

# 13

## Nuclear Magnetic Resonance Spectroscopy

### Solutions to In-Text Problems

- 13.1 (b) Apply Eq. 13.2b with  $\nu_0 = 360$  MHz.

$$\text{chemical shift in Hz} = \delta\nu_0 = (4.40)(360) = 1584 \text{ Hz}$$

- 13.2 (b) Follow the same procedure used in part (a).

$$\delta(1) - \delta(2) = \frac{\nu(1) - \nu(\text{TMS})}{\nu_0} - \frac{\nu(2) - \nu(\text{TMS})}{\nu_0} = \frac{\nu(1) - \nu(2)}{\nu_0} = \frac{45}{300} = 0.15 \text{ ppm}$$

- 13.3 (b) Because protons  $\text{H}^a$  and  $\text{H}^b$  are constitutionally nonequivalent, their chemical shifts are different.  
(d) Because protons  $\text{H}^a$  and  $\text{H}^b$  are enantiotopic, their chemical shifts are identical.

- 13.5 (b) The protons of dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) have the greatest chemical shift, because Cl is more electronegative than I, and because  $\text{CH}_2\text{Cl}_2$  has the largest number of these electronegative atoms.

- 13.6 (b)  $G_1 = \text{---Br}$ , and  $G_2 = \text{---I}$ . Eq. 13.3 gives  $\delta(0.2 + 2.3 + 1.8) = \delta 4.3$ .

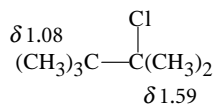
(d) Apply the first column of the table with  $G = \text{---Ph}$ .  $\delta = 2.3$ .

(f)  $G_1 = \text{CH}_3\text{CH}_2\text{---}$ , and  $G_2 = \text{---Br}$ . Eq. 13.3 gives  $\delta(0.2 + 0.6 + 2.3) = \delta 3.1$ .

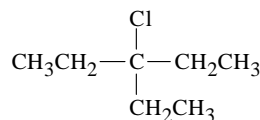
(h) Apply the first column of Table 13.3 with  $G = \text{alkyl}$ , for which  $\delta = 0.9$ . Notice that the bromine is not a  $\beta$ -halogen, but a  $\gamma$ -halogen; it has no significant effect on the chemical shift estimate.

- 13.7 (b) The proton NMR spectrum of *tert*-butyl bromide,  $(\text{CH}_3)_3\text{CBr}$ , consists of a single resonance.

- 13.8 (b) This is the structure given in Problem 13.7(a). As the solution to this problem postulated, there are indeed two absorptions.

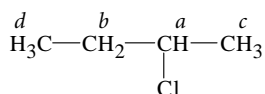


Another structure consistent with the data is the following:



This is a satisfactory answer at this point in the chapter. However, Section 13.3 of the text shows that the spectrum of this compound will consist of a number of lines that result from a phenomenon called splitting.

- 13.10 (b) The resonance for the methylene protons should be a doublet (one neighbor) with a chemical shift of about  $\delta (0.2 + 2.5 + 0.6 + 0.5 + 0.5) = \delta 4.3$ . The resonance for the methine proton should be a triplet (two neighbors) with a chemical shift of about  $\delta (5.3 + 0.7 + 0.5) = \delta 6.5$ . This calculation starts with the chemical shift of  $\text{CH}_2\text{Cl}_2$ ,  $\delta 5.3$ , from Table 13.1; to this is added a  $\delta 0.7$  ppm correction for a methine proton and  $\delta 0.5$  for a  $\beta$ -chlorine. Whatever the exact chemical shift of the resonance of this proton, it should be well downfield of the resonance of the methylene protons.
- 13.11 (b) The resonance for the methyl groups is a six-proton singlet at about  $\delta 3.3$ ; the resonance for the methylene protons  $\alpha$  to the oxygen should be a four-proton triplet at about  $\delta 3.2$ ; and the resonance for the central methylene group should be a two-proton quintet at about  $\delta 2.4$ .
- (d) The resonance for the methyl groups should be a six-proton singlet at about  $\delta 1.4$ ; and the resonance for the methylene protons should be a two-proton singlet at about  $\delta 3.8$ . (The basis of the  $\delta 1.4$  estimate was discussed in the solution to Problem 13.11(a).)
- 13.13 (b)  $\text{ClCH}_2\text{CHCl}_2$
- 13.16 (b) The resonance of proton  $\text{H}^b$  is split into a doublet by  $\text{H}^c$ , and each line of that doublet is split into another doublet by  $\text{H}^a$ . Thus, the resonance for proton  $\text{H}^b$  is a doublet of doublets, or four lines. By a similar analysis, the resonance for proton  $\text{H}^c$  is also a doublet of doublets, or four lines. The total number of lines accounted for by the resonances of  $\text{H}^b$  and  $\text{H}^c$  together is eight lines.
- 13.17 (b) In the NMR spectrum taken with a high-field spectrometer,  $\text{H}^a$  will be a sextet;  $\text{H}^b$  will be a quintet;  $\text{H}^c$  will be a doublet; and  $\text{H}^d$  will be a triplet. The order of chemical shifts, which is the same in spectra taken at various field strengths, is  $\text{H}^a < \text{H}^b < \text{H}^c < \text{H}^d$ .




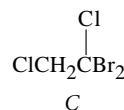
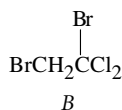
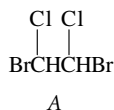
The protons  $\text{H}^b$  in this structure are diastereotopic and therefore are in principle chemically nonequivalent. The answer above assumes that protons  $\text{H}^b$  have identical chemical shifts. However, if their chemical shifts happen to be detectably different, then the NMR spectrum will be more complex than the spectrum described above.

- 13.20 (b) This triplet-quartet pattern indicates an ethyl group. Since there appear to be *only* ethyl resonances, the spectrum is that of diethyl ether,  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ .

- 13.22 (b) The unknown is *tert*-butyl alcohol,  $(\text{CH}_3)_3\text{C}-\text{OH}$ .
- 13.25 The resonance for the methyl group at room temperature is a singlet. When the temperature is lowered, the resonance of this methyl group should consist of two singlets, one for the conformation of 1-chloro-1-methylcyclohexane in which the methyl group is axial, and one for the conformation in which the methyl group is equatorial. The relative integrals of the two singlets will be proportional to the relative amounts of the two conformations. Since chlorine and methyl are about the same size, there should be about equal amounts of the two conformations.
- 13.27 (b) This structure contains four chemically nonequivalent sets of carbons and therefore would have a CMR spectrum consisting of four lines, not the three observed.
- 13.28 (b) Among the reasons that 2-chloro-1-butene does not fit the data are that it offers no explanation for the  $\delta$  4.5 absorption, and it has only two vinylic protons, whereas the observed NMR spectrum indicates three.
- 13.29 (b) The CMR of a compound with this structure should consist of four resonances, not the three observed, and there would be no CMR resonance that indicates two attached protons.

### Solutions to Additional Problems

- 13.31 (b) Only 1-hexene will have a complex vinylic proton absorption that integrates for 25% of the total absorption (that is, 3 protons); the vinylic proton absorption of *trans*-3-hexene will consist of a triplet integrating for 17% of the total absorption (that is, 2 protons).
- (d) Each spectrum will consist of a singlet; however, the singlet in 1,1,2,2-tetrabromoethane will occur at lower field.
- (f) The spectrum of *tert*-butyl methyl ether consists of two singlets; that of isopropyl methyl ether contains a singlet for the methoxy group, but a more complex doublet-septet pattern for the isopropyl group.
- 13.33 (b)  $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$  (d)  $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{C}(\text{CH}_3)_3$   
 2,3-dimethyl-2-butene 2,2,4,4-tetramethylpentane
- 13.34 (b)   
 cyclopentane (d)  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{CH}_2\text{C}(\text{CH}_3)_3$   
 2,4,4-trimethyl-1-pentene
- (f) Three compounds with the formula  $\text{C}_2\text{H}_2\text{Br}_2\text{Cl}_2$  would give NMR spectra all of which consist of one singlet:



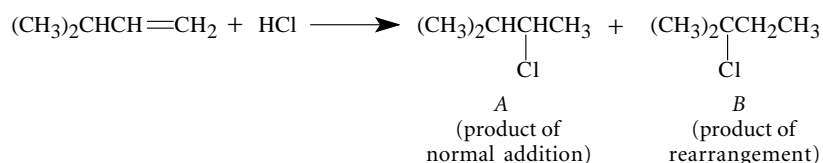
Compound A can be ruled out on the basis of the chemical shift. The chemical-shift prediction for this compound is  $\delta$   $(0.2 + 2.3$  [for Br]  $+ 2.5$  [for Cl]  $+ 0.7$  [methine correction]  $+ 1.0$  [two  $\beta$ -halogens]) =  $\delta$  6.7. This is not consistent with the observed chemical shift of  $\delta$  4.40. The chemical-shift estimate for compound B is  $\delta$   $(0.2 + 2.3 + 0.6 + 1.5$  [three  $\beta$ -halogens]) =  $\delta$  4.6. The estimate for compound C is  $\delta$   $(0.2 + 2.5 + 0.6 + 1.5)$  =  $\delta$  4.8. These estimates are too close to distinguish reliably between compounds

*B* and *C*. Consequently, either must be considered a correct answer. (It turns out that compound *B* has a chemical shift of  $\delta$  4.40.)

(h) The structure contains two equivalent protons split by three fluorines. The compound is 1,1,1-trifluoro-2-iodoethane,  $\text{I}-\text{CH}_2-\text{CF}_3$ .

(j) The compound is dichloromethyl methyl ether (dichloro(methoxy)methane,  $\text{CH}_3\text{OCHCl}_2$ ).

**13.37** First write the reaction in question.



The most characteristic difference between the spectra of these two compounds will be in the resonance at lowest field. Because compound *A* has a proton  $\alpha$  to the chlorine, it will have the resonance at lowest field, near  $\delta$  4.0; the splitting of this resonance could be either a quintet or an eight-line quartet of doublets, depending on whether the coupling constants with the neighboring protons are equal or not. The highest-field resonance in the spectrum of compound *B* should be a two-proton triplet near  $\delta$  1.9 characteristic of the  $-\text{CH}_2-$  group.

**13.39** From the triplet-quartet pattern in the integral ratio 3:2, and from the chemical shift of the  $-\text{CH}_2-$  quartet, the compound contains at least one ethoxy group. Hence, compounds (1) and (3) can be ruled out. Because there are no other absorptions indicating other types of ethyl groups, compound (2), which contains two ethyl groups, can be ruled out. In compound (4), the two CH protons are equivalent and hence, their resonances should be unsplit. Thus, compound (4) is also ruled out. Compound (5) is the correct one; the CH groups are chemically nonequivalent and split each other into doublets, and the ethoxy groups are chemically equivalent.

**13.41** (b) All methyl groups are homotopic; all methine carbons are homotopic; and all methylene carbons are homotopic. Each carbon of one type is constitutionally nonequivalent to all carbons of other types. Consequently, the CMR spectrum of this compound should consist of three resonances.

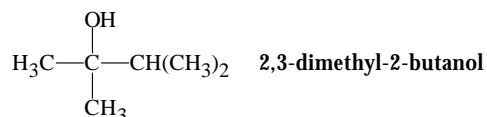
**13.42** (b) The NMR spectrum of the first compound should consist of the doublet-septet pattern characteristic of isopropyl groups; the NMR spectrum of the second compound should consist of a singlet at essentially the same chemical shift as the doublet in the first compound. (The splitting between H and D nuclei on adjacent carbons is nearly zero.)

(d) Because the two compounds are enantiomers, they have identical NMR spectra.

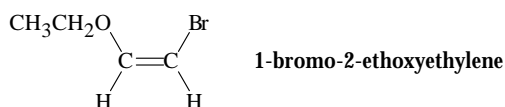
**13.43** (b) The reason the CMR spectrum of  $\text{CDCl}_3$  is a 1:1:1 triplet is the same reason that the proton NMR spectrum of  $^+\text{NH}_4$  is a 1:1:1 triplet [see part (a)]: deuterium, like nitrogen, can have spins of +1, 0, and -1, and splits  $^{13}\text{C}$  resonances just as it splits proton signals.

(d) The sample of  $\text{CH}_2\text{D}-\text{I}$  should be a triplet, the three lines of which are in the intensity ratio 1:1:1; the sample of  $\text{CHD}_2-\text{I}$  should be a quintet, the five lines of which are in the intensity ratio 1:2:3:2:1. Mass spectrometry could easily distinguish the two species on the basis of their differing masses.

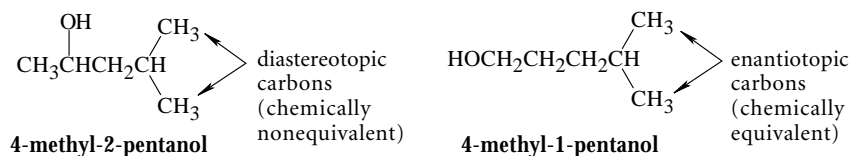
**13.45** The compound is an alcohol (exchangeable resonance at  $\delta$  1.25) with no rings or double bonds. The absence of an  $\alpha$ -proton resonance in the  $\delta$  3.5 region of the spectrum indicates that this is a tertiary alcohol. The alcohol has two unsplit methyl groups, one methyl group split into a doublet, and a complex methine absorption. The alcohol 2,3-dimethyl-2-butanol is consistent with these data.



- 13.47** The double molecular ion in the mass spectrum suggests the presence of one bromine. The NMR spectrum accounts for seven protons. After subtracting the hydrogens and the bromine from the molecular ion, 64 mass units remain to be accounted for. The typical ethyl pattern in the NMR, with the  $-\text{CH}_2-$  chemical shift of  $\delta$  3.91, suggests an ethyl ether,  $\text{CH}_3\text{CH}_2\text{O}-$ . If the compound contains an oxygen, then the 64 mass units can be accounted for by four carbons and the oxygen; the formula  $\text{C}_4\text{H}_7\text{OBr}$  fits the data. The IR spectrum shows strong  $\text{C}=\text{C}$  absorption at  $1644\text{ cm}^{-1}$ , but shows no *trans*-alkene,  $-\text{CH}=\text{CH}_2$ , or  $=\text{CH}_2$  absorptions; hence, a *cis*-alkene is reasonable. The NMR absorptions at  $\delta$  5.0 and  $\delta$  6.9 could be due to two vinylic hydrogens; their small coupling constant of 4 Hz suggests a *cis*-alkene. The compound is therefore 1-bromo-2-ethoxyethylene.



- 13.50** The two methyl groups at carbon-4 of 4-methyl-2-pentanol are diastereotopic and are therefore chemically nonequivalent. All other carbons are constitutionally (and chemically) nonequivalent. Thus, each of the six carbons should have a unique resonance in the CMR spectrum. In 4-methyl-1-pentanol, however, the two methyl groups at carbon-4 are *enantiotopic*, and therefore chemically equivalent. Consequently, this alcohol has only five chemically nonequivalent sets of carbons, and therefore five resonances in its CMR spectrum.



- 13.52** (b) Following a  $\text{D}_2\text{O}$  shake, the resonance of proton 1 should disappear; and the resonance of protons 2 should be the same as it is in the wet sample, that is, a triplet.
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