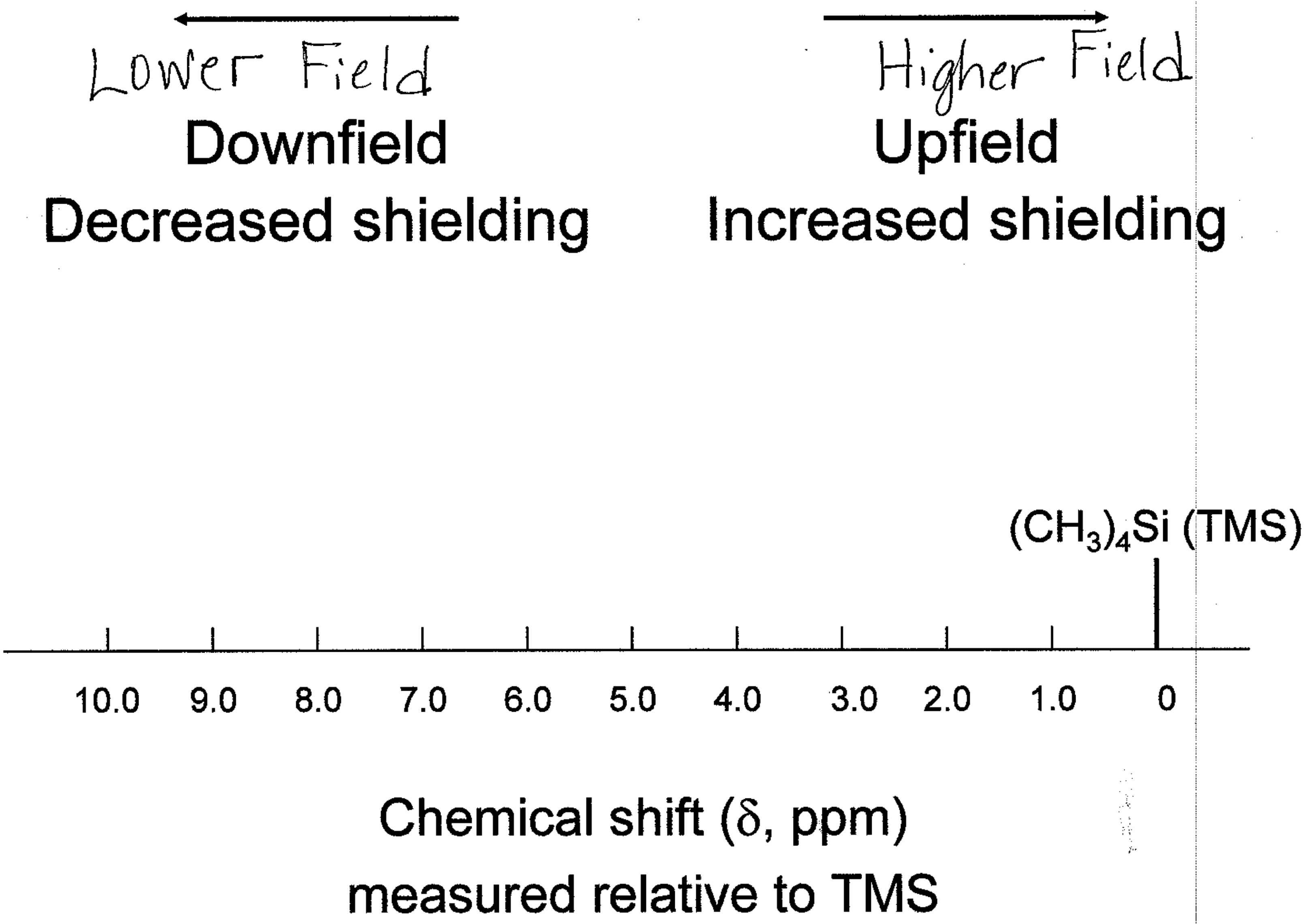

Lower Field
Downfield
Decreased shielding
Higher Field
Upfield
Increased shielding
(CH3)4Si (TMS)
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
Chemical shift (δ, ppm)
measured relative to TMS

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.

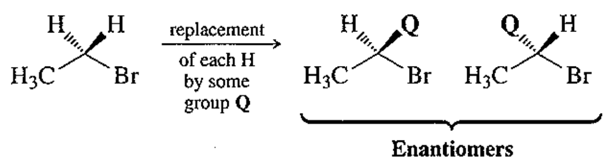
Review Problem 9.3 Carry out a similar analysis for 1,4-dimethylbenzene (Section 9.2C) and show that it has two sets of chemical shift equivalent protons, explaining why its spectrum (Fig. 9.3) has only two signals.

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

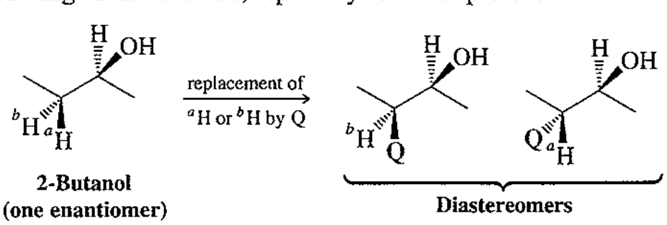
If replacement of each of two hydrogen atoms by the same group yields compounds that are enantiomers, the two hydrogen atoms are said to be **enantiotopic.** ***Enantiotopic hydrogen atoms have the same chemical shift and give only one ^{1}H NMR signal:****



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.***

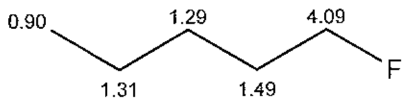
The two methylene hydrogens labeled ^{a}H and ^{b}H at C3 in 2-butanol are **diastereotopic.** We can illustrate this by imagining replacement of ^{a}H or ^{b}H with some imaginary group **Q**. The result is a pair of diastereomers. As diastereomers, they have different physical properties, including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



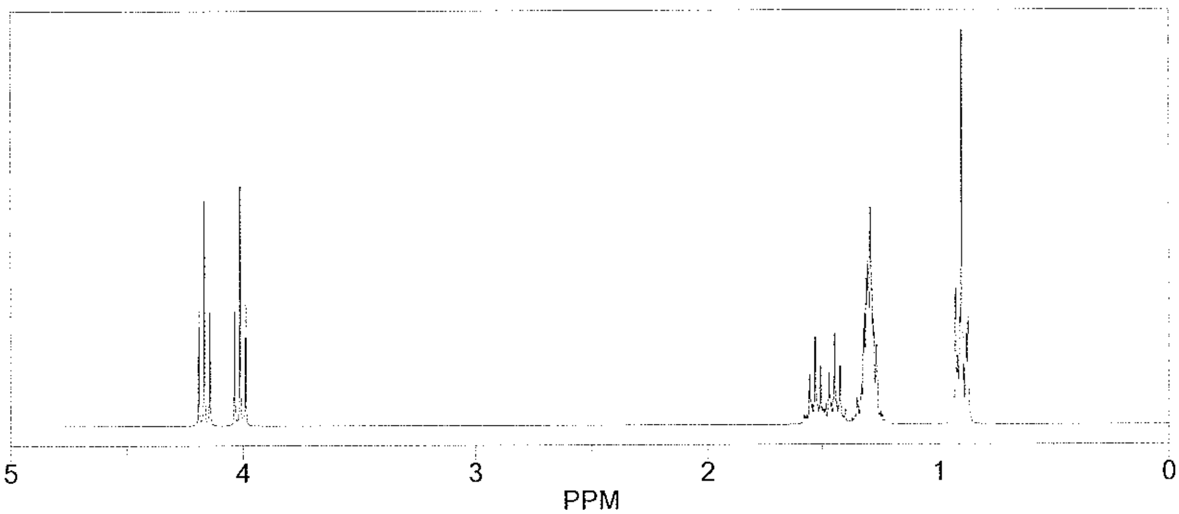
The diastereotopic nature of ^{a}H and ^{b}H at C3 in 2-butanol can also be appreciated by viewing Newman projections. In the conformations shown below (Fig. 9.16), as is the case for every possible conformation of 2-butanol, ^{a}H and ^{b}H experience different environments

*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.

ChemNMR ^{1}H Estimation



Estimation quality is indicated by color: good, medium, rough



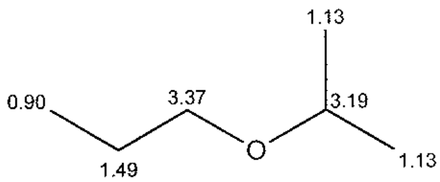
Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH2	4.09	1.37	methylene
		2.76	1 alpha -F
		-0.04	1 beta -C
CH2	1.49	1.37	methylene
		0.16	1 beta -F
		-0.04	1 beta -C
CH2	1.29	1.37	methylene
		-0.04	1 beta -C
		-0.04	1 beta -C
		0.00	general corrections
CH2	1.31	1.37	methylene
		0.00	1 alpha -C
		-0.04	1 beta -C
		-0.02	general corrections
CH3	0.90	0.86	methyl
		0.10	1 beta -C-R
		-0.06	general corrections

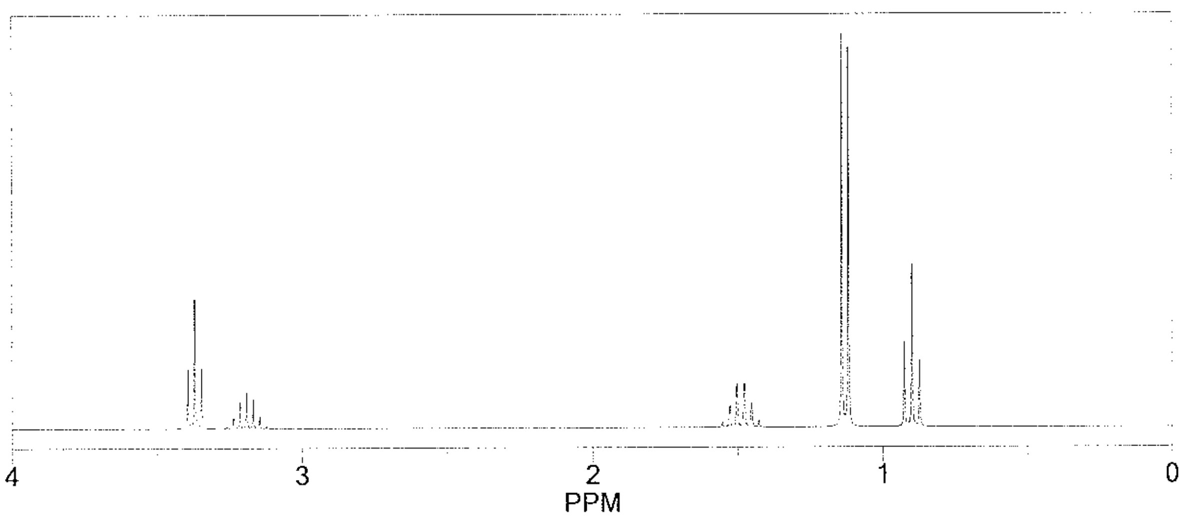
1H NMR Coupling Constant Prediction

shift	atom index	coupling partner, constant and vector		
4.09	5			
		6	46.4	H-CH-F
		4	7.1	H-CH-CH-H
1.49	4			
		6	25.2	H-CH-CH2-F
		5	7.1	H-CH-CH-H
		3	7.1	H-CH-CH-H
1.29	3			
		4	7.1	H-CH-CH-H

ChemNMR ^{1}H Estimation



Estimation quality is indicated by color: good, medium, rough



Protocol of the H-1 NMR Prediction:

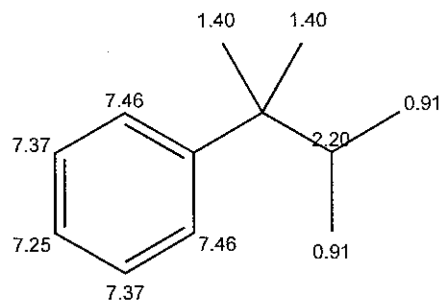
Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	3.19	1.50	methine
		0.34	2 alpha -C
		1.35	1 alpha -O-C
CH2	3.37	1.37	methylene
		2.04	1 alpha -O-C
		-0.04	1 beta -C
CH2	1.49	1.37	methylene
		0.00	1 alpha -C
		0.13	1 beta -O-C
		-0.01	general corrections
CH3	1.13	0.86	methyl
		0.25	1 beta -O-C
		0.05	1 beta -C
		-0.03	general corrections
CH3	1.13	0.86	methyl
		0.25	1 beta -O-C
		0.05	1 beta -C
		-0.03	general corrections
CH3	0.90	0.86	methyl
		0.10	1 beta -C-R
		-0.06	general corrections

1H NMR Coupling Constant Prediction

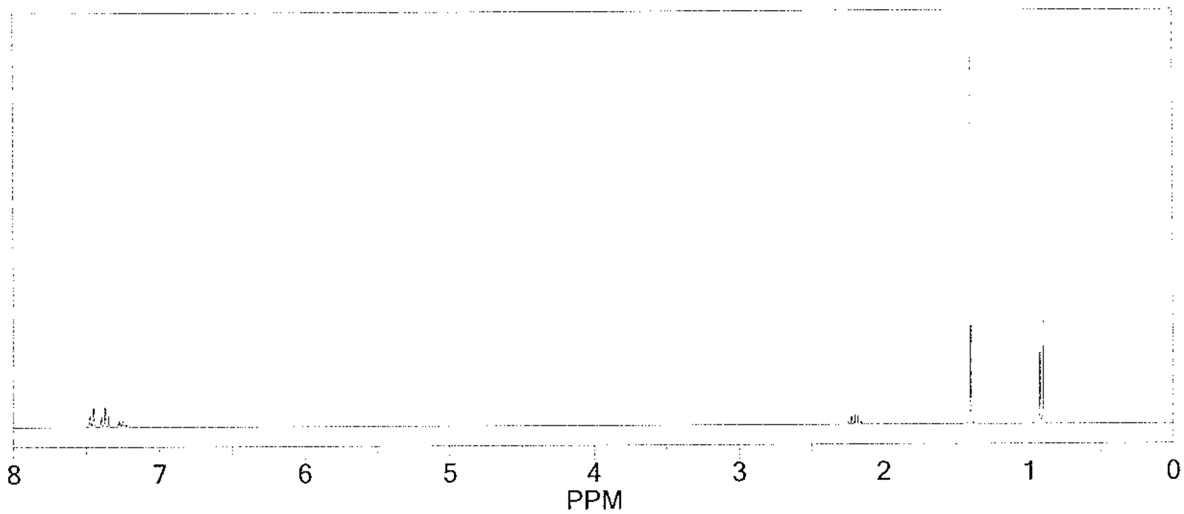
shift atom index coupling partner, constant and vector

3.19 5

ChemNMR ^{1}H Estimation



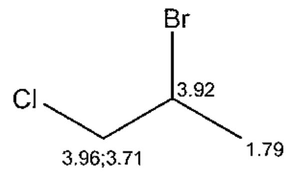
Estimation quality is indicated by color: good, medium, rough



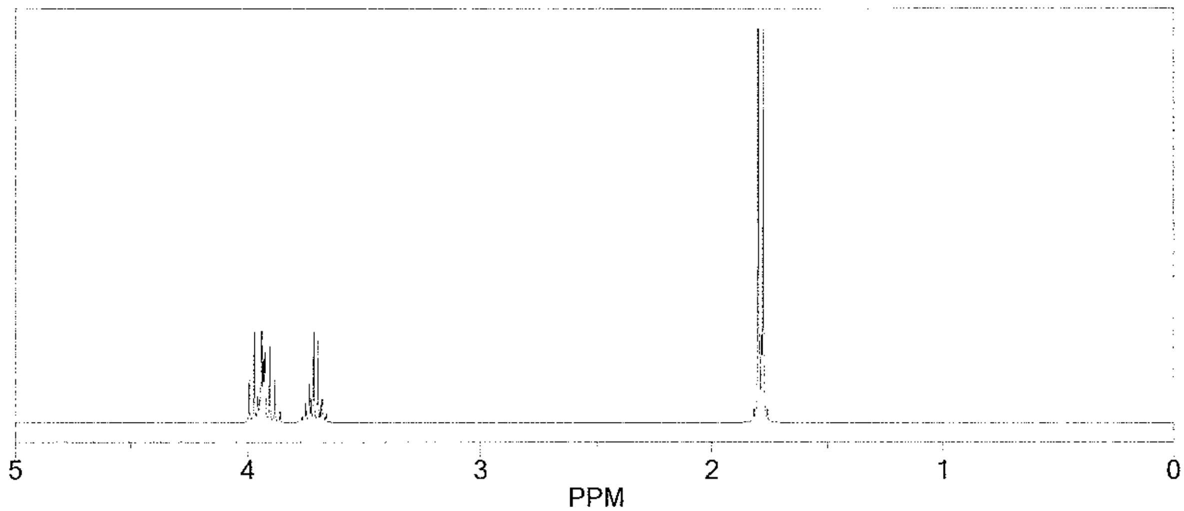
Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH 7.46		7.26	1-benzene
		0.03	1 -C(C)(C)C
		0.17	general corrections
CH 7.46		7.26	1-benzene
		0.03	1 -C(C)(C)C
		0.17	general corrections
CH 7.37		7.26	1-benzene
		-0.08	1 -C(C)(C)C
		0.19	general corrections
CH 7.37		7.26	1-benzene
		-0.08	1 -C(C)(C)C
		0.19	general corrections
CH 7.25		7.26	1-benzene
		-0.20	1 -C(C)(C)C
		0.19	general corrections
CH 2.20		1.50	methine
		0.34	2 alpha -C
		0.38	1 beta -1:C*C*C*C*C*C*1
		-0.02	2 beta -C
CH3 1.40		0.86	methyl
		0.38	1 beta -1:C*C*C*C*C*C*1
		0.10	1 beta -C-R
		0.05	1 beta -C

ChemNMR ^{1}H Estimation



Estimation quality is indicated by color: good, medium, rough



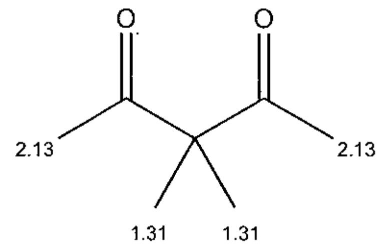
Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	3.92	1.50	methine
		0.17	1 alpha -C
		1.94	1 alpha -Br
		0.31	1 beta -Cl
CH2	3.96,3.715000	1.37	methylene
		2.05	1 alpha -Cl
		0.46	1 beta -Br
		-0.04	1 beta -C
CH3	1.79	0.86	methyl
		0.83	1 beta -Br
		0.10	1 beta -C-R

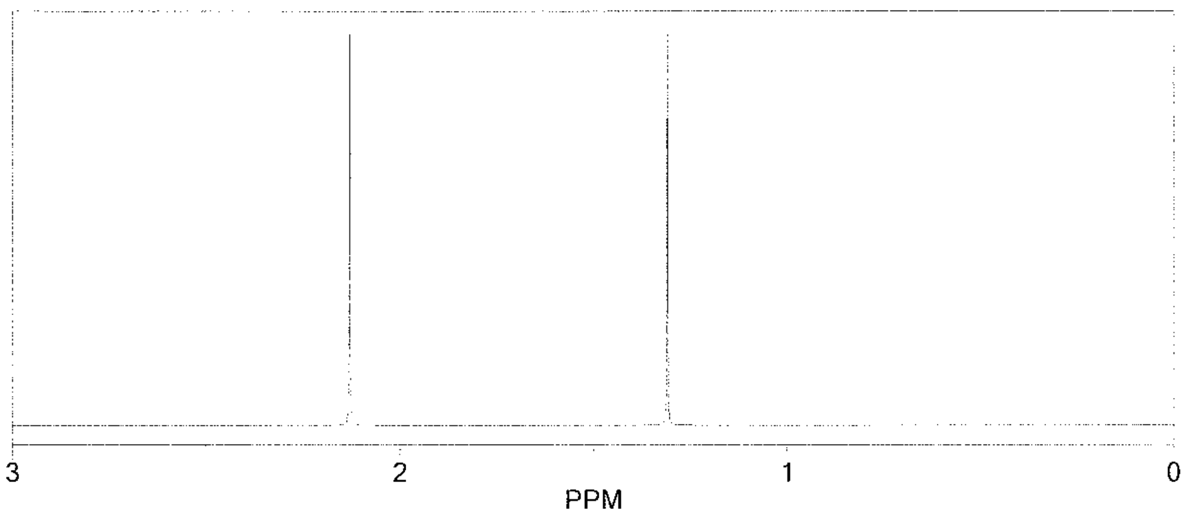
1H NMR Coupling Constant Prediction

shift	atom index	coupling partner, constant and vector
3.92	3	
		2 7.0 H-C-CH-H
		4 6.8 H-C-CH2-H
3.84	2	diastereotopic -12.4 H-C-H
		3 7.0 H-CH-C-H
1.79	4	
		3 6.8 H-CH2-C-H

ChemNMR ^{1}H Estimation



Estimation quality is indicated by color: good, medium, rough



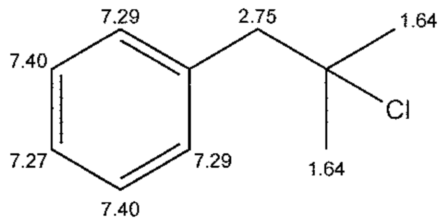
Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH3	2.13	0.86	methyl
		1.23	1 alpha -C(=O)C
		0.04	general corrections
CH3	2.13	0.86	methyl
		1.23	1 alpha -C(=O)C
		0.04	general corrections
CH3	1.31	0.86	methyl
		0.40	2 beta -C(=O)C
		0.05	1 beta -C
		0.00	general corrections
CH3	1.31	0.86	methyl
		0.40	2 beta -C(=O)C
		0.05	1 beta -C
		0.00	general corrections

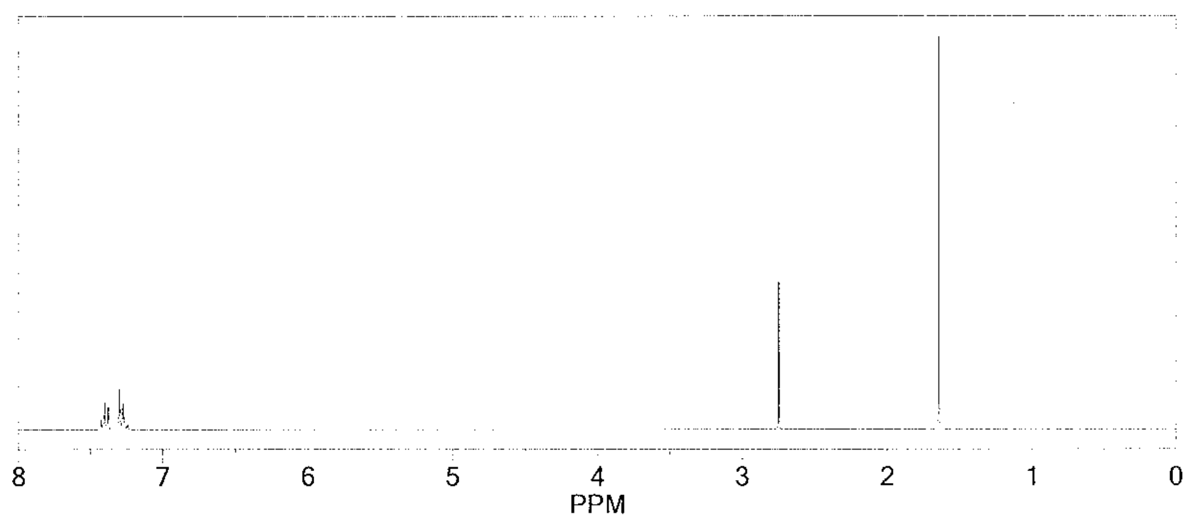
1H NMR Coupling Constant Prediction

shift	atom index	coupling partner, constant and vector
2.13	1	
2.13	5	
1.31	8	
1.31	9	

ChemNMR ^{1}H Estimation



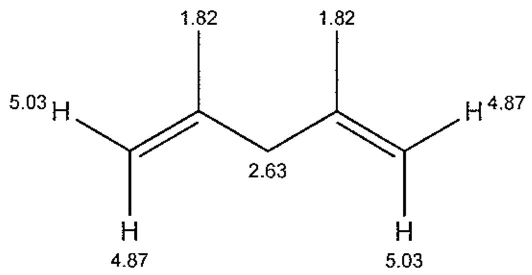
Estimation quality is indicated by color: good, medium, rough



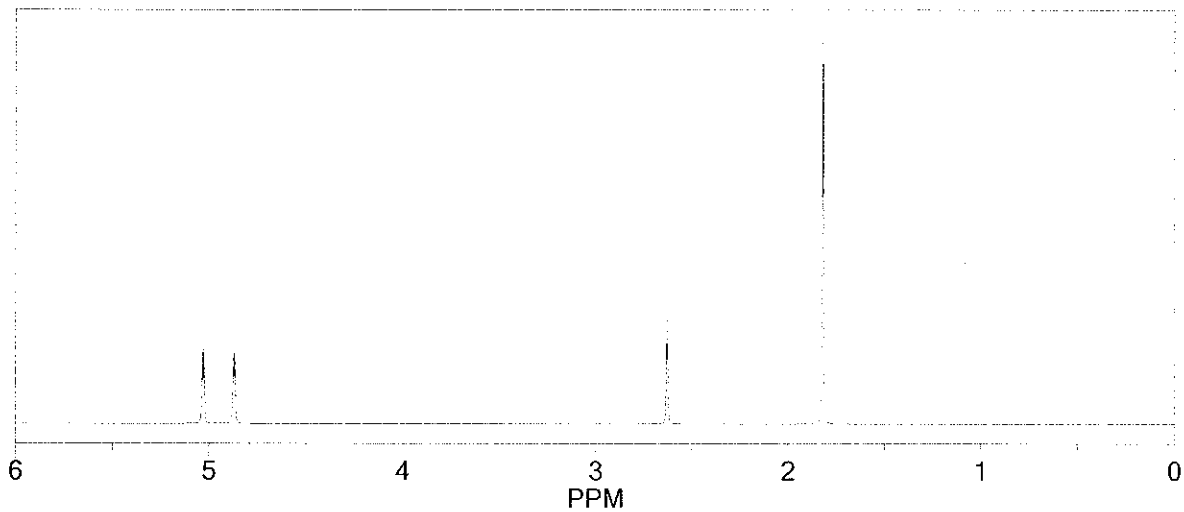
Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	7.29	7.26	1-benzene
		-0.14	1 -CC
		0.17	general corrections
CH	7.29	7.26	1-benzene
		-0.14	1 -CC
		0.17	general corrections
CH	7.40	7.26	1-benzene
		-0.05	1 -CC
		0.19	general corrections
CH	7.40	7.26	1-benzene
		-0.05	1 -CC
		0.19	general corrections
CH	7.27	7.26	1-benzene
		-0.18	1 -CC
		0.19	general corrections
CH2	2.75	1.37	methylene
		1.22	1 alpha -1:C*C*C*C*C*C*1
		0.24	1 beta -Cl
		-0.08	2 beta -C
CH3	1.64	0.86	methyl
		0.63	1 beta -Cl
		0.10	1 beta -C-R
		0.05	1 beta -C
CH3	1.64	0.86	methyl
		0.63	1 beta -Cl
		0.10	1 beta -C-R

ChemNMR ^{1}H Estimation



Estimation quality is indicated by color: good, medium, rough



Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH2	2.63	1.37	methylene
		1.26	2 alpha -C=C
CH3	1.82	0.86	methyl
		0.85	1 alpha -C=C
		0.11	general corrections
CH3	1.82	0.86	methyl
		0.85	1 alpha -C=C
		0.11	general corrections
H	5.03	5.25	1-ethylene
		-0.30	1 -CC=C cis
		-0.28	1 -C trans
		0.36	general corrections
H	4.87	5.25	1-ethylene
		-0.33	1 -CC=C trans
		-0.22	1 -C cis
		0.17	general corrections
H	5.03	5.25	1-ethylene
		-0.30	1 -CC=C cis
		-0.28	1 -C trans
		0.36	general corrections
H	4.87	5.25	1-ethylene
		-0.33	1 -CC=C trans
		-0.22	1 -C cis
		0.17	general corrections

Key

Name: ____________________ Date: ____________

1. If all the protons of 1-fluoropentane could be discerned, which would you expect to be at the lowest field in the ^1H NMR spectrum of this compound?
   downfield, deshielded

   $CH_3CH_2CH_2CH_2CH_2F$

   ↑ ↑ ↑ ↑ ↑

   V IV III II I

   A) Protons on carbon I
   B) ~~Protons on carbon II~~
   C) Protons on carbon III
   D) Protons on carbon IV
   E) Protons on carbon V

2. Which proton(s) of the compound below would appear as a septet in the ^1H NMR spectrum?

   I → CH_3

   $CH_3CH_2CH_2$-O-CH

   ↑ ↑ ↑ ↑ CH_3

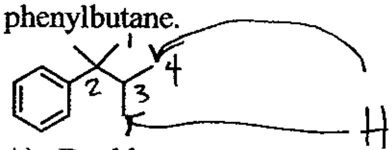
   V IV III II ↑

   I

   A) The protons on carbon I
   B) The proton on carbon II
   C) The protons on carbon III
   D) The protons on carbon IV
   E) The protons on carbon V

   1 type split by 6
   H on carbon II has 6 adjacent Hs on carbons I

3. Predict the splitting pattern you would observe for the proton at C3 of 2,3-dimethyl-2-phenylbutane.

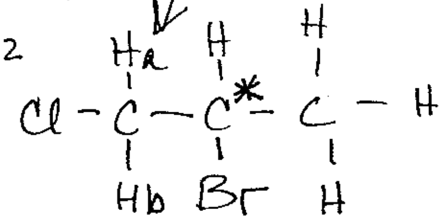


   H on carbon 3 is split by adjacent H's shown with arrows, split by 6

   A) Doublet
   B) Singlet
   C) Quartet
   D) Septet
   E) Octet

distereotopic, different chemical Shifts

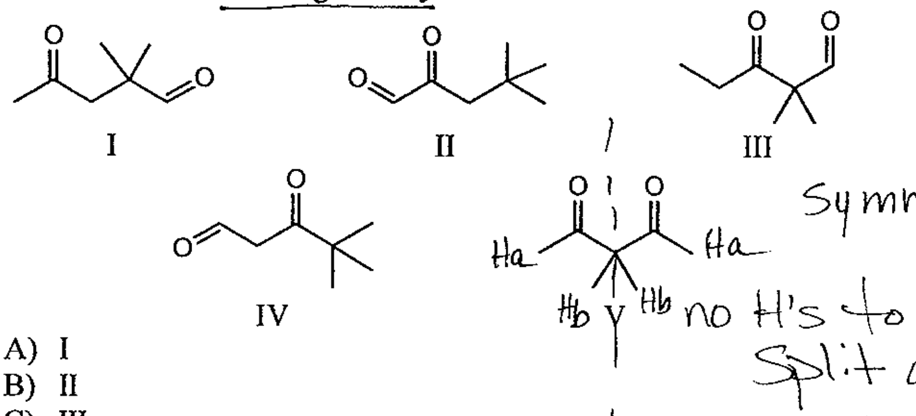
4. How many ^{1}H NMR signals would the following compound give?
$ClCH_2CHCH_3$ ← type 1 (with Br on CH; type 2 → CH, type 3 → CH_2)



A) 1
B) 2
C) 3
D) 4
E) 5

Replacement of either Ha or Hb results in diastereomers. (See handout)

5. The ^{1}H NMR spectrum of which of the compounds below, all of formula $C_7H_{12}O_2$, would consist of two singlets only?

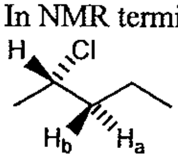


I II III IV

symmetrical
no H's to split on adjacent carbons

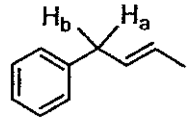
A) I
B) II
C) III
D) IV
E) V

6. In NMR terminology, protons H_a and H_b are said to be:



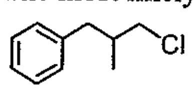
A) Identical
B) Enantiotopic
C) Diastereotopic and therefore have different chemical shifts
D) Homotopic
E) Mesotopic

7. In the structure shown, H_b and H_c are classified as:

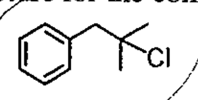


A) homotopic protons.
B) vicinal protons.
C) enantiotopic protons. — same chemical shift
D) diastereotopic protons.
E) isomeric protons.

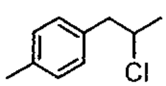
8. A compound with the molecular formula $C_{10}H_{13}Cl$ gave the following ^1H NMR spectrum:
singlet, δ 1.6
singlet, δ 3.1
multiplet, δ 7.2 (5H)
The most likely structure for the compound is:



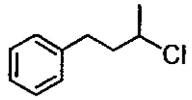
I



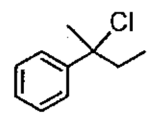
II



III

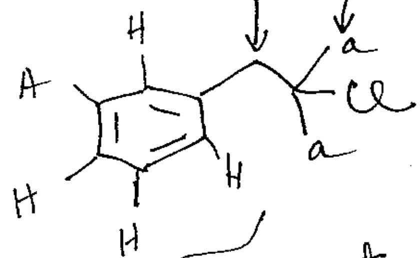


IV



V

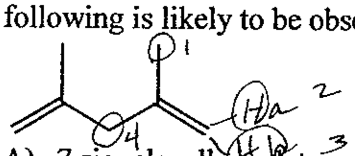
b also a singlet, no adj. H's
a's are a singlet no adjacent H's



multiplet 5 H

A) I
B) II
C) III
D) IV
E) V

9. Consider the expected ^1H NMR spectrum of 2,4-dimethyl-1,4-pentadiene. Which of the following is likely to be observed?



A) 7 signals: all singlets
B) 4 signals: all singlets
C) 3 signals: all singlets
D) 3 signals: one singlet, 2 doublets
E) 4 signals: two singlets, two doublets