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OpenCourseWare (2023)

CHEMISTRY II

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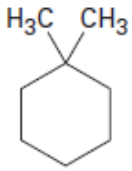
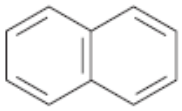
SOLUTIONS OF STRUCTURAL DETERMINATION EXERCISES

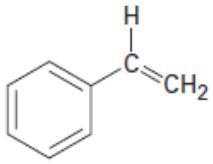
Exercice 1. How many types of non-equivalent protons are present in each of the following molecules?

(a) 

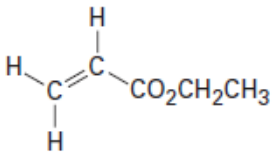
(b) $CH_3CH_2CH_2OCH_3$

(c) 

Naphthalene

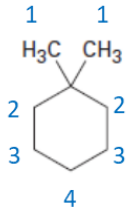
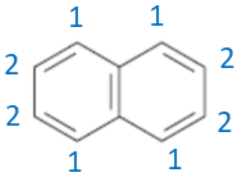
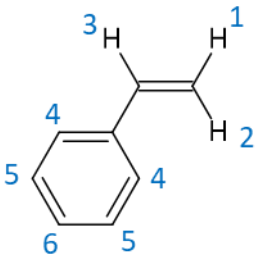
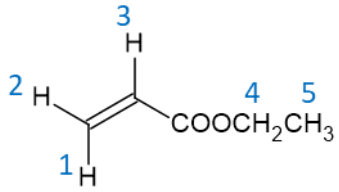
(d) 

Styrene

(e) 

Ethyl acrylate

SOLUTION

Compound	Kinds of non-equivalent protons	Compound	Kinds of non-equivalent protons
(a) 	4	(b) $CH_3CH_2CH_2OCH_3$ **1 2 3 4**	4
(c) 	2	(d) 	6
(e) 	5		

Exercise 2. *Structural Elucidation from ^1H NMR Spectra.* There are several isomeric alcohols and ethers of molecular formula $C_5H_{12}O$. Two of these, A and B, exhibit the following ^1H NMR spectra:

A: δ = 1.19 (s, 9 H), 3,21 (s, 3 H) ppm

B: δ = 0.93 (t, 3 H), 1.20 (t, 3 H), 1.60 (sextet, 2 H), 3.37 (t, 2H), 3.47 (q, 2 H) ppm.

Determine compounds A and B.

SOLUTION

Calculate the degree of unsaturation (equation shows the simplified general formula) to limit the number of possible structures. Each degree of unsaturation is a ring or π bond (likely an alkene or carbonyl).

$$Degree\ of\ unsaturation = (C + 1) - \left(\frac{H + X - N}{2}\right)$$

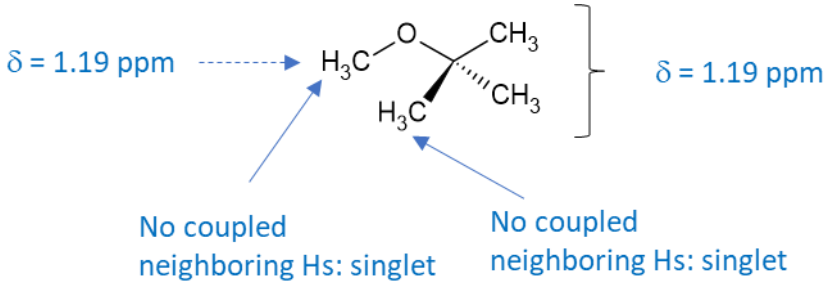
C: number of C atoms in the compound
H: number of H atoms in the compound
X: number of halogen atoms in the compound
N: number of N atoms in the compound

$$Degree\ of\ unsaturation = (5 + 1) - \frac{12}{2} = 0$$

Degree of unsaturation is 0, therefore, isomers have no rings or bonds.

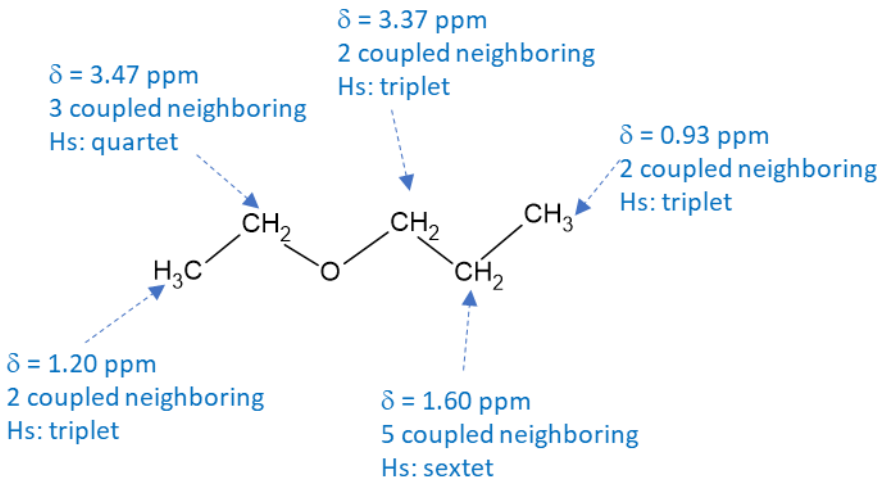
Compound A:

- The presence of two singlets is an indication of extensive symmetry.
- The absence of a peak integrating for 1 H excludes the presence of an OH function; hence, the molecule is an ether.
- A singlet integrating for 3 H is a strong indication of the presence of a CH_3 substituent. The singlet's chemical shift suggests that it is attached to the ether oxygen.
- Subtracting CH_3O from $C_3H_{12}O$ leaves C_4H_9, which must be the source of the other singlet at higher field, in the alkane region.
- A singlet integrating for 9 H is a strong indication for the presence of three equivalent CH_3 substituents: the solution is tert-butyl, $C(CH_3)_3$.
- The answer for A is $CH_3OC(CH_3)_3$.



Compound B:

- This molecule exhibits five signals, all of which are split. Again, there is no single hydrogen peak, that is no presence of a hydroxyl group.
- We note that two of the δ values are relatively large, identifying the two pieces attached to oxygen: the triplet for 2 H at δ = 3.37 ppm and the quartet for 2 H at δ = 3.47 ppm. This indicates an unsymmetrical substructure, X–CH_2OCH_2–Y.
- We can guess the nature of the neighbors X and Y from the coupling patterns of the CH_2 groups: One must be CH_3 to cause the appearance of a quartet; the other must be another CH_2 fragment to generate a triplet. Thus, you could consider strongly $CH_3CH_2OCH_2CH_2$– substructure.
- Subtracting this fragment from $C_5H_{12}O$ leaves only CH_3 as a final piece; hence a possible solution is $CH_3CH_2OCH_2CH_2CH_3$.
- Looking to higher field, we have two triplets, each arising from three equivalent hydrogens, that means two ethyl moieties. Finally, a sextet integrating for 2 H indicates the presence of a CH_2 group with five hydrogen neighbors. Both pieces of information are consistent with the proposed solution, leaving $CH_3CH_2OCH_2CH_2CH_3$, as the only viable structure.



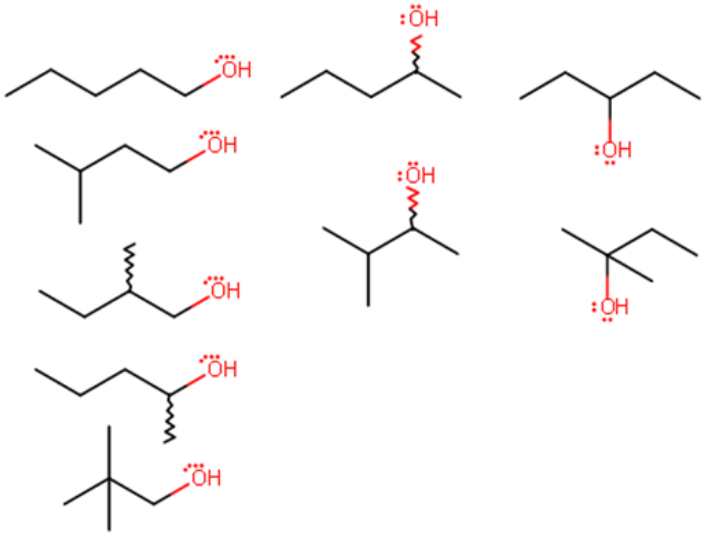
Exercise 3. An isomer of $C_5H_{12}O$ exhibits the following ^1H NMR spectrum: δ = 0.92 (t, 3 H), 1.20 (s, 6 H), 1.49 (q, 2 H), 1.85 (br s, 1 H) ppm. Determine its structure.

SOLUTION

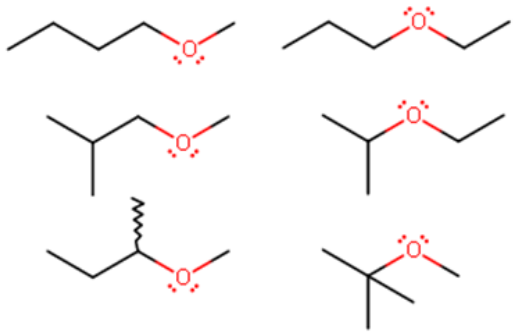
$$Degree\ of\ unsaturation = (5+1) - \frac{12}{2} = 0$$

Structures of the isomers that fit with molecular formula and degree of unsaturation:

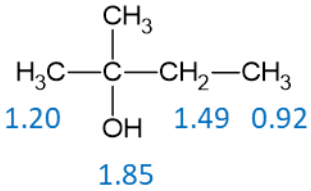
An alcohol:



Or an ether:

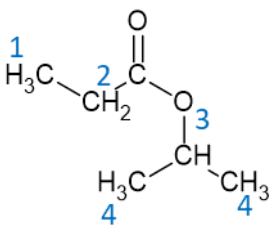


The correct structure is an alcohol:



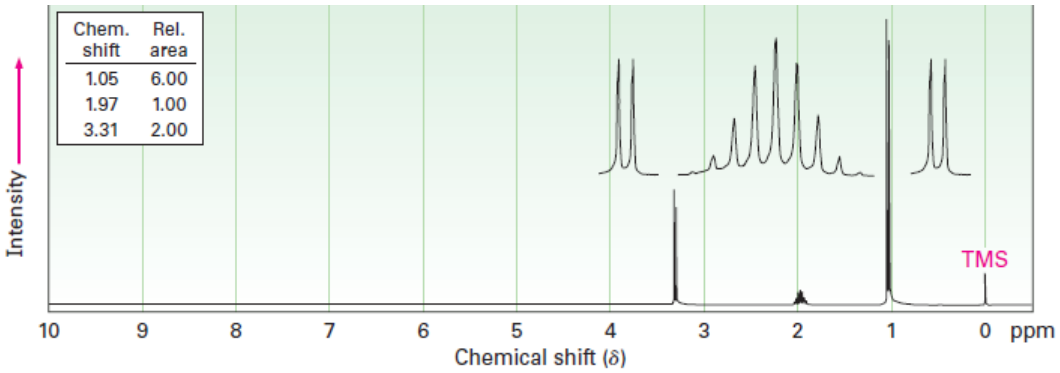
Exercise 4. Predict the splitting pattern for each kind of hydrogen in isopropyl propanoate, $CH_3CH_2CO_2CH(CH_3)_2$.

SOLUTION

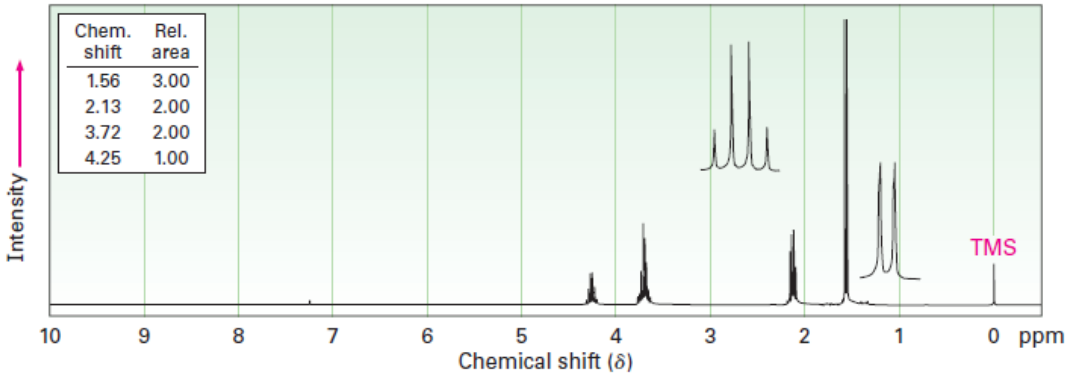
	Peak Assignment	***Splitting Pattern***	***Protons***
	1	triplet	(3H)
	2	quarter	(2H)
	3	septet	(1H)
	4	doublet	(6H)

Exercise 5. Propose structures for the two compounds whose ^{1}H NMR spectra are shown:

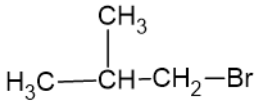
(a) C_4H_9Br



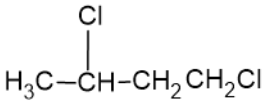
(b) $C_4H_8Cl_2$



SOLUTION

(a) 

1-bromo-2-methylpropane

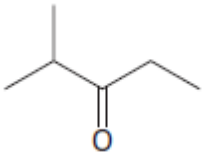
(b) 

1,3-dichlorobutane

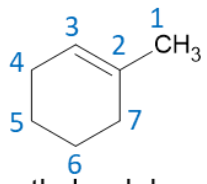
Exercise 6. Predict the number of carbon resonance lines you would expect in the ^{13}C NMR spectra of the following compounds:

(a) 1-Methylcyclohexene

(b) 2-Methyl-2-butene

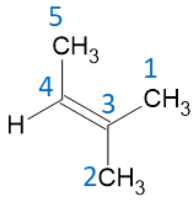
(c) 

SOLUTION



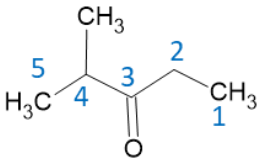
1-methylcyclohex-1-ene

Seven lines are seen because no two carbons are equivalents



2-methylbut-2-ene

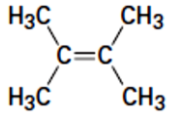
Five resonance lines are seen. Carbon 1 and 2 are non-equivalent because of teh double bond stereochemistry

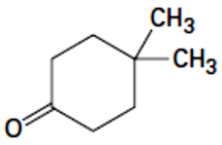


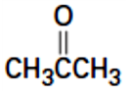
2-methylpentan-3-one

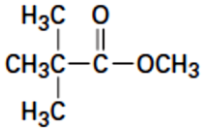
Five lines are observed.

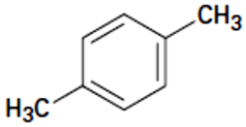
Exercise 7. How many signals would you expect each of the following molecules to have in its ^{1}H and ^{13}C spectra?

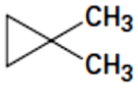
(a) 

(b) 

(c) 

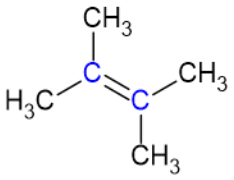
(d) 

(e) 

(f) 

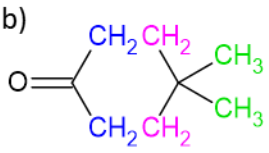
SOLUTION

(a)

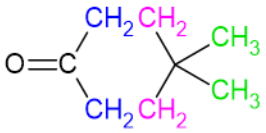


^{13}C: 2 absorptions
^{1}H: 1 absorption

(b)

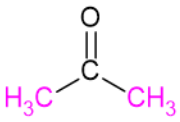


^{13}C: 5 absorptions



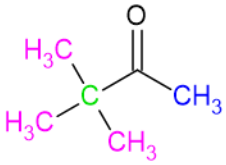
^{1}H: 3 absorptions

(c)

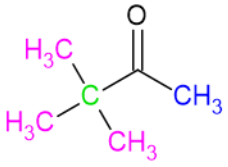


^{13}C: 2 absorptions
^{1}H: 1 absorption

(d)

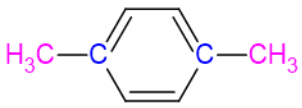


^{13}C: 4 absorptions



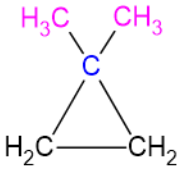
^{1}H: 2 absorptions

(e)



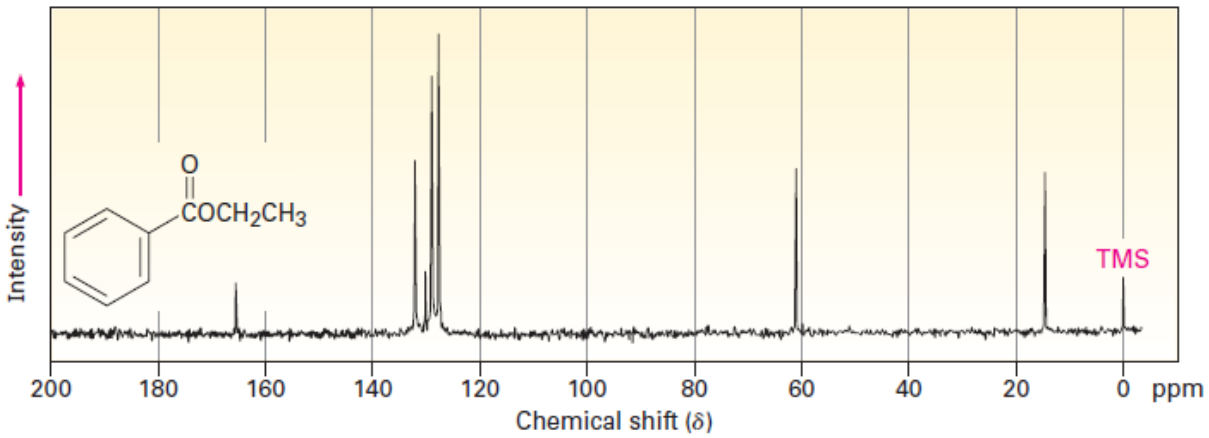
^{13}C: 3 absorptions
^{1}H: 2 absorption

(f)

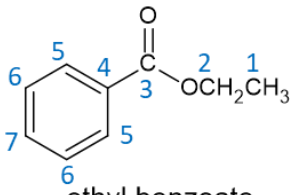


^{13}C: 3 absorptions
^{1}H: 2 absorption

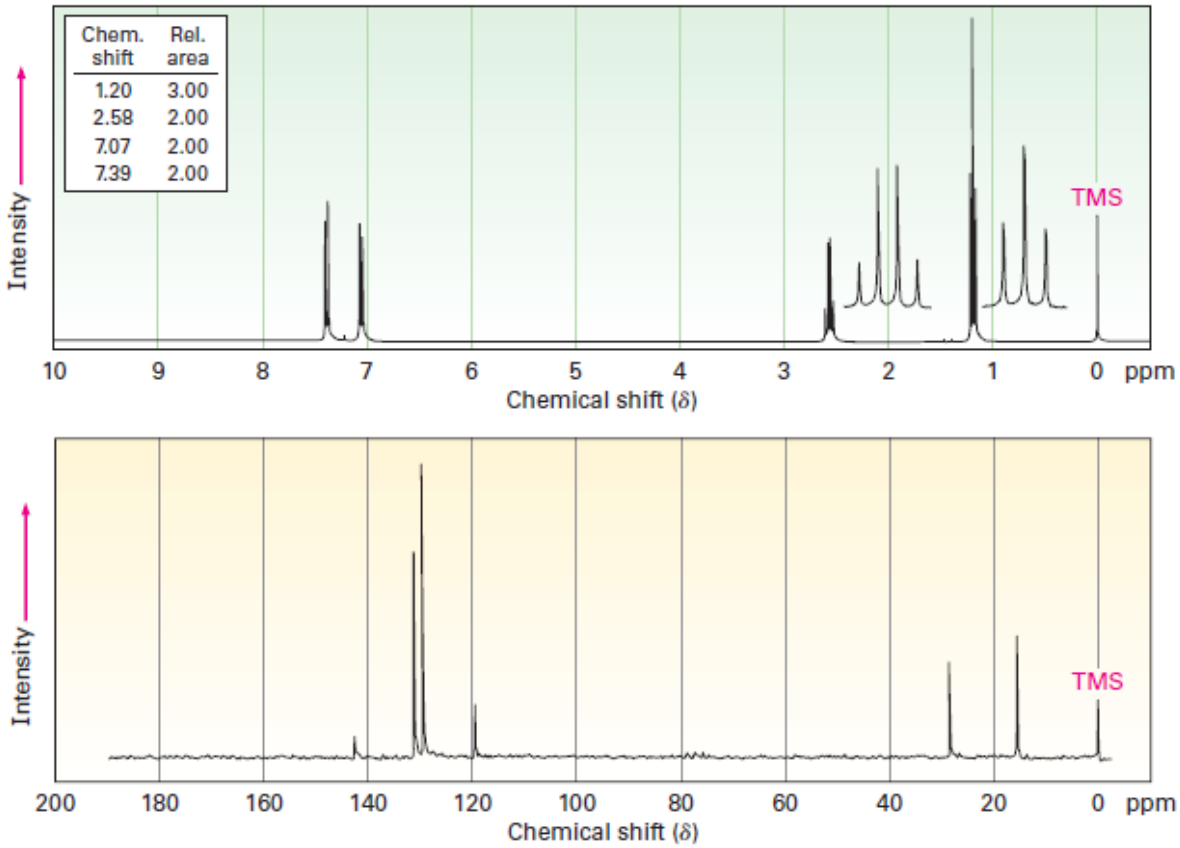
Exercise 8. Assign as many of the resonances as you can to specific carbon atoms in the ^{13}C NMR spectrum of ethyl benzoate.



SOLUTION

	Carbon	*δ (pmm)*
 ethyl benzoate	1	14
	2	61
	3	166
	4	127-133 (4 peaks)
	5	
	6	
	7	

Exercise 9. The ^{1}H and ^{13}C NMR spectra of compound A, C_8H_9Br, are shown. Propose a structure for A and assign peaks in the spectra to your structure.

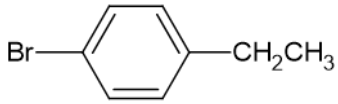


SOLUTION

$$Degree\ of\ unsaturation = (8+1) - \frac{(9+1)}{2} = 4$$

Compound A (4 multiple bonds and/or ring) must be symmetrical because it exhibits only six peaks in its ^{13}C NMR spectrum. Saturated carbons account for two of these peaks (15, 28 ppm), and unsaturated carbons account for the other four (119, 129, 131, 143 ppm).

^{1}H NMR shows a triplet (3 H at 1.2 δ) and a quartet (2 H at 2.58 δ), indicating the presence of an ethyl group. The other signal (4 H at 7.07 δ, 7,39 δ are due to aromatic protons.
The compound A is:



Exercise 10. Assume that you have a compound with formula C_3H_6O.

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

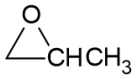
SOLUTION

(a) Calculate degree of unsaturation:

$$Degree\ of\ unsaturation = (3+1) - \frac{6}{2} = 1$$

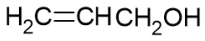
(a), (b) C_3H_6O contains 1 double bond or 1 ring. Possible structures:


oxetane

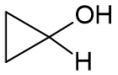


2-methyloxirane

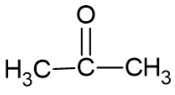
methoxyethene



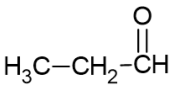
prop-2-en-1-ol



cyclopropanol



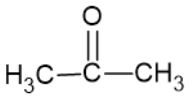
propan-2-one



propanal

(c) Carbonyl group can absorb at 1715 cm^{-1} in the IR. Only the last two compounds above show and infrared absorption in this region.

(d) because the aldehyde from part (b) has three different kinds of protons, its H NMR spectrum shows three peaks. The propan-2-one (a ketone) however, shows only one peak. Since the unknown compound of this problem shows only one H NMR absorption (in the methyl ketone region), it must be acetone: Propan-2-one (or acetone):



Exercise 11. How could you use infrared spectroscopy to distinguish between the following pairs of isomers?

(a) $HC{\equiv}CCH_2NH_2$ and $CH_3CH_2C{\equiv}N$

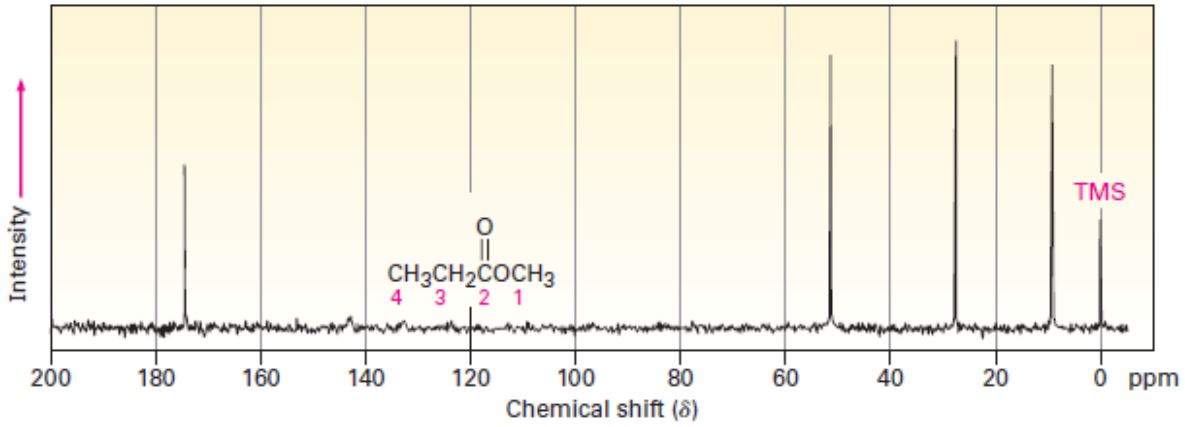
(b) CH_3COCH_3 and CH_3CH_2CHO

SOLUTION

(a) $HC{\equiv}CCH_2NH_2$ is an alkyne with absorptions at 3300 cm^{-1}, 2100-2260 cm^{-1}. Amine absorption at 3300-300 cm^{-1}. $CH_3CH_2C{\equiv}N$ has a nitrile group with absorption at 2200-2260 cm^{-1}

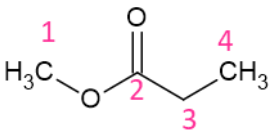
(b) CH_3COCH_3 present a strong ketone absorption at 1715 cm^{-1} and CH_3CH_2CHO a strong aldehyde absorption at 1730 cm^{-1}.

Exercise 12. Assign the resonances in the ^{13}C NMR spectrum of methyl propanoate, $CH_3CH_2CO_2CH_3$.



SOLUTION

Methyl propanoate has 4 unique carbons, and each one absorbs in a specific region of the ^{13}C spectrum. The absorption (4) has the lowest value of δ and occurs in the $-CH_3$ region of the ^{13}C spectrum. Absorption (3) occurs in the $-CH_2-$ region. The methyl group (1) is next to an electronegative atom and absorbs downfield from the other two absorptions. The carbonyl carbon (2) absorbs the farthest downfield.

	δ (ppm)	Assignment
	9.3	4
	27.6	3
	51.4	1
	174.6	2

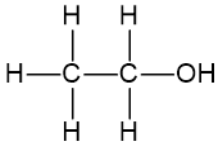
Exercise 13. Two compounds of molecular formula C_2H_6O show large intensity IR peaks at 2870 and 1150 cm^{-1} for the first isomer, and at 3400, 2950, and 1090 cm^{-1} for the second. What are their structures?

SOLUTION

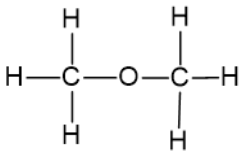
$$Degree\ of\ unsaturation = (2+1) - \frac{6}{2} = 0$$

Degree of unsaturation is 0, therefore, isomers has no rings or bonds.

Structures of the isomers that fit with molecular formula and degree of unsaturation:



Ethanol



dimethyl ether

From table, look at the IR absorption bands. Ethers are difficult to identify by IR spectroscopy. They show an absorption due to C–O single-bond stretching in the range 1050 to 1150 cm^{-1}; alcohols also present absorptions in the same range. Alkane C–H bonds show a strong absorption from 2850 to 2960 cm^{-1}. Alcohols have a characteristic band in the range 3400 to 3650 cm^{-1}. Therefore:

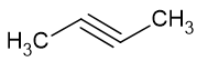
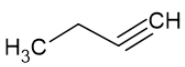
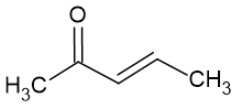
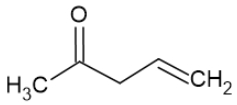
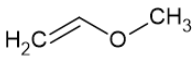
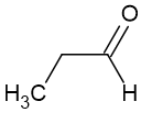
Isomer 1: dimethyl ether; *Isomer 2:* ethanol.

Exercise 14. How would you use infrared spectroscopy to distinguish between the following pairs of constitutional isomers?

(a) but-2-yne and but-1-yne; (b) pent-3-en-2-one and pent-4-en-2-one; (c) methoxyethene and propanal.

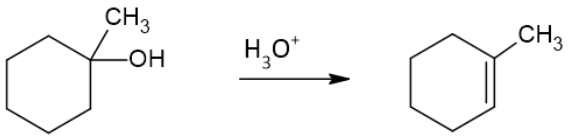
SOLUTION

	(a) But-2-yne exhibit no terminal =C-H stretching vibration at 3300 cm^{-1}, as but-1-yne does
	(b) pent-3-en-2-one a ketone next to a double bond, shows a strong ketone absorption at 1690 cm^{-1}; pent-4-en-2-one shows a ketone absorption at 1715 cm^{-1} and monosubstituted alkene absorptions at 910 cm^{-1} and 990 cm^{-1}

 but-2-yne  but-1-yne  pent-3-en-2-one  pent-4-en-2-one  methoxyethene  propanal	(c) propanal exhibits an aldehyde band at 1730 cm^{-1}; methoxyethene shows characteristics monosubstituted alkene absorptions at 910 cm^{-1} and 990 cm^{-1}

Exercise 15. Assume that you are carrying out the dehydration of 1-methylcyclohexanol to yields 1-methylcyclohexene. How could you use infrared spectroscopy to determine when the reaction is complete?

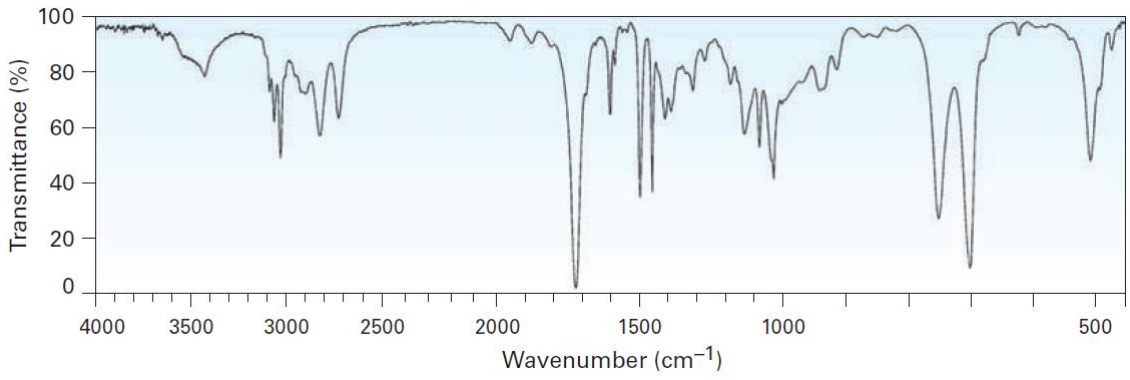
SOLUTION



1-methylcyclohexan-1-ol 1-methylcyclohex-1-ene

The IR spectrum of the starting alcohol shows a broad absorption at 3400-3640 cm^{-1} due to an O-H stretch. The alkene product exhibits medium intensity absorbances at 1645-1670 cm^{-1}. Monitoring the disappearance of the alcohol absorption makes it possible to decide when reaction is complete. It is also possible to monitor the appearance of the alkene absorptions.

Exercise 16. The figure shows the IR spectrum of a compound with the formula C_8H_8O. What functional groups does the compound contain?



SOLUTION

All IR spectra have many absorptions, but those useful for identifying specific functional groups are usually found in the region from 1500 to 3300 cm^{-1}. Pay particular attention to the carbonyl region (1670 to 1780 cm^{-1}), the aromatic region (1660 to 2000 cm^{-1}), the triple-bond region (2000 to 2500 cm^{-1}), and the C–H region (2500 to 3500 cm^{-1}).

$$Degree\ of\ unsaturation = (8 + 1) - \frac{8}{2} = 5$$

5 instaurations + rings

The spectrum shows an intense absorption at 1725 cm^{-1} due to a carbonyl group (perhaps an aldehyde, –CHO), a series of weak absorptions from 1800 to 2000 cm^{-1} characteristic of aromatic compounds, and a C–H absorption near 3030 cm^{-1}, also characteristic of aromatic compounds. In fact, the compound is 2-phenylacetaldehyde (with 1 ring and 4 instaurations: phenyl and carbonyl).

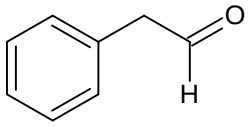


IMAGE CREDITS

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