

¹H NMR Problem-Solving Strategies

The goal of solving a ¹H NMR spectrum is to determine the structure that is consistent with ALL the NMR data. Since the NMR provides a lot of data, we must develop a systematic approach. First, we must determine what pieces are present. Next, we figure out how those pieces fit together. Finally, we check our structure to see if it matches the spectral data given.

1) If given an IR spectrum: what functional groups (FG) are present? These are pieces to your puzzle.

2) If given molecular formula: check for sites/degrees of unsaturation (DU).

If saturated, formula fits $C_nH_{2n+2+\#N}$.

every 2 missing H's = 1 DU

each DU = a π bond or a ring

4 DU = a possible benzene ring (3 π bonds, plus 1 ring)

3) Using the peak integration, determine the pieces of your molecule.

3 H signal = CH₃

2 H signal = CH₂

1 H signal = CH or OH or NH

4 H signal = 2 CH₂'s or a CH₃ + CH (overlapping signals?)

peaks around 7 ppm = aromatic H's (indicates presence of a benzene ring)

may be a single peak (singlet) or may be several signals in the region

a total of 5 H's around 7 ppm = monosubstituted benzene ring

a total of 4 H's around 7 ppm = disubstituted benzene ring, etc.

4) Do you have all your pieces? "Add up" your pieces and compare to your molecular formula

have you accounted for the calculated DU?

have you accounted for the FG in the IR?

5) Put the pieces together! Start with an end piece, such as a methyl (CH₃).

consider chemical shift

is it next to an oxygen? (~3.5 ppm)

is it next to a C=O or a benzene ring? (~2.2 ppm)

consider splitting patterns

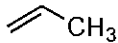
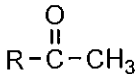
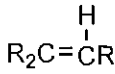
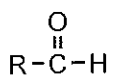
is it a triplet? It must be attached to a CH₂.

6) Check your answer! Final structure must match molecular formula, and IR and NMR spectra.

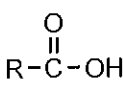
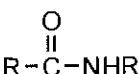
Look for symmetry. How many peaks should be in the NMR? What would integration be?

Calculate chemical shifts, predict splitting patterns, and compare to NMR spectrum.

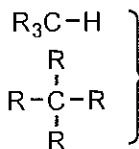

¹H NMR: Protons on Carbon

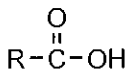
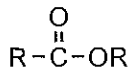
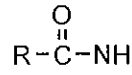
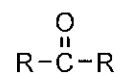
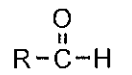
Type of C-H	δ (ppm)	Description
R-CH ₃	0.9	alkyl (methyl)
R-CH ₂ -R	1.3	alkyl (methylene)
R ₃ C-H	1.5-2	alkyl (methine)
	1.8	allylic
	2-2.3	α to carbonyl
Ar-CH ₃	2.3	benzylic
RC≡C-H	2.5	alkynyl
R ₂ N-CH ₃	2-3	α to nitrogen
R-CH ₂ -X	3-3.5	α to halogen
RO-CH ₃	3.8	α to oxygen
R-CH ₂ -F	4.5	α to fluorine
	5-5.3	vinyl
Ar-H	7.3	aromatic
	9.7	aldehyde

¹H NMR: Protons on Oxygen/Nitrogen

Type of H	δ (ppm)	Description
ROH	0.5-5	alcohol
ArOH	4-7	phenol
	10-13	carb. acid
RNH ₂	0.5-5	amine
ArNH ₂	3-5	aniline
	5-9	amide

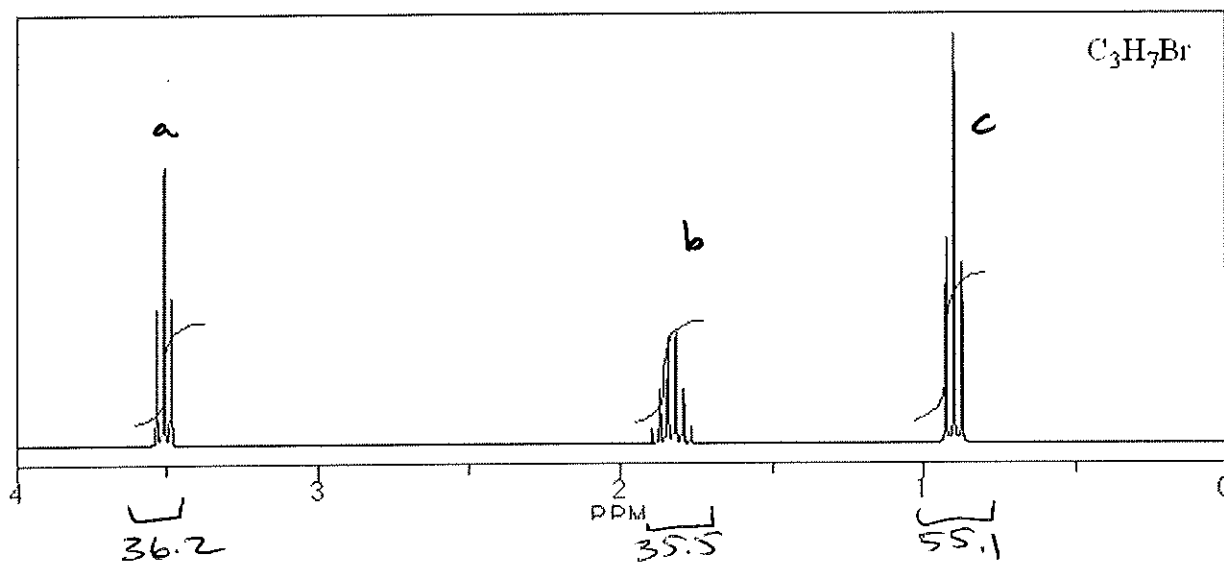
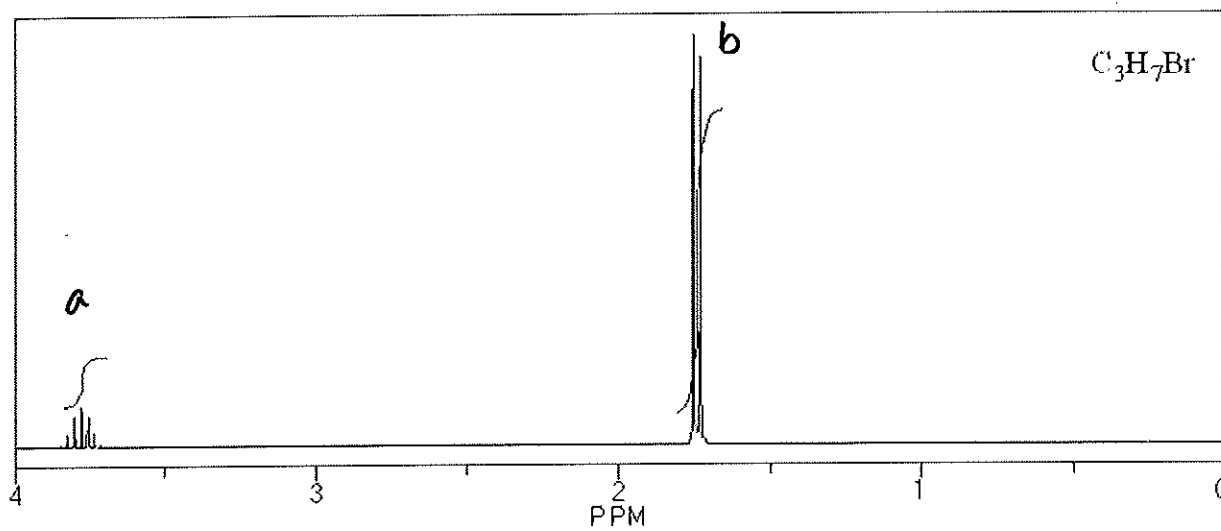
¹³C NMR: Carbons

Type of carbon	δ (ppm)	Description
R-CH ₃	10-30	methyl
R-CH ₂ -R	15-55	methylene
	20-60	methine or quaternary
C-I	0-40	
C-Br	25-65	
C-N	40-60	
C-Cl	35-80	
C-O	40-80	
RC≡CR	65-90	alkynyl
R ₂ C=CR ₂	100-150	alkenyl
	110-170	aromatic

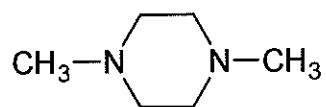
	} 165-185	C=O, carboxylic acid, ester, amide
		
		
	} 185-220	C=O, ketone or aldehyde
		

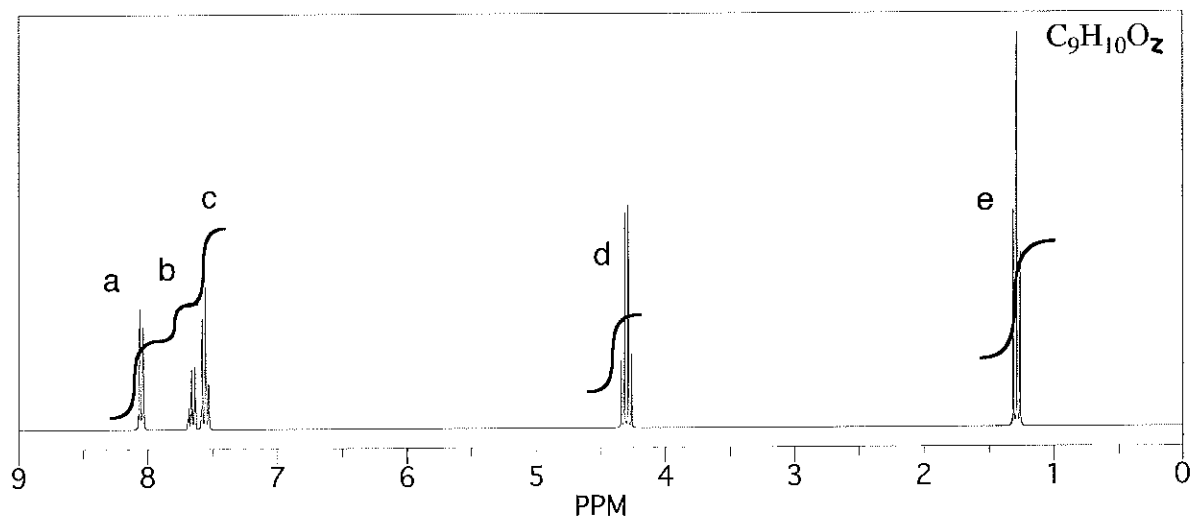
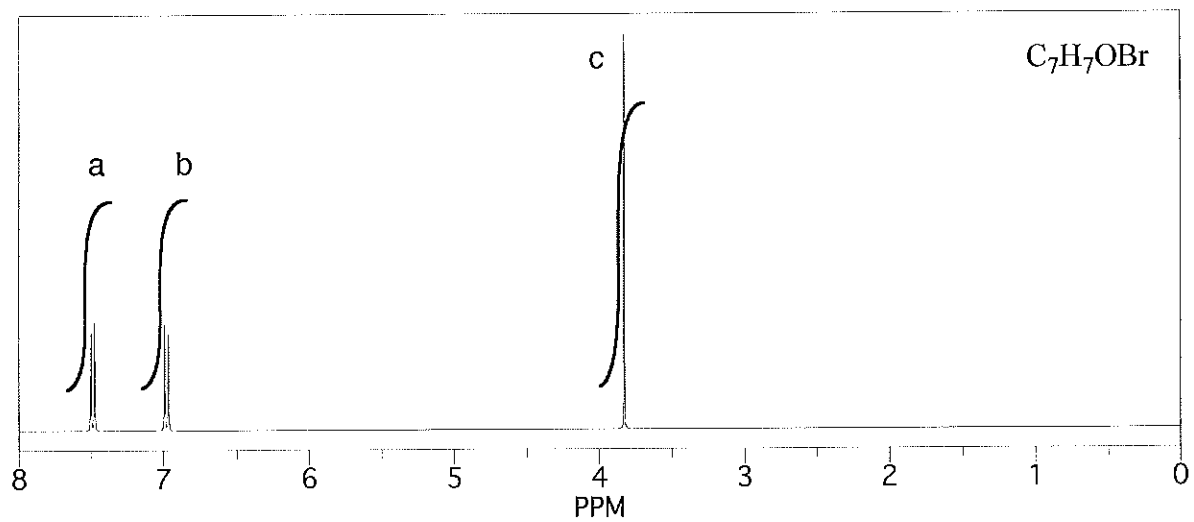
R = alkyl group
 Ar = aromatic ring, such as phenyl (Ph)

California State Polytechnic University, Pomona
Dr. Laurie S. Starkey, Organic Chemistry Laboratory, CHM 3140, Sample NMR



Predict the 1H NMR spectrum for the following compound (sketch it):



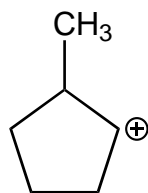


$C_9H_{10}O_2$ 1H NMR δ =
 7.4 ppm, singlet, 5H
 3.6 ppm, singlet, 2H
 3.5 ppm, singlet, 3H

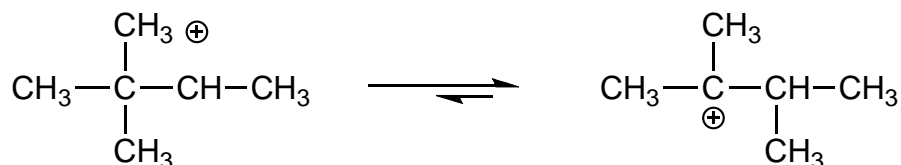
B) Carbocation rearrangements (6.11)

It is possible for neighboring groups to "shift" over to the positively charged carbon, if the relocated positive charge ends up in a more favorable position.

Hydride shift:



Methyl shift:



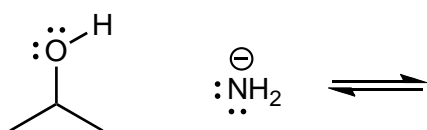
see SkillBuilder 6.6

IV) Mechanisms and arrow-pushing patterns (6.8, 6.9, 6.10)

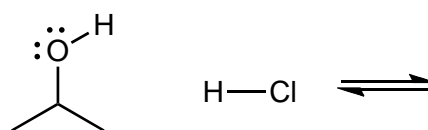
In addition to **carbocation rearrangements**, the following patterns of arrow-pushing will also be encountered in mechanisms found throughout organic chemistry:

Proton Transfer (Ch. 3) Draw curved arrows to show the mechanism and draw the organic product:

Deprotonation of a substrate



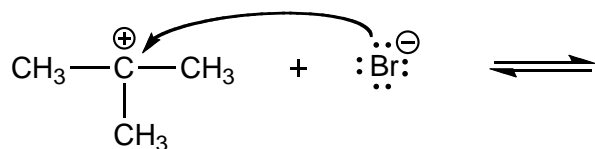
Protonation of a substrate



Loss of a Leaving Group (Ch. 7) Provide the products that result from the following curved arrows:



Nucleophilic Attack (Ch. 7) Provide the product that results from the following curved arrow:



see SkillBuilders 6.3, 6.4, 6.5