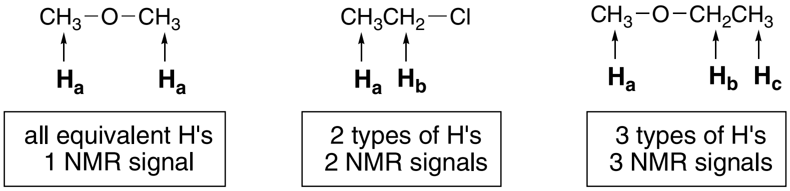
Chapter 14: Nuclear Magnetic Resonance Spectroscopy

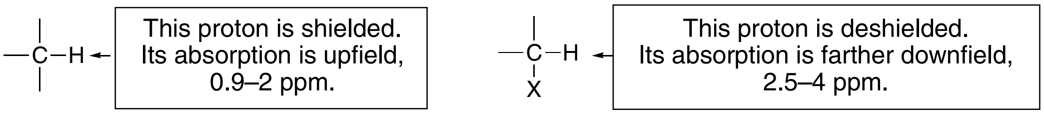
♦ ^{1}H NMR spectroscopy

[1] The **number of signals** equals the number of different types of protons (14.2).

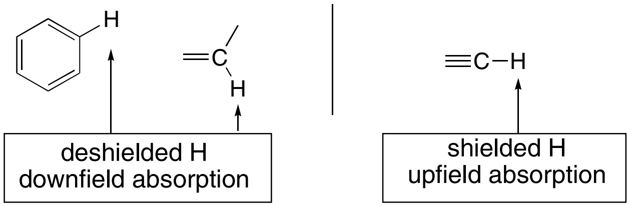


[2] The **position of a signal** (its chemical shift) is determined by shielding and deshielding effects.

- Shielding shifts an absorption upfield; deshielding shifts an absorption downfield.
- Electronegative atoms withdraw electron density, deshield a nucleus, and shift an absorption downfield (14.3).



- Loosely held π electrons can either shield or deshield a nucleus. Protons on benzene rings and double bonds are deshielded and absorb downfield, whereas protons on triple bonds are shielded and absorb upfield (14.4).



[3] The **area under an NMR signal** is proportional to the number of absorbing protons (14.5).

[4] **Spin-spin splitting** tells about nearby nonequivalent protons (14.6–14.8).

- Equivalent protons do not split each other's signals.
- A set of n nonequivalent protons on the same carbon or adjacent carbons split an NMR signal into $n + 1$ peaks.
- OH and NH protons do not cause splitting (14.9).
- When an absorbing proton has two sets of nearby nonequivalent protons that are equivalent to each other, use the $n + 1$ rule to determine splitting.
- When an absorbing proton has two sets of nearby nonequivalent protons that are not equivalent to each other, the number of peaks in the NMR signal = $(n + 1)(m + 1)$. In flexible alkyl chains, peak overlap often occurs, resulting in $n + m + 1$ peaks in an NMR signal.

♦ ^{13}C NMR spectroscopy (14.11)

[1] The number of signals equals the number of different types of carbon atoms. All signals are single lines.

[2] The relative position of ^{13}C signals is determined by shielding and deshielding effects.

- Carbons that are sp^3 hybridized are shielded and absorb upfield.
- Electronegative elements (N, O, and X) shift absorptions downfield.
- The carbons of alkenes and benzene rings absorb downfield.
- Carbonyl carbons are highly deshielded, and absorb farther downfield than other carbon types.

Chapter 14: Answers to Problems

14.1 Use the formula δ = [observed chemical shift (Hz)/ν of the NMR (MHz)] to calculate the chemical shifts.

a. **CH_3 protons:**
δ = [1715 Hz] / [500 MHz]
= **3.43 ppm**

OH proton:
δ = [1830 Hz] / [500 MHz]
= **3.66 ppm**

b. The positive direction of the δ scale is downfield from TMS. The CH_3 protons absorb upfield from the OH proton.

14.2 Calculate the chemical shifts as in Answer 14.1.

a. one signal:
δ = [1017 Hz] / [300 MHz]
= **3.39 ppm**

second signal:
δ = [1065 Hz] / [300 MHz]
= **3.55 ppm**

b. one signal:
3.39 = [x Hz] / [500 MHz]
x = **1695 Hz**

second signal:
3.55 = [x Hz] / [500 MHz]
x = **1775 Hz**

14.3 To determine if two H's are equivalent replace each by an atom X. If this yields the same compound or mirror images, the two H's are equivalent. Each kind of H will give one NMR signal.

a. CH_3CH_3
1 kind of H
1 NMR signal

b. $CH_3CH_2CH_3$
2 kinds of H's
2 NMR signals

c. $CH_3CH_2CH_2CH_3$
2 kinds of H's
2 NMR signals

d. $(CH_3)_2CHCH(CH_3)_2$
2 kinds of H's
2 NMR signals

e. $CH_3CH_2CO_2CH_2CH_3$
4 kinds of H's
4 NMR signals

f. $CH_3OCH_2CH(CH_3)_2$
4 kinds of H's
4 NMR signals

g. $CH_3CH_2OCH_2CH_3$
2 kinds of H's
2 NMR signals

h. $CH_3CH_2CH_2OH$
4 kinds of H's
4 NMR signals

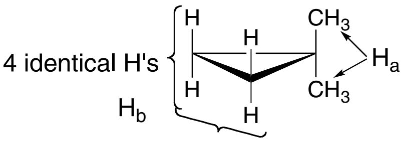
14.4

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2Cl$

Each C is a different distance from the Cl. This makes each C different, and each set of H's different. There are 8 different kinds of protons.

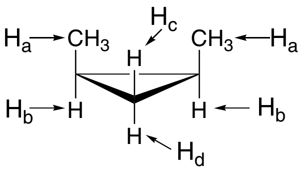
14.5 Draw in all of the H's and compare them. If two H's are cis and trans to the same group, they are equivalent.

a.



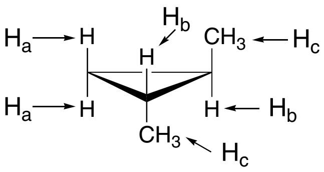
2 NMR signals

b.



4 NMR signals

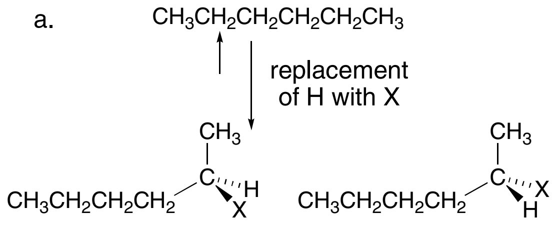
c.



3 NMR signals

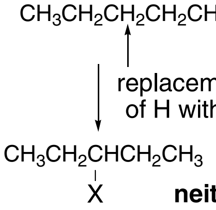
14.6 If replacement of H with X yields enantiomers, the protons are **enantiotopic**.
If replacement of H with X yields diastereomers, the protons are **diastereotopic**. In general, if the compound has **one stereogenic center**, the protons in a CH_2 group are **diastereotopic**.

a.



enantiomers =
enantiotopic H's

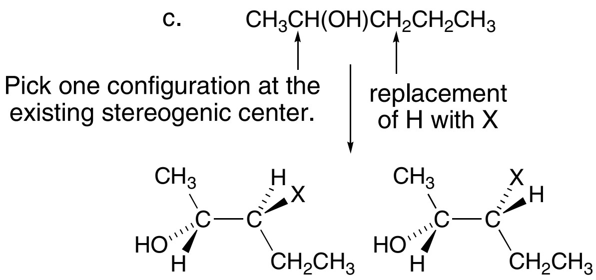
b.



no stereogenic center

neither enantiotopic nor diastereotopic

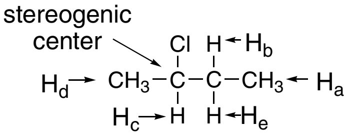
c.



diastereomers =
diastereotopic H's

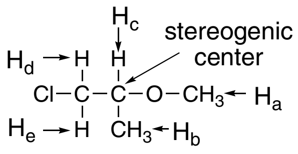
14.7 The two protons of a CH_2 group are different from each other if the compound has one stereogenic center. Replace one proton with X and compare the products.

a. The stereogenic center makes the H's in the CH_2 group diastereotopic and therefore different from each other.



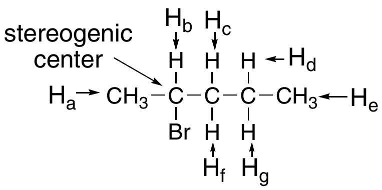
5 NMR signals

b.



5 NMR signals

c.



7 NMR signals

14.8 Decreased electron density deshields a nucleus and the absorption goes downfield. Absorption also shifts downfield with increasing alkyl substitution.

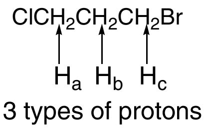
a. $FC\underline{\mathbf{H_2}}CH_2C\underline{H_2}Cl$
F is more electronegative than Cl. The CH_2 group adjacent to the F is more deshielded and the H's will absorb farther downfield.

b. $CH_3C\underline{H_2}CH_2C\underline{\mathbf{H_2}}OCH_3$
The CH_2 group adjacent to the O will absorb farther downfield because it is closer to the electronegative O atom.

c. $C\underline{\mathbf{H_3}}OC(C\underline{H_3})_3$
The CH_3 group bonded to the O atom will absorb farther downfield.

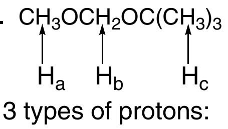
14.9

a.



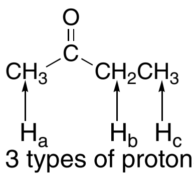
3 types of protons:
$H_b < H_c < H_a$

b.



3 types of protons:
$H_c < H_a < H_b$

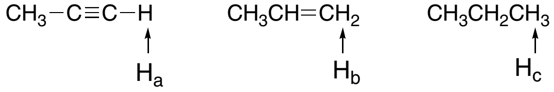
c.



3 types of protons:
$H_c < H_a < H_b$

14.10

a.

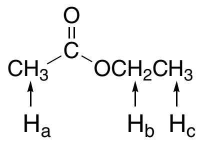


$CH_3-C\equiv C-H$ (H_a) $CH_3CH=CH_2$ (H_b) $CH_3CH_2CH_3$ (H_c)

H_c protons are shielded because they are bonded to an *sp*^{3} C.
H_a is shielded because it is bonded to an *sp* C.
H_b protons are deshielded because they are bonded to an *sp*^{2} C.

$H_c < H_a < H_b$

b.



$\underset{H_a}{CH_3}C(=O)O\underset{H_b}{CH_2}\underset{H_c}{CH_3}$

H_c protons are shielded because they are bonded to an *sp*^{3} C.
H_a protons are deshielded slightly because the CH_3 group is bonded to a C=O.
H_b protons are deshielded because the CH_2 group is bonded to an O atom.

$H_c < H_a < H_b$

14.11 An integration ratio of 2:3 means that there are two types of hydrogens in the compound, and that the ratio of one type to another type is 2:3.

a. CH_3CH_2Cl	b. $CH_3CH_2CH_3$	c. $CH_3CH_2OCH_2CH_3$	d. $CH_3OCH_2CH_2OCH_3$
2 types of H's	2 types of H's	2 types of H's	2 types of H's
3:2 - YES	6:2 or 3:1 - no	6:4 or 3:2 - YES	6:4 or 3:2 - YES

14.12 To determine how many protons give rise to each signal:

- Divide the total number of integration units by the total number of protons to find the number of units per H.
- Divide each integration value by this value and round to the nearest whole number.

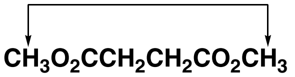
$C_8H_{14}O_2$

total number of integration units = 14 + 12 + 44 = 70 units
total number of protons = 14 H's
70 units/14 H's = **5 units per H**

Signal [A] = 14/5 = **3 H**
Signal [B] = 12/5 = **2 H**
Signal [C] = 44/5 = **9 H**

14.13

downfield absorption closer to O



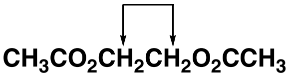
$CH_3O_2CCH_2CH_2CO_2CH_3$

A

ratio of absorbing signals 2:3

Signal [1] = **4 H = 2.64**
Signal [2] = **6 H = 3.69** ← 6 H's with downfield absorption

downfield absorption closer to O



$CH_3CO_2CH_2CH_2O_2CCH_3$

B

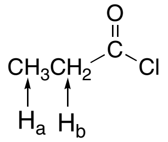
ratio of absorbing signals 3:2

Signal [1] = **6 H = 2.09**
Signal [2] = **4 H = 4.27** ← 4 H's with downfield absorption

14.14 To determine the **splitting pattern** for a molecule:

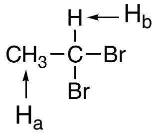
- Determine the number of different kinds of protons.
- Nonequivalent protons on the same C or adjacent C's split each other.
- Apply the *n* + 1 rule.

a.


CH_3CH_2COCl

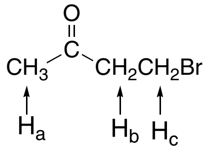
H_a: 3 peaks - triplet
H_b: 4 peaks - quartet

b.


CH_3CHBr_2

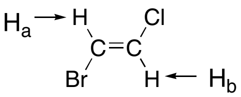
H_a: 2 peaks - doublet
H_b: 4 peaks - quartet

c.


$CH_3COCH_2CH_2Br$

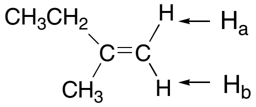
H_a: 1 peak - singlet
H_b: 3 peaks - triplet
H_c: 3 peaks - triplet

d.



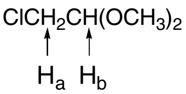
H_a: 2 peaks - doublet
H_b: 2 peaks - doublet

e.



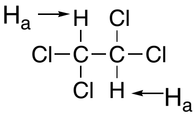
H_a: 2 peaks - doublet
H_b: 2 peaks - doublet

f.

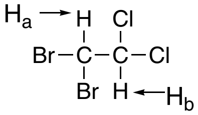

$ClCH_2CH(OCH_3)_2$

H_a: 2 peaks - doublet
H_b: 3 peaks - triplet

14.15 Identical protons do not split each other.



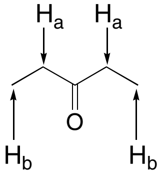
H_a: 1 singlet
All protons are equivalent.



H_a: 2 peaks - doublet
H_b: 2 peaks - doublet

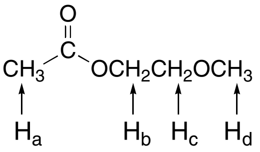
14.16 Use the directions from Answer 14.14.

a.



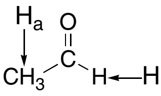
H_a: quartet
H_b: triplet
2 NMR signals

b.


$CH_3COOCH_2CH_2OCH_3$

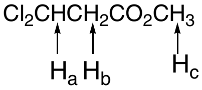
H_a and H_d are both singlets.
H_b: triplet
H_c: triplet
4 NMR signals

c.


CH_3CHO

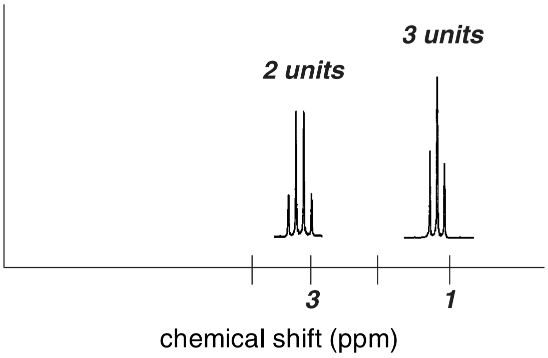
H_a: doublet
H_b: quartet
2 NMR signals

d.


$Cl_2CHCH_2CO_2CH_3$

H_a: triplet
H_b: doublet
H_c: singlet
3 NMR signals

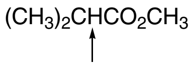
14.17 CH_3CH_2Cl



There are two kinds of protons, and they can split each other. The CH_3 signal will be split by the CH_2 protons into 2 + 1 = 3 peaks. It will be upfield from the CH_2 protons since it is farther from the Cl. The CH_2 signal will be split by the CH_3 protons into 3 + 1 = 4 peaks. It will be downfield from the CH_3 protons since the CH_2 protons are closer to the Cl. The ratio of integration units will be 3:2.

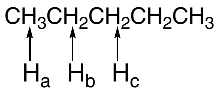
14.18

a.



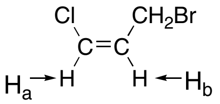
split by 6 equivalent H's
6 + 1 = **7 peaks**

b.



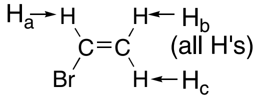
H_a: split by 2 H's
3 peaks
H_c: split by 4 equivalent H's
5 peaks
H_b: split by 2 sets of H's
(3 + 1)(2 + 1) = **12 peaks (maximum)**
Since this is a flexible alkyl chain, the signal due to H_b will have peak overlap, and 3 + 2 + 1 = **6 peaks** will likely be visible.

c.



H_a: split by 1 H
2 peaks
H_b: split by 2 sets of H's
(1 + 1)(2 + 1) = **6 peaks**

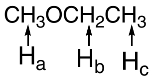
d.



H_a: split by 2 different H's
(1+1)(1+1) = **4 peaks**
H_b: split by 2 different H's
(1+1)(1+1) = **4 peaks**
H_c: split by 2 different H's
(1+1)(1+1) = **4 peaks**

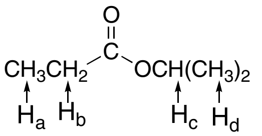
14.19

a.



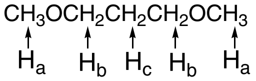
H_a: singlet at ~3 ppm
H_b: quartet at ~3.5 ppm
H_c: triplet at ~1 ppm

b.



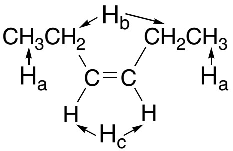
H_a: triplet at ~1 ppm
H_b: quartet at ~2 ppm
H_c: septet at ~3.5 ppm
H_d: doublet at ~1 ppm

c.



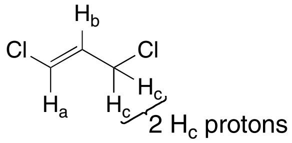
H_a: singlet at ~3 ppm
H_b: triplet at ~3.5 ppm
H_c: quintet at ~1.5 ppm

d.

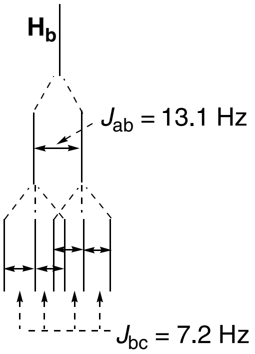


H_a: triplet at ~1 ppm
H_b: multiplet (8 peaks) at ~2.5 ppm
H_c: triplet at ~5 ppm

14.20



trans-1,3-dichloropropene

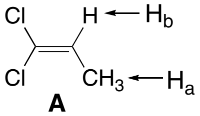


Splitting diagram for H_b

1 **trans** H_a proton splits H_b into
1 + 1 = 2 peaks
a doublet

2 H_c protons split H_b into
2 + 1 = 3 peaks
Now it's a doublet of triplets.

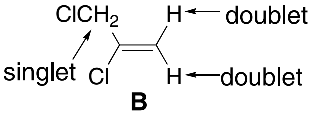
14.21



A

H_a: 1.75 ppm, doublet, 3 H, $J = 6.9$ Hz
H_b: 5.89 ppm, quartet, 1 H, $J = 6.9$ Hz

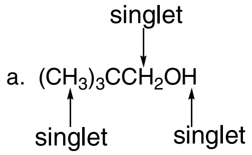
$C_3H_4Cl_2$



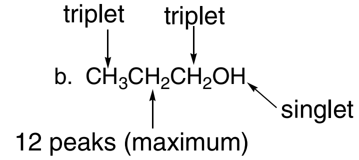
B

signal at 4.16 ppm, singlet, 2 H
signal at 5.42 ppm, doublet, 1 H, $J = 1.9$ Hz
signal at 5.59 ppm, doublet, 1 H, $J = 1.9$ Hz

14.22 Remember that OH (or NH) protons do not split other signals, and are not split by adjacent protons.

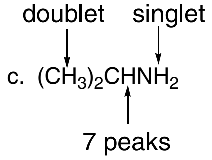


3 NMR signals



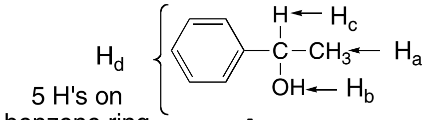
6 peaks (more likely, resulting from peak overlap)

4 NMR signals



3 NMR signals

14.23



A

H_a: doublet at ~1.4 due to the CH_3 group, split into two peaks by one adjacent nonequivalent H (H_c).

H_b: singlet at ~2.7 due to the OH group. OH protons are not split by nor do they split adjacent protons.

H_c: quartet at ~4.7 due to the CH group, split into four peaks by the adjacent CH_3 group.

H_d: Five protons on the benzene ring.

14.24 Use these steps to propose a structure consistent with the molecular formula, IR, and NMR data.

- Calculate the **degrees of unsaturation**.
- Use the IR data to determine what types of **functional groups** are present.
- Determine the number of different **types of protons**.
- Calculate the **number of H's** giving rise to each signal.
- Analyze the **splitting pattern** and put the molecule together.
- Use the **chemical shift** information to check the structure.

- Molecular formula $C_7H_{14}O_2$

  $2n + 2 = 2(7) + 2 = 16$
  $16 - 14 = 2/2 =$ **1 degree of unsaturation**
  1 π bond or 1 ring

- IR peak at 1740 cm^{-1}

  C=O absorption is around 1700 cm^{-1} (causes the degree of unsaturation).
  No signal at 3200–3600 cm^{-1} means there is no O–H bond.

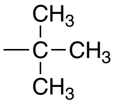
- NMR data:

absorption	ppm	integration	
singlet	1.2	26	→ 26 units/3 units per H = **9 H's**
triplet	1.3	10	→ 10 units/3 units per H = **3 H's** (probably a CH_3 group)
quartet	4.1	6	→ 6 units/3 units per H = **2 H's** (probably a CH_2 group)

  - 3 kinds of H's
  - number of H's per signal

    total integration units: 26 + 10 + 6 = 42 units
    42 units / 14 H's = 3 units per H
  - look at the splitting pattern

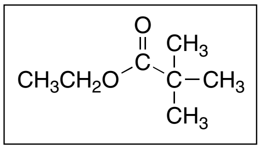
    The singlet (9 H) is likely from a *tert*-butyl group:



$$-C(CH_3)_3$$

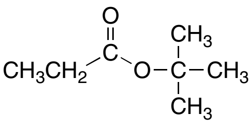
    The CH_3 and CH_2 groups split each other: CH_3-CH_2-

- Join the pieces together.



$$CH_3CH_2O\overset{O}{\overset{\|}{C}}\text{–}\underset{CH_3}{\overset{CH_3}{C}}\text{–}CH_3$$

or



$$CH_3CH_2\overset{O}{\overset{\|}{C}}\text{–}O\text{–}\underset{CH_3}{\overset{CH_3}{C}}\text{–}CH_3$$

Pick this structure due to the chemical shift data.
The CH_2 group is shifted downfield (4 ppm), so it
is close to the electron-withdrawing O.

14.25

- Molecular formula: C_3H_8O
- IR peak at 3200–3600 cm^{-1}
- NMR data:
  - doublet at ~1.2 (6 H)
  - singlet at ~2.2 (1 H)
  - septet at ~4 (1 H)

- Calculate degrees of unsaturation

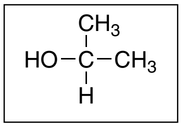
  $2n + 2 = 2(3) + 2 = 8$

  $8 - 8 =$ **0 degrees of unsaturation**

➢ Peak at 3200–3600 cm^{-1} is due to an **O–H bond.**

3 types of H's
septet from 1 H ← split by 6 H's
→ **singlet** from 1 H ← from the O–H proton
doublet from 6 H's ← split by 1 H

➢ Put information together:



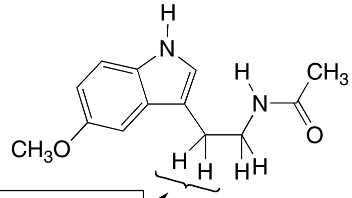
$$HO\text{–}\underset{H}{\overset{CH_3}{C}}\text{–}CH_3$$

14.26

a.

Absorption [**A**]:	singlet at ~3.8 ppm	CH_3O–
Absorption [**B**]:	multiplet at ~3.6 ppm	CH_2N
Absorption [**C**]:	triplet at ~2.9 ppm	CH_2 adjacent to five-membered ring
Absorption [**D**]:	singlet at ~1.9 ppm	CH_3C=O

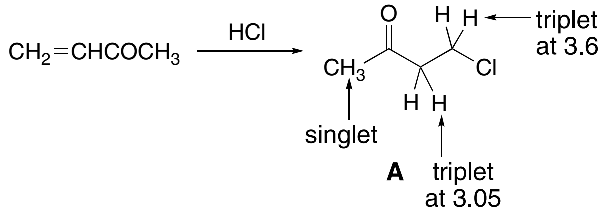
b.



split by 2 adjacent nonequivalent H's into a triplet

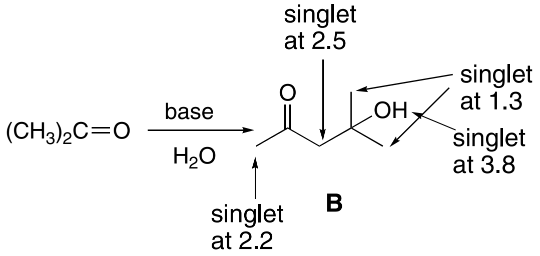
14.27 Identify each compound from the ^{1}H NMR data.

a.



A

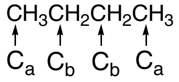
b.



B

14.28 Each different kind of carbon atom will give a different ^{13}C NMR signal.

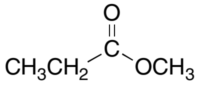
a.



2 kinds of C's

2 ^{13}C NMR signals

b.

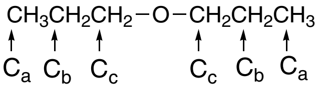


Each C is different.

4 kinds of C's

4 ^{13}C NMR signals

c.

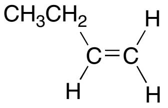


same groups on both sides of O

3 kinds of C's

3 ^{13}C NMR signals

d.



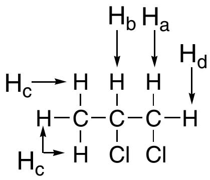
Each C is different.

4 kinds of C's

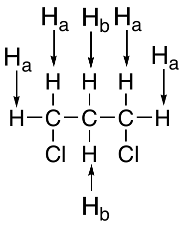
4 ^{13}C NMR signals

14.29

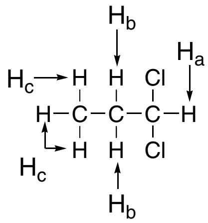
a.



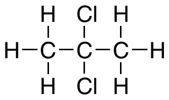
4 ^{1}H NMR signals



2 ^{1}H NMR signals



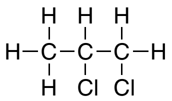
3 ^{1}H NMR signals



all H's identical

1 ^{1}H NMR signal

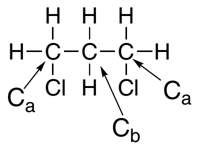
b.



Each C is different.

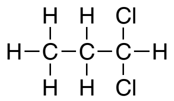
3 kinds of C's

3 ^{13}C NMR signals



2 kinds of C's

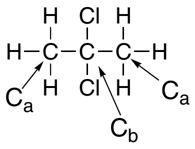
2 ^{13}C NMR signals



Each C is different.

3 kinds of C's

3 ^{13}C NMR signals



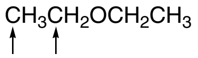
2 kinds of C's

2 ^{13}C NMR signals

c. Although the number of ^{13}C signals cannot be used to distinguish these isomers, each isomer exhibits a different number of signals in its ^{1}H NMR spectrum. As a result, the isomers are distinguishable by ^{1}H NMR spectroscopy.

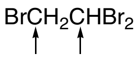
14.30 Electronegative elements shift absorptions downfield. The carbons of alkenes and benzene rings, and carbonyl carbons are also shifted downfield.

a.



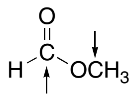
The CH_2 group is closer to the electronegative O and will be farther downfield.

b.



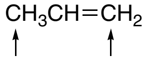
The C of the $CHBr_2$ group has two bonds to electronegative Br atoms and will be farther downfield.

c.



The carbonyl carbon is highly deshielded and will be farther downfield.

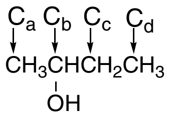
d.



The CH_2 group is part of a double bond and will be farther downfield.

14.31

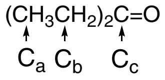
a. In order of lowest to highest chemical shift:



$\overset{C_a}{\overset{\downarrow}{CH_3}}\underset{\underset{OH}{\mid}}{\overset{C_b}{\overset{\downarrow}{C}}H}\overset{C_c}{\overset{\downarrow}{CH_2}}\overset{C_d}{\overset{\downarrow}{CH_3}}$

$C_d < C_a < C_c < C_b$

b. In order of lowest to highest chemical shift:

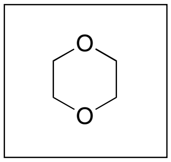


$(\underset{C_a}{\underset{\uparrow}{C}}H_3\underset{C_b}{\underset{\uparrow}{C}}H_2)_2\underset{C_c}{\underset{\uparrow}{C}}{=}O$

$C_a < C_b < C_c$

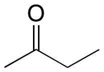
14.32

- molecular formula $C_4H_8O_2$
  $2n + 2 = 2(4) + 2 = 10$
  $10 - 8 = 2/2 =$ **1 degree of unsaturation**
- no IR peaks at 3200–3600 or 1700 cm^{-1}
  no O–H or C=O
- ^1H NMR spectrum at 3.69 ppm
  only one kind of proton
- ^{13}C NMR spectrum at 67 ppm
  only one kind of carbon

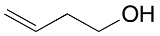


This structure satisifies all the data. One ring is one degree of unsaturation. All carbons and protons are identical.

14.33



- molecular formula C_4H_8O
  $2n + 2 = 2(4) + 2 = 10$
  $10 - 8 = 2/2 =$ **1 degree of unsaturation**
- ^{13}C NMR signal at > 160 ppm due to C=O



- molecular formula C_4H_8O
  $2n + 2 = 2(4) + 2 = 10$
  $10 - 8 = 2/2 =$ **1 degree of unsaturation**
- all ^{13}C NMR signals at < 160 ppm
  NO C=O

14.34 Use the directions from Answer 14.3.

a. $(CH_3)_3CH$

2 kinds of H's

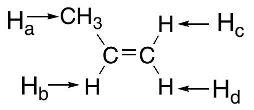
b. $(CH_3)_3CC(CH_3)_3$

1 kind of H

c. $CH_3CH_2OCH_2CH_2CH_2CH_2CH_3$

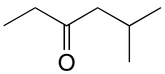
7 kinds of H's

d.



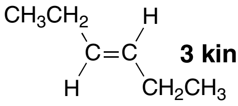
4 kinds of H's

e.



5 kinds of H's

f.

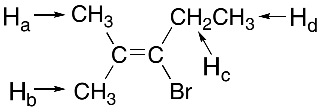


3 kinds of H's

g. $CH_3CH_2CH_2OCH_2CH_2CH_3$

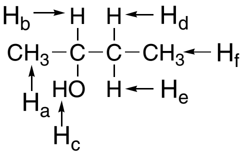
3 kinds of H's

h.



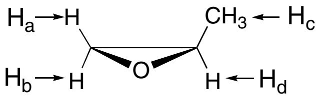
4 kinds of H's

i.



6 kinds of H's

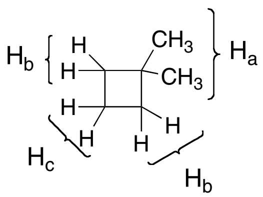
j.



4 kinds of H's

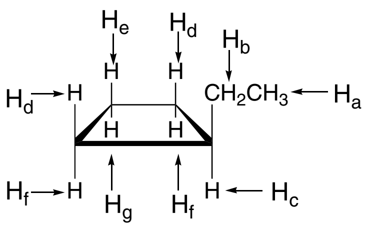
14.35

a.



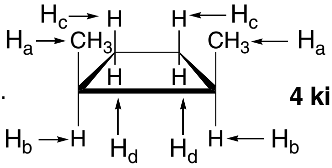
3 kinds of protons

b.



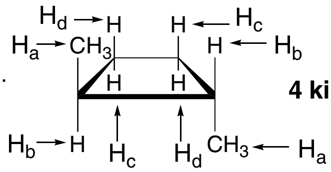
7 kinds of protons

c.



4 kinds of protons

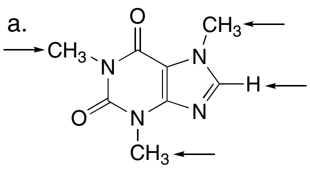
d.



4 kinds of protons

14.36

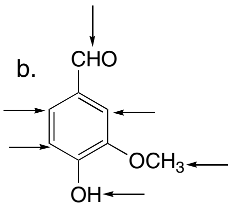
a.



caffeine

4 NMR signals

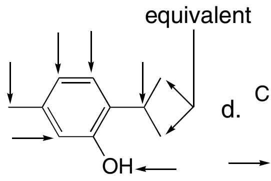
b.



vanillin

6 NMR signals

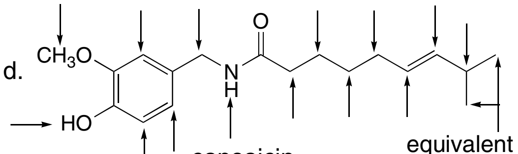
c.



thymol

7 NMR signals

d.



capsaicin

15 NMR signals

14.37

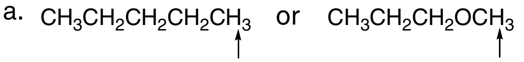
δ (in ppm) = [observed chemical shift (Hz)] / ν of the NMR (MHz)]

a. 2.5 = x Hz/300 MHz
x = **750 Hz**
b. ppm = 1200 Hz/300 MHz
= **4 ppm**
c. 2.0 = x Hz/300 MHz
x = **600 Hz**

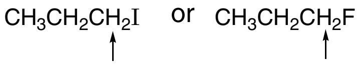
14.38

2.16 = x Hz/500 MHz
x = 1080 Hz (chemical shift of acetone in Hz)
1080 Hz + 1570 Hz = **2650 Hz**
2650 Hz/500 MHz = **5.3 ppm**, chemical shift of the CH_2Cl_2 signal

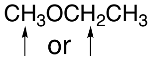
14.39 Use the directions from Answer 14.8.

a. 
$CH_3CH_2CH_2CH_2CH_3$ or $CH_3CH_2CH_2OCH_3$

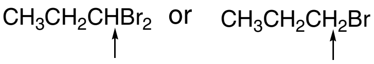
Adjacent O deshields the H's.
farther downfield

b. 
$CH_3CH_2CH_2I$ or $CH_3CH_2CH_2F$

More electronegative F deshields the H's.
farther downfield

c. 
$CH_3OCH_2CH_3$

Increasing alkyl substitution
farther downfield

d. 
$CH_3CH_2CHBr_2$ or $CH_3CH_2CH_2Br$

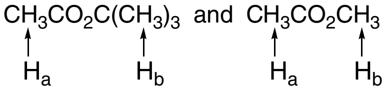
Two electronegative Br's deshield the H.
farther downfield

14.40 Use the directions from Answer 14.12.

[total number of integration units] / [total number of protons]
[13 + 33 + 73] / 10 = ~12 units per proton

Signal of 13 units is from **1 H.**
Signal of 33 units is from **3 H's.**
Signal of 73 units is from **6 H's.**

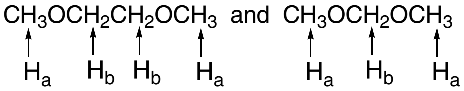
14.41

a. 
$CH_3CO_2C(CH_3)_3$ and $CH_3CO_2CH_3$

$H_a : H_b = 1:3$ $H_a : H_b = 1:1$

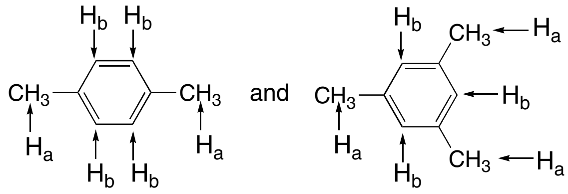
different ratio of peak areas

H_b in $CH_3CO_2CH_3$ is farther downfield than all H's in $CH_3CO_2C(CH_3)_3$.

b. 
$CH_3OCH_2CH_2OCH_3$ and $CH_3OCH_2OCH_3$

$H_a : H_b = 3:2$ $H_a : H_b = 3:1$

different ratio of peak areas

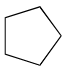
c. 

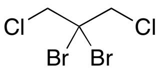
$H_a : H_b = 3:2$ $H_a : H_b = 3:1$

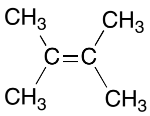
different ratio of peak areas

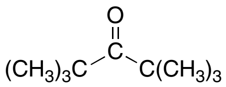
14.42 The following compounds give one singlet in a ^1H NMR spectrum:

CH_3CH_3 $CH_3-C\equiv C-CH_3$

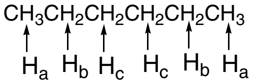






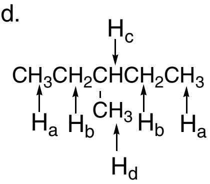


14.43



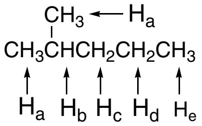
$CH_3CH_2CH_2CH_2CH_2CH_3$

3 signals:
H_a: split by 2 H_b protons - triplet
H_c: split by 2 H_b protons - triplet
H_b: split by 3 H_a + 2 H_c protons - 12 peaks (maximum)
Since H_b is located in a flexible alkyl chain, peak overlap occurs, so that only 3 + 2 + 1 = 6 peaks will likely be observed.



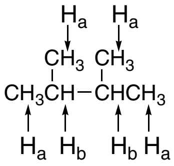
$CH_3CH_2CH(CH_3)CH_2CH_3$

4 signals:
H_a: split by 2 H_b protons - triplet
H_b: split by 3 H_a + 1 H_c protons - 8 peaks (maximum)
H_c: split by 4 H_b + 3 H_d protons - 20 peaks (maximum)
H_d: split by 1 H_c proton - doublet
Since H_b and H_c are located in a flexible alkyl chain, it is likely that peak overlap occurs, so that the following is observed: H_b (3 + 1 + 1 = 5 peaks) and H_c (4 + 3 + 1 = 8 peaks).



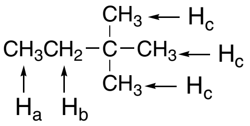
$CH_3CH(CH_3)CH_2CH_2CH_3$

5 signals:
H_a: split by 1 H_b proton - doublet
H_b: split by 6 H_a + 2 H_c protons - 21 peaks (maximum)
H_c: split by 1 H_b + 2 H_d protons - 6 peaks (maximum)
H_d: split by 2 H_c + 3 H_e protons - 12 peaks (maximum)
H_e: split by 2 H_d protons - triplet
Since H_b, H_c, and H_d are located in a flexible alkyl chain, it is likely that peak overlap occurs, so that the following is observed:
H_b (6 + 2 + 1 = 9 peaks), H_c (1 + 2 + 1 = 4 peaks), and H_d (2 + 3 + 1 = 6 peaks).



$CH_3CH(CH_3)-CH(CH_3)CH_3$

2 signals:
H_a: split by 1 H_b proton - doublet
H_b: split by 6 H_a protons - septet

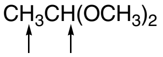


$CH_3CH_2-C(CH_3)_2-CH_3$

3 signals:
H_a: split by 2 H_b protons - triplet
H_b: split by 3 H_a protons - quartet
H_c: no splitting - singlet

14.44

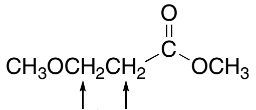
a.



$CH_3CH(OCH_3)_2$

CH_3 protons split by 1 H = **doublet**
CH proton split by 3 H's = **quartet**

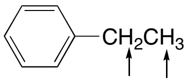
b.



$CH_3OCH_2CH_2COOCH_3$

both CH_2 groups split each other = **triplets**

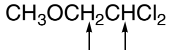
c.



$C_6H_5-CH_2CH_3$

CH_3 protons split by 2 H's = **triplet**
CH_2 protons split by 3 H's = **quartet**

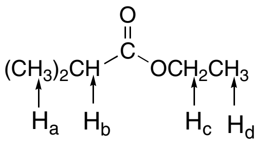
d.



$CH_3OCH_2CHCl_2$

CH_2 protons split by 1 H = **doublet**
CH proton split by 2 H's = **triplet**

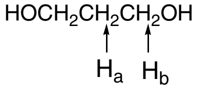
e.



$(CH_3)_2CHCOOCH_2CH_3$

H_a protons split by 1 H = **doublet**
H_b proton split by 6 H's = **septet**
H_c protons split by 3 H's = **quartet**
H_d protons split by 2 H's = **triplet**

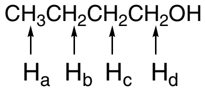
f.



$HOCH_2CH_2CH_2OH$

H_a protons split by 2 CH_2 groups = **quintet**
H_b protons split by 2 H's = **triplet**

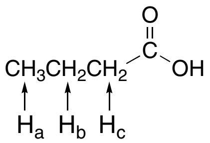
g.



$CH_3CH_2CH_2CH_2OH$

H_a protons split by 2 H's = **triplet**
H_b protons split by CH_3 + CH_2 protons = **12 peaks** (maximum)
H_c protons split by 2 different CH_2 groups = **9 peaks** (maximum)
H_d protons split by 2 H's = **triplet**
Since H_b and H_c are located in a flexible alkyl chain, it is likely that peak overlap occurs, so that the following is observed: H_b (3 + 2 + 1 = 6 peaks), H_c (2 + 2 + 1 = 5 peaks).

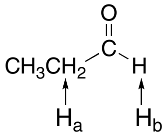
h.



$CH_3CH_2CH_2COOH$

H_a protons split by 2 H's = **triplet**
H_c protons split by 2 H's = **triplet**
H_b protons split by CH_3 + CH_2 protons = **12 peaks** (maximum)
Since H_b is located in a flexible alkyl chain, it is likely that peak overlap occurs, so that only 3 + 2 + 1 = 6 peaks will be observed.

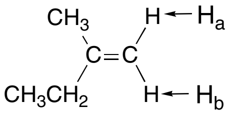
i.



CH_3CH_2CHO

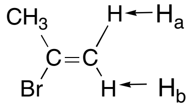
H_a: split by CH_3 group + H_b = **8 peaks** (maximum)
H_b: split by 2 H's = **triplet**

j.



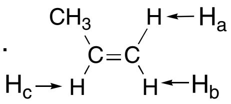
H_a: split by 1 H = **doublet**
H_b: split by 1 H = **doublet**

k.



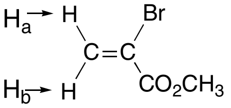
H_a: split by 1 H = **doublet**
H_b: split by 1 H = **doublet**

l.

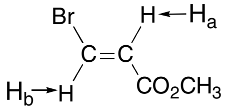


H_a: split by H_b + H_c -
doublet of doublets (4 peaks)
H_b: split by H_a + H_c -
doublet of doublets (4 peaks)
H_c: split by CH_3, H_a + H_b - **16 peaks**

14.45



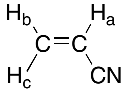
H_a: split by 1 H = **doublet**
H_b: split by 1 H = **doublet**
H_a and H_b are geminal.



H_a: split by 1 H = **doublet**
H_b: split by 1 H = **doublet**
H_a and H_b are trans.

Both compounds exhibit two doublets for the H's on the C=C, but the coupling constants (J_{geminal} and J_{trans}) are different. J_{geminal} is much smaller than J_{trans} (0–3 Hz versus 11–18 Hz).

14.46



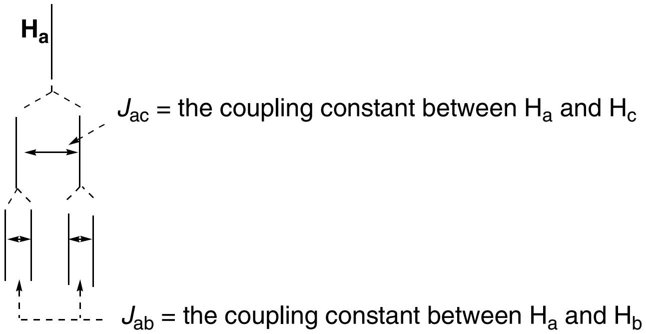
J_{ab} = 11.8 Hz
J_{bc} = 0.9 Hz
J_{ac} = 18 Hz

H_a: doublet of doublets at 5.7 ppm. Two large J values are seen for the H's cis (J_{ab} = 11.8 Hz) and trans (J_{ac} = 18 Hz) to H_a.
H_b: doublet of doublets at ~6.2 ppm. One large J value is seen for the cis H (J_{ab} = 11.8 Hz). The geminal coupling (J_{bc} = 0.9 Hz) is hard to see.
H_c: doublet of doublets at ~6.6 ppm. One large J value is seen for the trans H (J_{ac} = 18 Hz). The geminal coupling (J_{bc} = 0.9 Hz) is hard to see.

Splitting diagram for H_a

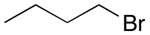
1 **trans** H_c proton splits H_a into
1 + 1 = 2 peaks
a doublet

1 **cis** H_b proton splits H_a into
1 + 1 = 2 peaks
Now it's a doublet of doublets.

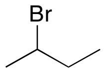


14.47

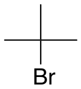
Four constitutional isomers of **C_4H_9Br**:



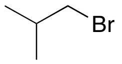
4 different C's



4 different C's



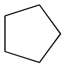
2 different C's



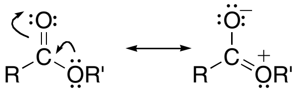
3 different C's

14.48 Only two compounds in Problem 14.42 give one signal in their ^{13}C NMR spectrum:

CH_3CH_3



14.49



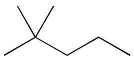
The O atom of an ester donates electron density so the carbonyl carbon has less δ^+, making it less deshielded than the carbonyl carbon of an aldyhyde or ketone. Therefore, the carbonyl carbon of an aldehyde or ketone is more deshielded and absorbs farther downfield.

14.50

a. $HC(CH_3)_3$

2 signals

b.

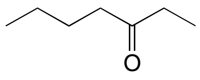


5 signals

c. $CH_3OCH(CH_3)_2$

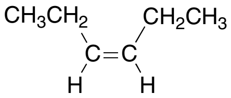
3 signals

d.



7 signals

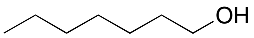
e.



$CH_3CH_2CH{=}CHCH_2CH_3$

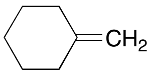
3 signals

f.



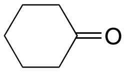
7 signals

g.



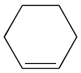
5 signals

h.



4 signals

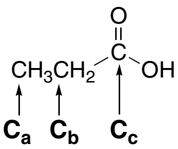
i.



3 signals

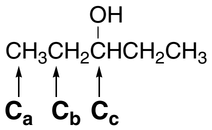
14.51

a.



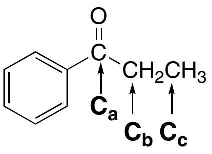
$C_a < C_b < C_c$

b.



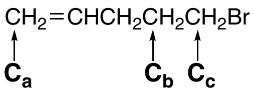
$C_a < C_b < C_c$

c.



$C_c < C_b < C_a$

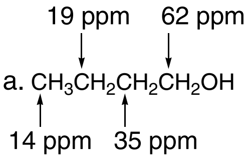
d.



$C_b < C_c < C_a$

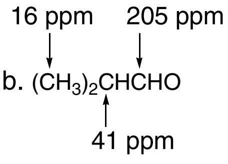
14.52

a.



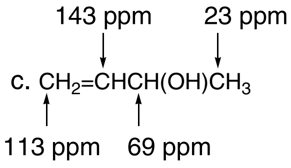
$CH_3CH_2CH_2CH_2OH$

b.



$(CH_3)_2CHCHO$

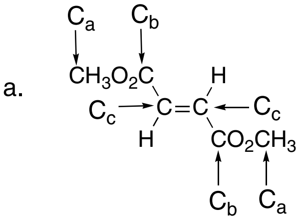
c.



$CH_2{=}CHCH(OH)CH_3$

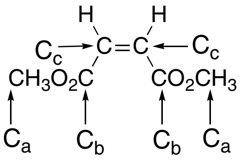
14.53

a.

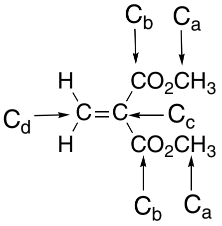


3 different C's
3 signals

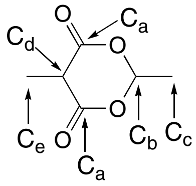
b.



3 signals



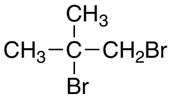
4 signals



5 signals

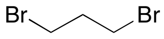
14.54 Use the directions from Answer 14.24.

a. **$C_4H_8Br_2$**: 0 degrees of unsaturation
IR peak at 3000–2850 cm^{-1}: **C_{sp^3}–H bonds**
NMR: singlet at 1.87 ppm (6 H) (2 CH_3 groups)
singlet at 3.86 ppm (2 H) (CH_2 group)

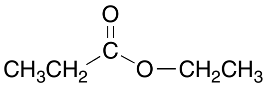


$CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_2Br$

b. **$C_3H_6Br_2$**: 0 degrees of unsaturation
IR peak at 3000–2850 cm^{-1}: **C_{sp^3}–H bonds**
NMR: quintet at 2.4 ppm (split by 2 CH_2 groups)
triplet at 3.5 ppm (split by 2 H's)

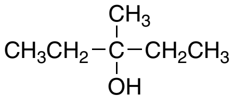


c. **$C_5H_{10}O_2$**: **1 degree of unsaturation**
IR peak at 1740 cm^{-1}: **C=O**
NMR: triplet at 1.15 ppm (3 H) (CH_3 split by 2 H's)
triplet at 1.25 ppm (3 H) (CH_3 split by 2 H's)
quartet at 2.30 ppm (2 H) (CH_2 split by 3 H's)
quartet at 4.72 ppm (2 H) (CH_2 split by 3 H's)



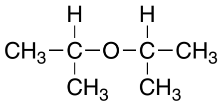
$CH_3CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$

d. **$C_6H_{14}O$**: 0 degrees of unsaturation
IR peak at 3600–3200 cm^{-1}: **O–H**
NMR: triplet at 0.8 ppm (6 H) (2 CH_3 groups split by CH_2 groups)
singlet at 1.0 ppm (3 H) (CH_3)
quartet at 1.5 ppm (4 H) (2 CH_2 groups split by CH_3 groups)
singlet at 1.6 ppm (1 H) (O–H proton)



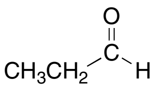
$CH_3CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_2CH_3$

e. **$C_6H_{14}O$**: 0 degrees of unsaturation
IR peak at 3000–2850 cm^{-1}: **C_{sp^3}–H bonds**
NMR: doublet at 1.10 ppm (integration = 30 units) (from 12 H's)
septet at 3.60 ppm (integration = 5 units) (from 2 H's)



$CH_3-\overset{H}{\underset{CH_3}{C}}-O-\overset{H}{\underset{CH_3}{C}}-CH_3$

f. **C_3H_6O**: **1 degree of unsaturation**
IR peak at 1730 cm^{-1}: **C=O**
NMR: triplet at 1.11 ppm
multiplet at 2.46 ppm
triplet at 9.79 ppm



$CH_3CH_2-\overset{O}{\overset{\|}{C}}-H$

14.55

Two isomers of $C_9H_{10}O$: 5 degrees of unsaturation (benzene ring likely)

Compound A:

IR absorption at 1742 cm^{-1}: **C=O**

NMR data:

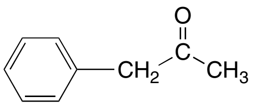
Absorptions:

singlet at 2.15 (3 H) (CH_3 group)

singlet at 3.70 (2 H) (CH_2 group)

broad singlet at 7.20 (5 H)

(likely a monosubstituted benzene ring)



Compound B:

IR absorption at 1688 cm^{-1}: **C=O**

NMR data:

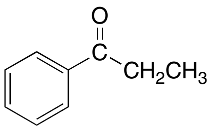
Absorptions:

triplet at 1.22 (3 H) (CH_3 group split by 2 H's)

quartet at 2.98 (2 H) (CH_2 group split by 3 H's)

multiplet at 7.28–7.95 (5 H)

(likely a monosubstituted benzene ring)



14.56

Compound C:

molecular ion 146 (molecular formula $C_6H_{10}O_4$)

IR absorption at 1762 cm^{-1}: **C=O**

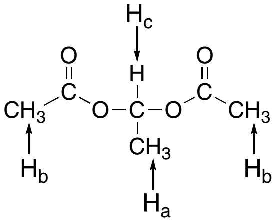
^{1}H NMR data:

Absorptions:

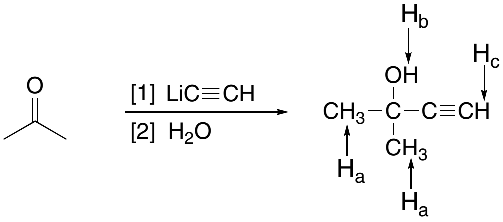
H_a: doublet at 1.47 (3 H) (CH_3 group adjacent to CH)

H_b: singlet at 2.07 (6 H) (2 CH_3 groups)

H_c: quartet at 6.84 (1 H adjacent to CH_3)



14.57



D

Compound D:

molecular ion 84 (molecular formula C_5H_8O)

IR absorptions at 3600–3200 cm^{-1}: OH

3303 cm^{-1}: C_{sp}–H

2938 cm^{-1}: C_{sp^3}–H

2120 cm^{-1}: C≡C

^{1}H NMR data:

Absorptions:

H_a: singlet at 1.53 (6 H) (2 CH_3 groups)

H_b: singlet at 2.37 (1 H)

H_c: singlet at 2.43 (1 H)

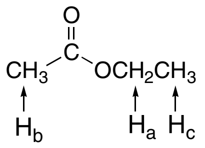
alkynyl CH and OH

14.58

Compound E:
$C_4H_8O_2$:
1 degree of unsaturation
IR absorption at 1743 cm^{-1}: **C=O**
NMR data:

total integration units/# H's
(23 + 29 + 30)/8 = ~10 units per H

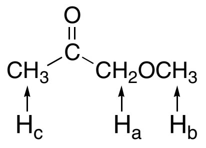
H_a: quartet at 4.1 (23 units - **2 H**)
H_b: singlet at 2.0 (29 units - **3 H**)
H_c: triplet at 1.4 (30 units - **3 H**)


$CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3$

Compound F:
$C_4H_8O_2$:
1 degree of unsaturation
IR absorption at 1730 cm^{-1}: **C=O**
NMR data:

total integration units/# H's
(18 + 30 + 31)/8 = ~10 units per H

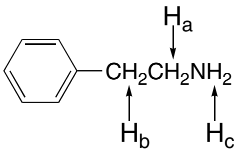
H_a: singlet at 4.1 (18 units - **2 H**)
H_b: singlet at 3.4 (30 units - **3 H**)
H_c: singlet at 2.1 (31 units - **3 H**)


$CH_3\overset{O}{\overset{\|}{C}}CH_2OCH_3$

14.59

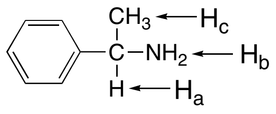
Compound H:
$C_8H_{11}N$:
4 degrees of unsaturation
IR absorptions at 3365 cm^{-1}: N–H
3284 cm^{-1}: N–H
3026 cm^{-1}: C_{sp^2}–H
2932 cm^{-1}: C_{sp^3}–H
1603 cm^{-1}: due to benzene
1497 cm^{-1}: due to benzene
NMR data:

multiplet at 7.2–7.4 ppm, **5 H** on a benzene ring
H_a: triplet at 2.9 ppm, **2 H**, split by 2 H's
H_b: triplet at 2.8 ppm, **2 H**, split by 2 H's
H_c: singlet at 1.1 ppm, **2 H,** no splitting (on NH_2)



Compound I:
$C_8H_{11}N$:
4 degrees of unsaturation
IR absorptions at 3367 cm^{-1}: N–H
3286 cm^{-1}: N–H
3027 cm^{-1}: C_{sp^2}–H
2962 cm^{-1}: C_{sp^3}–H
1604 cm^{-1}: due to benzene
1492 cm^{-1}: due to benzene
NMR data:

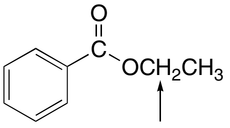
multiplet at 7.2–7.4 ppm, **5 H** on a benzene ring
H_a: quartet at 4.1 ppm, **1 H**, split by 3H's
H_b: singlet at 1.45 ppm, **2 H**, no splitting (NH_2)
H_c: doublet at 1.4 ppm, **3 H**, split by 1 H



14.60

a. **$C_9H_{10}O_2$:**
5 degrees of unsaturation
IR absorption at 1718 cm^{-1}: **C=O**
NMR data:

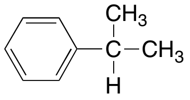
multiplet at 7.4–8.1 ppm, **5 H** on a benzene ring
quartet at 4.4 ppm, **2 H**, split by 3 H's
triplet at 1.3 ppm, **3 H**, split by 2 H's



downfield due to the O atom

b. **C_9H_{12}:**
4 degrees of unsaturation
IR absorption at 2850–3150 cm^{-1}:
C–H bonds
NMR data:

singlet at 7.1–7.4 ppm, **5 H**, benzene
septet at 2.8 ppm, **1 H**, split by 6 H's
doublet at 1.3 ppm, **6 H**, split by 1 H



14.61

a. Compound **J** has a molecular ion at 72: molecular formula **C_4H_8O**

1 degree of unsaturation

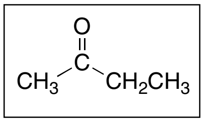
IR spectrum at 1710 cm^{-1}: **C=O**

^1H NMR data (ppm):

1.0 (triplet, 3 H), split by 2 H's

2.1 (singlet, 3 H)

2.4 (quartet, 2 H), split by 3 H's



b. Compound **K** has a molecular ion at 88: molecular formula **$C_5H_{12}O$**

0 degrees of unsaturation

IR spectrum at 3600–3200 cm^{-1}: **O–H bond**

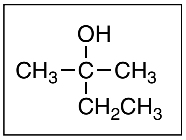
^1H NMR data (ppm):

0.9 (triplet, 3 H), split by 2 H's

1.2 (singlet, 6 H), due to 2 CH_3 groups

1.5 (quartet, 2 H), split by 3 H's

1.6 (singlet, 1 H), due to the OH proton



14.62

Compound **L** has a molecular ion at 90: molecular formula **$C_4H_{10}O_2$**

0 degrees of unsaturation

IR absorptions at 2992 and 2941 cm^{-1}: C_{sp^3}–H

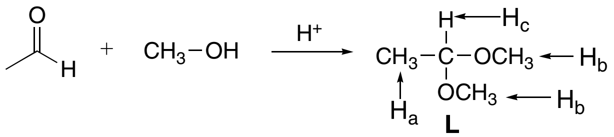
^1H NMR data (ppm):

H_a: 1.2 (doublet, 3 H), split by 1 H

H_b: 3.3 (singlet, 6 H), due to 2 CH_3 groups

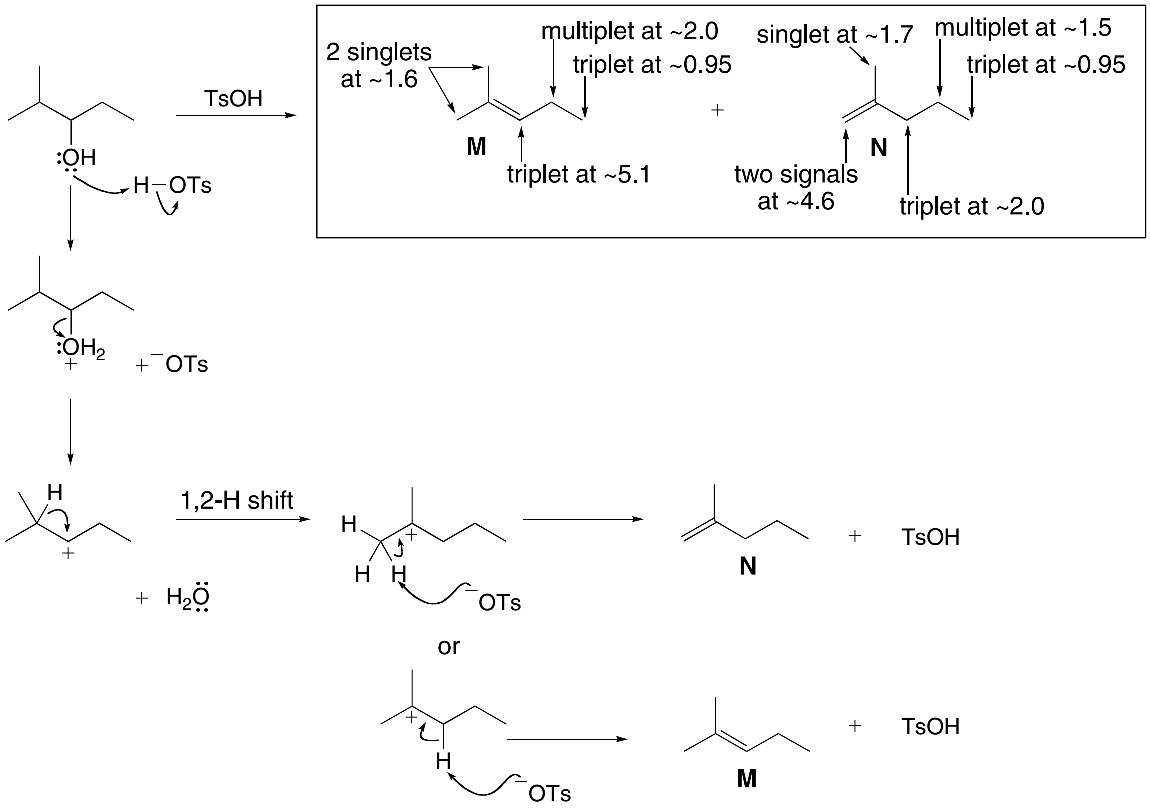
H_c: 4.8 (quartet, 1 H), split by 3 adjacent H's

total integration units/# H's
(25 + 46 + 7)/10 = ~8 units per H



L

14.63



14.64

Compound **O** has a molecular formula **$C_{10}H_{12}O$.**

5 degrees of unsaturation

IR absorption at 1687 cm^{-1}

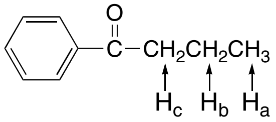
^1H NMR data (ppm):

H_a: 1.0 (triplet, 3 H), due to CH_3 group, split by 2 adjacent H's

H_b: 1.7 (sextet, 2 H), split by CH_3 and CH_2 groups

H_c: 2.9 (triplet, 2 H), split by 2 H's

7.4–8.0 (multiplet, 5 H), benzene ring



O

14.65

Compound **P** has a molecular formula **$C_5H_9ClO_2$.**

1 degree of unsaturation

^{13}C NMR shows 5 different C's, including a C=O.

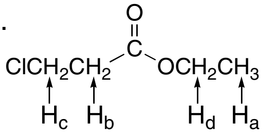
^1H NMR data (ppm):

H_a: 1.3 (triplet, 3 H), split by 2 H's

H_b: 2.8 (triplet, 2 H), split by 2 H's

H_c: 3.7 (triplet, 2 H), split by 2 H's

H_d: 4.2 (quartet, 2 H), split by CH_3 group



P

14.66

Compound Q: Molecular ion at 86.

Molecular formula: **$C_5H_{10}O$:**

1 degree of unsaturation

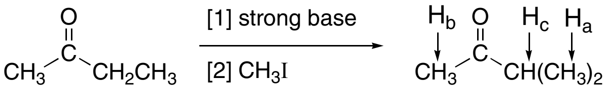
IR absorption at ~1700 cm^{-1}: **C=O**

NMR data:

H_a: doublet at 1.1 ppm, 2 CH_3 groups split by 1 H

H_b: singlet at 2.1 ppm, CH_3 group

H_c: septet at 2.6 ppm, 1 H split by 6 H's



= **Q**

MW = 86

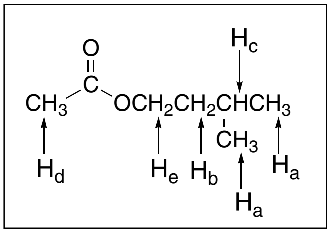
14.67

a. Compound **R**, the odor of banana: $C_7H_{14}O_2$

1 degree of unsaturation

^1H NMR (ppm):

H_a: 0.93 (doublet, 6 H)
H_b: 1.52 (multiplet, 2 H)
H_c: 1.69 (multiplet, 1 H)
H_d: 2.04 (singlet, 3 H)
H_e: 4.10 (triplet, 2 H)

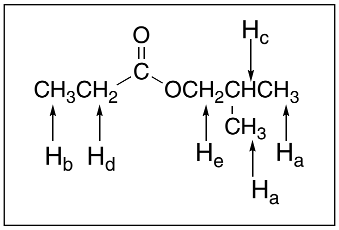


b. Compound **S**, the odor of rum: $C_7H_{14}O_2$

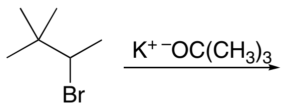
1 degree of unsaturation

^1H NMR (ppm):

H_a: 0.94 (doublet, 6 H)
H_b: 1.15 (triplet, 3 H)
H_c: 1.91 (multiplet, 1 H)
H_d: 2.33 (quartet, 2 H)
H_e: 3.86 (doublet, 2 H)



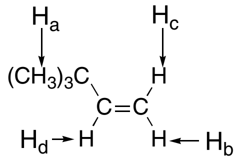
14.68

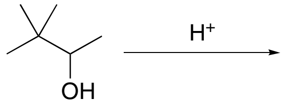


T

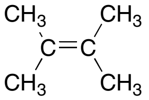
C_6H_{12}:
1 degree of unsaturation

^{1}H NMR of **T** (ppm):
H_a: 1.01 (singlet, 9 H)
H_b: 4.82 (doublet of doublets, 1 H, J = 10, 1.7 Hz)
H_c: 4.93 (doublet of doublets, 1 H, J = 18, 1.7 Hz)
H_d: 5.83 (doublet of doublets, 1 H, J = 18, 10 Hz)



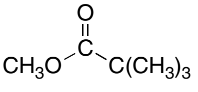


U ^{1}H NMR of **U**: 1.60 (singlet) ppm.



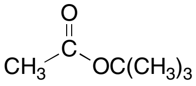
All H's are identical, so there is only one singlet in the NMR.

14.69 Both **A** and **B** have the same molecular ion—since they are isomers—and show a C=O peak in their IR spectra. ^{1}H NMR spectroscopy is the best way to distinguish the two compounds.



A

or



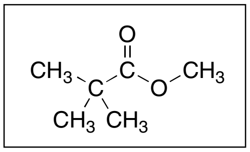
B

Both **A** and **B** have two singlets in a 3:1 ratio in their ^{1}H NMR spectra. But **A** has a peak at ~3 ppm due to the deshielded CH_3 group bonded to the O atom. **B** has no proton that is so deshielded. Both of its singlets are in the 1–2.5 ppm region.

14.70

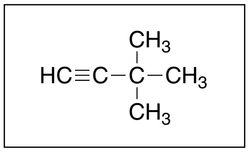
a.

$C_6H_{12}O_2$:
1 degree of unsaturation
IR peak at 1740 cm^{-1}: **C=O**
^{1}H NMR 2 signals: 2 types of H's
^{13}C NMR: 4 signals: 4 kinds of C's, including one at ~170 ppm due a C=O



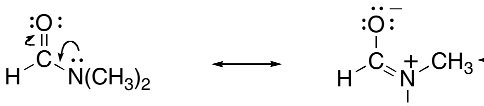
b.

C_6H_{10}:
2 degrees of unsaturation
IR peak at 3000 cm^{-1}: **C*sp*^{3}–H bonds**
peak at 3300 cm^{-1}: **C$_{sp}$–H bond**
peak at ~2150 cm^{-1}: **C≡C bond**
^{13}C NMR: 4 signals: 4 kinds of C's



$$HC{\equiv}C{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_3$$

14.71



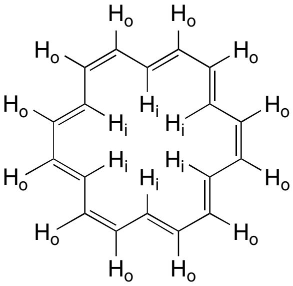
N,N-dimethylformamide

cis to the O atom

cis to the H atom

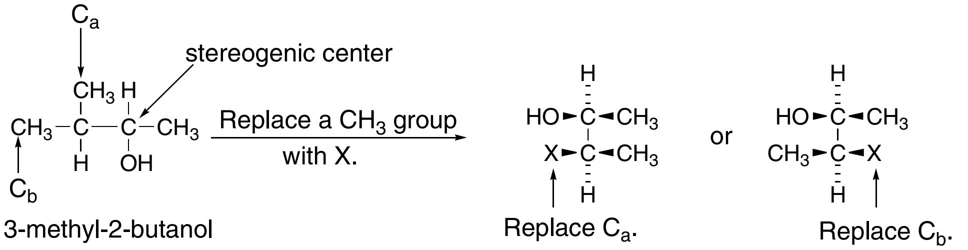
A second resonance structure for *N,N*-dimethylformamide places the two CH_3 groups in different environments. One CH_3 group is cis to the O atom, and one is cis to the H atom. This gives rise to two different absorptions for the CH_3 groups.

14.72



18-Annulene has 18 π electrons that create an **induced magnetic field** similar to the 6 π electrons of benzene. 18-Annulene has 12 protons that are oriented on the outside of the ring (labeled H_o), and 6 protons that are oriented inside the ring (labeled H_i). The induced magnetic field reinforces the external field in the vicinity of the protons on the outside of the ring. These protons are deshielded and so they absorb downfield (8.9 ppm). In contrast, the induced magnetic field is opposite in direction to the applied magnetic field in the vicinity of the protons on the inside of the ring. This shields the protons and the absorption is therefore very far upfield, even higher than TMS (–1.8 ppm).

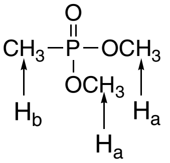
14.73



The CH_3 groups are not equivalent to each other, since replacement of each by X forms two diastereomers.

Thus, every C in this compound is different and there are five ^{13}C signals.

14.74



$CH_3-P(=O)(OCH_3)-OCH_3$

One P atom splits each nearby CH_3 into a doublet by the *n* + 1 rule, making two doublets.

All 6 H_a protons are equivalent.