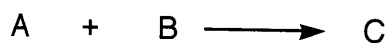Attention Students:

The notes that follow are for your use in class. They are incomplete. You are expected to add important information and details during class. You cannot survive Organic II with these notes alone!

CHAPTER 13: NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Structure determination:

A + B ⟶ C

IR / MS / NMR / UV

Energy required: (see electromagnetic spectrum, p. 502 of Wade)

The Basics of NMR Theory:

1. All nuclei are charged.

2. Some nuclei have a nuclear spin.

3. The spinning charge generates a magnetic field (magnetic moment).

4. These magnetic fields are randomly oriented.

5. If an external magnetic field (H_0) is applied, the orientations of the nuclear magnetic fields are no longer random.

H_0 increases

H_0
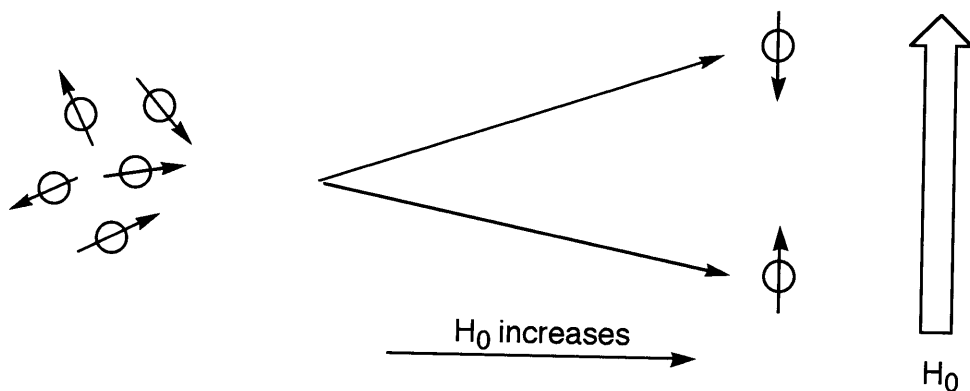
6. Energy is required to "flip" the nucleus from its lower energy state to its higher energy state. When the "flip" occurs, the nucleus is said to be "in resonance." Energy required is proportional to the magnetic field strength.

NMR - continued

To obtain an NMR spectrum:
- sample is irradiated with a constant amount of radio frequency (rf) energy (such as 60 MHz) by a transmitter
- the magnetic field strength is varied
- at the appropriate magnetic field strength (for the rf energy) the nucleus absorbs energy and "flips"
- a detector measures the energy absorbed and a peak is recorded at that field strength
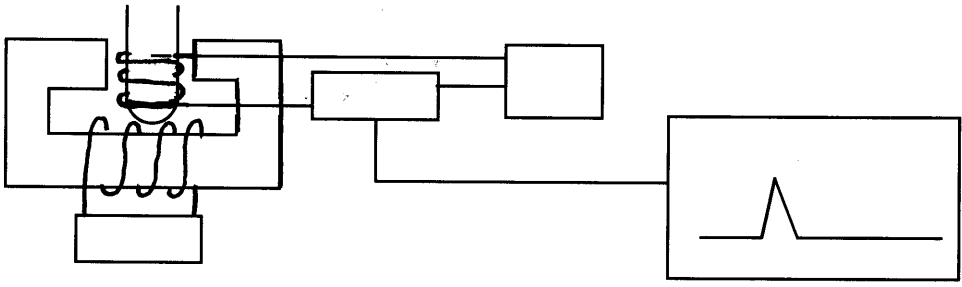
If examining isolated nuclei (protons) -

Nuclei are not isolated -

circulating electrons generate magnetic fields -

$$H_{effective} = H_0 - H_i$$

Example: naked proton absorbs at 14,092.0 gauss
            assume shielding of 0.3 gauss
H_{eff} = 14,092.0 - 0.3 = 14,091.7 gauss

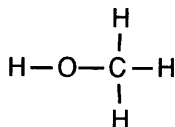Heff = 14,092.3 - 0.3 = 14,092.0 gauss

Nuclei in different magnetic environments absorb energy at different magnetic field strengths -

the more shielded a nucleus -

the more deshielded a nucleus -

Example: see Fig. 13-9, The Proton NMR Spectrum of Methanol

$$H-O-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$$
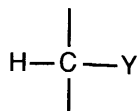
Chemical shift:

The variations in magnetic field strength necessary to bring nuclei in different magnetic environments in to resonance are actually quite small. If field strength (in gauss) were used as the scale for NMR spectra, it would be difficult to distinguish different types of protons.
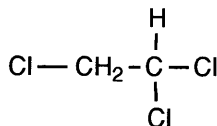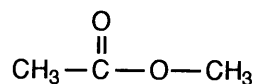
Solution:

$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-CH_3$$
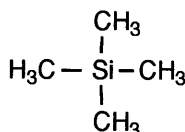
Structural features that contribute to shielding/deshielding:

1. an electronegative atom

$$H-\overset{\overset{\displaystyle |}{|}}{\underset{\underset{\displaystyle |}{|}}{C}}-Y$$

examples:

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3 \qquad\qquad Cl-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-Cl$$
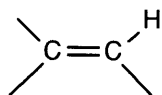
2. π electrons

a. aromatic π electrons - induced field reinforces the applied field

$$H_3C-\langle\bigcirc\rangle-H$$
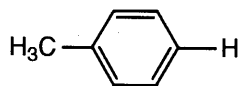
b. π electrons of double bond - induced field reinforces the applied field

$$\overset{\diagdown}{\underset{\diagup}{C}}=\overset{\diagup}{\underset{\diagdown}{C}}H$$

c. π electrons of triple bond - induced field opposes the applied field

$$-C\equiv C-H$$

Fig. 13-10   Deshielding of Benzene Protons
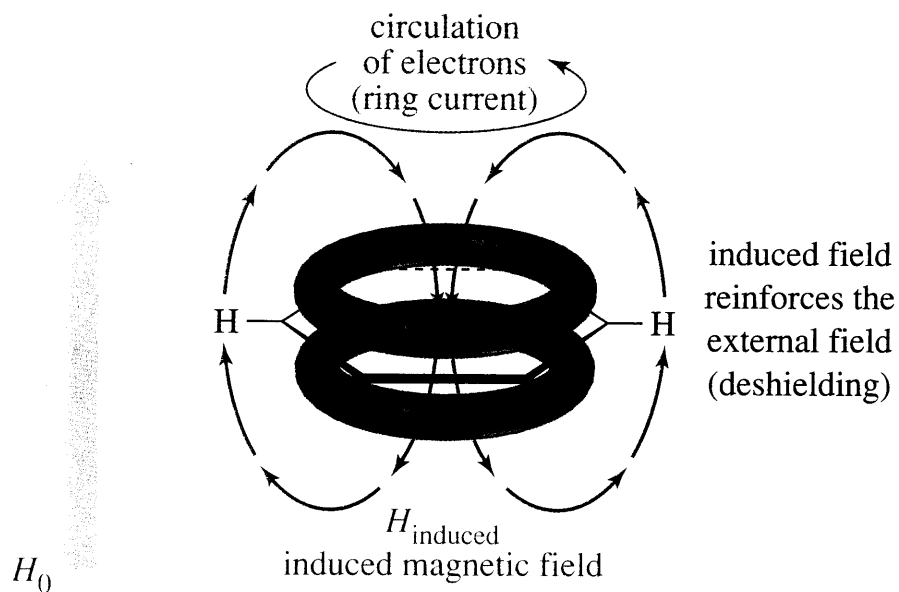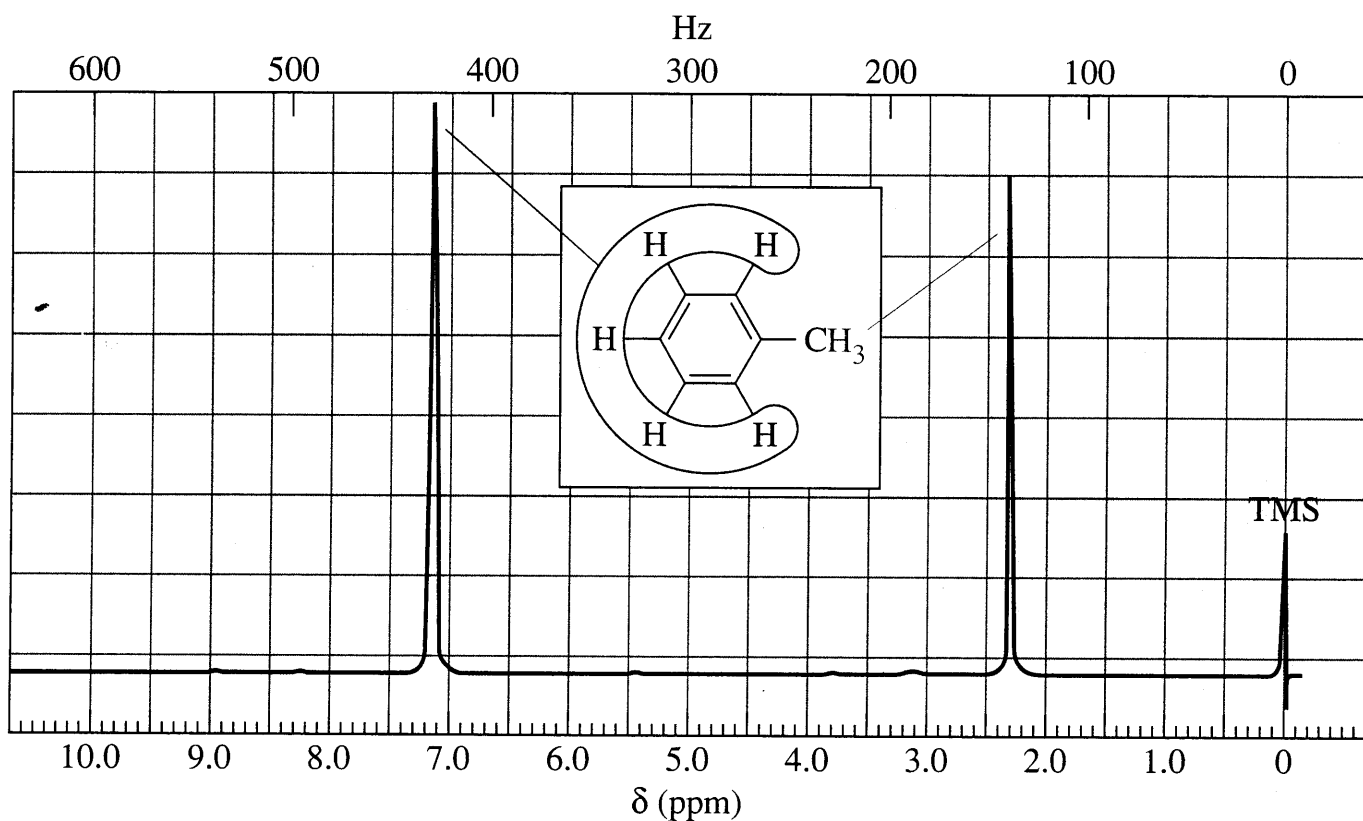

Fig. 13-11   Proton NMR Spectrum of Toluene

Fig. 13-12   Deshielding of Vinyl Protons

$H_{induced}$

induced field
reinforces the
external field
(deshielding)

$H_{induced}$

H_0
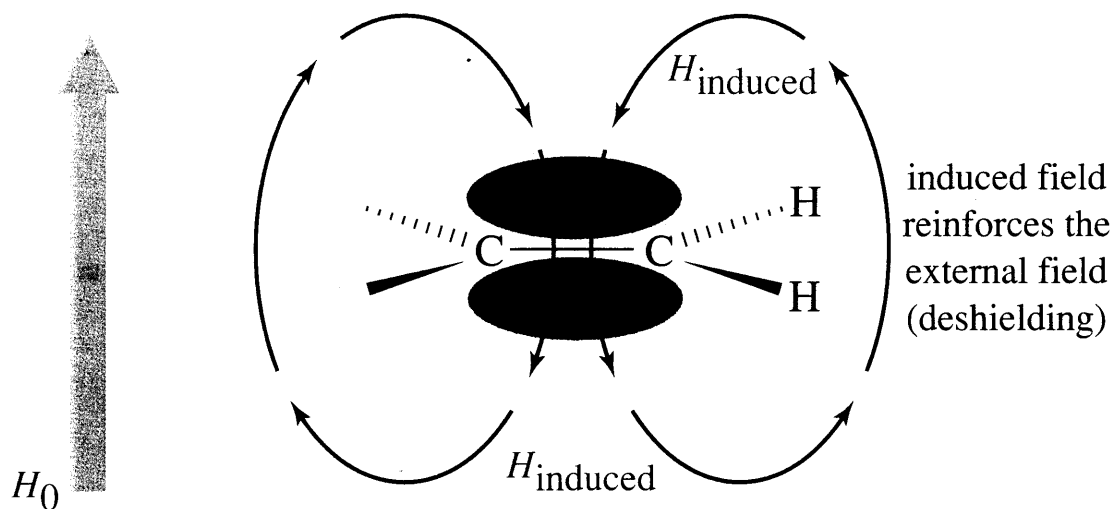
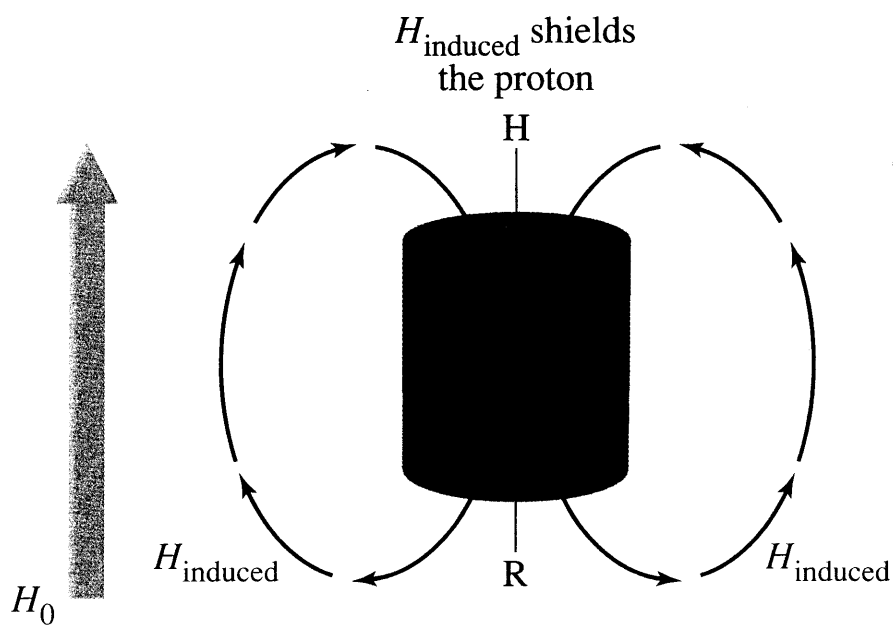**Fig. 13-13   Shielding of Acetylenic Protons**

$H_{induced}$ shields
the proton

$H_{induced}$

$H_{induced}$

H_0

TABLE 13-3 Typical Values of Chemical Shifts

Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane (—CH_3)	0.9	$\diagup C=C \diagdown$ CH₃	1.7
alkane (—CH_2—)	1.3	Ph—H	7.2
alkane (—CH—)	1.4	Ph—CH_3	2.3
O ‖ —C—CH_3	2.1	R—CHO	9–10
		R—COOH	10–12
—C≡C—H	2.5	R—OH	variable, about 2–5
R—CH_2—X (X = halogen, O)	3–4	Ar—OH	variable, about 4–7
		R—NH_2	variable, about 1.5–4
$\diagup C=C \diagdown$ H	5–6		

Note: These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present. A more complete table of chemical shifts appear in Appendix 1.

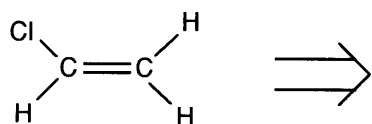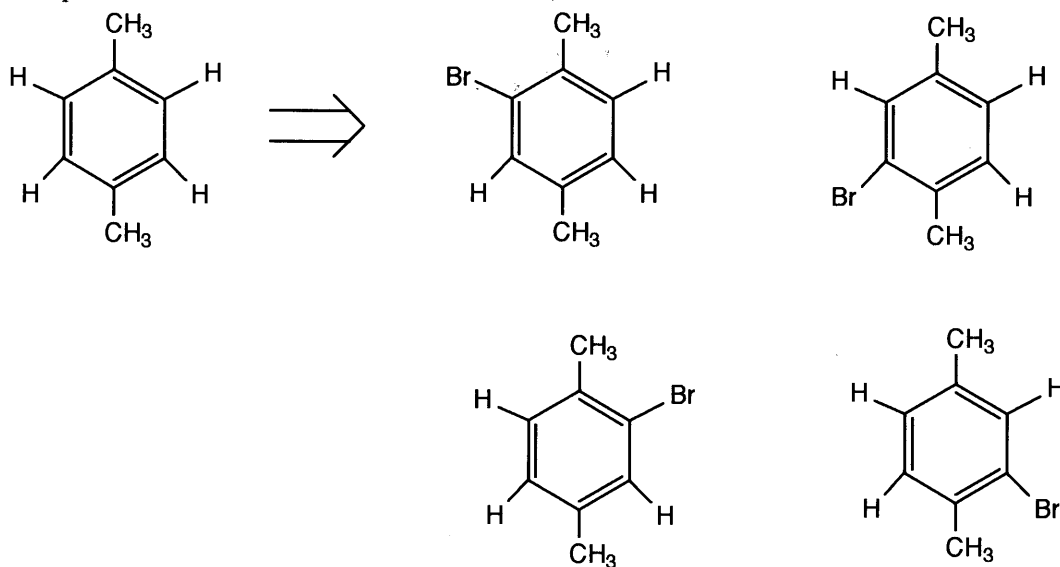## Fig. 13-40   Common Chemical Shifts in the Proton NMR Spectrum
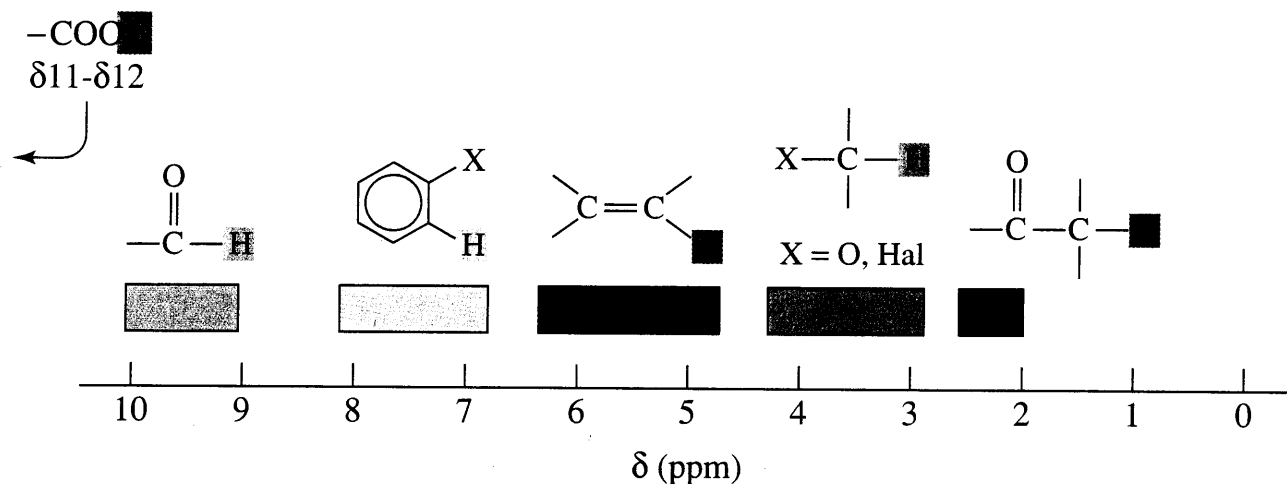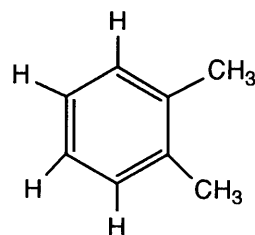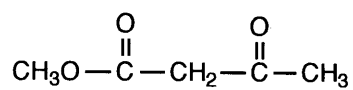
Equivalent vs Nonequivalent Protons

IMPORTANT to recognize!

If two hydrogens can be replaced in turn (one at a time) by the same group to obtain a chemically equivalent compound, the two hydrogens are chemically equivalent.
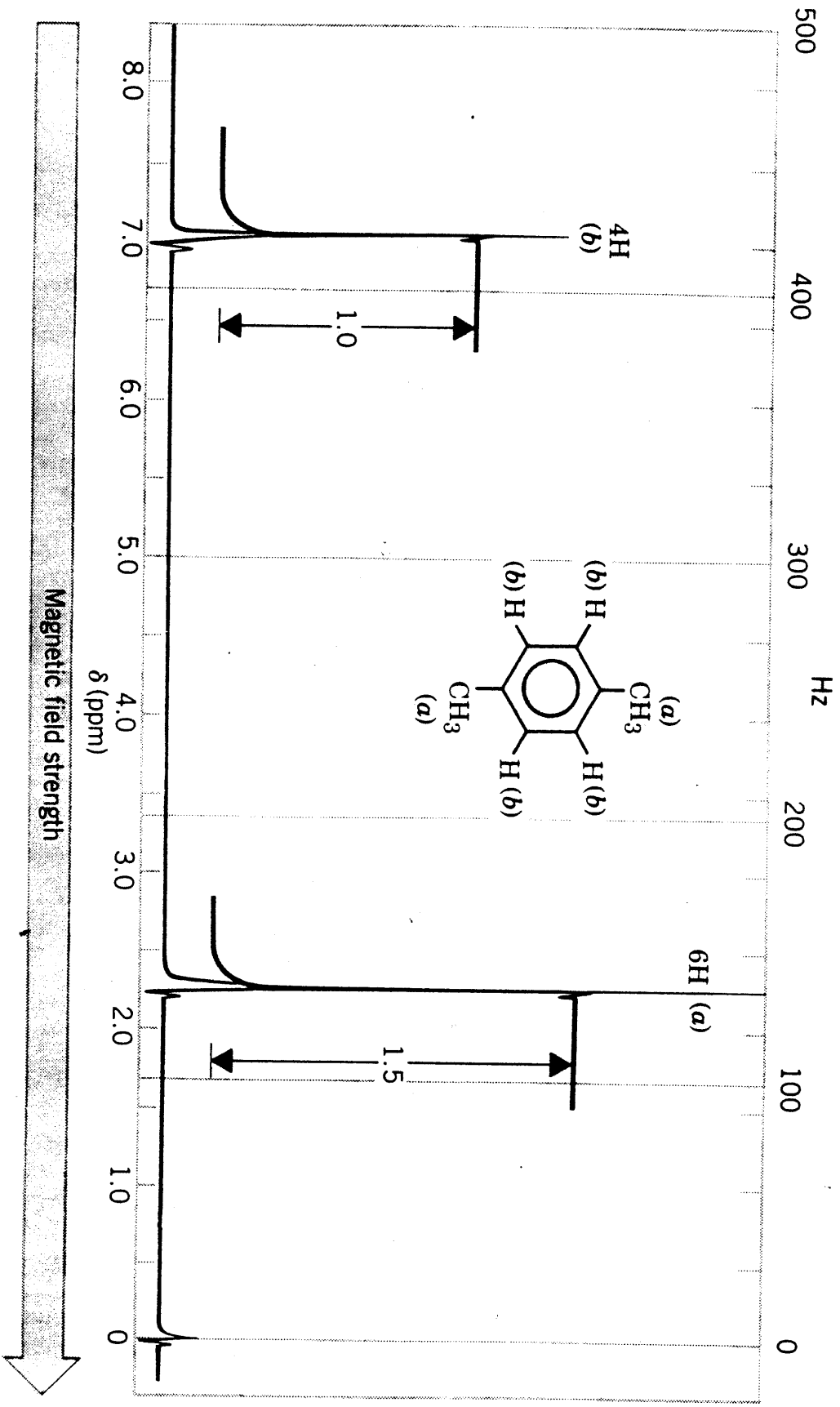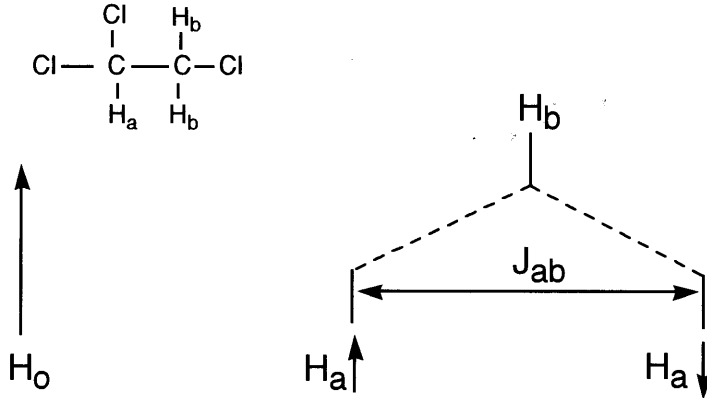
examples:

Practice:

$CH_3O-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

FIGURE 14.10   86   98

9

FIGURE 14.10

Spin-spin splitting:

- occurs only between nonequivalent protons
- does not occur between equivalent protons
- most splitting is between protons on adjacent carbon atoms
- also occurs between nonequivalent protons on the same carbon atom

- H_a mag. field aligned with applied field
- effective field, or field "felt" by H_b, is increased by H_a
- H_b resonates at lower magnetic field strength - downfield

- H_a mag. field aligned against applied field
- effective field, or field "felt" by H_b, is decreased by H_a
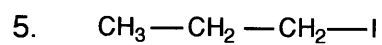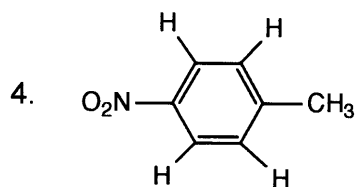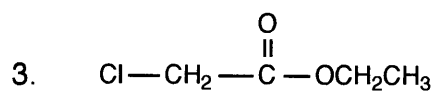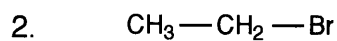- H_b resonates at higher magnetic field strength - upfield

observed signal for H_b:

opposing H_b magnetic fields cancel
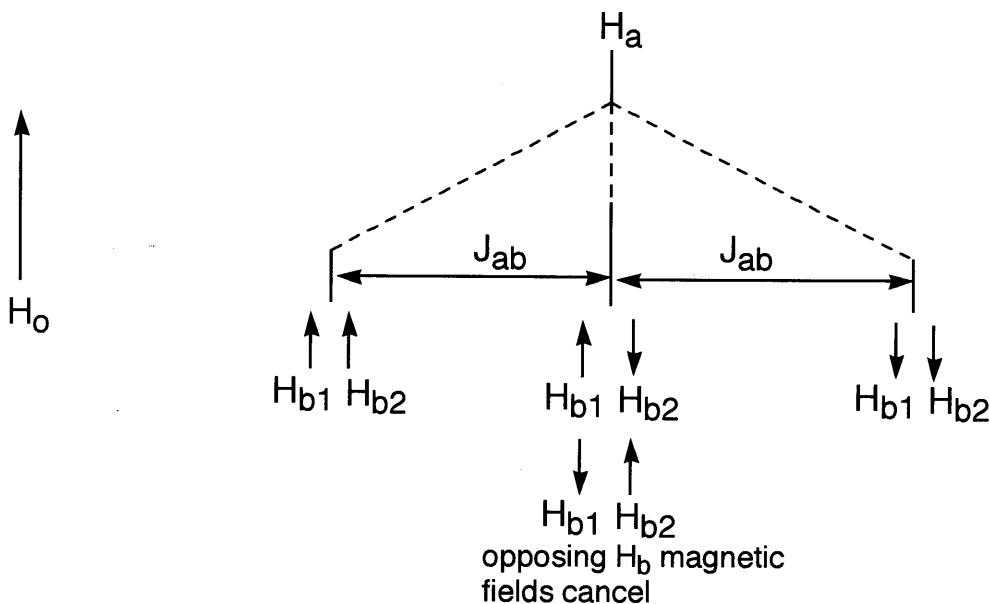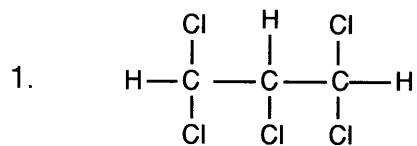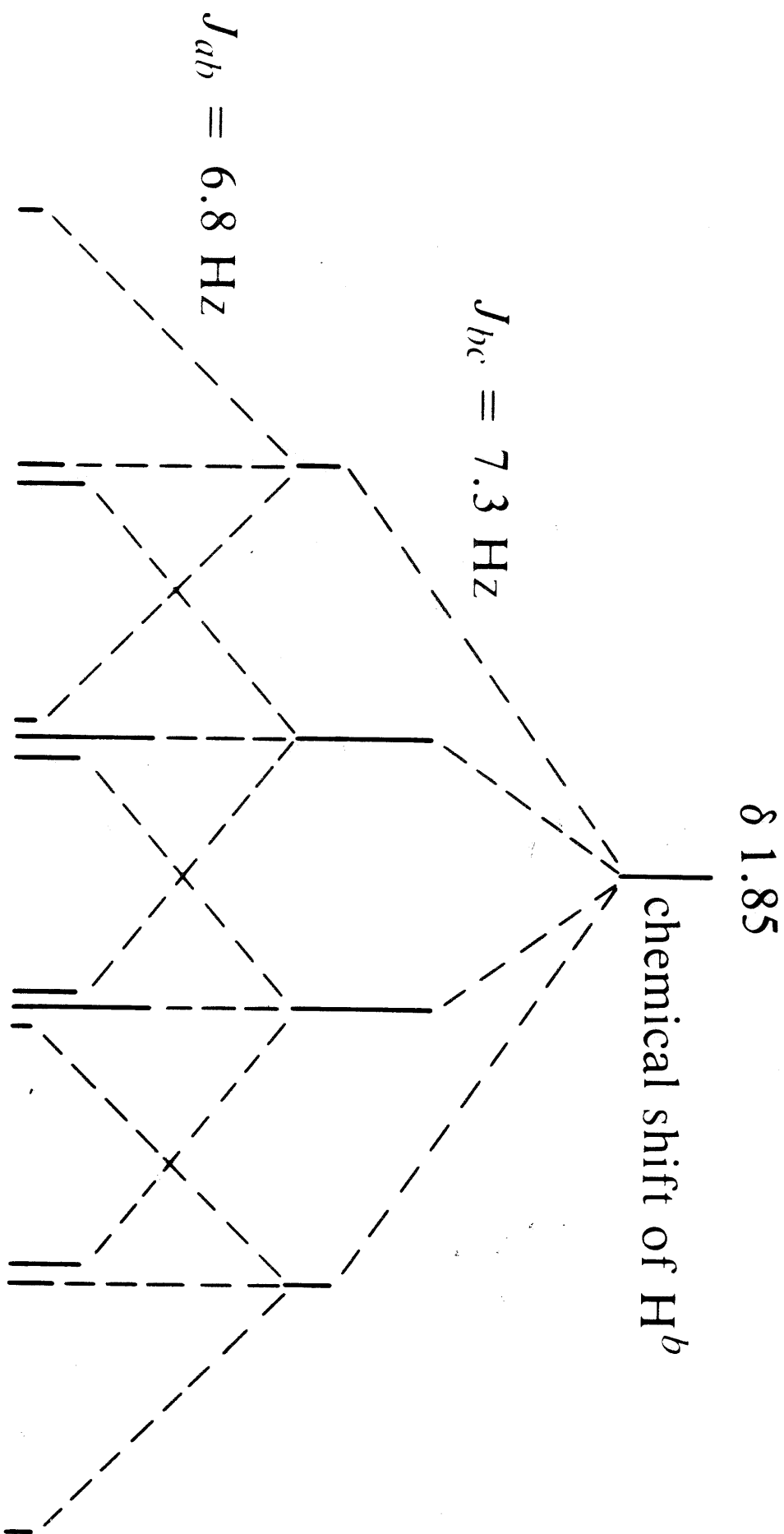
observed signal for H_a:

The N + 1 Rule: If a signal is split by N equivalent protons, it is split into N + 1 peaks.

Examples:

1.

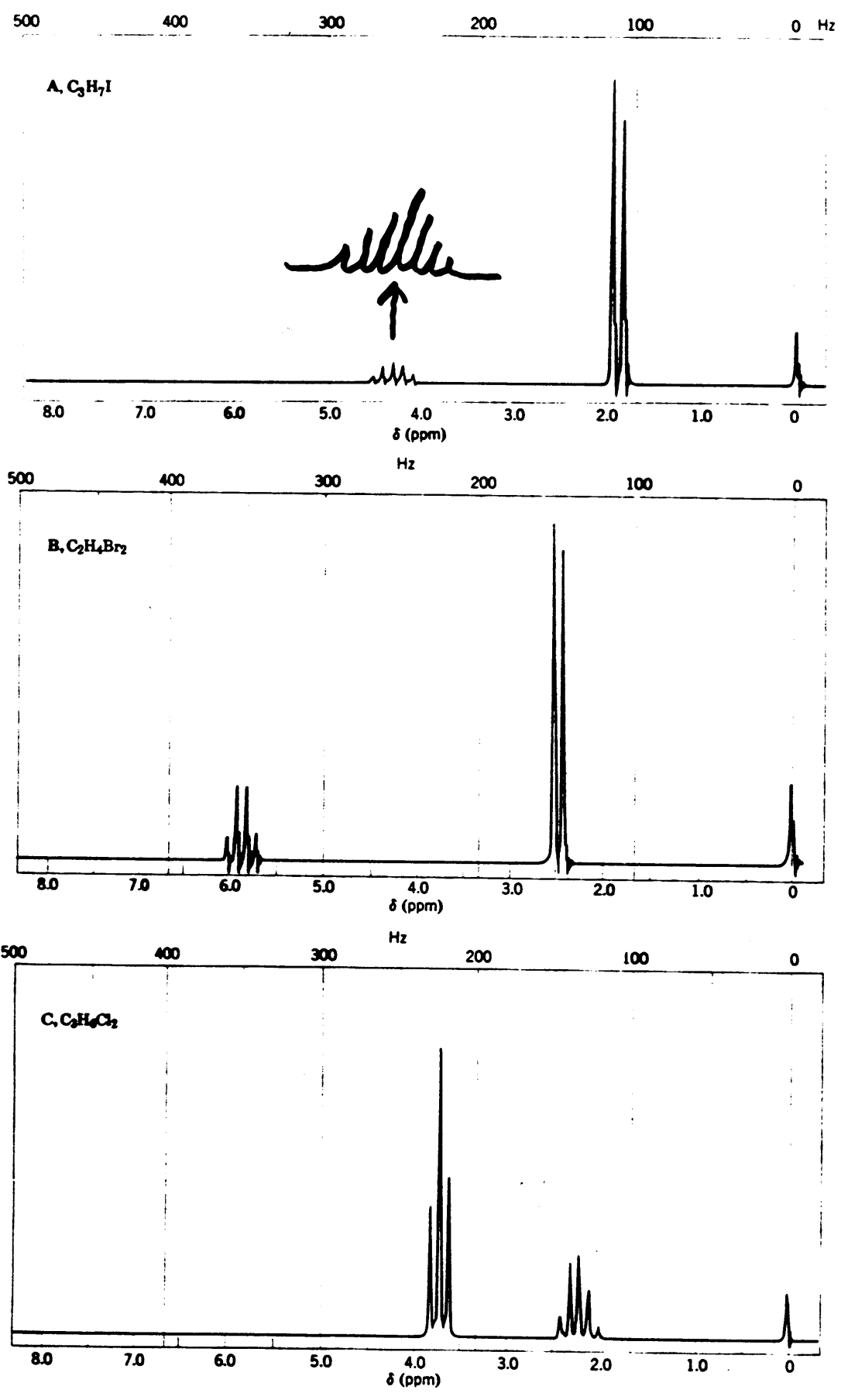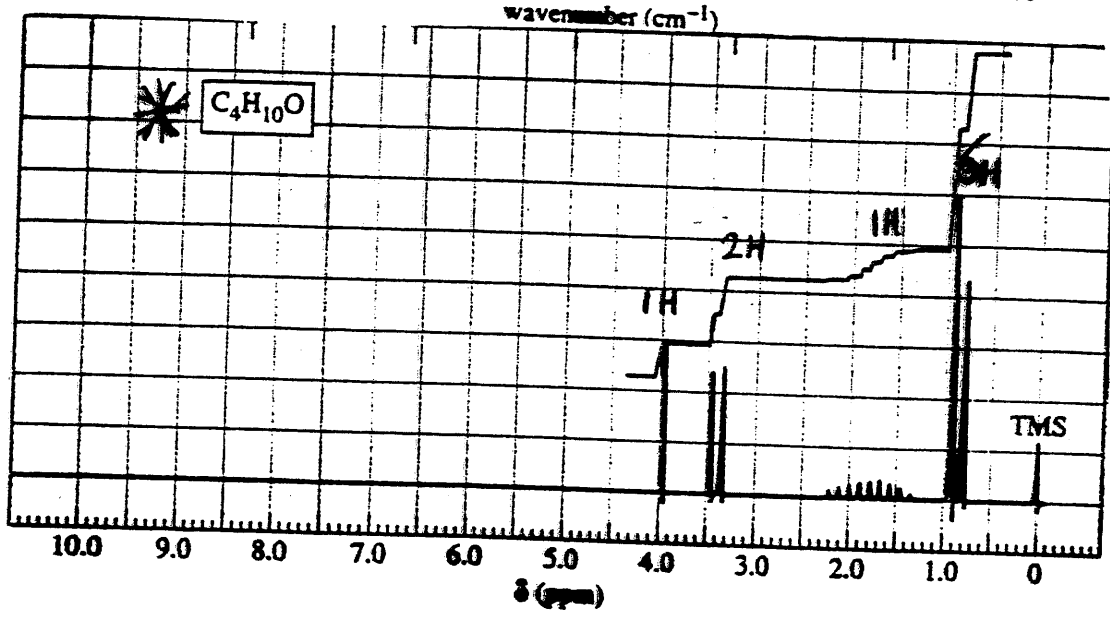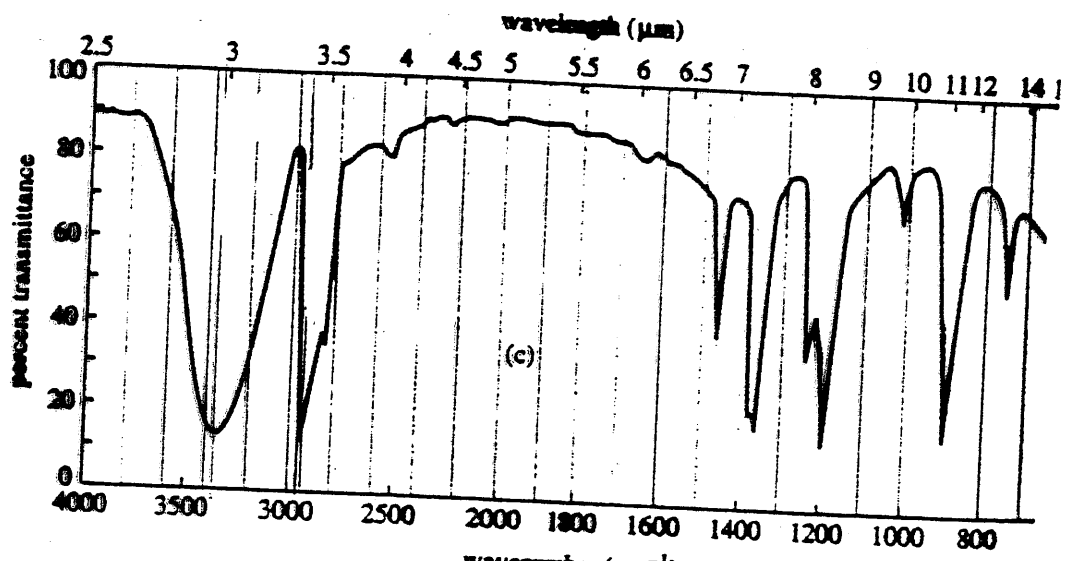$$\begin{array}{ccccc} & Cl & & H & & Cl & \\ & | & & | & & | & \\ H-&C&-&C&-&C&-H \\ & | & & | & & | & \\ & Cl & & Cl & & Cl & \end{array}$$

2. $CH_3 — CH_2 — Br$

3. $$Cl — CH_2 — \overset{\overset{O}{\|}}{C} — OCH_2CH_3$$

4.

5. $CH_3 — CH_2 — CH_2 — I$

SPLITTING PATTERN of the *b* PROTONS
in *n*-PROPYL IODIDE

$J_{ab} = 6.8 \text{ Hz}$

$J_{bc} = 7.3 \text{ Hz}$

$\delta 1.85$

chemical shift of H^b

13

¹H NMR

A, C₃H₇I

B, C₂H₄Br₂

C, C₂H₄Cl₂

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FIGURE 14.27   94

IR spectrum (c): wavelength (µm) vs. percent transmittance / wavenumber (cm⁻¹)

$C_4H_{10}O$

¹H NMR spectrum: integrations 1H (~3.9 ppm), 2H (~3.4 ppm), 1H (~1.6 ppm), 3H (~0.9 ppm), TMS reference at 0 ppm. δ (ppm) scale from 10.0 to 0.

Carbon-13 NMR:

Theory -

Important Differences Between ^{13}C and ^1H NMR:

1. Techniques for obtaining spectra are different. Since % natural abundance of ^{13}C is low (approx. 99% of carbon atoms are ^{12}C), we would obtain very weak signals using the techniques discussed for ^1H NMR spectroscopy. Solutions: Use computer to average many scans taken in the "normal" continuous wave manner (time consuming) or use FT NMR spectroscopy.

2. Carbon signals occur over much wider range, 0 - 220 ppm (0 - 10ppm for ^1H), so less signal overlap.

3. Peak area is not necessarily proportional to the number of carbons.

4. No carbon - carbon splitting is observed (adjacent ^{13}C atoms unlikely).
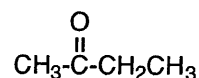Carbon - hydrogen splitting may be observed depending on instrument mode.

Proton Spin Decoupling: all carbon signals appear as singlets; observe a singlet for each type of carbon

$$CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2CH_3$$
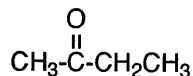
Off - Resonance Decoupling: observe splitting of ^{13}C signal by its directly bonded protons only; N + 1 Rule applies

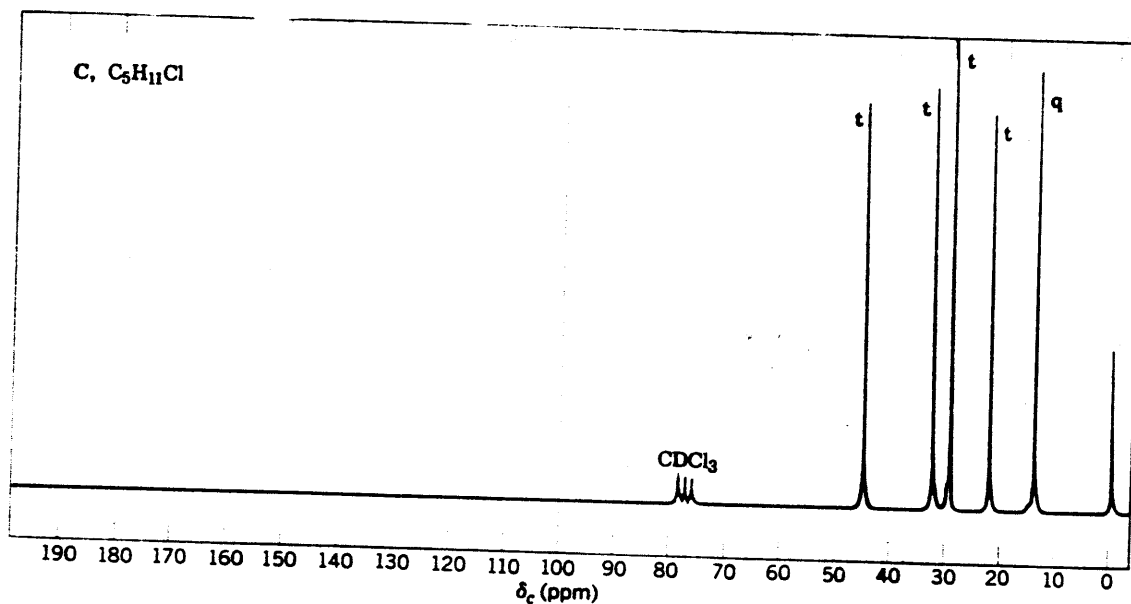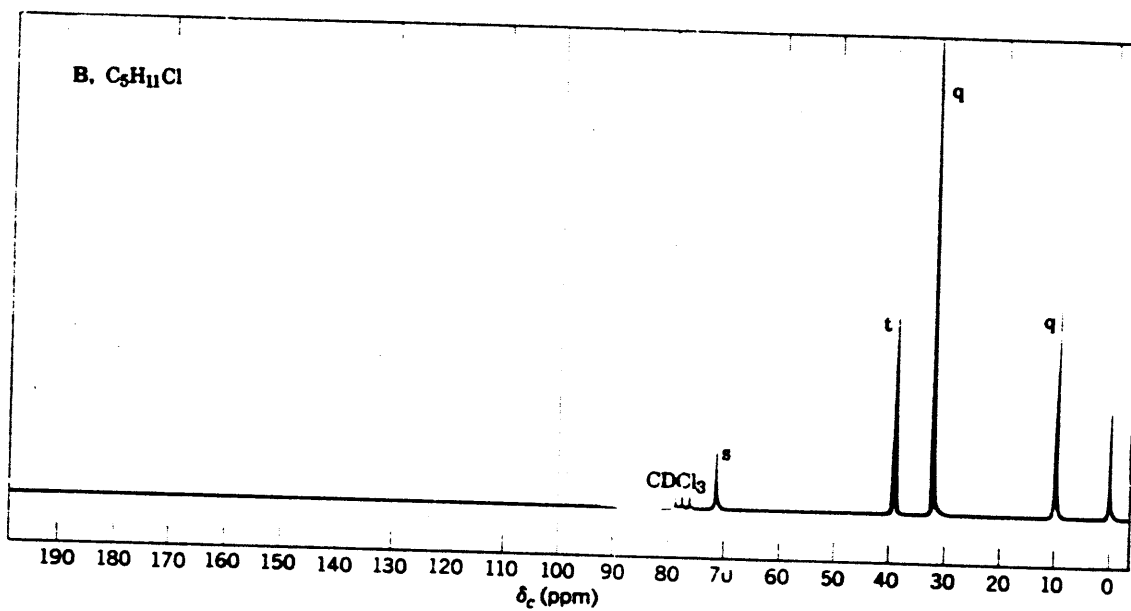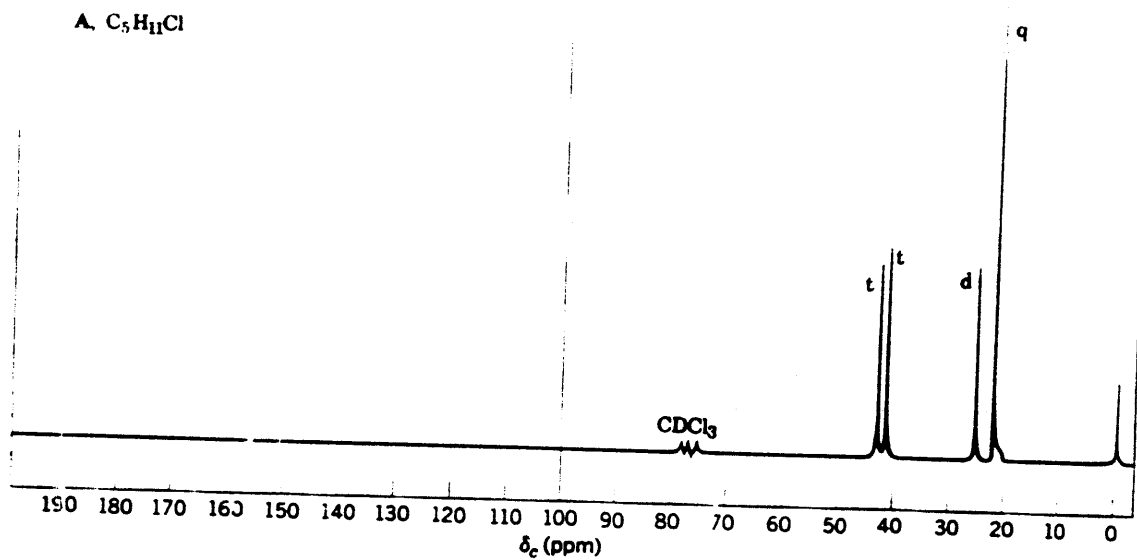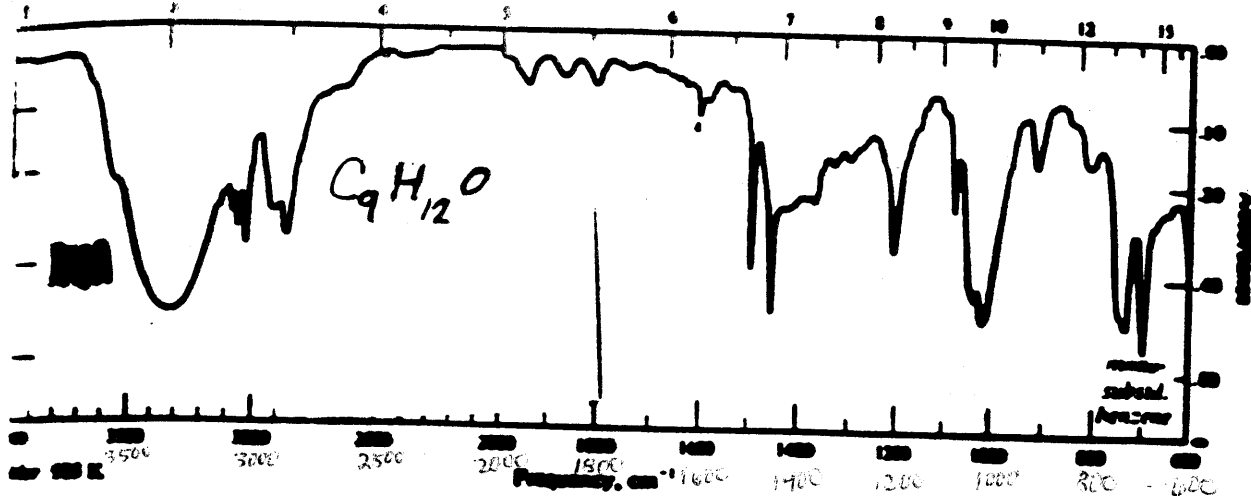CH_3 CH $CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2CH_3$

CH_2 C

A. $C_5H_{11}Cl$

B. $C_5H_{11}Cl$

C. $C_5H_{11}Cl$

FIGURE 14.37   102

$C_9H_{12}O$

^{13}C-NMR:

15 δ, q

25 δ, t

60 δ, d

130-140 δ, 3d and 1 s

$C_{10}H_{12}O$

IR: 1700 cm^{-1}, strong

^{1}H·NMR

5

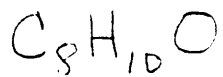2 2

3

7.7 ppm

2.9 2.4

1.1

0
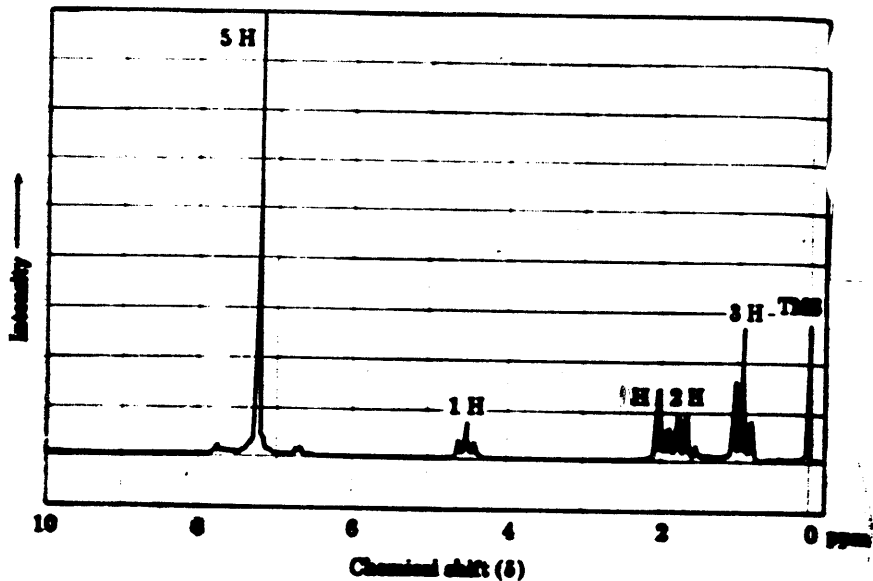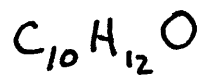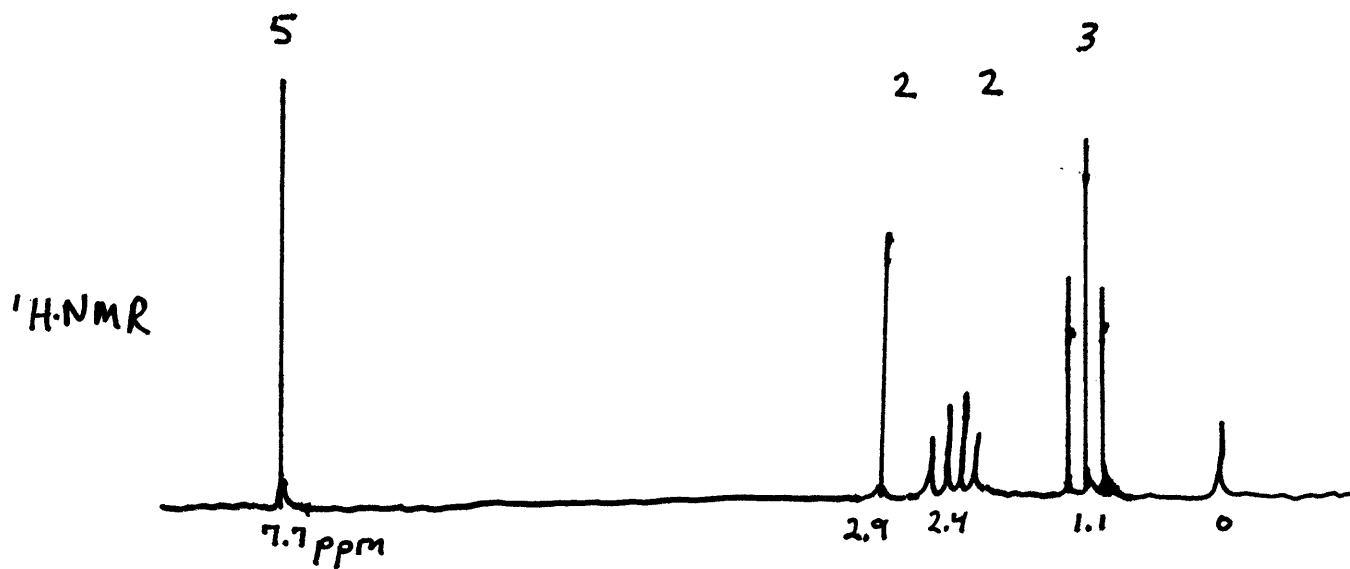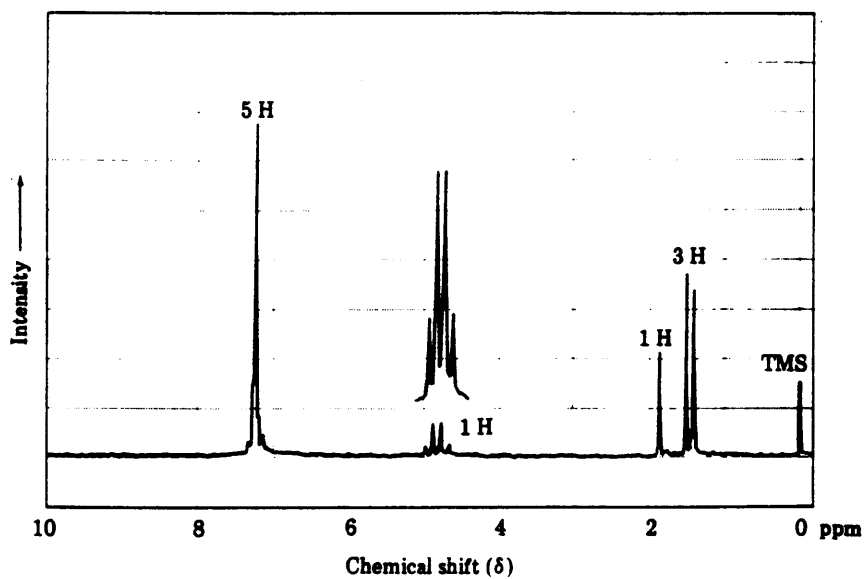
^{13}C NMR data:

S, 200 ppm

1s, 3d, 135 – 120 ppm

t, 45 ppm

t, 40 ppm

q, 10 ppm

$C_8H_{10}O$
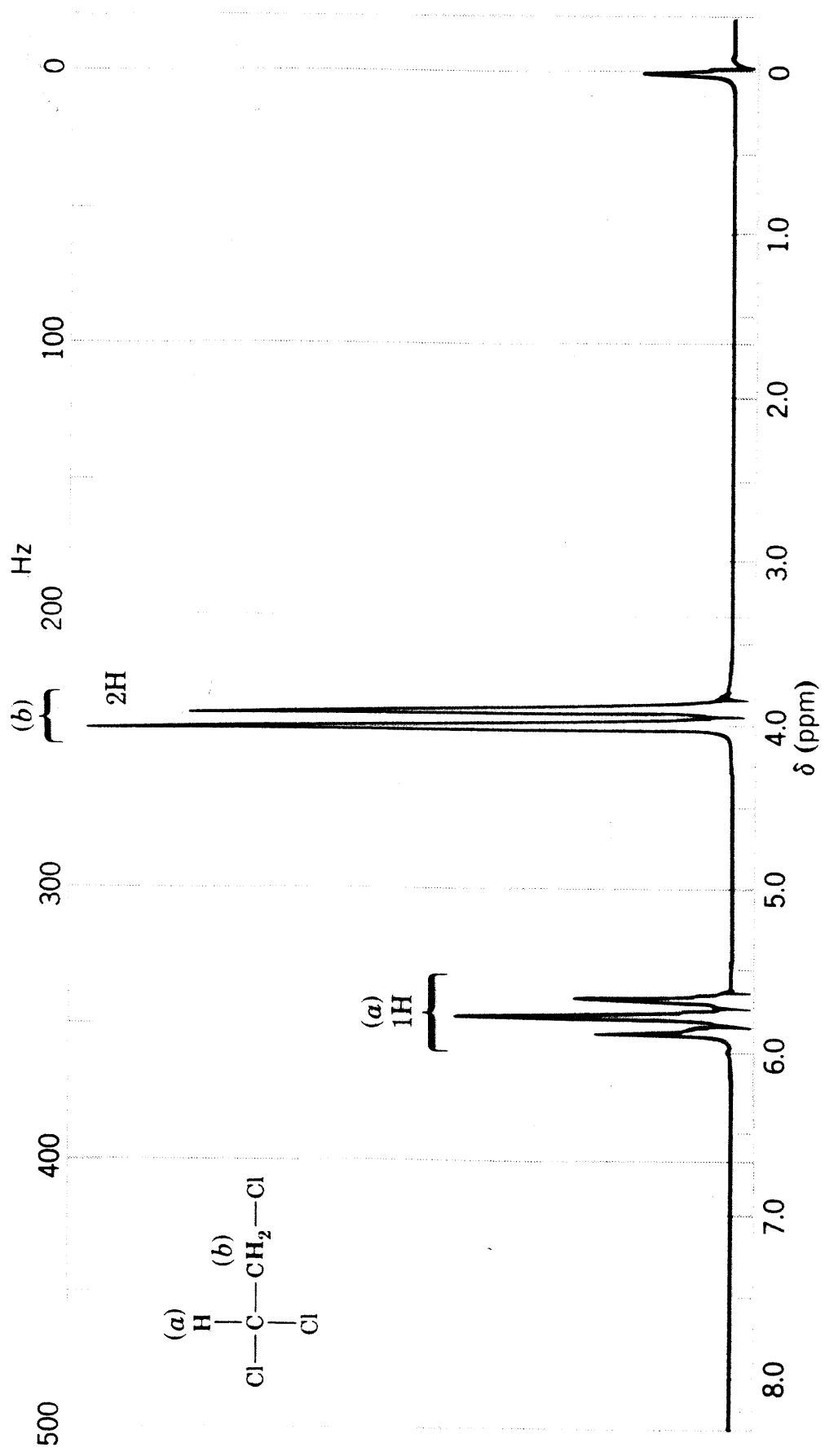

IR: 3350 cm^{-1}, strong
1500, 1600 cm^{-1}, 2 peaks

^{13}C NMR:

δ 130-140, 3d, 1s
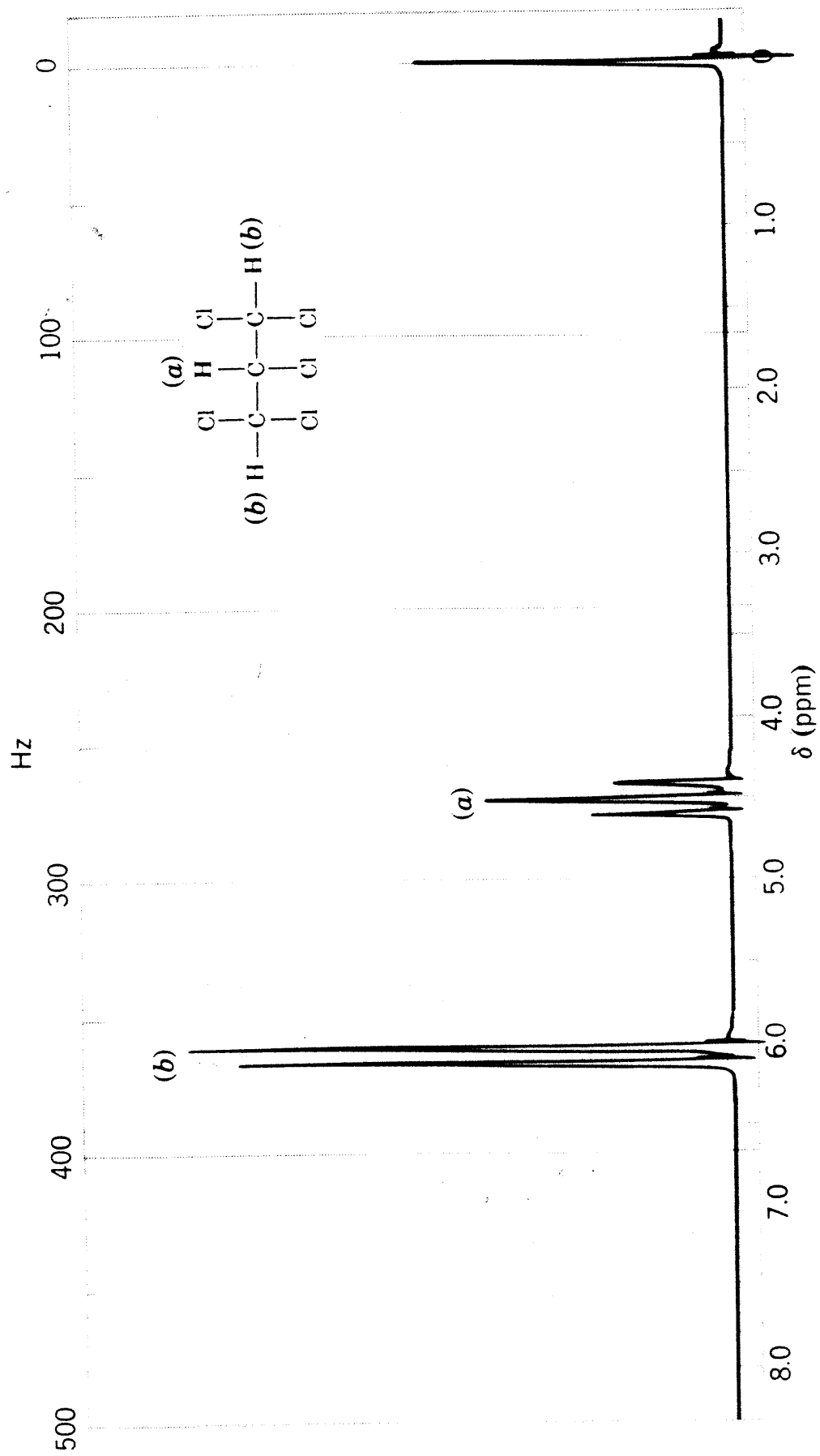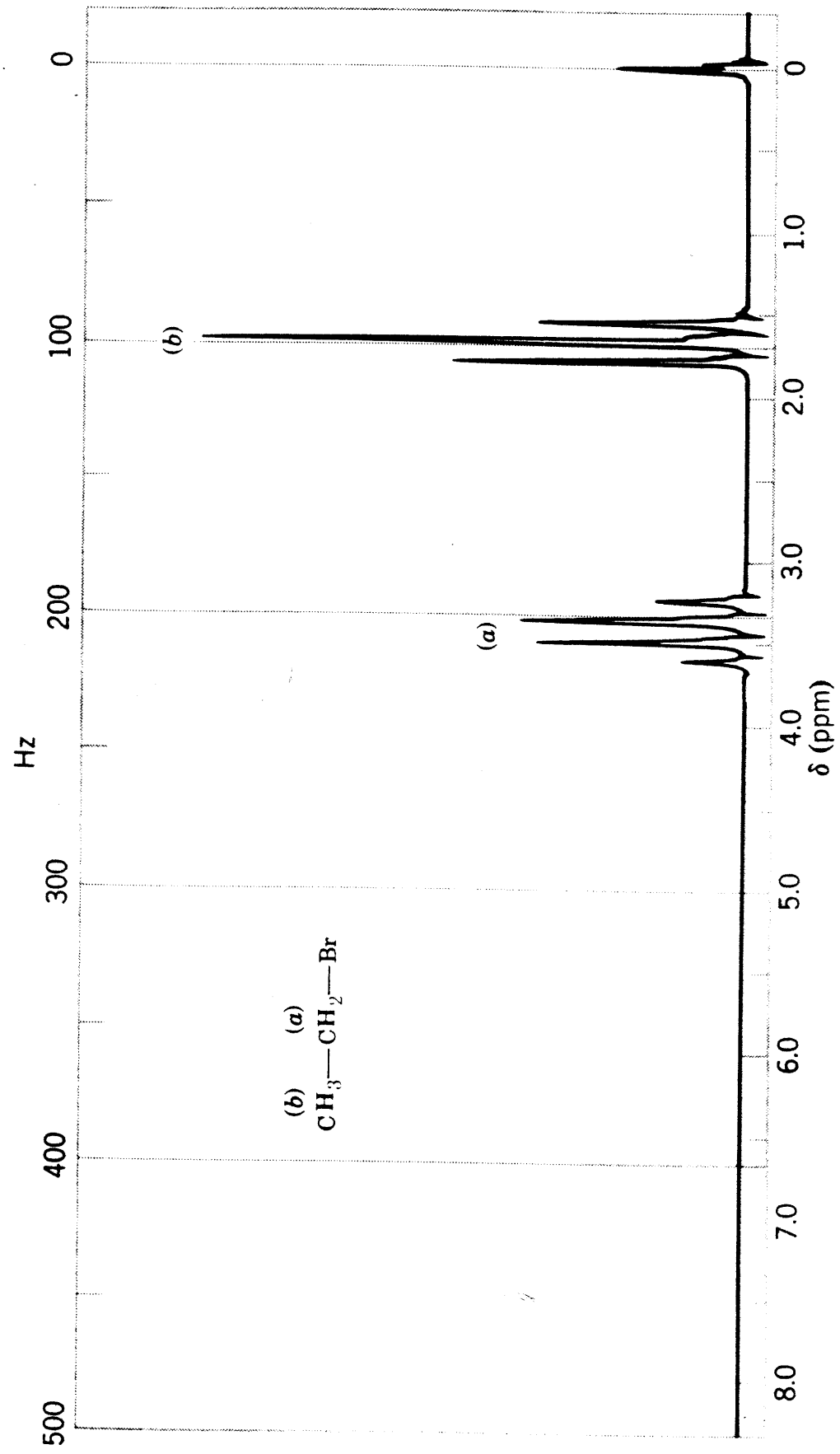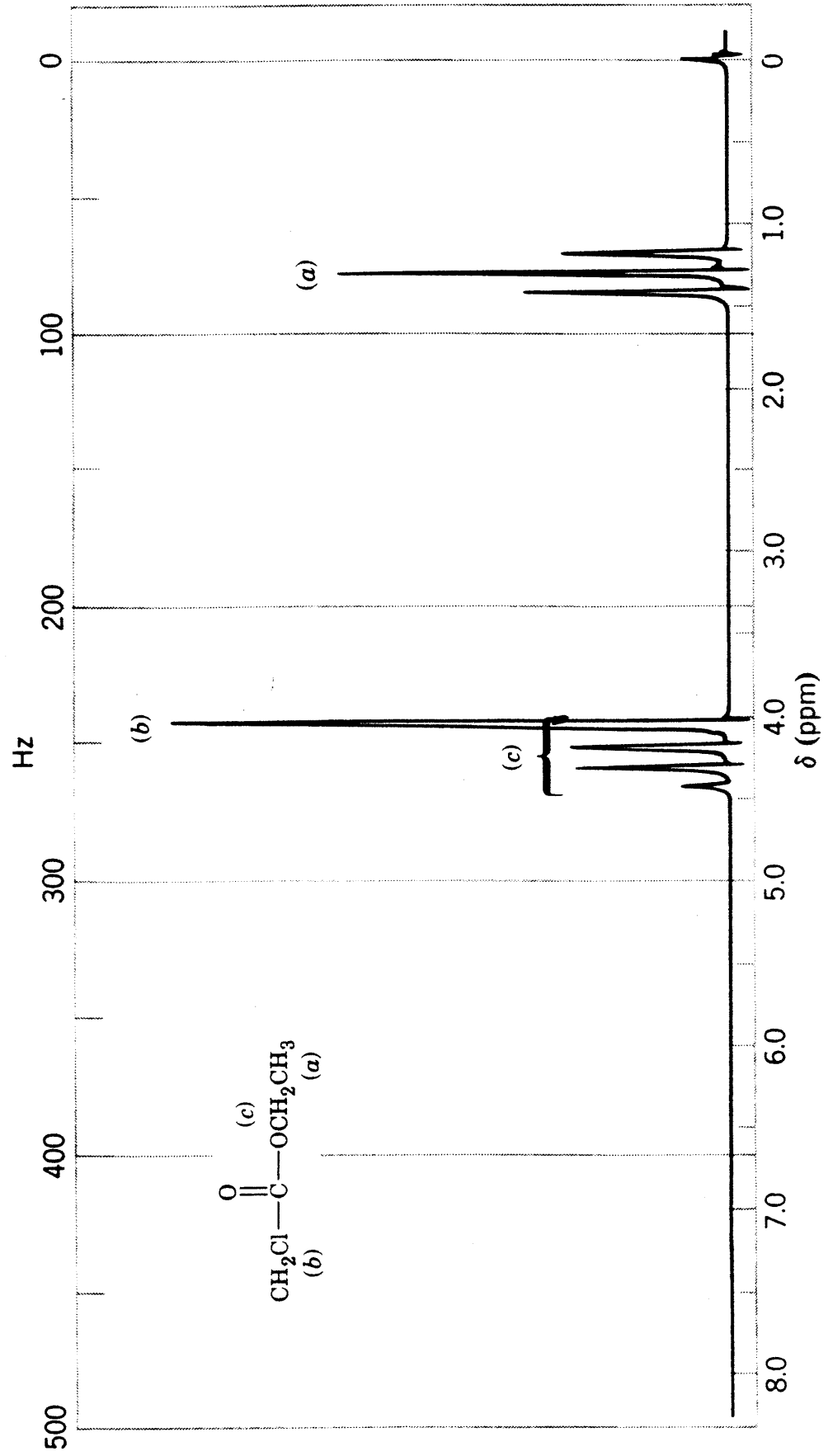δ 20, q
δ 60, d

20

FIGURE 14.11   87

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FIGURE 14.24 92

22

(b) (a)
CH₃—CH₂—Br

FIGURE 14.26 93

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23

Ⓓ

Hz

(a)

(b)

(c)

δ (ppm)

$$CH_2Cl - \overset{\overset{\displaystyle O}{\|}}{C} - OCH_2CH_3$$
(b)   (c)   (a)

0   100   200   300   400   500

0.0   1.0   2.0   3.0   4.0   5.0   6.0   7.0   8.0

FIGURE 14.29   95

NMR