

Chapter 13

13.1 The amount of energy required to spin-flip a nucleus depends both on the strength of the external magnetic field and on the nucleus. At a field strength of 4.7T, rf energy of 200 MHz is required to bring a ^1H nucleus into resonance, but energy of only 187 MHz will bring a ^{19}F nucleus into resonance. Use the equation given in Problem 12.7 to calculate the amount of energy required to spin-flip a ^{19}F nucleus. Is this amount greater or less than that required to spin-flip a ^1H nucleus?

Solution:

$$^1\text{H}: E = 6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 200 \times 10^6 = 8.0 \times 10^{-5} \text{ KJ/mol}$$

$$^{19}\text{F}: E = 6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 187 \times 10^6 = 7.5 \times 10^{-5} \text{ KJ/mol}$$

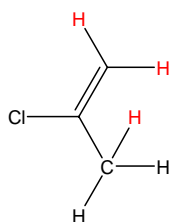
13.2 Calculate the amount of energy required to spin-flip a proton in a spectrometer operating at 300 MHz. Does increasing the spectrometer frequency from 200 to 300 MHz increase or decrease the amount of energy necessary for resonance?

Solution:

$$E = 6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 300 \times 10^6 = 1.2 \times 10^{-4} \text{ KJ/mol}$$

13.3 2-chloropropene shows signals for three kinds of protons in its ^1H NMR spectrum, explain.

Solution:



because the protons in red are not equivalent, so it shows signals for three kinds of protons in its ^1H NMR spectrum.

13.4 When the ^1H NMR spectrum of acetone, CH_3COCH_3 , is recorded on an instrument operating at 200 MHz, a single sharp resonance at is seen.

(a) How many hertz downfield from TMS does the acetone resonance correspond to?

Solution:

$$200 \times 2.1 = 420 \text{ Hz}$$

(b) If the ^1H NMR spectrum of acetone were recoded at 500 MHz, what would be the position of the absorption in δ units ?

Solution:

the position of the absorption in δ units will be 2.1 δ .

(c) How many hertz downfield from TMS does this 500 MHz resonance correspond to?

Solution:

$$500 \times 2.1 = 1050 \text{ Hz}$$

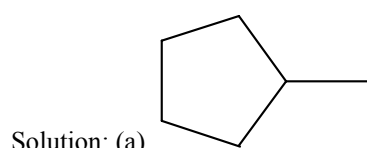
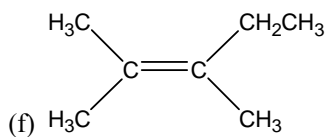
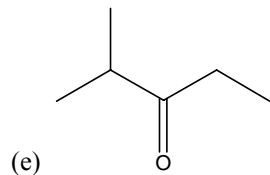
13.5 The following ^1H NMR peaks were recorded on a spectrometer operating at 200 MHz. Convert each into δ units.

(a) CHCl_3 ; 1454 Hz (b) CH_3Cl ; 610 Hz (c) CH_3OH ; 693 Hz (d) CH_2Cl_2 ; 1060 Hz

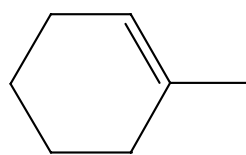
Solution: (a): 7.27 (b): 3.05 (c): 3.465 (d): 5.3

13.6 Predict the number of carbon resonance lines you would expect in the ^{13}C NMR spectra of the following compounds:

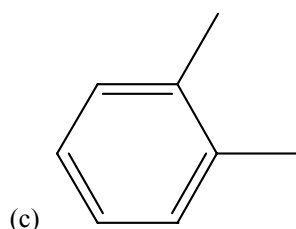
- (a) Methylcyclopentane (b) 1-methylcyclohexene
 (c) 1,2-Dimethylbenzene (d) 2-methyl-2-butene



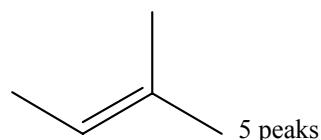
4 single peaks



7 single peaks



4 single peaks



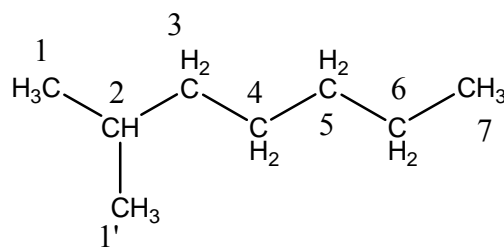
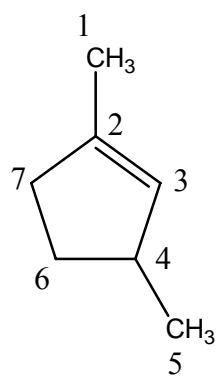
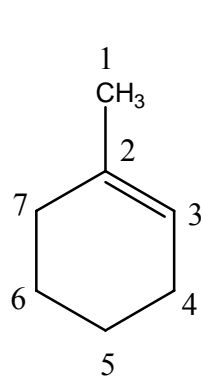
5 peaks

(e) 5 peaks because of the free rotation of single bond (f) 7 peaks

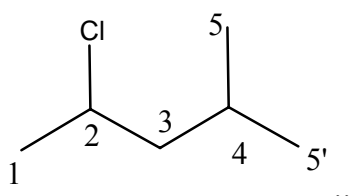
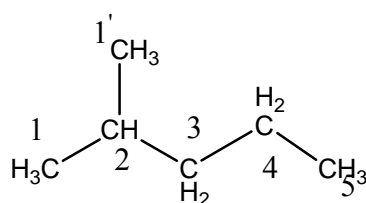
13.7 Propose structures for compounds that fit the following descriptions:

- (a) A hydrocarbon with seven lines in its ^{13}C NMR spectrum

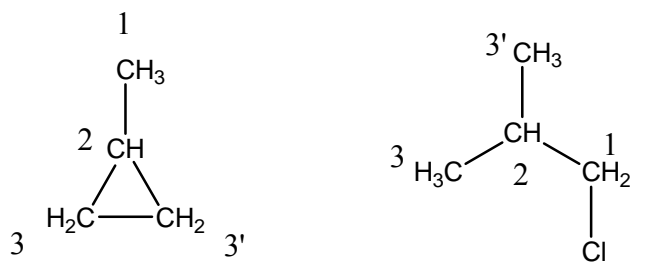
There are many compounds according to the problem, and several of them are drawn following:



- (b) A six-carbon compound with only five lines in its ^{13}C NMR spectrum

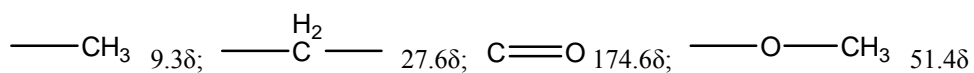


(c) A four-carbon compound with three lines in its ^{13}C NMR spectrum

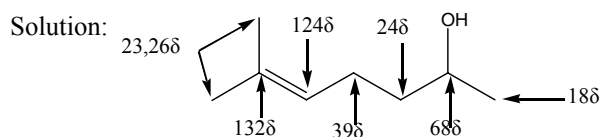


13.8 Assign the resonances in the ^{13}C NMR spectrum of methyl propanoate, $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3$

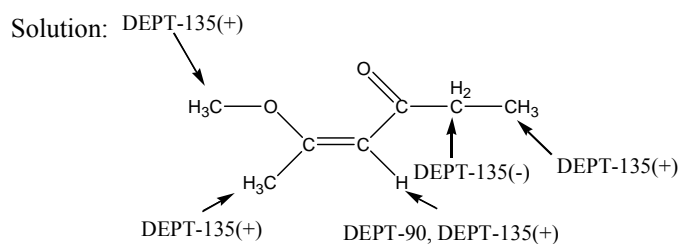
Solution



13.9 Assign a chemical shift to each carbon in 6-methyl-5-hepten-2-ol.



13.10 Estimate the chemical shift of each carbon in the following molecule. Predict which carbons will appear in the DEPT-90 spectrum, which will give positive peaks in the DEPT-135 spectrum, and which will give negative peaks in the DEPT-135 spectrum.



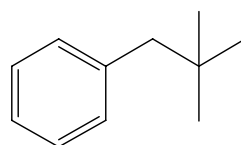
13.11 Propose a structure for an aromatic hydrocarbon, $\text{C}_{11}\text{H}_{16}$, that has the following ^{13}C NMR spectral data.

Broadband decoupled ^{13}C NMR : 29.5, 31.8, 50.2, 125.5, 130.3, 139.8δ;

DEPT-90: 125.5, 127.5, 130.3δ;

DEPT-135: positive peaks at 29.5, 125.5, 127.5, 130.3δ; negative peak at 50.2δ.

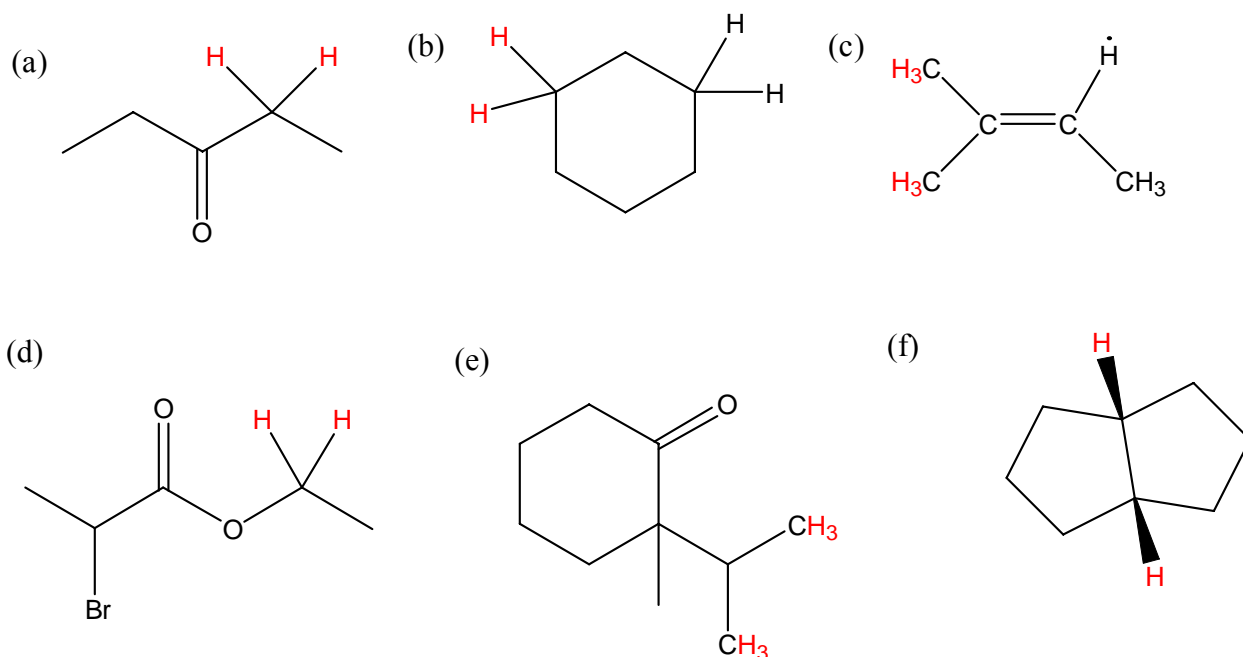
Solution: The structure for this aromatic hydrocarbon is



13.12 We saw in section 8.4 that addition of HBr to a terminal alkyne leads to the Markovnikov addition product, with the Br bonding to the more highly substituted carbon. How could you use ^{13}C NMR to identify the product of the addition of 1 equivalent of HBr to 1-hexyne?

Solution: The best way to identify whether the product is Markovnikov addition product or non Markovnikov addition product is to use the DEPT-90 ^{13}C NMR. A non Markovnikov addition product has two absorptions in a DEPT-90 ^{13}C NMR spectrum, but the Markovnikov addition product has no absorption in a DEPT-90 ^{13}C NMR spectrum.

13.13 Identify the indicated sets of protons as unrelated, homotopic, enantiotopic, or diastereotopic:



Solution:

- (a) enantiotopic
- (b) diastereotopic
- (c) diastereotopic (since replacement of a hydrogen would form Z-R diastereomers)
- (d) diastereotopic
- (e) diastereotopic
- (f) homotopic

13.14 How many kinds of electronically nonequivalent protons present in each of the following compounds, and thus how many NMR absorption might you expect in each?

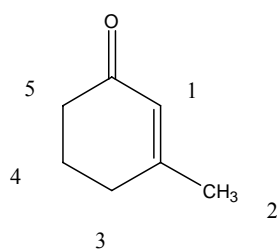
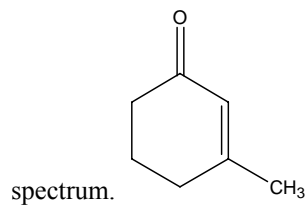
- (a) $\text{CH}_3\text{CH}_2\text{Br}$ (b) $\text{CH}_3\text{OCH}_2\text{CH}(\text{CH}_3)_2$ (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$ (d) Methylbenzene (e) 2-Methyl-1-butene (f) cis-3-Hexene

Solution:

	Nonequivalent protons	NMR absorptions
(a)	unrelated enantiotopic	2
(b)	unrelated enantiotopic	4

- (c) unrelated enantiotopic 3
 (d) unrelated 4
 (e) unrelated enantiotopic 5
 (f) unrelated 3

13-15 How many absorptions would you expect the following compound to have in the ^1H NMR



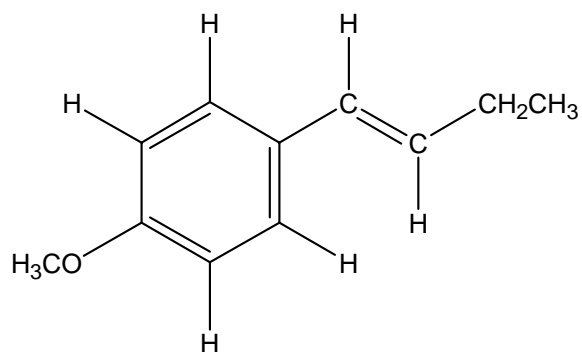
Solution: From the , we can see they will be 5 absorptions.

13-16 Each of the following compounds has a single ^1H NMR peak. Approximately where would you expect each compound to absorb.

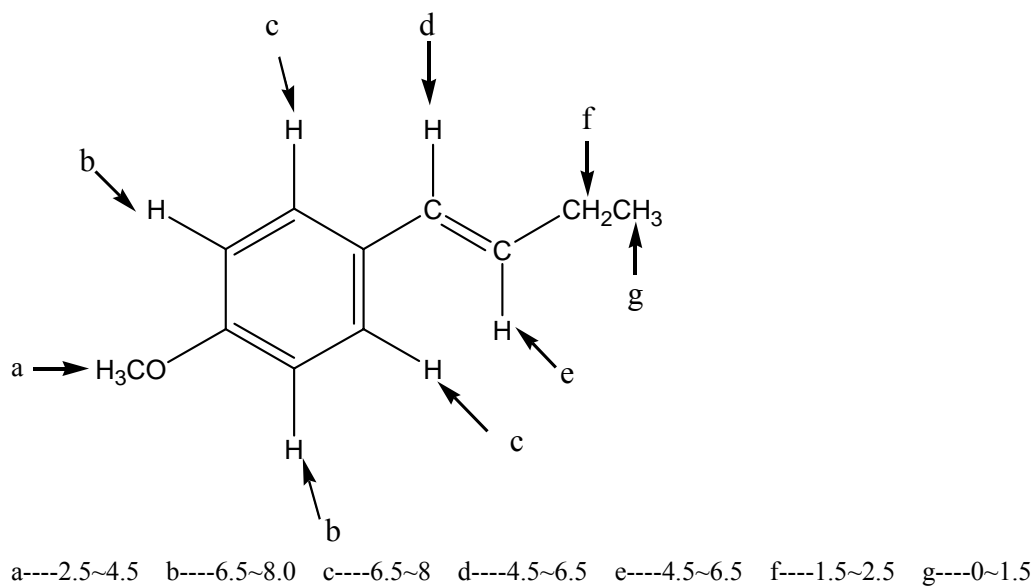
Solution:

- (a): Cyclohexane: 1.2-1.6 δ
 (b): CH_3OCH_3 : 1.7-2.3 δ
 (c): Benzene: 6.5-8.0 δ
 (d): Glyoxal: 9.7-10.0 δ
 (e): CH_2Cl_2 : 2.5-5.5 δ
 (f): $(\text{CH}_3)_3\text{N}$: 1.7-2.3 δ

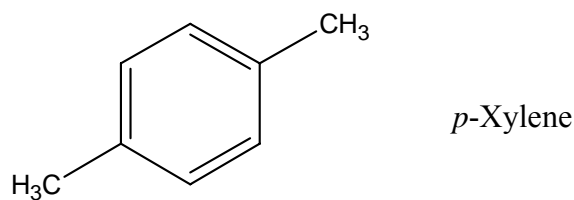
13.17 Identify the different kinds of nonequivalent protons in the following molecule, and tell where you would expect each to absorb:



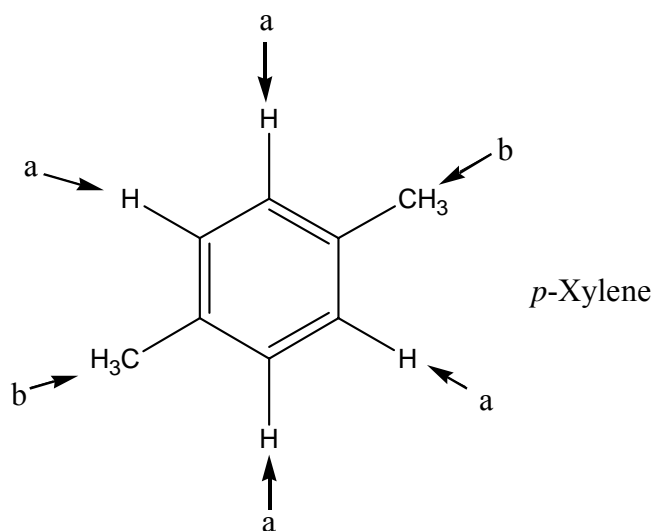
Solution: There are seven different kinds of nonequivalent protons.



13.18 How many peaks would you expect in the ^1H NMR spectrum of 1,4-dimethylbenzene (*p*-xylene)? What ratio of peak areas would you expect on integration of the spectrum? Refer to Table 13.3 for approximate chemical shifts, and sketch what the spectrum would look like. (remember from Section 2.4 that aromatic rings have 2 resonance forms.)



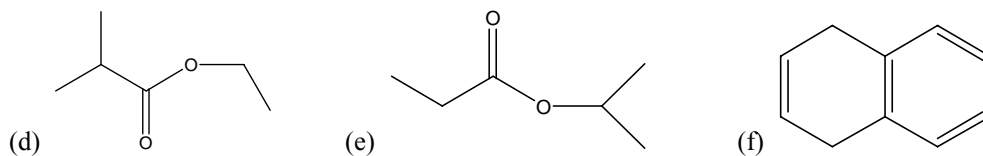
Solution:



The number of H labeled by a is 4 and labeled by b is 6. So there are 2 peaks and the ratio of peak areas is 2:3.

13.19 Predict the splitting patterns you would expect for each proton in the following molecules.

- (a) CHBr_2CH_3 (b) $\text{CH}_3\text{OCH}_2\text{CH}_2\text{Br}$ (c) $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}$



Solution:

(a): As there are two kinds of protons, so there would be one quartet which is caused by $-\text{CHBr}_2$ and one doublet caused by $-\text{CH}_3$.

(b): There are three kinds of protons, so there are one singlet caused by $-\text{CH}_3$, two triplets caused by $-\text{CHBr}_2$ and $-\text{CH}_2-$.

(c): There are two kinds of protons, so there are one quintet caused by $-\text{CH}_2-$, and one triplet caused by two $-\text{CH}_2\text{Cl}$.

(d): There are four kinds of protons, so there are one doublet caused by two methyl bonded to $-\text{CH}-$, one triplet caused by methyl bonded to $-\text{CH}_2-$, one quartet caused by $-\text{CH}_2-$ and one septet caused by $-\text{CH}-$.

(e): There are four kinds of protons, so there are one doublet caused by two methyl bonded to $-\text{CH}-$, one triplet caused by methyl bonded to $-\text{CH}_2-$, one quartet caused by $-\text{CH}_2-$ and one septet caused by $-\text{CH}-$.

(f): There are four kinds of protons, so there are one quartet caused by $=\text{CH}$, one doublet caused by $-\text{CH}_2-$, one doublet caused by aromatic carbons on departure, one triplet caused by aromatic carbons on other places.

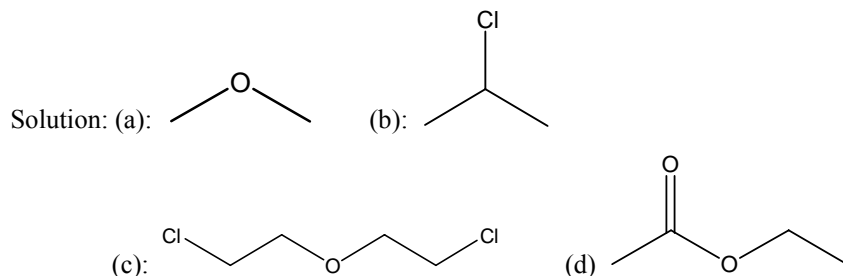
13.20 Draw structure for compounds that meet the following descriptions:

(a) $\text{C}_2\text{H}_6\text{O}$; one singlet

(b) $\text{C}_3\text{H}_7\text{Cl}$; one doublet

(c) $\text{C}_4\text{H}_8\text{Cl}_2\text{O}$; two triplets

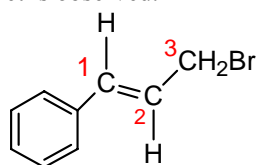
(d) $\text{C}_4\text{H}_8\text{O}_2$; one singlet, one quartet



13.21 The integrated ^1H NMR spectrum of a compound of formula $\text{C}_4\text{H}_{10}\text{O}$ is shown in Figure 13.17. Propose a structure consistent with the data.

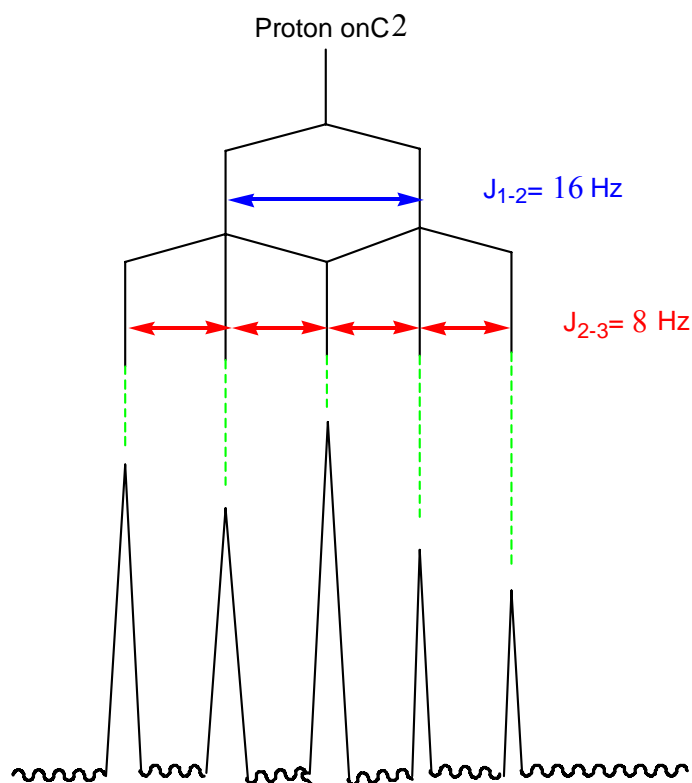
Solution: The structure is: $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$

13.22 3-Bromo-1-propene shows a complex NMR spectrum in which the vinylic proton at C_2 is coupled with both the C_1 vinylic proton ($J=16\text{Hz}$) and the C_3 methylene protons ($J=8\text{Hz}$). Draw a tree diagram for the C_2 proton signal, and account for the fact that a five-line multiplet is observed.



3-Bromo-1-phenyl-1-propene

Solution:



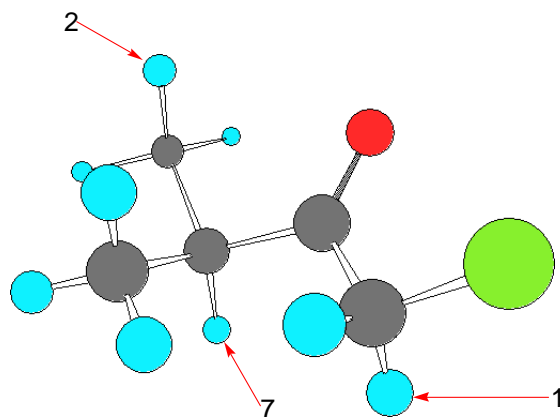
Coupling with the C1 proton splits the signal of the C2 proton into a doublet with $J=16\text{Hz}$. Further coupling with the C3 protons then splits each peak of the doublet into triplet with $J=8\text{Hz}$, and two peaks of them overlap, so we therefore observe a five-line spectrum for the C2 proton.

13.23 How could you use ^1H NMR to determine the regiochemistry of electrophilic addition to alkenes?

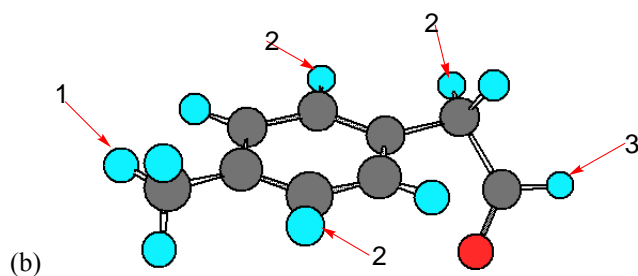
For example, does addition of HCl to 1-methylcyclohexene yield 1-chloro-1-methylcyclohexane or 1-chloro-2-methylcyclohexane?

Solution: the product of the reaction will be 1-chloro-1-methylcyclohexane, for in the spectrum we will see a three-proton singlet absorption near 1δ , not a doublet one.

13.24 Into how many peaks would you expect the ^1H NMR signals of the indicated protons to be split? (yellow-green = Cl)



Solution: (a)

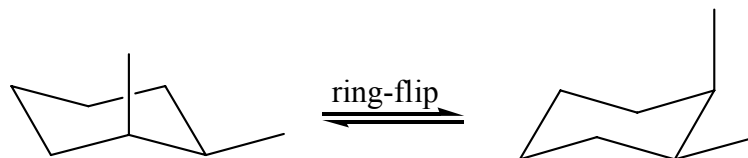


13.25 How many absorptions would you expect the following compound to have in its ^{13}C NMR spectrum?

Solution: There are two absorptions in its ^{13}C NMR spectrum.

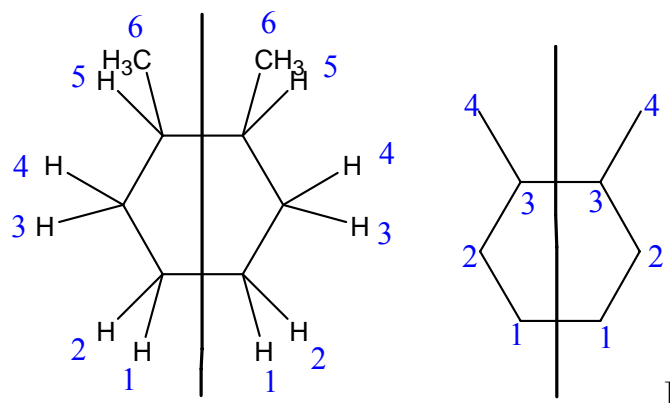
13.26 Missing

13.27 How many electronically nonequivalent kinds of protons and how many kinds of carbons are there in the following compound? Don't forget that cyclohexane rings can ring-flip.



Solution:

There are 6 kinds of protons and 4 kinds of carbons in the compound.



13.28 The following ^1H NMR absorptions were obtained on a spectrometer operating at 200 MHz and given in hertz downfield from the TMS standard. Convert the absorptions to δ units.

- (a) 436Hz
- (b) 956Hz
- (c) 1504Hz

Solution:

$$\delta = \frac{\text{Observed chemical shift (number of Hz away from TMS)}}{\text{Spectrometer frequency in MHz}}$$

- (a) $436/200=2.18\delta$
 (b) $956/200=4.78\delta$
 (c) $1504/200=7.52\delta$

13.29 The following ^1H NMR absorptions were obtained on a spectrometer operating at 300 MHz.
 Convert the chemical shift from δ unit to hertz downfield from TMS.

- (a). 2.1δ (b). 3.45δ (c). 6.30δ (d). 7.70δ

Solution:

- (a). $2.1 \times 300 = 630\text{Hz}$
 (b). $3.45 \times 300 = 1035\text{Hz}$
 (c). $6.30 \times 300 = 1890\text{Hz}$
 (d). $7.70 \times 300 = 2310\text{Hz}$

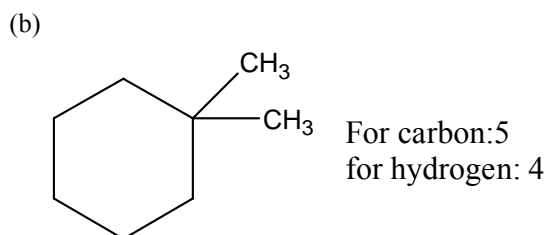
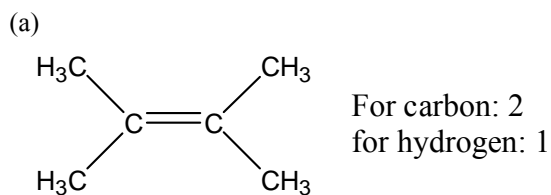
13.30 When measured on a spectrometer operating at 200MHz, chloroform (CHCl_3) show a single sharp absorption at 7.3δ :

- (a). How many parts per million downfield from the TMS does chloroform absorb?
 (b). How many hertz downfield from TMS would chloroform absorb if the measurement were carried out on a spectrometer operating at 360 Hz?
 (c). What would be the position of the chloroform absorption in δ units when measured on a 360Mhz spectrometer?

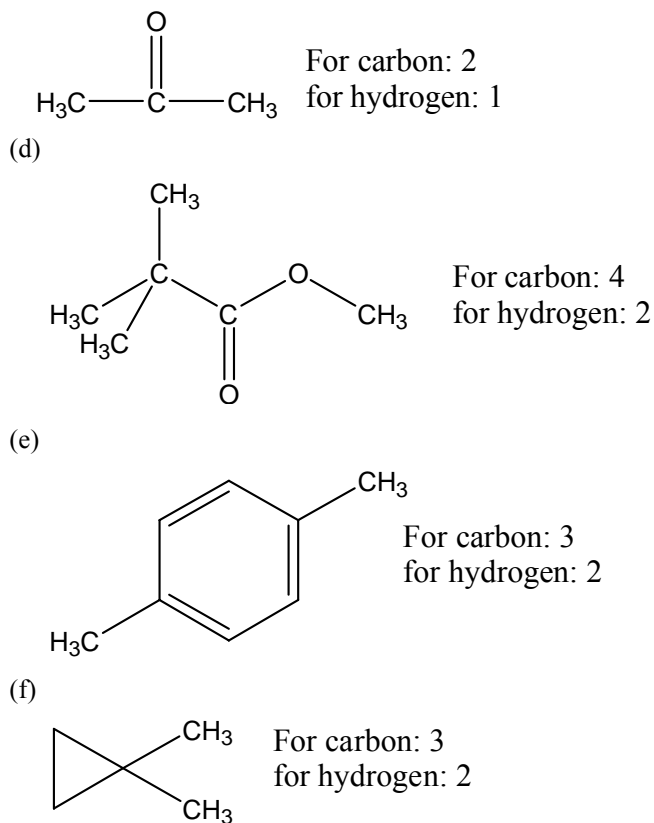
Solution:

- (a). 7.3 ppm
 (b). $7.3 \times 360 = 2628 \text{ Hz}$
 (c). 7.3 ppm

13.31 How many signals would you expect each of the following molecules to have in its ^1H and ^{13}C spectra?

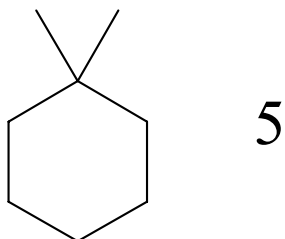


(c)



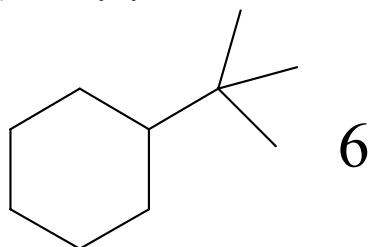
13.32 How many absorptions would you expect to observe in the ^{13}C NMR spectra of the following compounds?

(a) 1,1-Dimethylcyclohexane

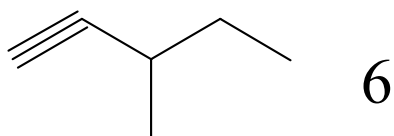


(b) $\text{CH}_3\text{CH}_2\text{OCH}_3$ 3

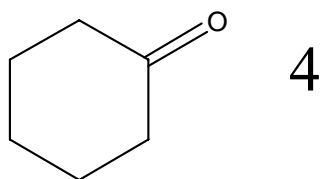
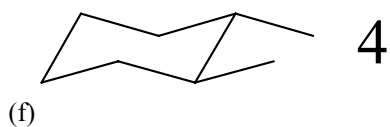
(c) tert-Butylcyclohexane



(d) 3-Methyl-1-pentyne



(e) cis-1,2-Dimethylcyclohexane



13.33 Suppose you ran a DEPT-135 spectrum for each substance in Problem 13.32. Indicate which carbon atoms in each molecule would show positive peaks and which would show negative peaks?

Solution: The CH_2 will be negative and others will be positive.

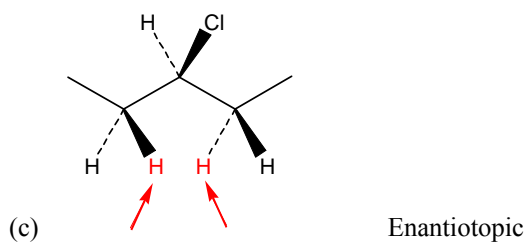
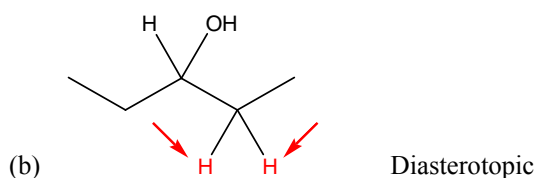
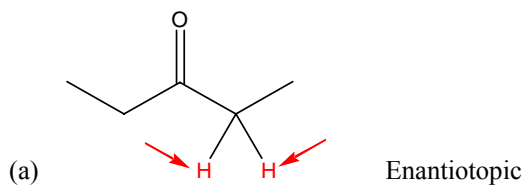
13.34 Why do you suppose accidental overlap of signals is much more common in ^1H NMR than in ^{13}C NMR?

Solution: Normally, C will have signals between 1~220 ppm, while H will have signals between 0~10 ppm. Therefore, accidental overlap of signals will be more common in proton NMR than in carbon NMR.

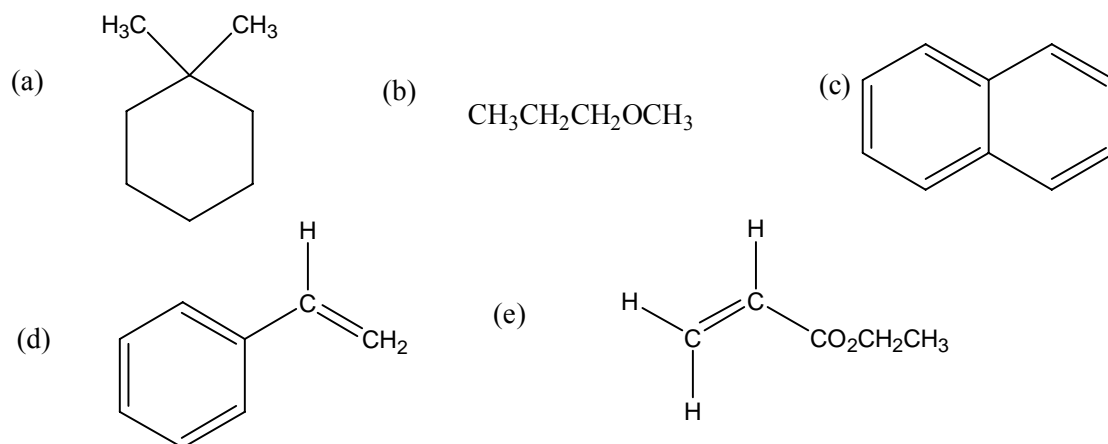
13.35 Is a nucleus that absorbs at 6.50δ more shielded or less shielded than a nucleus that absorbs at 3.20δ ? Does the nucleus that absorbs at 6.50δ require a stronger applied field or a weaker applied field to come into resonance than the nucleus that absorbs at 3.20δ ?

Conclusion: The nucleus that absorbs at 6.50δ is less shielded and requires a weaker applied field to come into resonance.

13.36 Identify the indicated sets of protons as unrelated, homotopic, enantiotopic, or diastereotopic:

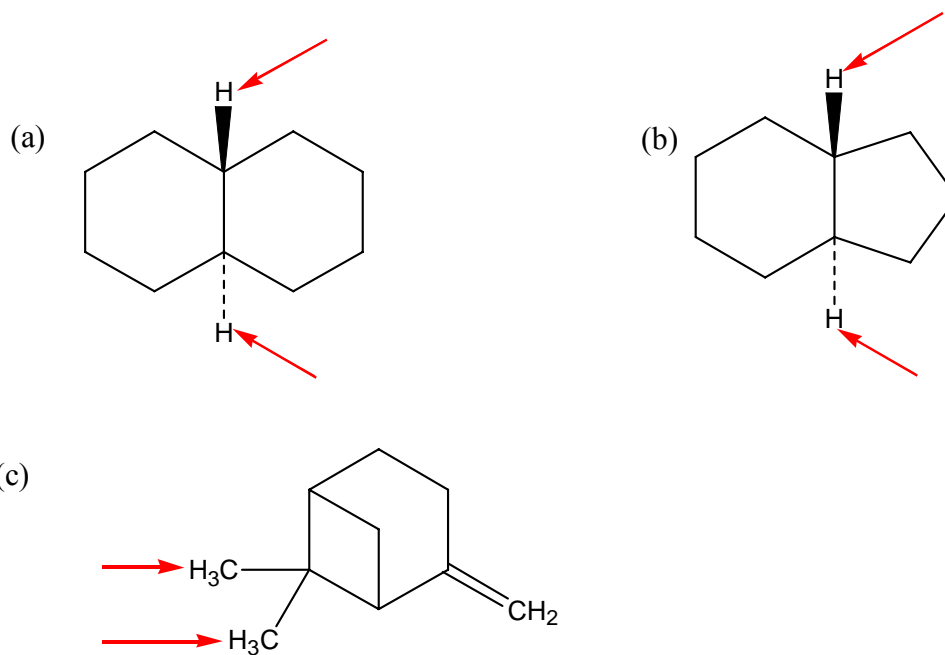


13.37 How many types of nonequivalent protons are in each of the following molecules?



Solution: (a) has four types nonequivalent protons.
 (b) has four types nonequivalent protons.
 (c) has two types nonequivalent protons.
 (d) has six types nonequivalent protons.
 (e) has five types nonequivalent protons.

13.38 Identify the indicated sets of protons as unrelated, homotopic, enantiotopic, or diastereotopic:

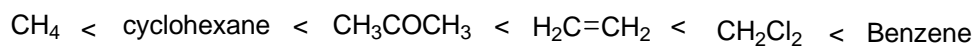


Solution: (a) is homotopic
 (b) is enantiotopic.
 (c) is diastereotopic.

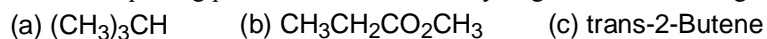
13.39 The following compounds all show a single line in their ^1H NMR spectra. List them in expected order of increasing chemical shift:

CH_4 , CH_2Cl_2 , cyclohexane, CH_3COCH_3 , $\text{H}_2\text{C}=\text{CH}_2$, Benzene

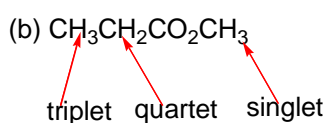
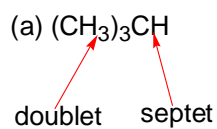
Solution:



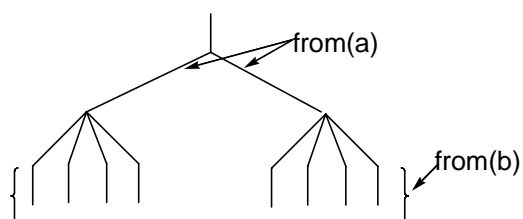
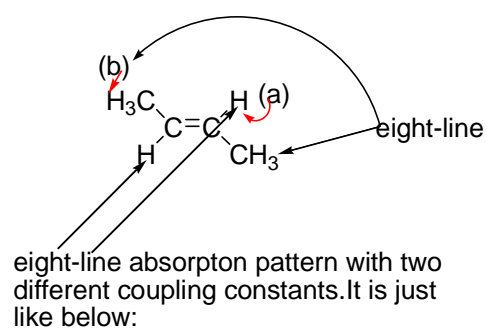
13.40 Predict the splitting pattern for each kind of hydrogen in the following molecules:



Solution:

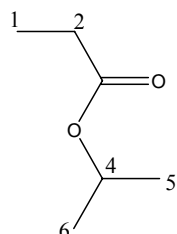


(c) trans-2-Butene



13.41 Predict the splitting pattern for each kind of hydrogen in isopropyl propanoate, $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}(\text{CH}_3)_2$.

Solution:



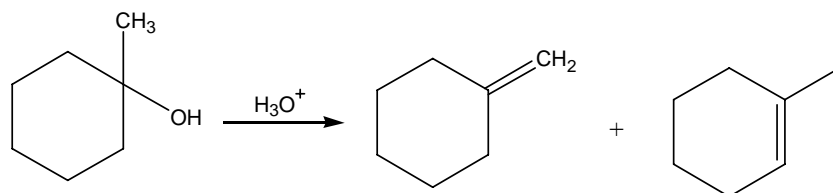
C1 has three signals;

C2 has four signals;

C4 has seven signals;

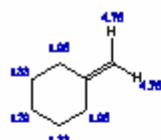
C5 and C6 are equivalent and have two signals.

13.42 The acid-catalyzed dehydration of 1-methylcyclohexanol yields a mixture of two alkenes. How would you use ^1H NMR to help you decide which was which?

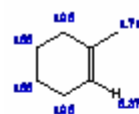


Solution:

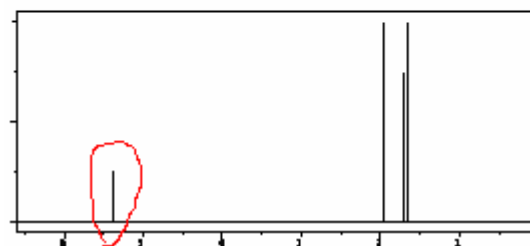
The first structure will have four signals in proton NMR, while the second structure has six signals in proton NMR. The specific one will be the methyl group for the second structure.



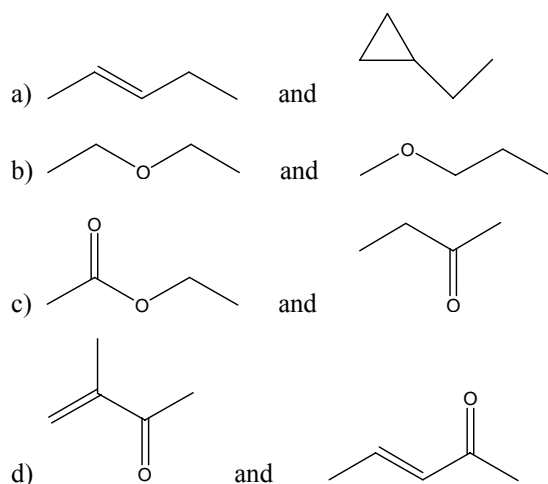
Estimation Quality: blue = good, magenta = medium, red = rough



Estimation Quality: blue = good, magenta = medium, red = rough



13.43 How would you use ^1H NMR to distinguish between the following pairs of isomers?



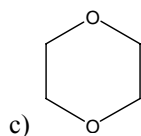
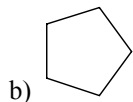
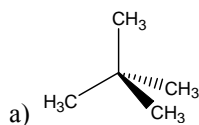
Solution:

- We can find peaks between 4.5-6.5ppm of the first structure but we can't find any peak in that position of the second structure.
- The splitting pattern is different. The first one has ethyl group splitting pattern, while the second structure has a singlet for methyl group.
- We can find peaks between 3.3-4.5ppm of the first structure but we can't find any peak in that position of the second structure.
- The second structure has a trans alkene unit, coupling constant will be 8-15 Hz.

13.44 Propose structures for compounds with the following formulas that show only one peak in their ^1H NMR spectra:

- a) C_5H_{12} b) C_5H_{10} c) $\text{C}_4\text{H}_8\text{O}_2$

Solution:



13.45 How many ^{13}C NMR absorptions would you expect for cis-1,3-dimethylcyclohexane? For trans-1,3-dimethylcyclohexane? Explain.

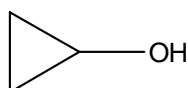
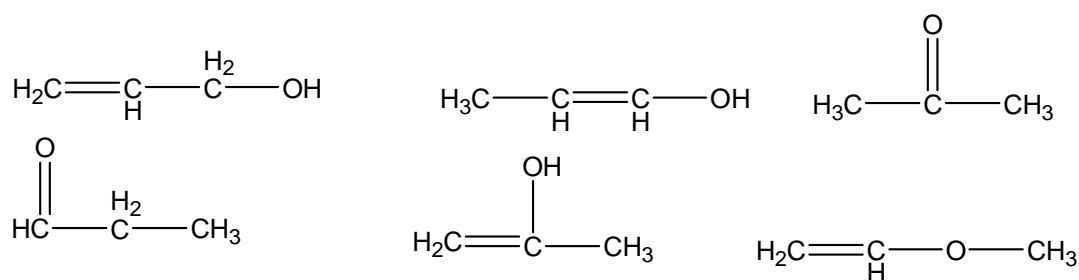
SOLUTION: For cis-1,3-dimethylcyclohexane, there will be 5 ^{13}C NMR absorptions because of its symmetry. For trans-1,3-dimethylcyclohexane, there will be 5 ^{13}C NMR absorptions because of its faster ring-flips than the time frame of NMR spectrum.

13.46 Assume that you have a compound with formula $\text{C}_3\text{H}_6\text{O}$

- How many double bonds and/or rings does your compound contain?
- Propose as many structures as you can that fit the molecular formula.
- If your compound shows an infrared absorption peak at 1715cm^{-1} , what functional group does it have?
- If your compound shows a single ^1H NMR absorption peak at 2.1δ , what is its structure?

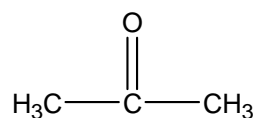
SOLUTION: (a) There is one double bond or one ring.

(b)

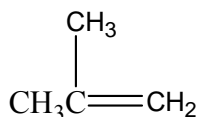
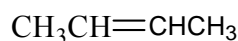
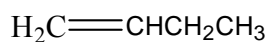
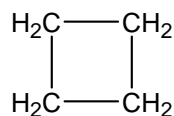


(c) $\text{C}=\text{O}$

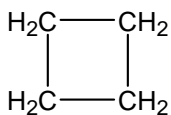
(d)



13.47 How would you use ^1H and ^{13}C NMR to help you distinguish among the following isomeric compounds of formula C_4H_8 ?



Solution:



The ^1H NMR spectrum for $\text{H}_2\text{C} - \text{CH}_2$ shows only 1 peak for its H, so it is the first one to be distinguished.

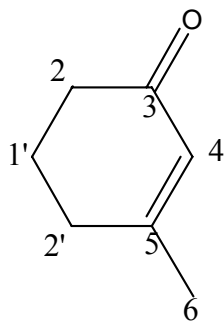
For $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_3$, we can see four multiple peaks in its ^1H NMR spectrum because of the four H which are indicated in four different colors are chemically nonequivalent.

For $\text{CH}_3\text{CH}=\text{CHCH}_3$ and $\text{CH}_3\text{C}=\text{CH}_2$, they both have 2 different kinds of chemically nonequivalent H, so it's hard to distinguish them in using ^1H NMR.

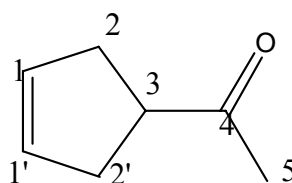
Since $\text{CH}_3\text{CH}=\text{CHCH}_3$ has 2 different kinds of chemically nonequivalent C, while

$\text{CH}_3\text{C}=\text{CH}_2$ has 3 different kinds of chemically nonequivalent C, we can distinguish them with ^{13}C NMR which shows different number of peaks for them.

13.48 How could you use ^1H NMR, ^{13}C NMR and IR spectroscopy to help you distinguish between the following structures?



3-methyl-2-cyclohexenone



3-cyclopentenyl methyl ketone

Solution:

3-Methyl-2-cyclohexenone is a ketone next to a double bond and absorbs at about 1690 cm^{-1} in the infrared absorption spectrum while 3-Cyclopentenyl methyl ketone absorbs at about 1715 cm^{-1} , where saturated open-chain ketones usually absorb.

3-Methyl-2-cyclohexenone has 6 different kinds of chemically nonequivalent C, and shows 6 peaks in the ^{13}C NMR spectrum. While 3-Cyclopentenyl methyl ketone has 5 different kinds of chemically nonequivalent C, and shows 5 peaks in the ^{13}C NMR spectrum.

3-Methyl-2-cyclohexenone has 5 different kinds of chemically nonequivalent H, and shows 5

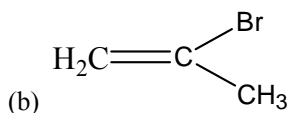
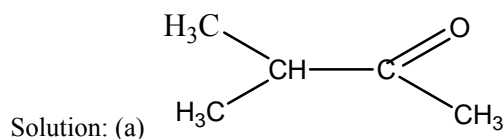
multiple peaks in the ^1H NMR spectrum. While 3-Cyclopentyl methyl ketone has 4 different kinds of chemically nonequivalent H, and shows 5 multiple peaks in the ^1H NMR spectrum.

13.49 The compound whose ^1H NMR spectrum is shown has the molecular formula $\text{C}_3\text{H}_6\text{Br}_2$. Propose a structure.

Solution: $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br}$

13.50 Propose structure for compounds that fit the following ^1H NMR data:

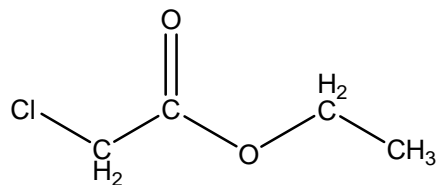
- (a) $\text{C}_5\text{H}_{10}\text{O}$ 0.95 δ (6H, doublet, $J=7\text{Hz}$) 2.10 δ (3H, singlet) 2.43 δ (1H, multiplet)
 (b) $\text{C}_3\text{H}_5\text{Br}$ 2.32 δ (3H, singlet) 5.35 δ (1H, broad singlet) 5.54 δ (1H, broad singlet)



13.51 The compound whose ^1H NMR spectrum is shown has the molecular formula $\text{C}_4\text{H}_7\text{O}_2\text{Cl}$ and has an infrared absorption peak at 1740 cm^{-1} . Propose structure.

Solution:

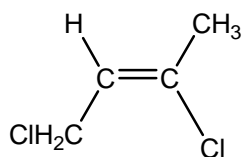
The structure may be as follow:



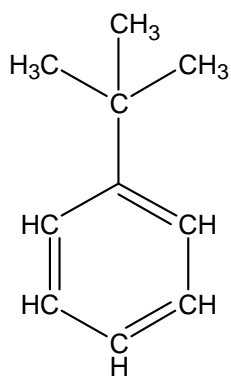
13.52 Propose structures for compounds that fit the following ^1H NMR data:

- | | |
|---|---|
| (a) $\text{C}_4\text{H}_6\text{Cl}_2$ | (b) $\text{C}_{10}\text{H}_{14}$ |
| 2.18 δ (3H, singlet) | 1.30 δ (9H, singlet) |
| 4.16 δ (2H, doublet, $J=7\text{ Hz}$) | 7.30 δ (5H, singlet) |
| 5.71 δ (1H, triplet, $J=7\text{ Hz}$) | |
| (c) $\text{C}_4\text{H}_7\text{BrO}$ | (d) $\text{C}_9\text{H}_{11}\text{Br}$ |
| 2.11 δ (3H, singlet) | 2.15 δ (2H, quintet, $J=7\text{ Hz}$) |
| 3.52 δ (2H, triplet, $J=6\text{ Hz}$) | 2.75 δ (2H, triplet, $J=7\text{ Hz}$) |
| 4.40 δ (2H, triplet, $J=6\text{ Hz}$) | 3.38 δ (2H, triplet, $J=7\text{ Hz}$) |
| | 7.02 δ (5H, singlet) |

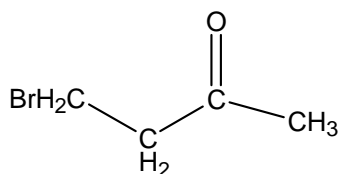
Solution: (a) is



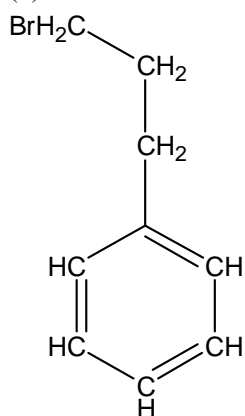
(b)



(c)



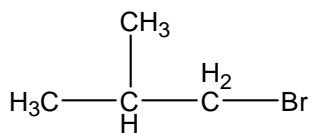
(d)



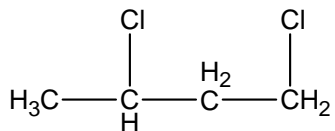
13.53 Propose structures for the two compounds whose ^1H NMR spectra are shown.

- (a) $\text{C}_4\text{H}_9\text{Br}$
 (b) $\text{C}_4\text{H}_8\text{Cl}_2$

Solution: (a)

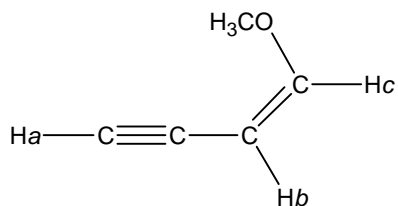


(b)



13.54 Long-range coupling between protons more than two carbon atoms apart is sometimes observed when bonds intervene. An example is found in 1-methoxy-1-buten-3-yne. Not only does the acetylenic proton, H_a , couple with the vinylic proton H_b , it also couples with the vinylic

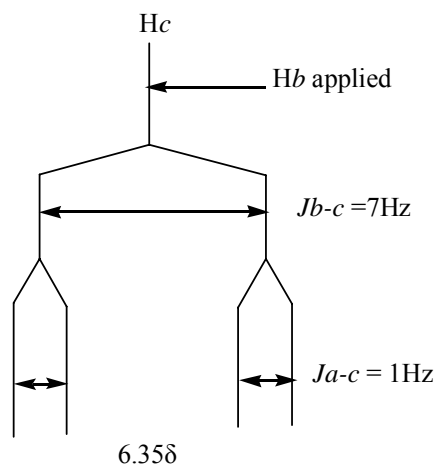
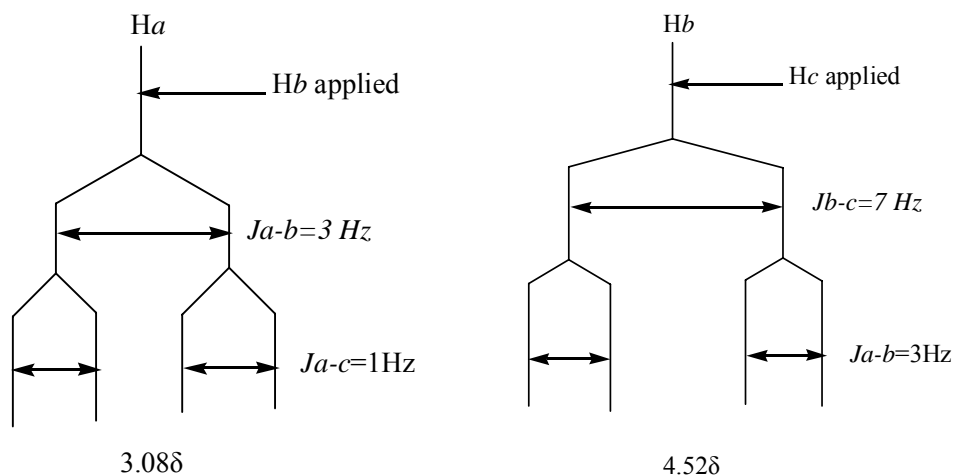
proton Hc, four carbon atoms away. The data are:



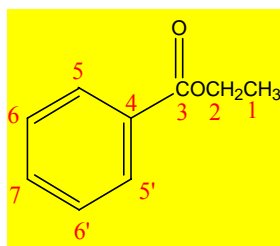
Ha(3.08 δ) Hb(4.52 δ) Hc(6.35 δ)
*J*_{a-b} = 3 Hz *J*_{a-c} = 1 Hz *J*_{b-c} = 7 Hz

Construct tree diagrams that account for the observed splitting patterns of Ha, Hb, Hc.

Solution:



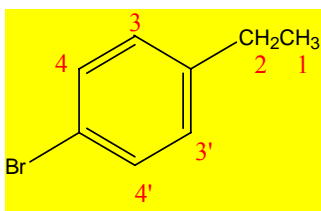
13.55 Assign as many of the resonance as you can to specific carbon atoms in the C NMR spectrum of ethyl benzene.



Answer:

From left to right the resonance stands for 3, 4, 7, 6&6', 5&5', 2, 1.

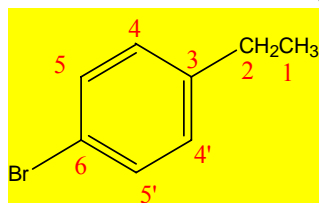
13.56 The H and C NMR spectra of compound A, C₈H₉Br, are shown. Propose a structure for A, and assign peaks in the spectra to your structure.



Answer:

To the H NMR from left to right: 3&3', 4&4', 2, 1.

To the C NMR from left to right: 3, 4&4', 5&5', 6, 2, 1.



13.57 Propose structures for the three compounds whose ^1H NMR spectra are shown.

(a) $\text{C}_5\text{H}_{10}\text{O}$

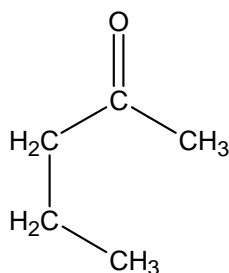
(b) $\text{C}_7\text{H}_7\text{Br}$

(c) $\text{C}_8\text{H}_9\text{Br}$

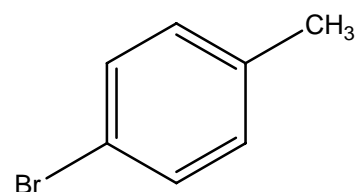
Solution:

The structure is:

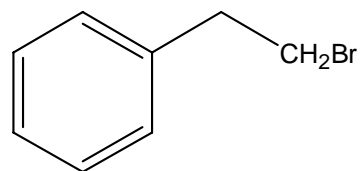
(a)



(b)



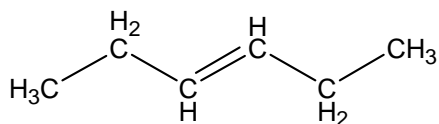
(c)



13.58 The mass spectrum and ^{13}C NMR spectrum of a hydrocarbon are shown. Propose a structure for this hydrocarbon, and explain the spectral data.

Solution:

The structure is:



3-hexene

- CH₃ (17ppm)
- CH₂- (24ppm)
- =CH- (131ppm)

13.59 Compound A, a hydrocarbon with $M^+=96$ in its mass spectrum, has the ^{13}C spectral data given below. On reaction with BH_3 followed by treatment with basic H_2O_2 , A is converted into B, whose ^{13}C spectral data are also given below. Propose structures for A and B.

Compound A

Broadband-decoupled ^{13}C NMR: 26.8, 28.7, 35.7, 106.9, 149.7 δ

DEPT-90: no peaks

DEPT-135: no positive peaks; negative peaks at 26.8, 28.7, 35.7, 106.9 δ

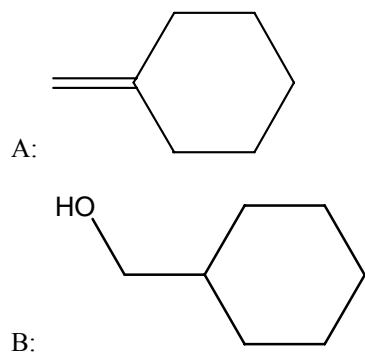
Compound B

Broadband-decoupled ^{13}C NMR: 26.1, 26.9, 29.9, 40.5, 68.2 δ

DEPT-90: 40.5 δ

DEPT-135: positive peak at 40.5 δ ; negative peaks at 26.1, 26.9, 29.9, 68.2 δ

Solution:



13.60 Propose a structure for compound C, which has $M^+=86$ in its mass spectrum, an IR absorption at 3400 cm^{-1} , and the following ^{13}C NMR spectral data:

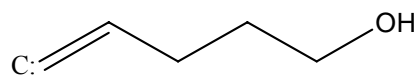
Compound C

Broadband-decoupled ^{13}C NMR: 30.2, 31.9, 61.8, 114.7, 138.4 δ

DEPT-90: 138.4 δ

DEPT-135: positive peak at 138.4 δ ; negative peaks at 30.2, 31.9, 61.8, 114.7 δ

Solution:



13.61 Compound D is isomeric with compound C and has the following ^{13}C NMR spectral data. Propose a structure.

Compound D

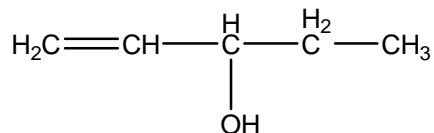
Broadband-decoupled ^{13}C NMR :9.7,29.9,74.4,114.4,141.4 δ

DEPT-90: 74.4,141.4δ

DEPT-135: positive peaks at 9.7,74.4,141.4δ

Negative peaks at 29.9,114.4δ

Solution:



13.62 Propose a structure for compound E, $\text{C}_7\text{H}_{12}\text{O}_2$, which has the following ^{13}C NMR spectral data:

Compound E

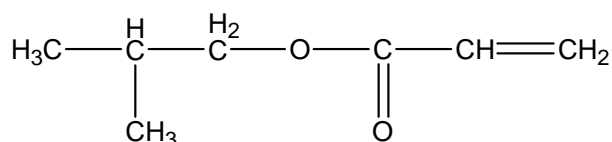
Broadband-decoupled ^{13}C NMR : 19.1,28.0,70.5,129.0,129.8,165.8δ

DEPT-90: 28.0,129.8δ

DEPT-135: positive peaks at 19.1,28.0,129.8δ

Negative peaks at 70.5,129.0δ

Solution:



13.63 Compound F, a **hydrocarbon** with $M^+ = 96$ in its mass spectrum, undergoes reaction with HBr to yield compound G. Propose structure for F and G, whose ^{13}C NMR spectral data are given below.

Compound F

Broadband-decoupled ^{13}C NMR : 27.6, 29.3, 32.2, 132.4δ

DEPT-90: 132.4δ

DEPT-135: positive peak at 132.4δ; negative peaks at 27.6,29.3,32.2δ]

Compound F

Broadband-decoupled ^{13}C NMR : 25.1, 27.7,39.9, 56.0 δ

DEPT-90: 56.0δ

DEPT-135: positive peak at 56.0δ; negative peaks at 25.1,27.7,39.9δ

Reasoning and solutions :

There is some difference between the Two DEPT-90 NMR, so I think there is a carbon-carbon double bond was replaced by a carbon-halogen bond.

Remark the chemical shift with color: CH, CH₂, CH₃,

Compound F

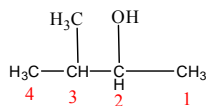
Broadband-decoupled ^{13}C NMR : 27.6, 29.3, 32.2, 132.4δ

Compound G

Broadband-decoupled ^{13}C NMR : 25.1, 27.7, 39.9, 56.0 δ

So the compound F is **cyclohepten**, and the compound G is **bromocyclohepten**.

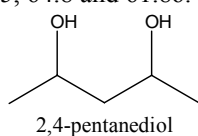
13.64 3-Methyl-2-butanol has five signals in its ^{13}C NMR spectrum at 17.9, 18.15, 20.00, 35.05, and 72.75 δ . Why are the two methyl groups attached to the C3 nonequivalent?



Solutions :

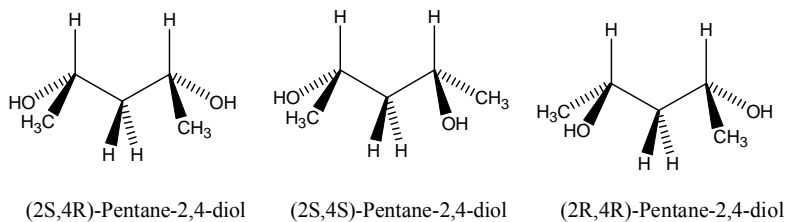
Because of chirality center at C2, the two methyl groups are nonequivalent.

13.65 A ^{13}C NMR spectrum of commercially available 2,4-pentanediol, show five peaks at 23.3, 23.9, 46.5, 64.8 and 61.8 δ . Explain.

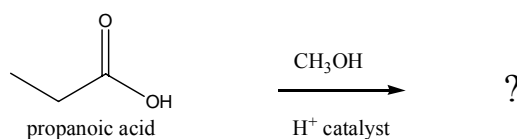


Solution:

Five kinds carbons:



13.66 Carboxylic acids (RCO_2H) react with alcohols ($\text{R}'\text{OH}$) in the presence of an acid catalyst. The reaction product of propanoic acid with methanol has the following spectroscopic properties. Propose a structure.



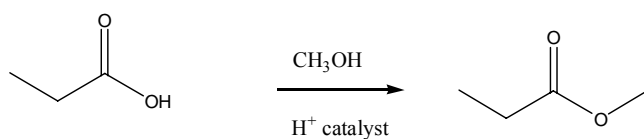
MS: $\text{M}^+ = 88$

IR: 1735 cm^{-1}

^1H NMR: 1.11 δ (3H, triplet, $J=7\text{Hz}$); 2.32 δ (2H, quartet, $J=7\text{Hz}$); 3.65 δ (3H, singlet)

^{13}C NMR: 9.3, 27.6, 51.4, 174.6 δ

Solution:



There are three kinds of hydrogen. CH_3 -, CH_2 and CH_3 - bonded to oxygen.

13.67 Nitrile ($\text{RC}\equiv\text{N}$) react with Grignard reagents ($\text{R}'\text{MgBr}$). The reaction product from 2-methylpropanenitrile with methylmagnesium bromide has the following spectroscopic properties. Propose a structure.

Solution:

The product is a methyl ketone:

