9.7A PPM and the δ Scale

The chemical shift of a proton, when expressed in hertz, is proportional to the strength of the external magnetic field. Since spectrometers with different magnetic field strengths are commonly used, it is desirable to express chemical shifts in a form that is independent of the strength of the external field. This can be done easily by dividing the chemical shift by the frequency of the spectrometer, with both numerator and denominator of the fraction expressed in frequency units (hertz). Since chemical shifts are always very small (typically <5000 Hz) compared with the total field strength (commonly the equivalent of 60, 300, or 600 *million* hertz), it is convenient to express these fractions in units of *parts per million* (ppm). This is the origin of the delta scale for the expression of chemical shifts relative to TMS:

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

For example, the chemical shift for benzene protons is 2181 Hz when the instrument is operating at 300 MHz. Therefore,

$$\delta = \frac{2181 \text{ Hz} \times 10^6}{300 \times 10^6 \text{ Hz}} = 7.27$$

The chemical shift of benzene protons in a 60-MHz instrument is 436 Hz:

$$\delta = \frac{436 \text{ Hz} \times 10^6}{60 \times 10^6 \text{ Hz}} = 7.27$$

Thus, the chemical shift expressed in ppm is the same whether measured with an instrument operating at 300 or 60 MHz (or any other field strength).

Figure 9.2 (Section 9.2A) gives the *approximate* values of proton chemical shifts for some common hydrogen-containing groups.

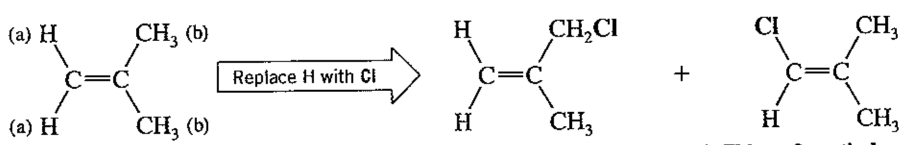
9.8 *Chemical Shift Equivalent and Nonequivalent Protons*

Two or more protons that are in identical environments have the same chemical shift and, therefore, give only one ^{1}H NMR signal. How do we know when protons are in the same environment? For most compounds, protons that are in the same environment are also equivalent in chemical reactions. That is, **chemically equivalent** protons are **chemical shift equivalent** in ^{1}H NMR spectra.

9.8A Homotopic Hydrogen Atoms

A simple way to decide whether two or more protons in a given compound are chemical shift equivalent is to replace each hydrogen in turn by some other group. The group may be real or imaginary. If, in making these replacements, you get the same compound, then the hydrogens being replaced are said to be **chemically equivalent** or **homotopic,** and **homotopic atoms (or groups) are chemical shift equivalent.**

Consider 2-methylpropene as an example:



3-Chloro-2-methylpropene **1-Chloro-2-methylpropene**

The six methyl hydrogens (b) are one set of homotopic hydrogens; replacing any one of them with chlorine, for example, leads to the same compound, 3-chloro-2-methylpropene. The two vinyl hydrogens (a) are another set of homotopic hydrogens; replacing either of these leads to 1-chloro-2-methylpropene. 2-Methylpropene, therefore, gives two ^{1}H NMR signals.

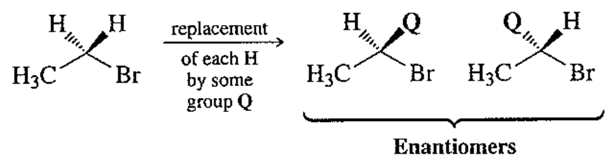
Review Problem 9.3 Carry out a similar analysis for 1,4-dimethylbenzene (Section 9.2C) and show that it has two sets of chemical shift equivalent protons, explaining why its spectrum (Fig. 9.3) has only two signals.

Review Problem 9.4 How many signals would each compound give in its ^{1}H NMR spectrum?

(a) Ethane
(b) Propane
(c) *tert*-Butyl methyl ether
(d) 2,3-Dimethyl-2-butene
(e) (*Z*)-2-Butene
(f) (*E*)-2-Butene

9.8B Enantiotopic and Diastereotopic Hydrogen Atoms

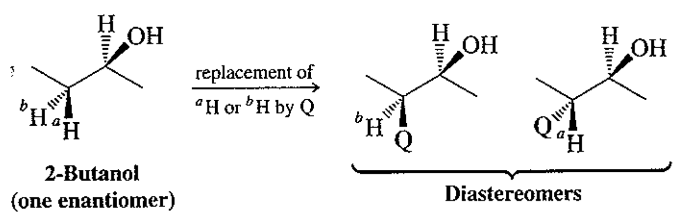
If replacement of each of two hydrogen atoms by the same group yields compounds that are enantiomers, the two hydrogen atoms are said to be **enantiotopic.** ***Enantiotopic hydrogen atoms have the same chemical shift and give only one ^{1}H NMR signal:****



The two hydrogen atoms of the —CH_2Br group of bromoethane are enantiotopic. Bromoethane, then, gives two signals in its ^{1}H NMR spectrum. The three equivalent protons of the —CH_3 group give one signal; the two enantiotopic protons of the —CH_2Br group give the other signal. [The ^{1}H NMR spectrum of bromoethane, as we shall see, actually consists of seven peaks (three in one signal, four in the other). This is a result of signal splitting, which is explained in Section 9.9.]

If replacement of each of two hydrogen atoms by a group, **Q**, gives compounds that are diastereomers, the two hydrogens are said to be **diastereotopic.** Except for accidental coincidence, ***diastereotopic protons do not have the same chemical shift and give rise to different ^{1}H NMR signals.***

The two methylene hydrogens labeled ^{a}H and ^{b}H at C3 in 2–butanol are **diastereotopic.** We can illustrate this by imagining replacement of ^{a}H or ^{b}H with some imaginary group **Q**. The result is a pair of diastereomers. As diastereomers, they have different physical properties, including chemical shifts, especially for those protons near the chirality center.



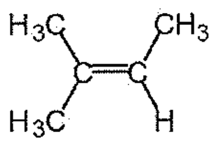
The diastereotopic nature of ^{a}H and ^{b}H at C3 in 2–butanol can also be appreciated by viewing Newman projections. In the conformations shown below (Fig. 9.16), as is the case for every possible conformation of 2–butanol, ^{a}H and ^{b}H experience different environments

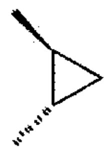
*Enantiotopic hydrogen atoms may not have the same chemical shift if the compound is dissolved in a chiral solvent. However, most ^{1}H NMR spectra are determined using achiral solvents, and in this situation enantiotopic protons have the same chemical shift.

NMR Key

1. How many different kinds of protons are present in each of the following molecules?

a. $(CH_3)_2CHOCH_2CH_3$ b. $CH_3CH_2CH_2CH_2OH$ c. $CH_3CH(Br)CH_2OH$

d. 

e. 

a. a: 3; b: 5; c: 5; d: 4; e: 3
b. a: 4; b: 5; c: 4; d: 4; e: 3
C. a: 4; b: 5; c: 5; d: 4; e: 3
d. a: 4; b: 5; c: 5; d: 3; e: 4
e. a: 4; b: 5; c: 5; d: 4; e: 4

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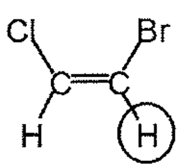
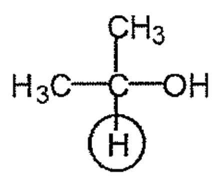
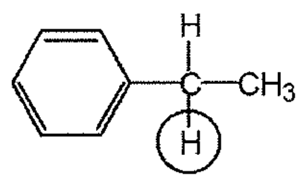
2. Into how many peaks will each of the circled protons be split?

A. 

B. 

C. 

a. A: 3; B: 7; C: 4
B. A: 2; B: 7; C: 4
c. A: 2; B: 7; C: 3
d. A: 2; B: 6; C: 4
e. A: 2; B: 8; C: 4

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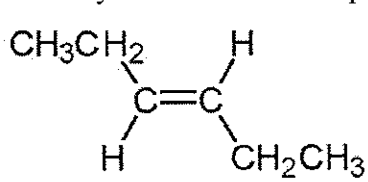
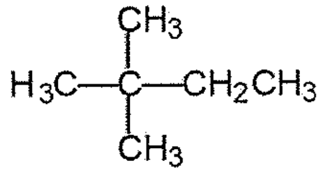
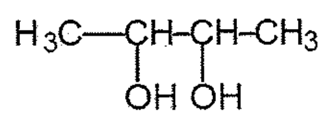
3. How many different kinds of protons are present in each of the following compounds?

a. 

b. 

c. 

a. a: 2; b: 3; c: 4
b. a: 2; b: 3; c: 3
<u>C</u>. a: 3; b: 3; c: 3
d. a: 3; b: 3; c: 4
e. a: 3; b: 2; c: 3

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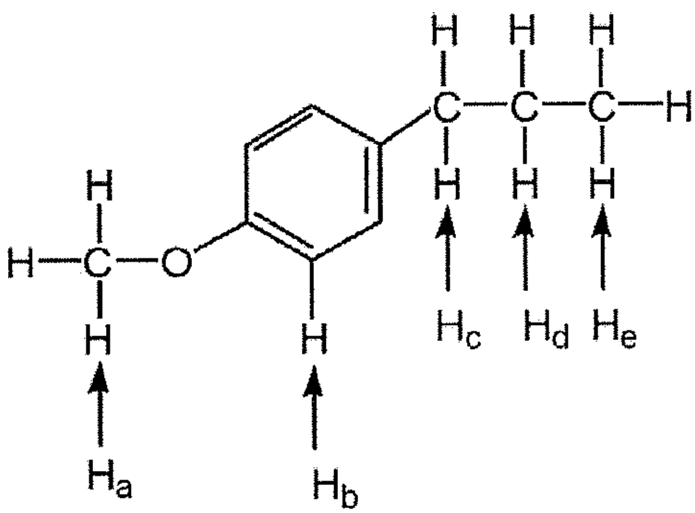
4. Which of the labeled hydrogens absorbs furthest *upfield* in the NMR?



a. H_a
b. H_b
c. H_c
d. H_d
<u>E</u>. H_e

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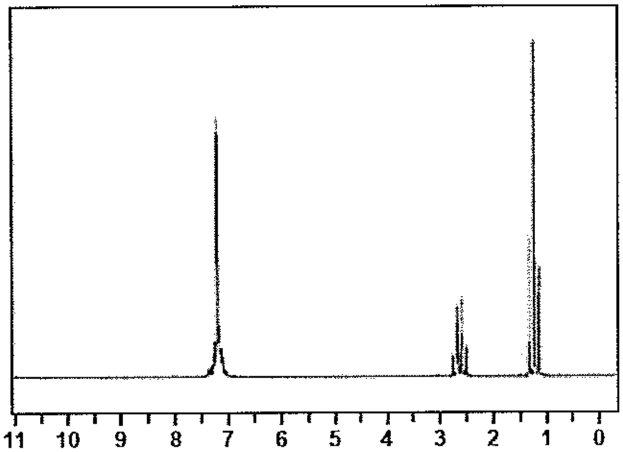
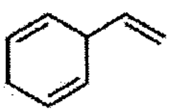
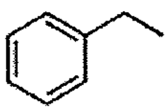
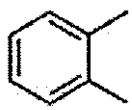
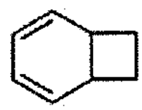
5. Compound X has a molecular formula C_8H_{10}, and gives the ^1H NMR below. What is the structure of X?



^1H NMR

A.  B.  C.  D. 

a. A
B. B
c. C
d. D

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