

^1H NMR \rightarrow tells us "type" $\frac{1}{3}$ relative #s of protons in molecules

(1) Chemically Equivalent

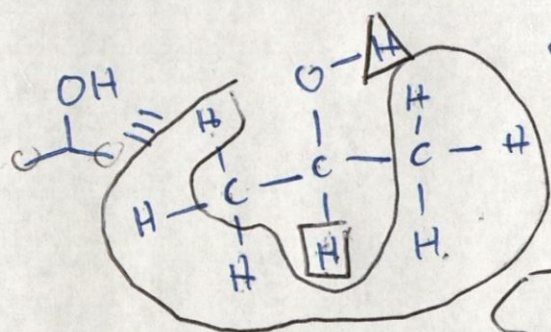
(2) e^- density around given ^1H nuclei \rightarrow Chemical Shift

(4) "Adjacent" ^1H nuclei \rightarrow splitting

Ratio of area under curve

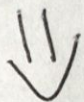
(1) Equivalent Sets of Protons (^1H Atoms)

\rightarrow Similar Chemical environment



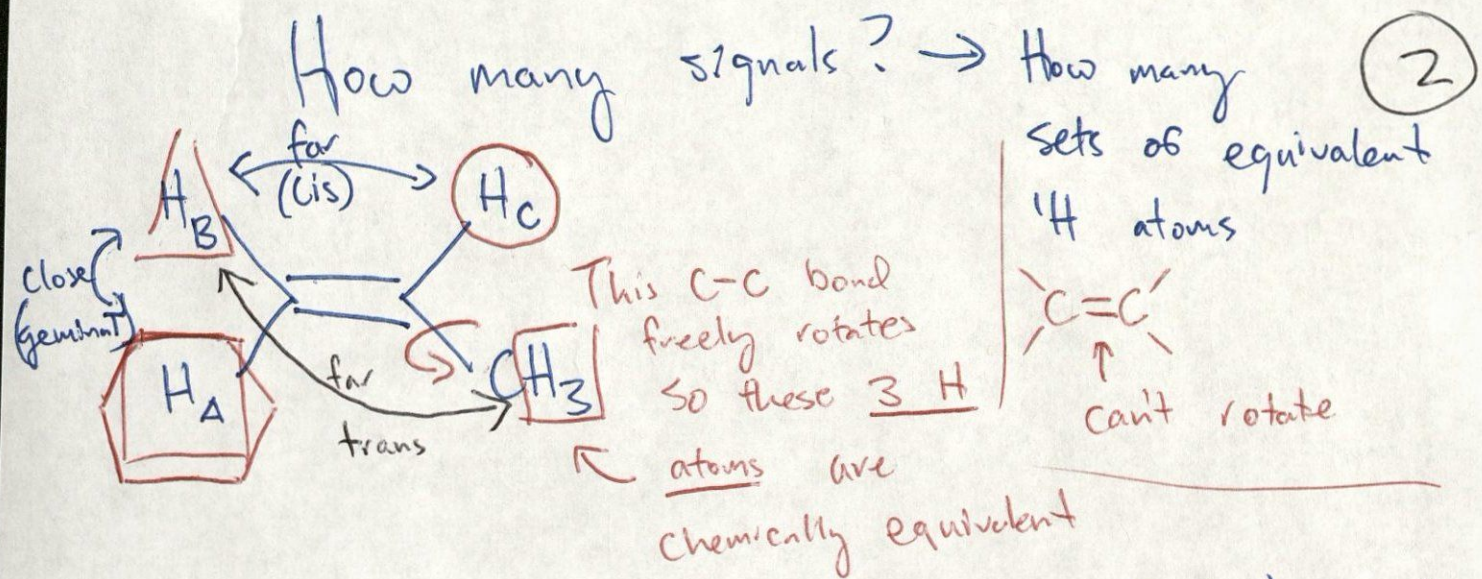
All 11 bonds in this molecule rotate freely \rightarrow Single bonds, no rings

3 sets of protons



3 signals

These 6 atoms are in the same chemical environment \rightarrow bound to the same freely rotating atoms/groups \rightarrow Equivalent \rightarrow all 6 ^1H nuclei show up as one ^1H NMR signal



Consider what H_B feels: H_B is 'geminal' to H_A
 cis to H_C
 trans to $-CH_3$

→ Why →
 4 sets of Protons ⇒ 4 signals

(2) Chemical Shift (ppm) → Changes in e^- density around a proton nucleus due to electronegative atoms nearby that pull e^- density away (desshielding)

Desielding ← → Shielding

10 0
 Chemical Shift (ppm)

3

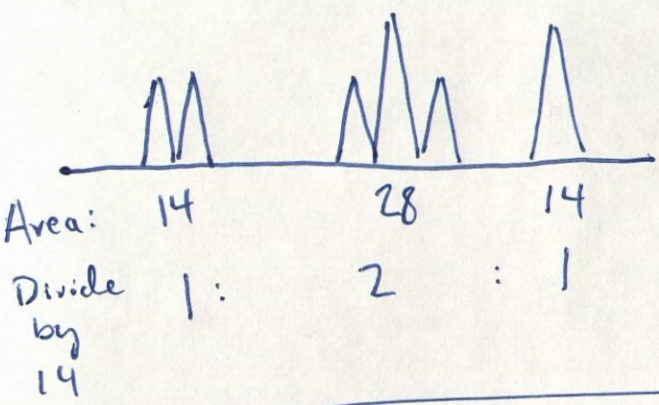
③ Integration $\int dx \rightarrow$ Area under curve



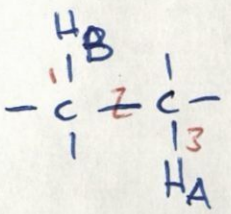
relative amounts of protons



ratio of the # of sets of equivalent protons



④ Splitting \rightarrow Adjacent ^1H nuclei (H_A) change the net magnetic field felt by a given ^1H nucleus (H_B)



3 bonds or fewer away

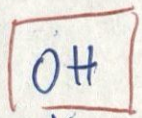
NOTE: Equivalent H atoms don't split other equivalent H atoms!

One signal can have multiple peaks!

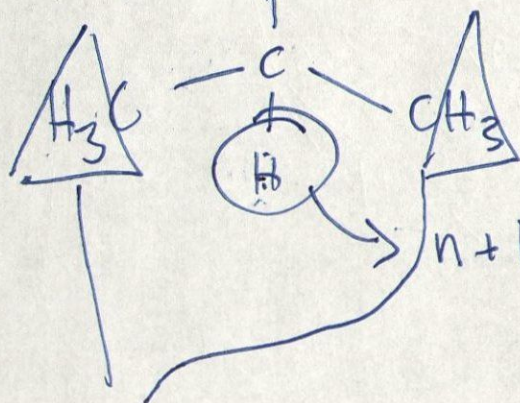
★ For proton nuclei on a freely rotating C atom $\rightarrow n+1$ peaks for n adjacent H_A atoms

★ Non-freely rotating (alkenes, rings) \rightarrow multiplicative splitting $(n+1) \cdot (m+1) \cdot (p+1)$ "n" set of equivalent adjacent nuclei

(4) are not



$\rightarrow -\text{OH}, -\text{NH}_2 \rightarrow$ Broad peaks, ~~don't~~ split and don't split adjacent nuclei.



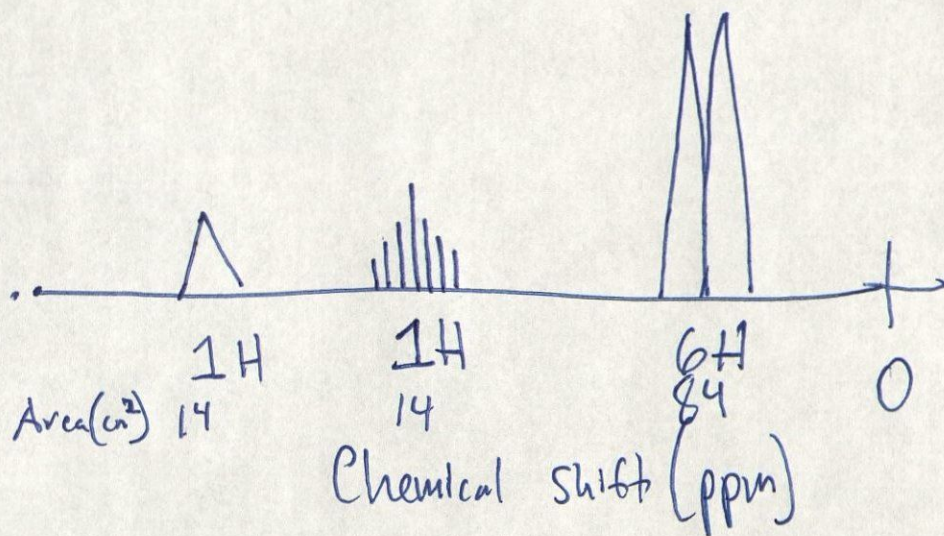
$n+1$ splitting $\Rightarrow 6+1 = 7$ peaks

integrates to

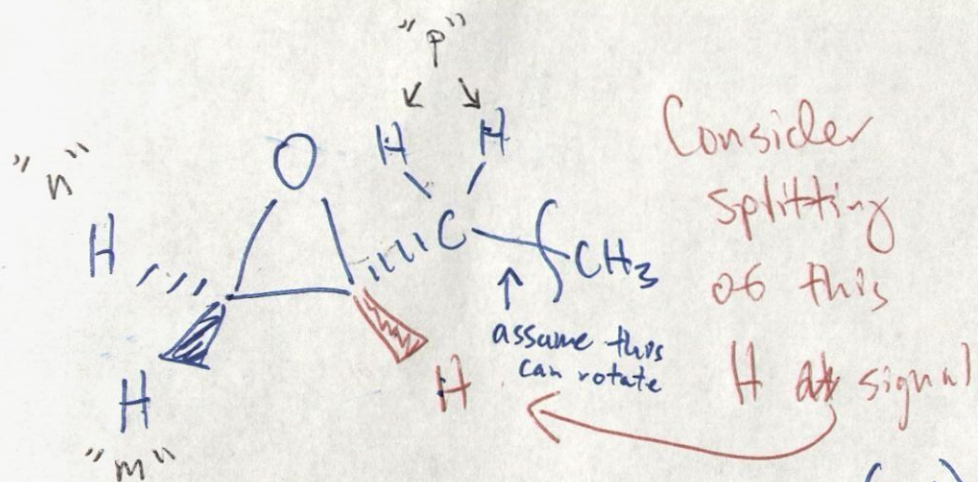
1 H atom

$n+1 \Rightarrow 1+1 = 2$ peaks

integrates to 6 H atoms



(5)



Consider
splitting
of this

H at signal

Splitting

->

H

$$= (n+1)(m+1)(p+1)$$

$$= (2) \cdot (2) \cdot (2+1)$$

$$= 2 \cdot 2 \cdot 3 = 12 \text{ peaks}$$

for that

one H atom's

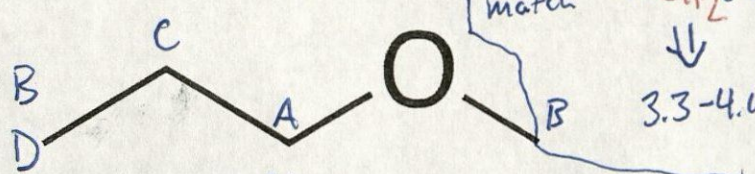
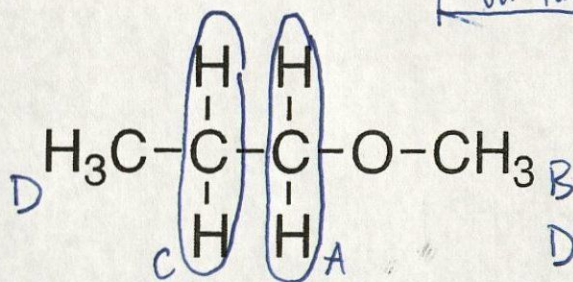
signal

¹H NMR

Finding Chemical Shift on table →

A is -CH₂- bound to one O atom and one C atom

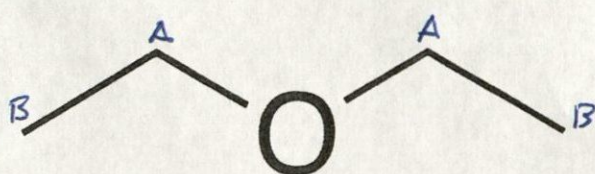
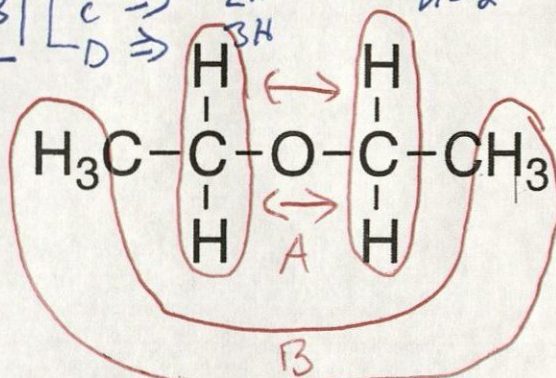
(2)



closest match = RCH₂OR
↓
3.3-4.0

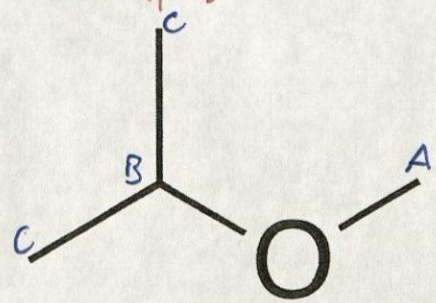
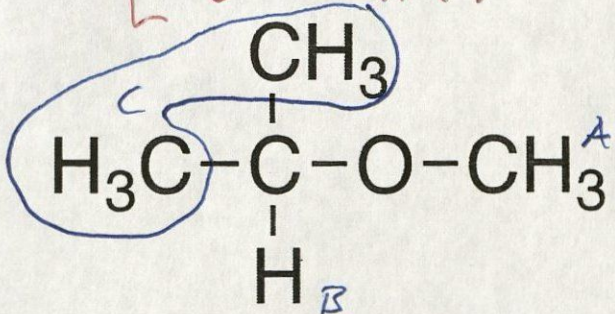
4 sets
 Ratio: 2:3:2:3
 Integrations
 A ⇒ 2H
 B ⇒ 3H
 C ⇒ 2H
 D ⇒ 3H

Splitting
 n=2 2+1=3=Triplet 3.3-4 ppm
 n=0 0+1=1=Singlet 3.3-4 ppm
 n=5 5+1=6=sextet 1.2-1.4 ppm
 n=2 2+1=3=Triplet 0.8-1 ppm



Ratio 2:3

2 Sets
 Set A 4H (2) Simplified Ratio
 Set B 6H (3) Ratio
 Splitting 4 (quartet) 3.3-4
 3 (triplet) 0.8-1



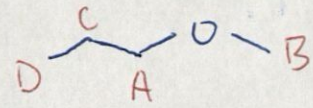
3 Sets
 A 3H
 B 1H
 C 6H

Split
 1 = singlet 3.3-4
 7 = septet/multiplet 3.3-4
 2 = Doublet 0.8-1

Ratio: 3:1:6

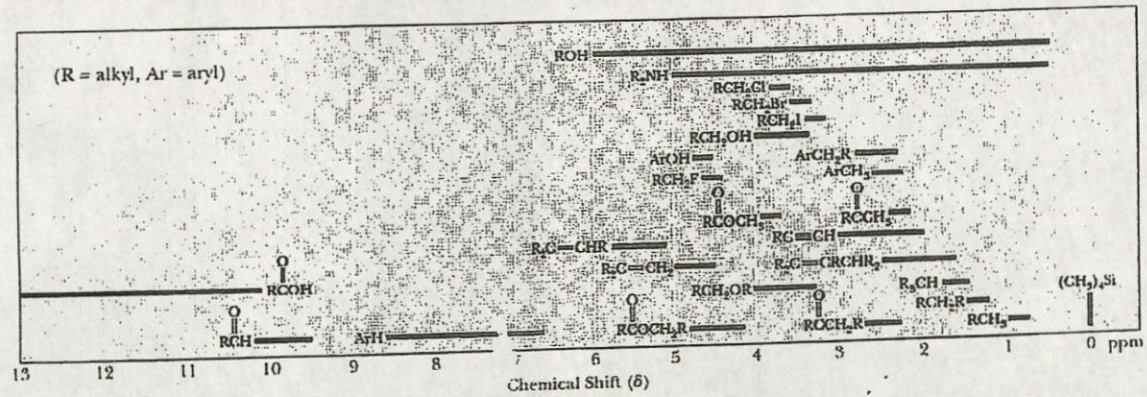
Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
R_2NH	0.5-5.0	RCH_2OH	3.4-4.0
ROH	0.5-6.0	RCH_2Br	3.4-3.6
RCH_3	0.8-1.0	RCH_2Cl	3.6-3.8
RCH_2R	1.2-1.4	$\begin{matrix} O \\ \\ RCOCH_3 \end{matrix}$	3.7-3.9
R_3CH	1.4-1.7	$\begin{matrix} O \\ \\ RCOCH_2R \end{matrix}$	4.1-4.7
$R_2C=CRCHR_2$	1.6-2.6	RCH_2F	4.4-4.5
$RC\equiv CH$	2.0-3.0	$ArOH$	4.5-4.7
$\begin{matrix} O \\ \\ RCOCH_3 \end{matrix}$	2.1-2.3	$R_2C=CH_2$	4.6-5.0
$\begin{matrix} O \\ \\ RCOCH_2R \end{matrix}$	2.2-2.6	$R_2C=CHR$	5.0-5.7
$ArCH_3$	2.2-2.5	$\begin{matrix} O \\ \\ H_2C-CH_2 \end{matrix}$	3.3-4.0
RCH_2NR_2	2.3-2.8	$\begin{matrix} O \\ \\ RCH \end{matrix}$	9.5-10.1
RCH_2I	3.1-3.3	$\begin{matrix} O \\ \\ RCOH \end{matrix}$	10-13
RCH_2OR	3.3-4.0		

For this molecule!



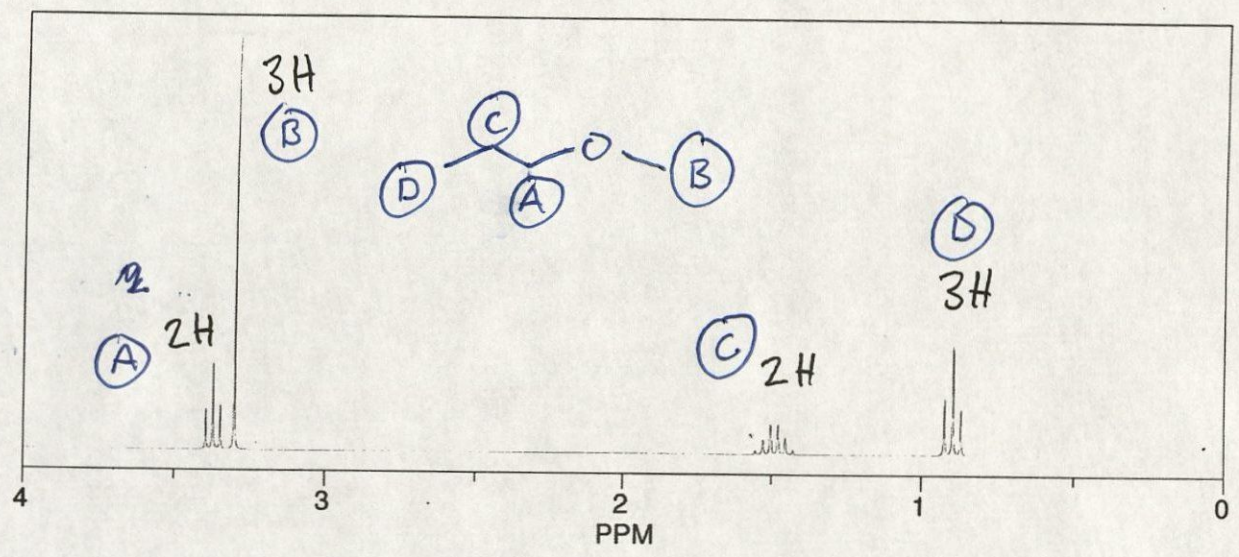
A = RCH_2OR ← Similar shifts!
 B = $ROCH_2R$ ← This R is a "H" atom
 C = RCH_2R
 D = RCH_3

* Values are relative to tetramethylsilane. Other atoms within the molecule may cause the signal to appear outside these ranges.

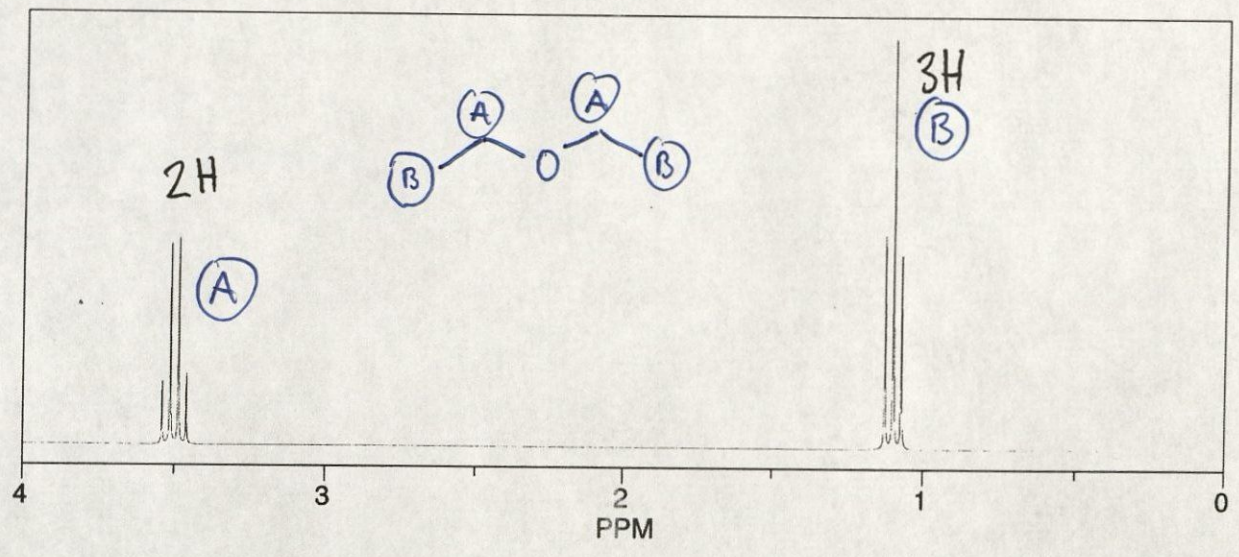


¹H NMR

10 H



5H?
x2
10H
Symmetric



10H

