Chapter 16
Nuclear Magnetic Resonance Spectroscopy

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 16. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

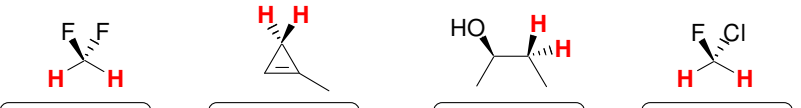
- A spinning proton generates a **magnetic** _____, which must align either with or against an imposed external magnetic field.
- All protons do not absorb the same frequency because of _____, a weak magnetic effect due to the motion of surrounding electrons that either **shield** or **deshield** the proton.
- _____ solvents are generally used for acquiring NMR spectra.
- In a ^{1}H NMR spectrum, each signal has three important characteristics: location, area and shape.
- When two protons are interchangeable by rotational symmetry, the protons are said to be _____.
- When two protons are interchangeable by rotational symmetry, the protons are said to be _____.
- The left side of an NMR spectrum is described as _____**field**, and the right side is described as _____**field**.
- In the absence of inductive effects, a methyl group (CH_3) will produce a signal near _____ppm, a **methylene group** (CH_2) will produce a signal near _____, and a _____ **group** (CH) will produce a signal near _____. The presence of nearby groups increases these values somewhat predictably.
- The _____, or area under each signal, indicates the number of protons giving rise to the signal.
- _____represents the number of peaks in a signal. A _____has one peak, a _____has two, a _____has three, a _____has four, and a _____has five.
- Multiplicity is the result of **spin-spin splitting**, also called _____, which follows **the n+1 rule**.
- When signal splitting occurs, the distance between the individual peaks of a signal is called the **coupling constant**, or _____ **value**, and is measured in Hz.
- Complex splitting occurs when a proton has two different kinds of neighbors, often producing a _____.
- ^{13}C is an _____of carbon, representing _____% of all carbon atoms.
- All ^{13}C-^{1}H splitting is suppressed with a technique called **broadband** _____, causing all of the ^{13}C signals to collapse to _____.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 16. The answers appear in the section entitled *SkillBuilder Review*.

16.1 Determining the Relationship between Two Protons in a Compound

FOR EACH OF THE FOLLOWING COMPOUNDS, IDENTIFY THE RELATIONSHIP BETWEEN THE TWO INDICATED PROTONS (ARE THEY HOMOTOPIC, ENANTIOPTOPIC OR DIASTEREOTOPIC?) AND DETERMINE WHETHER THEY ARE CHEMICALLY EQUIVALENT.



RELATIONSHIP _____ _____ _____ _____

CHEMICALLY EQUIVALENT? _____ _____ _____ _____

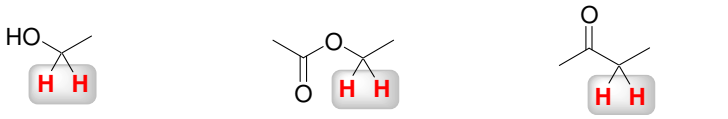
16.2 Identifying the Number of Expected Signals in a ^{1}H NMR Spectrum

FOR EACH OF THE FOLLOWING COMPOUNDS, DETERMINE WHETHER THE TWO INDICATED PROTONS ARE CHEMICALLY EQUIVALENT.

CHEMICALLY EQUIVALENT? _____ _____ _____ _____

16.3 Predicting Chemical Shifts

FOR EACH OF THE FOLLOWING COMPOUNDS, PREDICT THE EXPECTED CHEMICAL SHIFT OF THE INDICATED PROTONS.



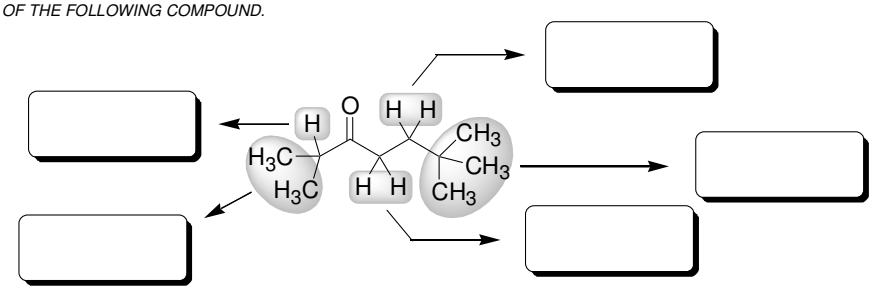
_____ ppm _____ ppm _____ ppm

16.4 Determining the Number of Protons Giving Rise to a Signal

STEP 1 - *COMPARE THE RELATIVE _____ VALUES, AND CHOOSE THE LOWEST NUMBER*	***STEP 2 -*** *DIVIDE ALL INTEGRATION VALUES BY THE NUMBER FROM STEP #1, WHICH GIVES THE RATIO OF _____*	***STEP 3 -*** *IDENTIFY THE NUMBER OF PROTONS IN THE COMPOUND (FROM THE MOLECULAR FORMULA) AND THEN ADJUST THE RELATIVE INTEGRATION VALUES SO THAT THE SUM TOTAL EQUALS THE NUMBER OF _____.*

16.5 Predicting the Multiplicity of a Signal

IDENTIFY THE EXPECTED MULTIPLICITY FOR EACH SIGNAL IN THE PROTON NMR SPECTRUM OF THE FOLLOWING COMPOUND.



16.6 Drawing the Expected ^{1}H NMR Spectrum of a Compound

STEP 1 - *IDENTIFY THE NUMBER OF _____*	***STEP 2***- *PREDICT THE _____ _____ OF EACH SIGNAL*	***STEP 3*** - *DETERMINE THE _____ OF EACH SIGNAL BY COUNTING THE NUMBER OF _____ GIVING RISE TO EACH SIGNAL*	***STEP 4***- *PREDICT THE _____ OF EACH SIGNAL*	***STEP 5*** - *DRAW EACH SIGNAL*

16.7 Using ^{1}H NMR Spectroscopy to Distinguish Between Compounds

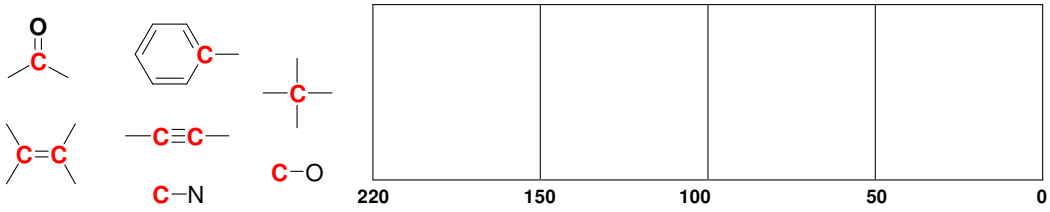
STEP 1 - *IDENTIFY THE NUMBER OF _____ THAT EACH COMPOUND WILL PRODUCE.*	***STEP 2*** - *IF EACH COMPOUND IS EXPECTED TO PRODUCE THE SAME NUMBER OF SIGNALS, THEN DETERMINE THE _____, _____, AND _____ OF EACH SIGNAL IN BOTH COMPOUNDS*	***STEP 3*** - *LOOK FOR DIFFERENCES IN THE CHEMICAL SHIFTS, MULTIPLICITIES OR INTEGRATION VALUES OF THE EXPECTED SIGNALS*

16.8 Analyzing a ^{1}H NMR Spectrum and Proposing the Structure of a Compound

STEP 1 - *USE THE _____ _____ TO DETERMINE THE HDI. AN HDI OF _____ INDICATES THE POSSIBILITY OF AN AROMATIC RING*	***STEP 2 -*** *CONSIDER THE NUMBER OF SIGNALS AND INTEGRATION OF EACH SIGNAL (GIVES CLUES ABOUT THE _____ OF THE COMPOUND)*	***STEP 3 -*** *ANALYZE EACH SIGNAL (____, ____, AND ____), AND THEN DRAW FRAGMENTS CONSISTENT WITH EACH SIGNAL. THESE FRAGMENTS BECOME OUR PUZZLE PIECES THAT MUST BE ASSEMBLED TO PRODUCE A MOLECULAR STRUCTURE*	***STEP 4 -*** *ASSEMBLE THE FRAGMENTS*

16.9 Predicting the Number of Signals and Approximate Location of Each Signal in a ^{13}C NMR Spectrum

BELOW ARE SEVEN DIFFERENT TYPES OF CARBON ATOMS. EACH OF THEM IS EXPECTED TO PRODUCE A SIGNAL IN ONE OF FOUR POSSIBLE REGIONS IN A CARBON NMR SPECTRUM. IDENITFY THE EXPECTED REGION FOR EACH TYPE OF CARBON ATOM.



16.10 Determining Molecular Structure using DEPT ^{13}C NMR Spectroscopy

COMPLETE THE FOLLOWING CHART BY DRAWING THE EXPECTED SHAPE OF EACH SIGNAL:

	CH_3	CH_2	CH	C
BROADBAND DECOUPLED				
DEPT-90				
DEPT-135				

Solutions

16.1.

a) homotopic
b) enantiotopic
c) diastereotopic
d) enantiotopic
e) homotopic

16.2.

a) All four protons can be interchanged either via rotation or reflection.
b) The three protons of a methyl group are always equivalent, and in this case, the two methyl groups are equivalent to each other because they can be interchanged by rotation. Therefore, all six protons are equivalent.
c) Three
d) Three
e) Six

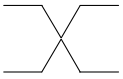
16.3.

16.4.

a) 8	b) 4	c) 2	d) 3	e) 5	f) 3
g) 4	h) 2	i) 4	j) 7	k) 4	l) 7

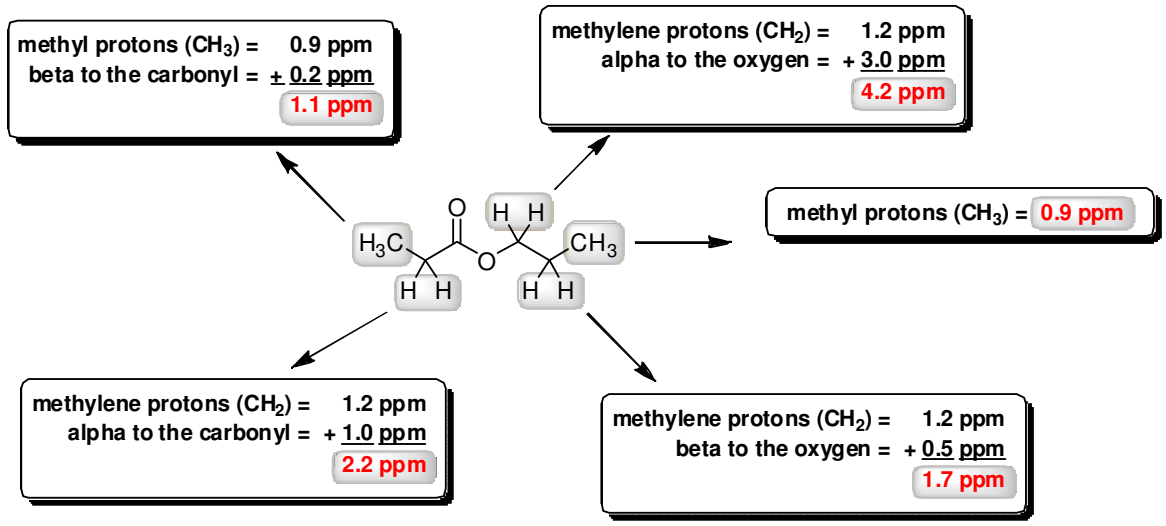
16.5. The presence of the bromine atom does not render C3 a chirality center because there are two ethyl groups connected to C3. Nevertheless, the presence of the bromine atom does prevent the two protons at C2 from being interchangeable by reflection. The replacement test gives a pair of diastereomers, so the protons are diastereotopic.

16.6. This compound will exhibit two signals in its ^{1}H NMR spectrum:

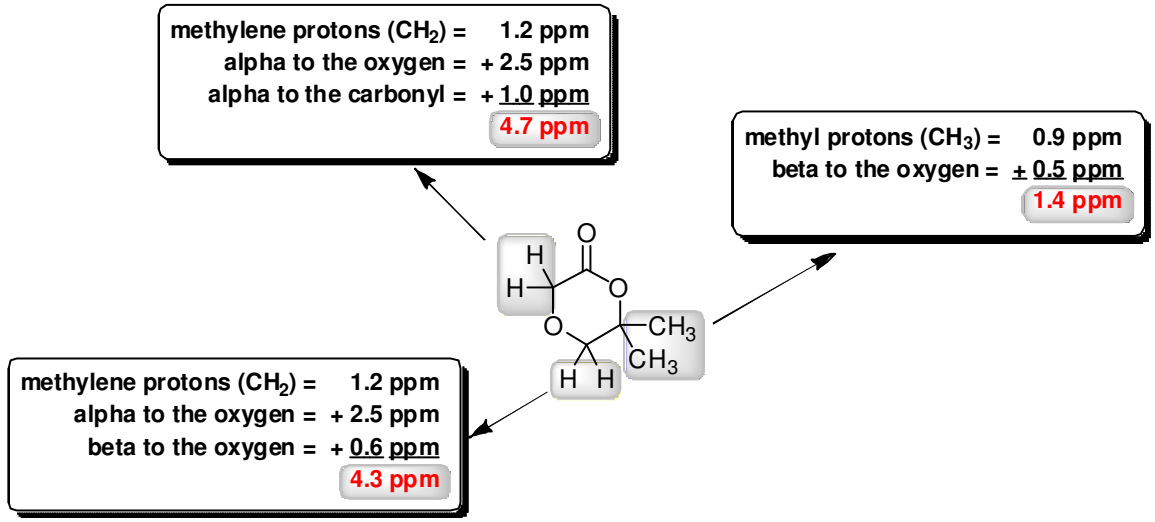


16.7.

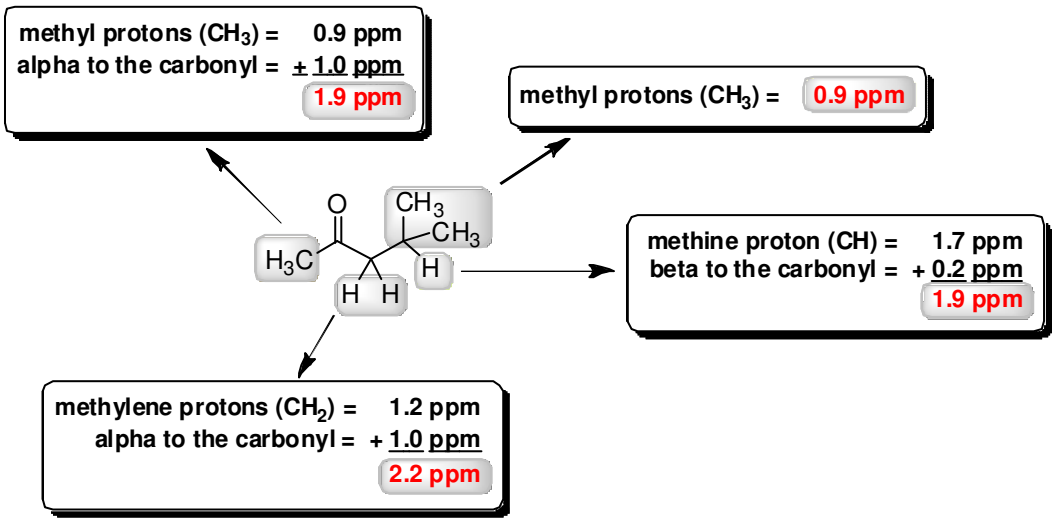
a)


methyl protons (CH3) = 0.9 ppm
beta to the carbonyl = + 0.2 ppm
1.1 ppm
methylene protons (CH2) = 1.2 ppm
alpha to the oxygen = + 3.0 ppm
4.2 ppm
methyl protons (CH3) = 0.9 ppm
methylene protons (CH2) = 1.2 ppm
alpha to the carbonyl = + 1.0 ppm
2.2 ppm
methylene protons (CH2) = 1.2 ppm
beta to the oxygen = + 0.5 ppm
1.7 ppm

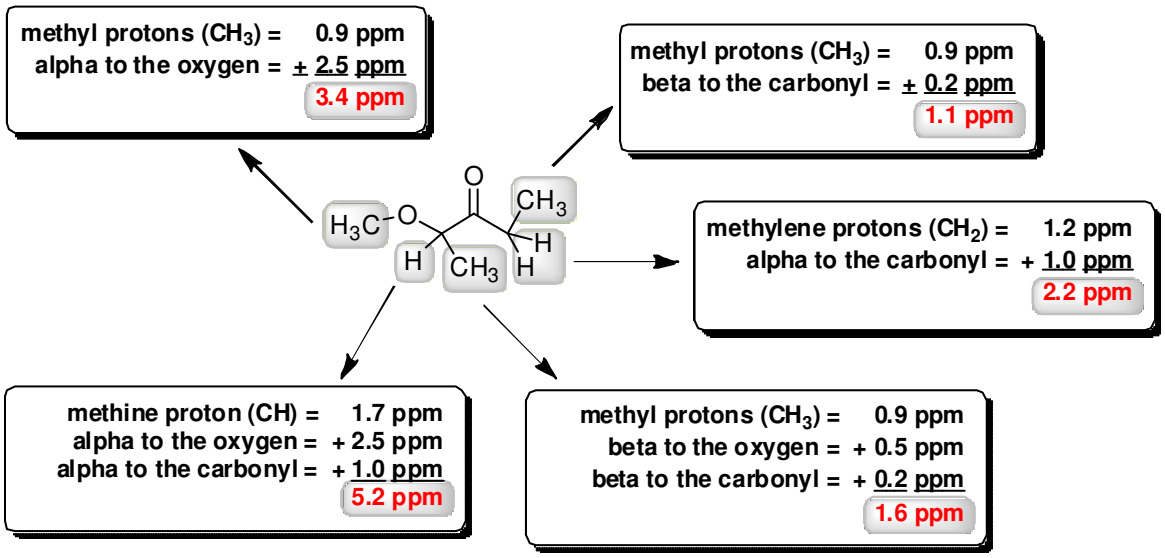
b)


methylene protons (CH2) = 1.2 ppm
alpha to the oxygen = + 2.5 ppm
alpha to the carbonyl = + 1.0 ppm
4.7 ppm
methyl protons (CH3) = 0.9 ppm
beta to the oxygen = + 0.5 ppm
1.4 ppm
methylene protons (CH2) = 1.2 ppm
alpha to the oxygen = + 2.5 ppm
beta to the oxygen = + 0.6 ppm
4.3 ppm

c)

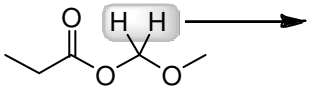


d)



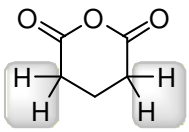
e) All four methylene groups are equivalent, so the compound will have only one signal in its ^{1}H NMR spectrum. That signal is expected to appear at approximately (1.2 + 2.5 + 0.5) = 4.2 ppm.

16.8.



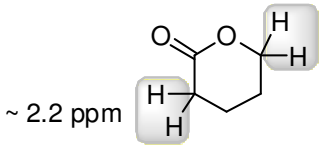
methylene protons (CH_2) = 1.2 ppm
alpha to the oxygen = + 3.0 ppm
alpha to the oxygen = + 2.5 ppm
6.7 ppm

16.9.



~ 2.2 ppm

Only one signal downfield of 2.0 ppm
(the four highlighted protons are equivalent)



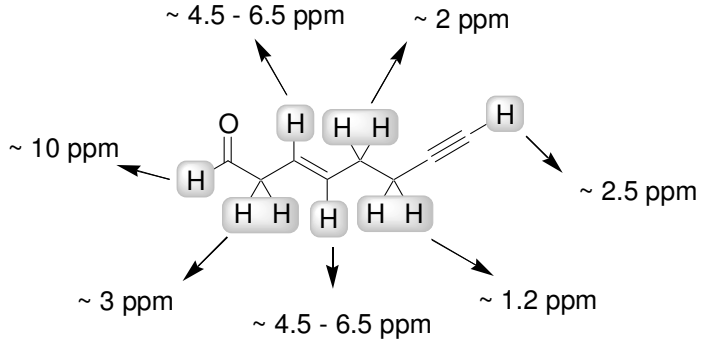
~ 2.2 ppm

~ 4.2 ppm

Two signals downfield of 2.0 ppm

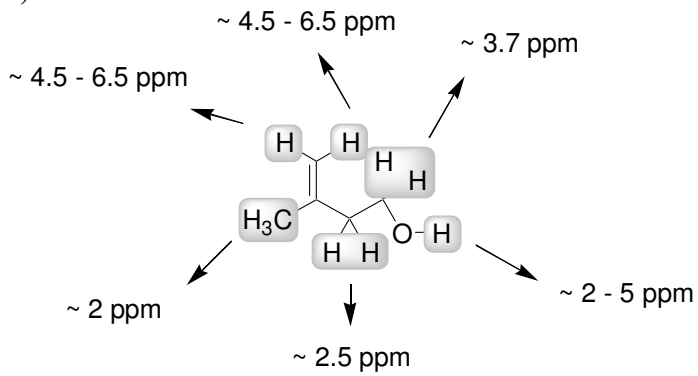
16.10.

a)



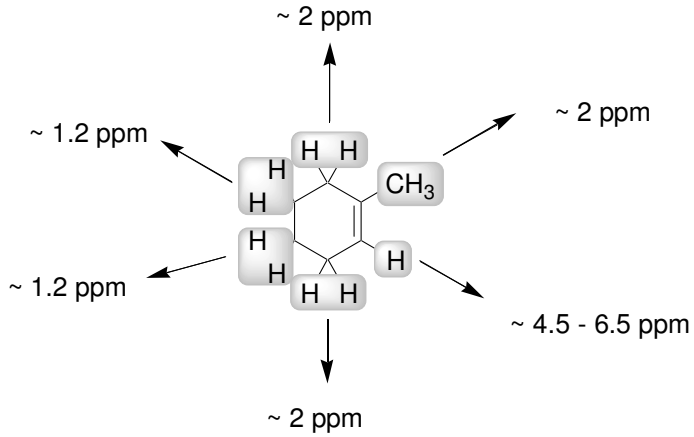
~ 4.5 - 6.5 ppm
~ 2 ppm
~ 10 ppm
~ 2.5 ppm
~ 3 ppm
~ 4.5 - 6.5 ppm
~ 1.2 ppm

b)

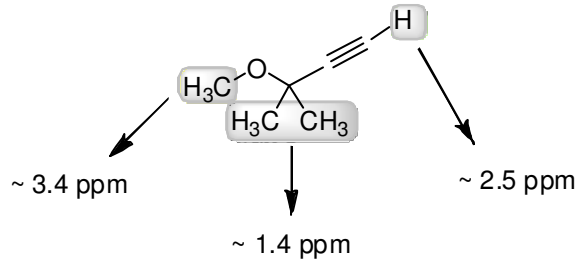


~ 4.5 - 6.5 ppm
~ 3.7 ppm
~ 4.5 - 6.5 ppm
~ 2 ppm
~ 2 - 5 ppm
~ 2.5 ppm

c)



d)

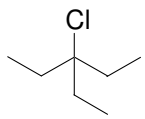


16.11.
The signal at 4.0 ppm represents two protons.
The signal at 2.0 ppm represents three protons.
The signal at 1.6 ppm represents two protons.
The signal at 0.9 ppm represents three protons.

16.12.
The signal at 9.6 ppm represents one proton.
The signal at 7.5 ppm represents five protons.
The signal at 7.3 ppm represents one proton.
The signal at 2.1 ppm represents three protons.

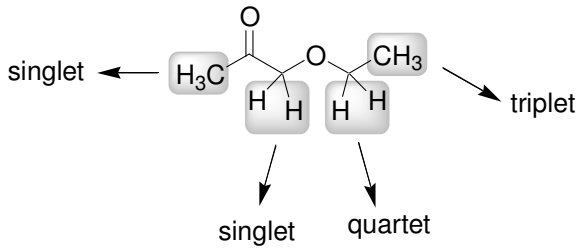
16.13. Each signal represents two protons.

16.14.

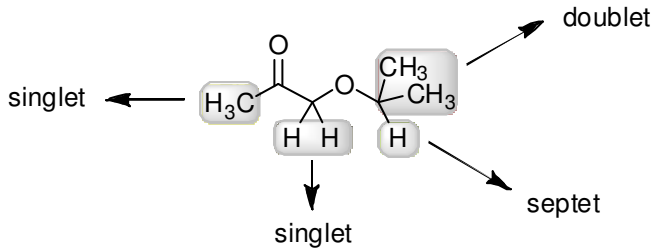


16.15.

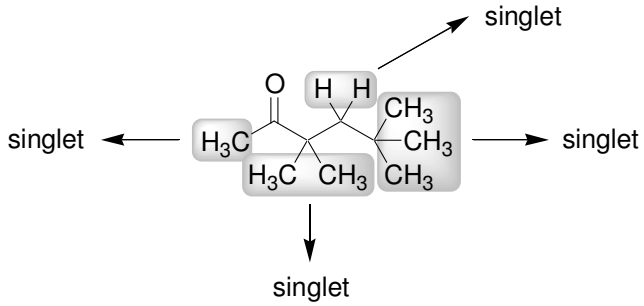
a)


singlet
triplet
singlet
quartet

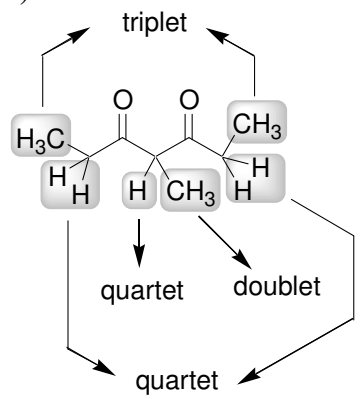
b)


doublet
singlet
septet
singlet

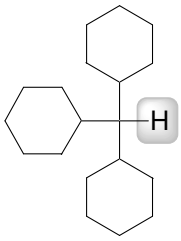
c)


singlet
singlet
singlet
singlet

d)


triplet
quartet
doublet
quartet

16.16.

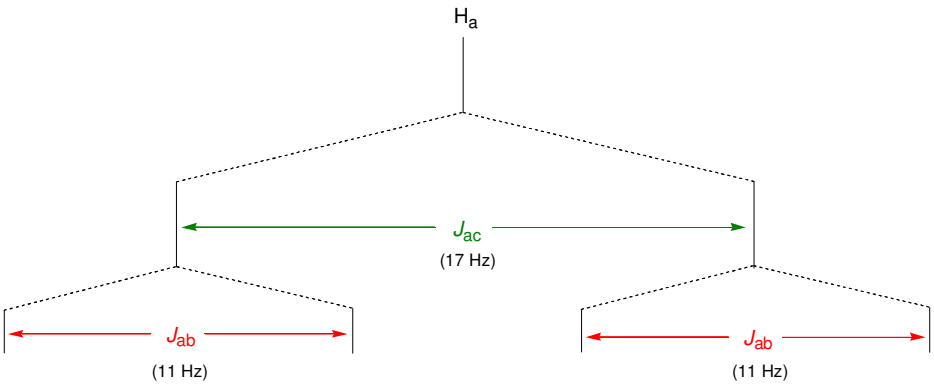


16.17.

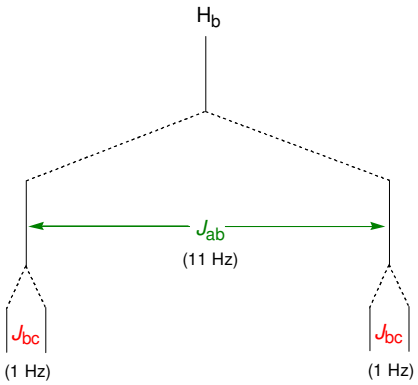
a) The spectrum exhibits the characteristic pattern of an isopropyl group.
b) The spectrum exhibits the characteristic pattern of an isopropyl group as well as the characteristic pattern of an ethyl group.
c) The spectrum exhibits the characteristic pattern of a *tert*-butyl group.
d) The spectrum does not exhibit the characteristic pattern of an ethyl group, an isopropyl group, or a *tert*-butyl group.

16.18.

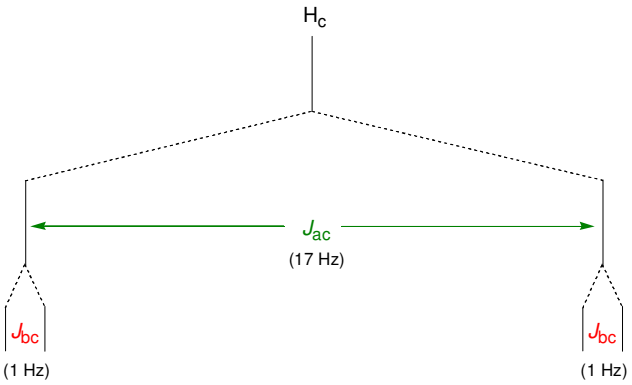
a)



b)

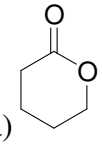


c)

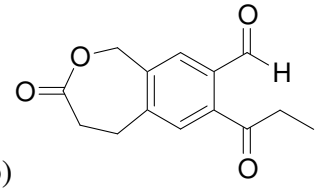


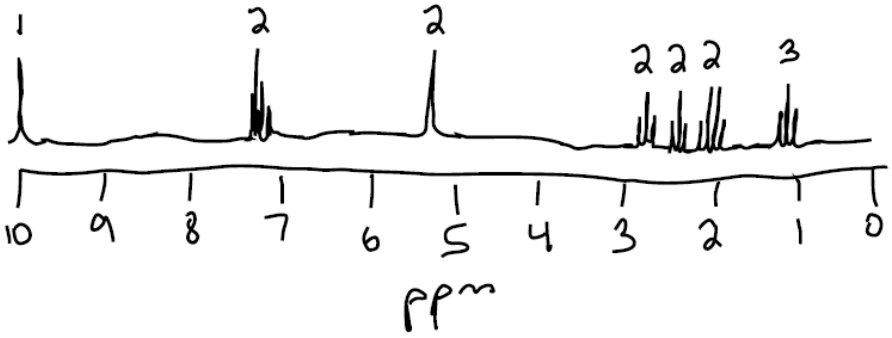
16.19. Draw the expected ^{1}H NMR spectrum for each of the following compounds

a)

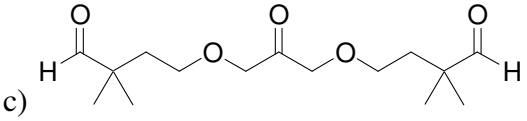


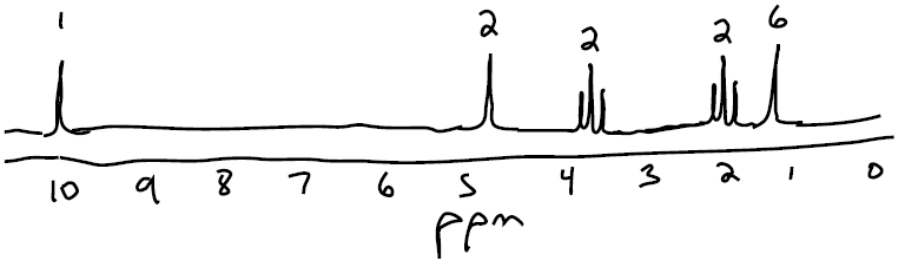
b)



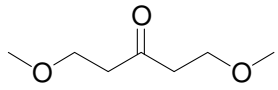


c)





16.20.



16.21.

a) The first compound will have only three signals in its ^{1}H NMR spectrum, while the second compound will have six signals.

b) Both compounds will exhibit ^{1}H NMR spectra with only two singlets. In each spectrum, the relative integration of the two singlets is 1:3. In the first compound, the singlet with the smaller integration value will be at approximately 2 ppm. In the second compound, the singlet with the smaller integration value will be at approximately 4 ppm.

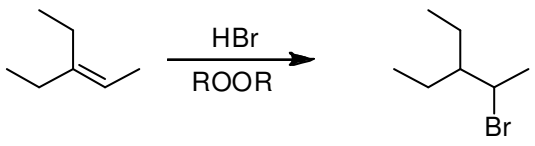
d) The first compound will have only two signals in its ^{1}H NMR spectrum, while the second compound will have three signals.

e) The first compound will have five signals in its ^{1}H NMR spectrum, while the second compound will have only three signals.

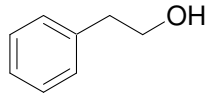
f) The first compound will have only four signals in its ^{1}H NMR spectrum, while the second compound will have five signals.

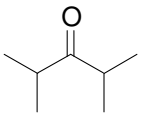
g) The first compound will have only one signal in its ^{1}H NMR spectrum, while the second compound will have two signals.

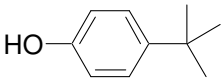
16.22. The presence of peroxides caused an *anti*-Markovnikov addition of HBr:

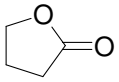


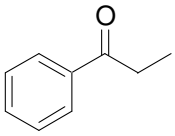
16.23.

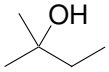
a) 

b) 

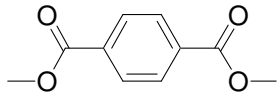
c) 

d) 

e) 

f) 

16.24.



16.25.

a) Four signals. Three appear in the region 0 – 50 ppm, and the fourth signal (the C=O) appears in the region 150 – 220 ppm.

b) Five signals. All five appear in the region 0 – 50 ppm.

c) Six signals. Two appear in the region 0 – 50 ppm, and four signals appear in the region 100-150 ppm.

d) Nine signals. Two appear in the region 0 – 50 ppm, one appears in the region 50 – 100 ppm and six signals appear in the region 100 – 150 ppm.

e) Seven signals. Two appear in the region 0 – 50 ppm, one appears in the region 50 – 100 ppm and four signals appear in the region 100 – 150 ppm.

f) Five signals. Three appear in the region 0 – 50 ppm and two signals appear in the region 100 – 150 ppm.

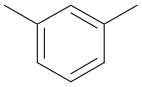
g) Seven signals. Five appear in the region 0 – 50 ppm and two signals appear in the region 100 – 150 ppm.

h) Two signals. One appears in the region 0 – 50 ppm and the other appears in the region 100 – 150 ppm.

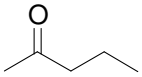
i) One signal appears in the region 50 – 100.
j) Five signals. One appears in the region 0 – 50 ppm, one appears in the region 50 – 100 ppm, two appear in the region 100-150, and one signal appears in the region 150 – 200 ppm.

16.26. The first compound lacks a chirality center. The two methyl groups are enantiotopic and are therefore chemically equivalent. The second compound has a chirality center (the position bearing the OH group). As such, the two methyl groups are diastereotopic and are therefore not chemically equivalent. For this reason, the ^{13}C NMR spectrum of the second compound exhibits six signals, rather than five.

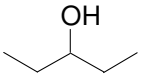
16.27.



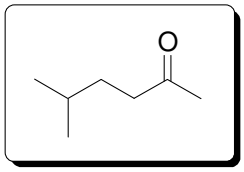
16.28.



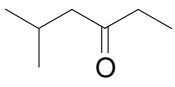
16.29.



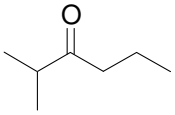
16.30.



Consistent with
^{1}H NMR and ^{13}C NMR spectra



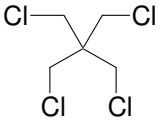
Consistent only with
^{13}C NMR spectrum

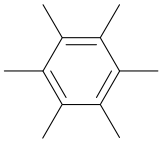


Consistent only with
^{13}C NMR spectrum

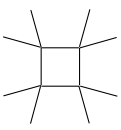
16.31.

a) 

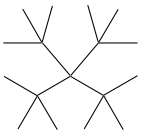
b) 

c) 

16.32.



16.33. This compound will exhibit three signals in its ^{13}C NMR spectrum:



16.34.

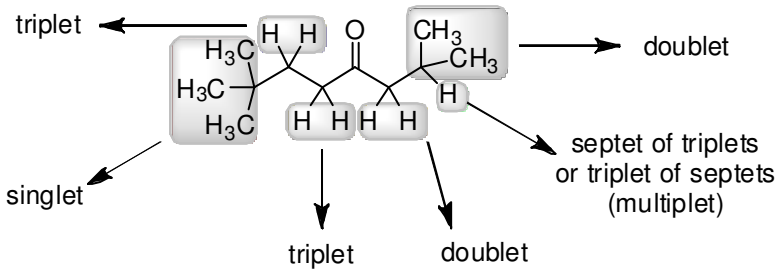
a) 2 b) 4 c) 4 d) 2 e) 2 f) 5

16.35.

a) 4 b) 6 c) 6 d) 4 e) 2 f) 4

16.36. The first compound will have five signals in its ^{13}C NMR spectrum, while the second compound will have seven signals.

16.37.



16.38.

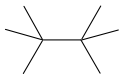
a) The first compound will have four signals in its ^{13}C NMR spectrum, while the second compound will have twelve signals.
The first compound will have two signals in its ^{1}H NMR spectrum, while the second compound will have eight signals.

b) The first compound is a meso compound. Two of the protons are enantiotopic (the protons that are alpha to the chlorine atoms) and are therefore chemically equivalent. The first compound will only have two signals in its ^{1}H NMR spectrum, while the second compound will have three signals. For a similar reason, first compound will only have two signals in its ^{13}C NMR spectrum, while the second compound will have three signals.

c) The ^{13}C NMR spectrum of the second compound will have one more signal than the ^{13}C NMR spectrum of the other first compound. The ^{1}H NMR spectra will differ in the following way: the first compound will have a singlet somewhere between 2 and 5 ppm with an integration of 1, while the second compound will have a singlet at approximately 3.4 ppm with an integration of 3.

d) The first compound will have three signals in its ^{13}C NMR spectrum, while the second compound will have five signals.
The first compound will have two signals in its ^{1}H NMR spectrum, while the second compound will have four signals.

16.39. This compound will exhibit two signals in its ^{13}C NMR spectrum:



16.40.

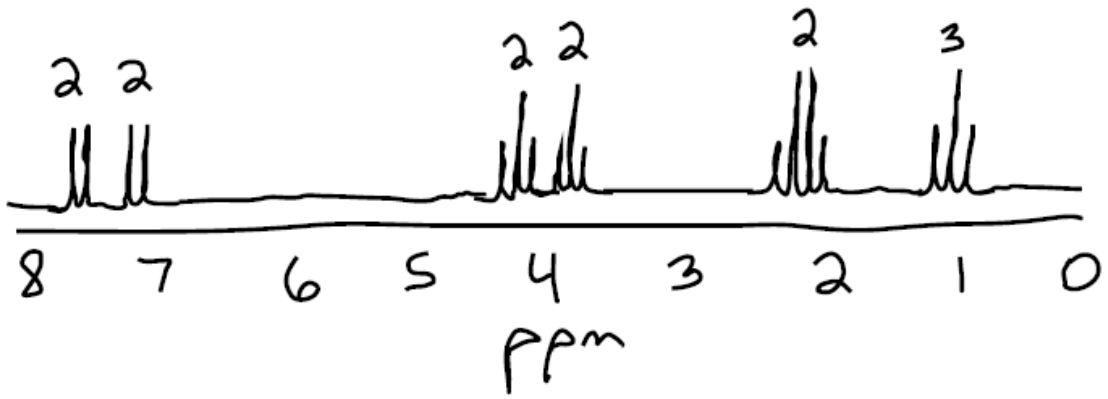
a) homotopic b) enantiotopic c) enantiotopic d) homotopic

e) diastereotopic f) homotopic g) diastereotopic h) diastereotopic

i) homotopic j) homotopic k) homotopic l) diastereotopic

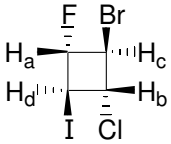
m) enantiotopic n) diastereotopic o) homotopic

16.41.



16.42.

a) Four signals are expected in the ^{1}H NMR spectrum of this compound.



b) Increasing chemical shift ←

$H_a > H_b > H_c > H_d$

c) Four signals are expected in the ^{13}C NMR spectrum of this compound.

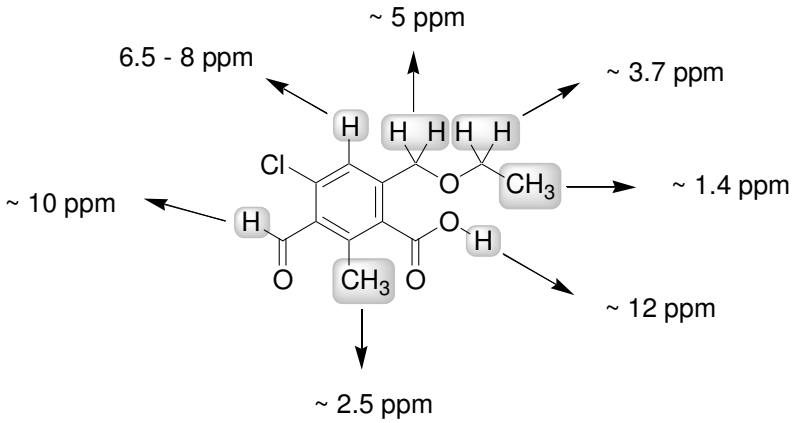
d) The carbon atoms follow the same trend exhibited by the protons.

16.43.

16.44.

a) Nine b) Eight c) Six

16.45.



16.46.

a) Six signals, all of which appear in the region 100 – 150 ppm.
b) Seven signals. One appears in the region 150 – 220 ppm, and the remaining six signals appear in the region 0 – 50 ppm.
c) Four signals. One appears in the region 0 – 50 ppm, two appear in the region 50 – 100 ppm, and one signal appears in the region 150 – 200 ppm.

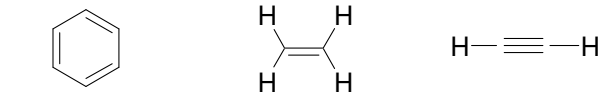
16.47. The ^{1}H NMR spectrum of the Markovnikov product should have only four signals, while the anti-Markovnikov product should have many more signals in its ^{1}H NMR spectrum.

16.48.

a) 2 b) 8 c) 4 d) 2 e) 3 f) 6 g) 2 h) 3

16.49.

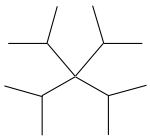
Increasing chemical shift in ^{1}H NMR spectroscopy



16.50.

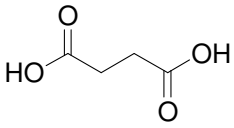
$$\delta = \frac{\text{(observed shift from TMS in hertz)} \times 10^6}{\text{(operating frequency of the instrument in hertz)}}$$

(Observed shift from TMS in hertz) = (δ)(operating frequency) / 10^6

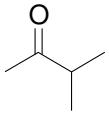
16.51. 

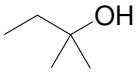
16.52. 

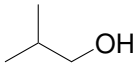
16.53. 

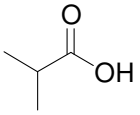
16.54. 

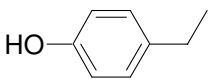
16.55.

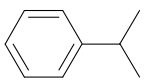
a) 

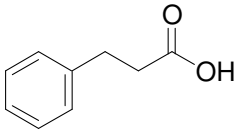
b) 

c) 

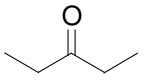
d) 

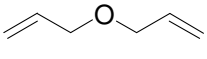
16.56. 

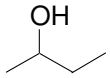
16.57. 

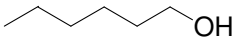
16.58. 

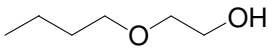
16.59.

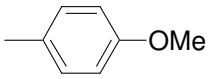
a) 

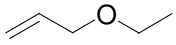
b) 

16.60. 

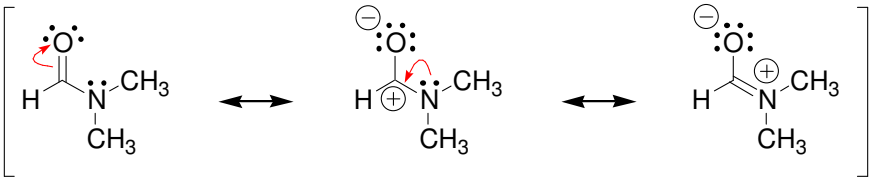
16.61. 

16.62. 

16.63. 

16.64. 

16.65. N,N-dimethylformamide (DMF) has several resonance structures:



Consider the third resonance structure shown above, in which the C-N bond is a double bond. This indicates that this bond is expected to have some double bond character. As such, there is an energy barrier associated with rotation about this bond, such that rotation of this bond occurs at a rate that it slower than the timescale of the NMR spectrometer. At high temperature, more molecules will have the requisite energy to undergo free rotation about the C-N bond, so the process can occur on a time scale that is faster than the timescale of the NMR spectrometer. For this reason, the signals are expected to collapse into one signal at high temperature.

16.66. In a concentrated solution of phenol, the OH groups are engaged in extensive, intermolecular hydrogen-bonding interactions. These interactions cause the average distance to increase between the O and H of each OH group. This effectively deshields the protons of the hydroxyl groups. These protons therefore show up downfield. In a dilute solution, there are fewer hydrogen bonding interactions, and the effect described above is not observed.

16.67. The methyl group on the right side is located in the shielding region of the π bond, so the signal for this proton is moved upfield to 0.8 ppm.

16.68. Bromine is significantly larger than chlorine, and the electron density of a bromine atom partially surrounds any carbon atom attached directly to the bromine, thereby shielding it. In CBr_4, the carbon atom in the center of the compound is significantly shielded because it is positioned within the electron clouds of the four bromine atoms. In fact, it is so strongly shielded that it produces a signal even higher upfield than TMS.