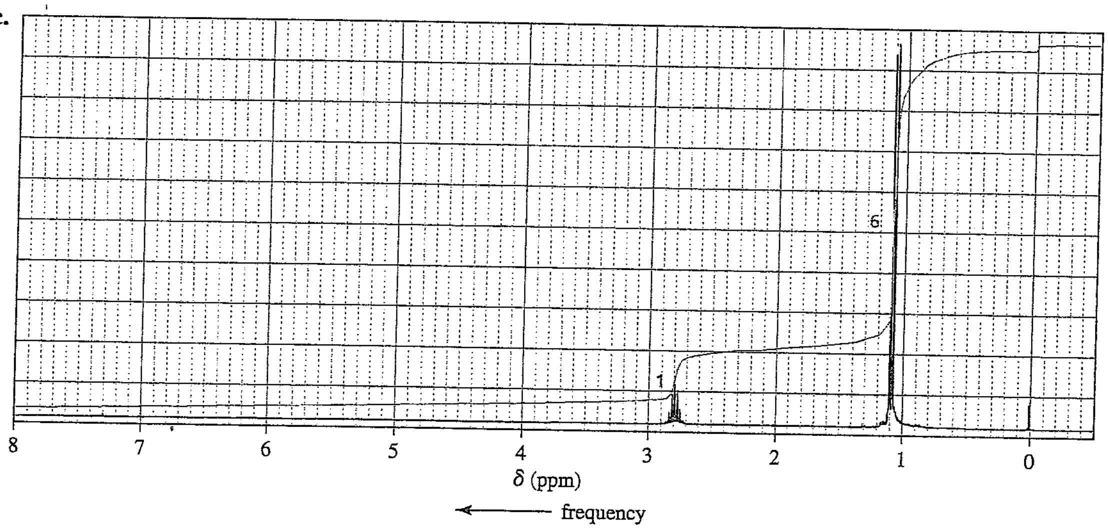




b.



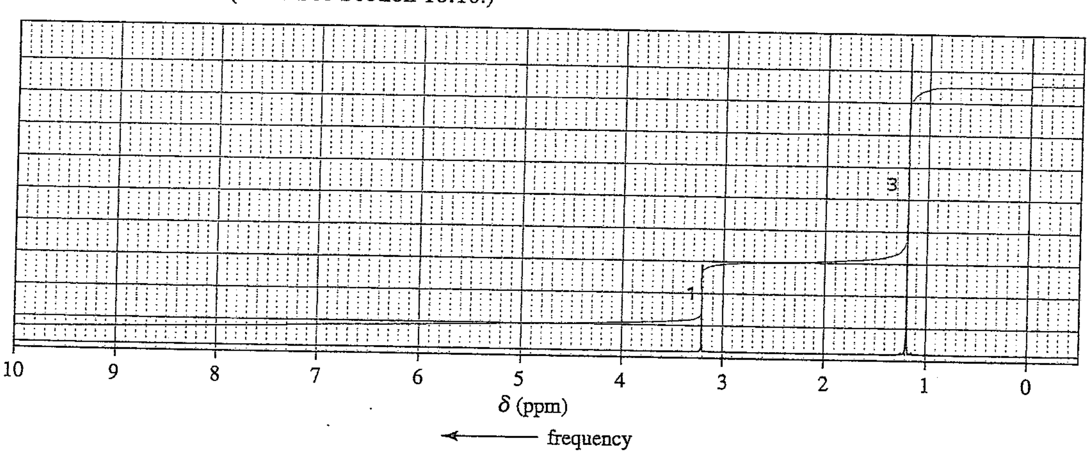
c.



59. Would it be better to use ^1H NMR or ^{13}C NMR spectroscopy to distinguish among 1-butene, *cis*-2-butene, and 2-methylpropene? Explain your answer.

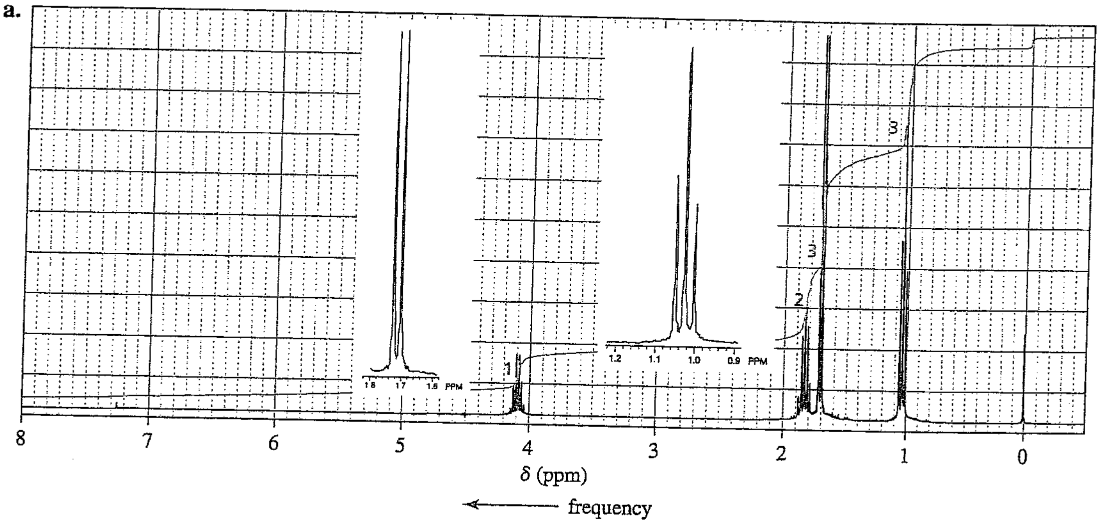
60. There are four esters with molecular formula $C_4H_8O_2$. How can they be distinguished by ^1H NMR?

61. An alkyl halide reacts with an alkoxide ion to form a compound whose ^1H NMR spectrum is shown here. Identify the alkyl halide and the alkoxide ion. (*Hint:* See Section 10.10.)

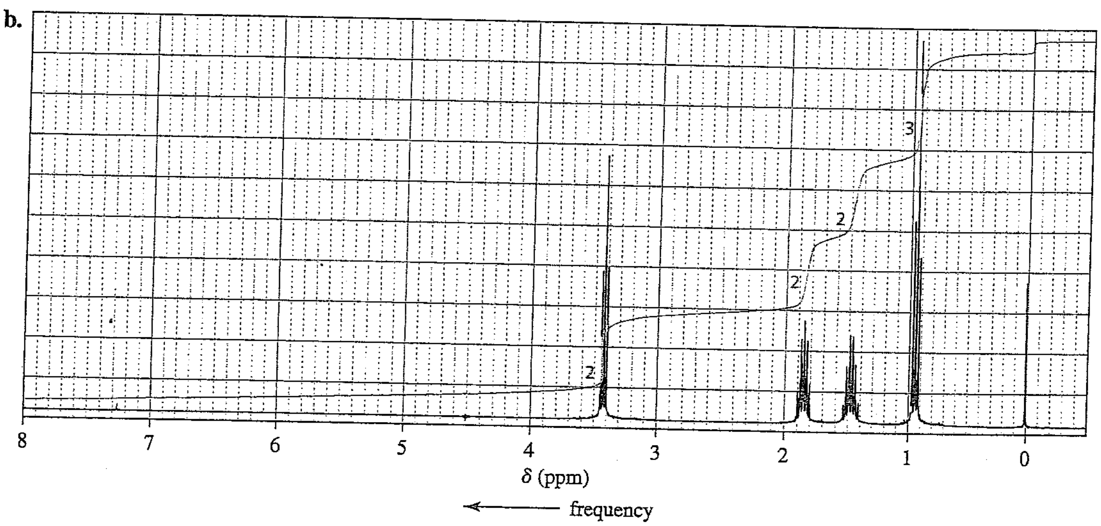


53. The ^1H NMR spectra of three isomers with molecular formula C_4H_9Br are shown here. Which isomer produces which spectrum?

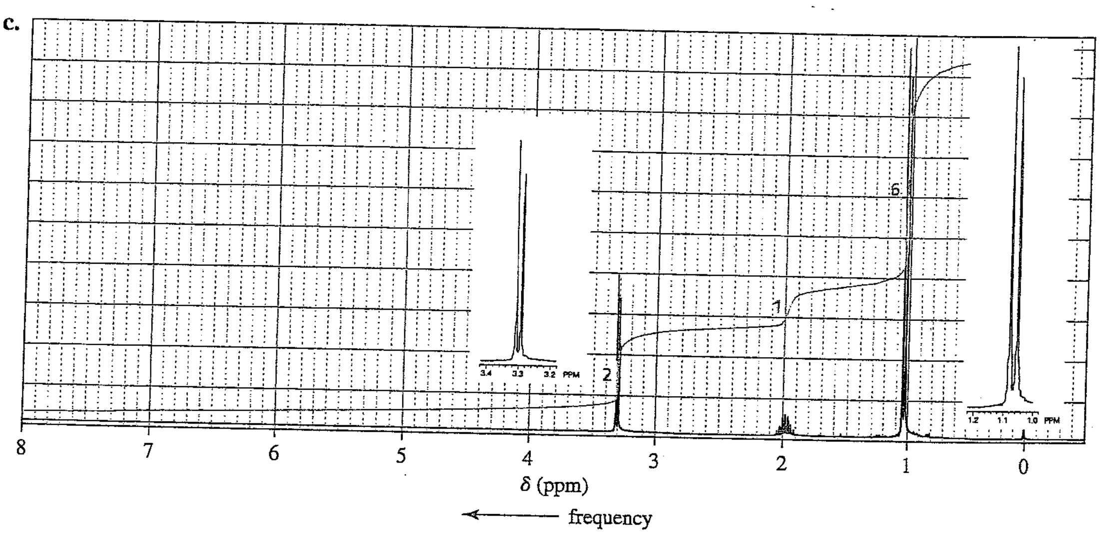
a.



b.

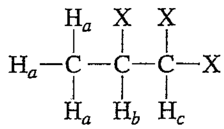


c.

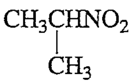


47. Draw a splitting diagram for the H_b proton and give its multiplicity if

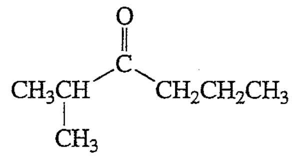
a. $J_{ba} = J_{bc}$ **b.** $J_{ba} = 2J_{bc}$

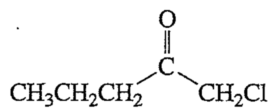


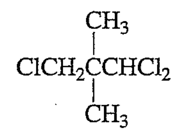
48. Label each set of chemically equivalent protons, using ***a*** for the set that will be at the lowest frequency (farthest upfield) in the [1]H NMR spectrum, ***b*** for the next lowest, and so on. Indicate the multiplicity of each signal.

a. 

b. $CH_3CH_2CH_2OCH_3$

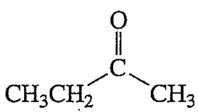
c. 

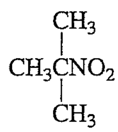
d. 

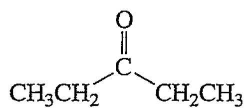
e. 

f. $ClCH_2CH_2CH_2CH_2CH_2Cl$

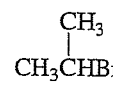
49. Match each of the [1]H NMR spectra with one of the following compounds:



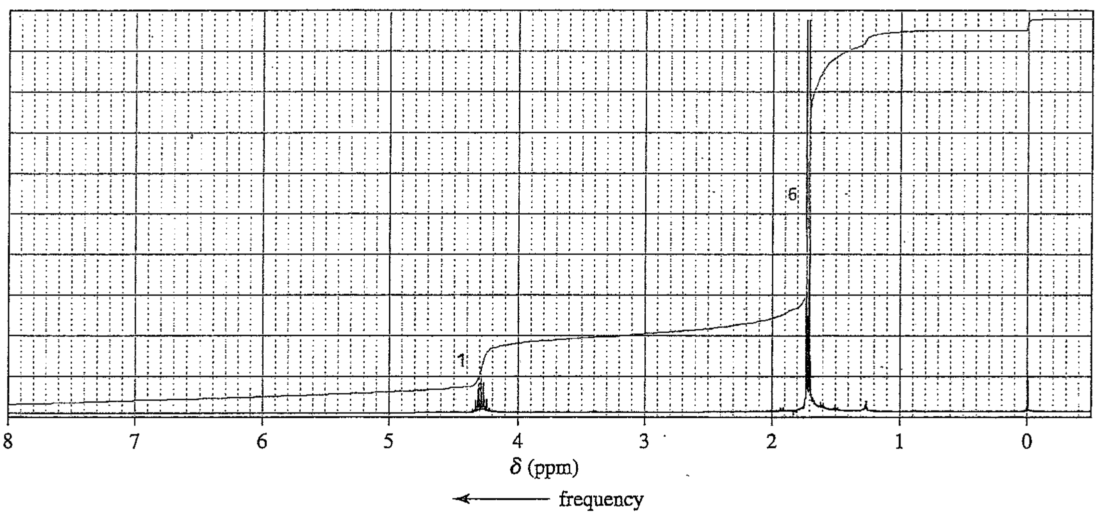




$CH_3CH_2CH_2NO_2$ $CH_3CH_2NO_2$



a.



b.