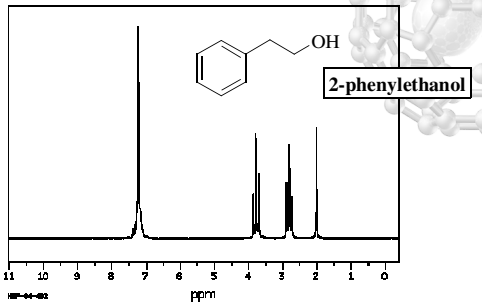
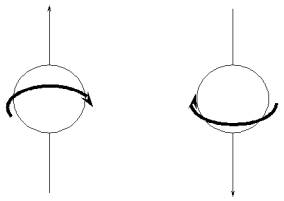
Chapter 13: Spectroscopy – Proton Nuclear Magnetic Resonance (^{1}H NMR)



Nuclear Spin States – Hydrogen Nucleus

Just like electrons, the proton in the nucleus of a hydrogen atom has a *spin number*



+ 1/2 - 1/2

The two states are equivalent in energy in the *absence* of a magnetic or an electric field.

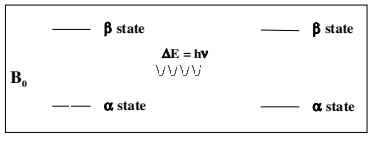
Hydrogen nuclei have two options in the presence of external magnetic field (B_0):

B_0

Proton spins aligned with B_0	Proton spins aligned against B_0
α state	β state
(a lower energy state)	(a higher energy state)

A small energy difference between α and β states: $\Delta E = E_\beta - E_\alpha$

Use matching energy (radio frequency "rf" photon) to promote spin from α to β state (also called: α→ β transition, "spin flip", spin *resonance*)

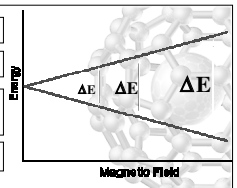


Energy difference (ΔE) depends on

i) type of nucleus (^{1}H, ^{13}C, ^{19}F, *etc.*)

ii) molecular environment around nucleus

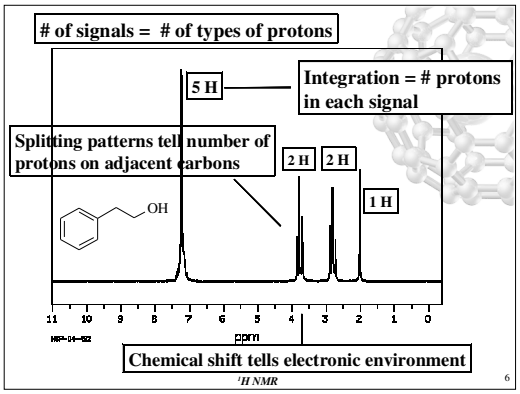
iii) strength of B_0



Different types of hydrogens release different amounts of rf energy depending on their chemical environment, i.e., *chemical structure*. Thus, chemically different types of hydrogens absorb and then release different energies.

TYPES OF INFORMATION FROM ^{1}H NMR SPECTRA

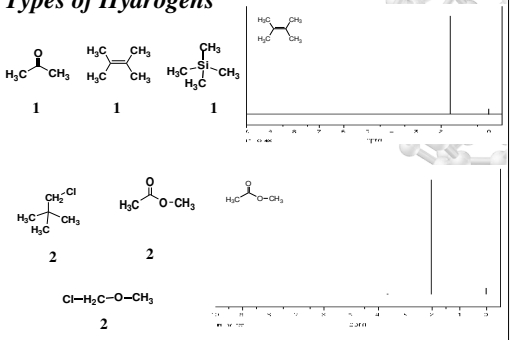
1. **Each different type of hydrogen gives a signal.**
2. **The chemical shift (δ, in ppm) gives a clue as to the type of hydrogen generating the peak (alkane, alkene, benzene, aldehyde, etc.)**
3. **The integral gives the relative numbers of each type of hydrogen.**
4. **Spin-spin splitting gives the number of hydrogens on adjacent carbons.**

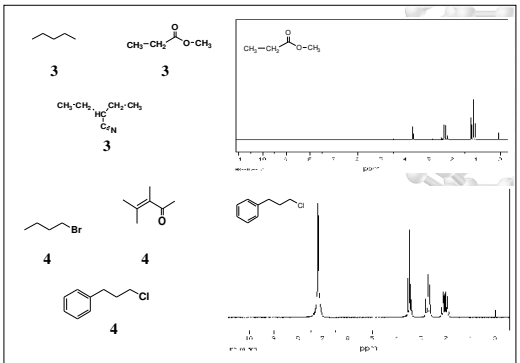


Number of Signals

Number of signals = number of chemically different types of hydrogens in a molecule

Types of Hydrogens





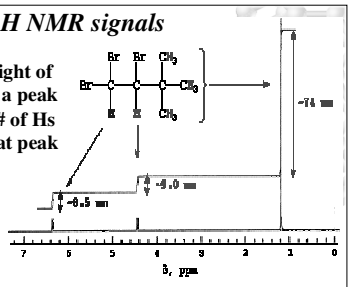
INTEGRATION

Integration = determination of the area under a peak

The area under a peak is proportional to the number of hydrogens that generate the peak.

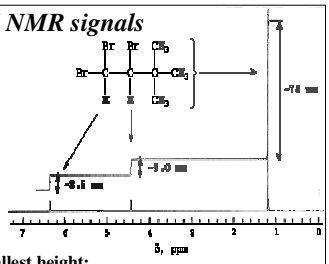
Integration of ^{1}H NMR signals

Generally true: height of integration step of a peak is proportional to # of Hs that give rise to that peak



The peak integration heights are measured:
8.5mm, 9.0mm and 74mm

Integration of ^{1}H NMR signals

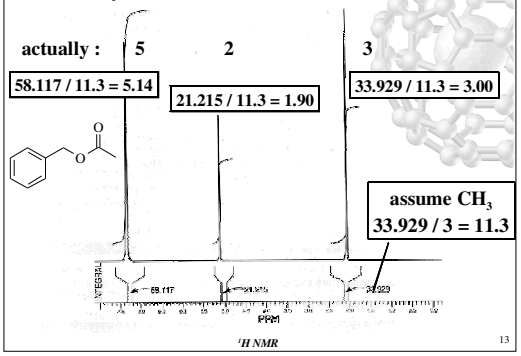


Divide each by the smallest height:

$$\frac{8.5\text{ mm}}{8.5\text{ mm}} \quad \frac{9.0\text{ mm}}{8.5\text{ mm}} \quad \frac{74\text{ mm}}{8.5\text{ mm}} = 1.0 \quad 1.1 \quad 8.7$$

Thus the hydrogen ratios are most likely to be 1 : 1 : 9

Benzyl Acetate (FT-NMR)

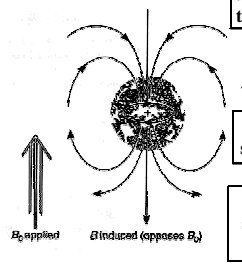


CHEMICAL SHIFT

Chemical shift = the position of each peak in the spectrum

Diamagnetic Anisotropy

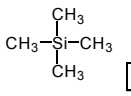
Valence electron density around an atom helps "protect" it from the magnetic field



More electron density = more shielding = B_0 has smaller effect

Less electron density = less shielding (more deshielding) = B_0 has larger effect

THE CHEMICAL SHIFT

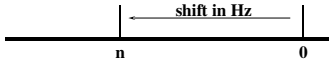


tetramethylsilane TMS

reference compound

the shift observed depends on the frequency of the instrument used

TMS $(CH_3)_4Si$

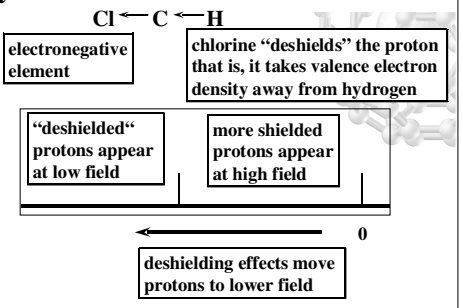


parts per million

chemical shift = δ = $\frac{\text{shift in Hz}}{\text{spectrometer frequency in MHz}}$ = **ppm**

this division gives a number independent of the instrument used

Electronegativity Dependence of Chemical Shift



Electronegativity Dependence of Chemical Shift

Dependence of the Chemical Shift of CH_3X on the Element X

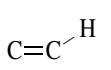
Compound CH_3X	CH_3F	CH_3OH	CH_3Cl	CH_3Br	CH_3I	CH_4	$(CH_3)_4Si$
Element X	F	O	Cl	Br	I	H	Si
Electronegativity of X	4.0	3.5	3.0	2.8	2.6	2.1	1.8
Chemical shift δ	4.26	3.40	3.05	2.68	2.16	0.23	0

Substitution Effects on Chemical Shift

$CHCl_3$	CH_2Cl_2	CH_3Cl	
7.27	5.30	3.05	ppm

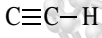
$-CH_2-Br$	$-CH_2-CH_2Br$	$-CH_2-CH_2CH_2Br$	
3.30	1.69	1.25	ppm

Hybridization Effects on Chemical Shift



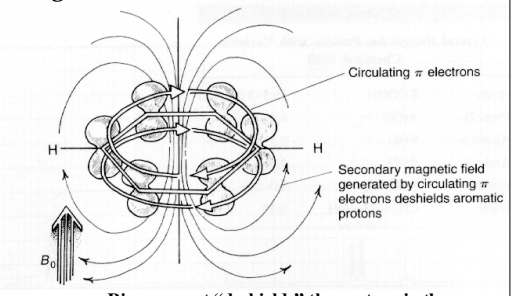
5-6

10



2-3

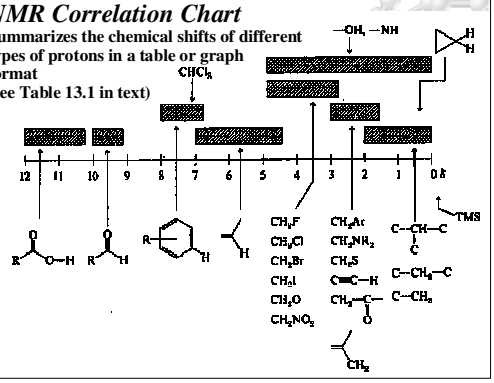
Ring Current in Benzene



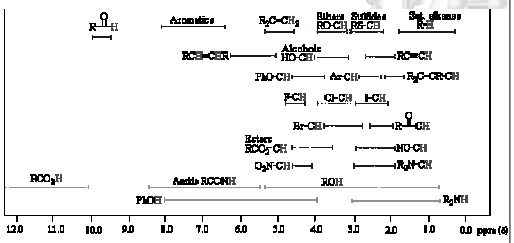
Ring current "deshields" the protons in the benzene ring, causes them to appear downfield

NMR Correlation Chart

Summarizes the chemical shifts of different types of protons in a table or graph format (see Table 13.1 in text)



NMR Correlation Chart



SPIN-SPIN SPLITTING

Most ^{1}H NMR peaks are not single lines.

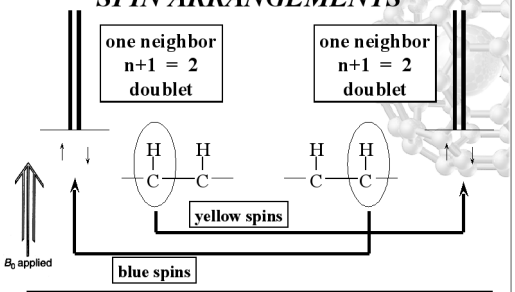
Signal splitting occurs when non-equivalent protons are on adjacent carbons

Only occurs between *non-equivalent* protons; equivalent protons do not split each other

n + 1 RULE

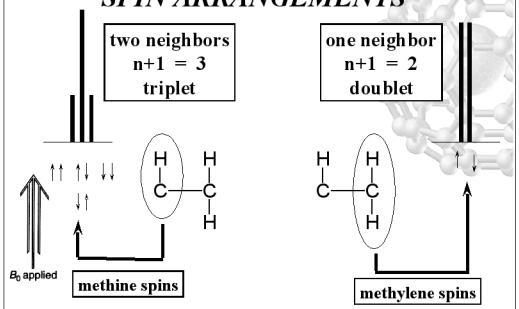
Any peak in a ^{1}H NMR spectrum shows up as n+1 lines, where *n* is the total number of *non-equivalent* hydrogens on all carbons adjacent to the carbon of interest.

SPIN ARRANGEMENTS

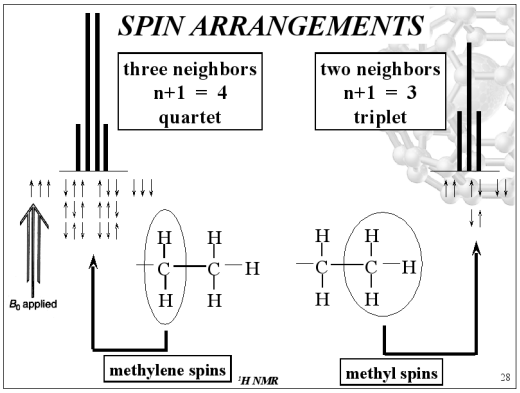


The resonance positions (splitting) of a given hydrogen is affected by the possible spins of its neighbor.

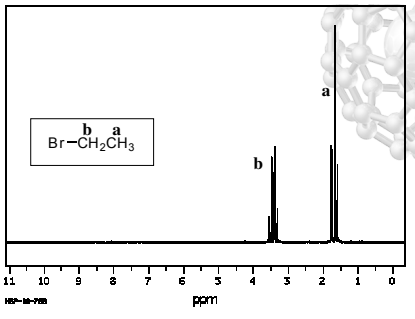
SPIN ARRANGEMENTS



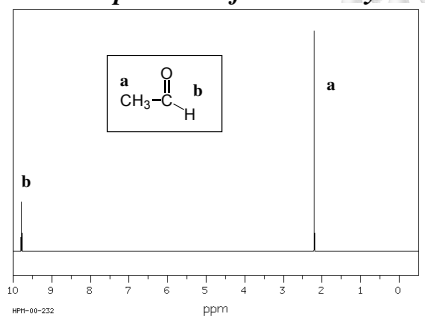
SPIN ARRANGEMENTS



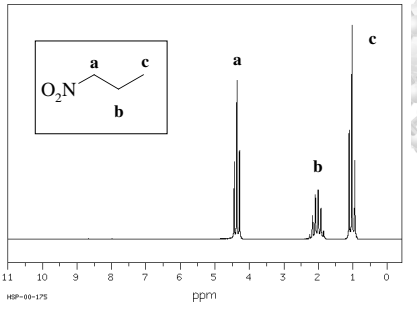
^{1}H NMR Spectrum of Bromoethane



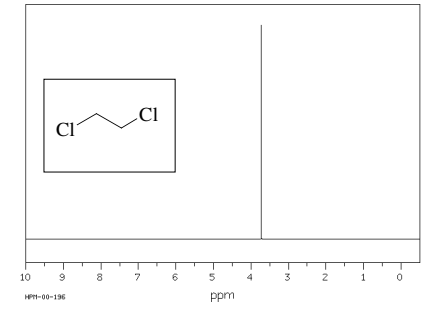
^{1}H NMR Spectrum of Acetaldehyde



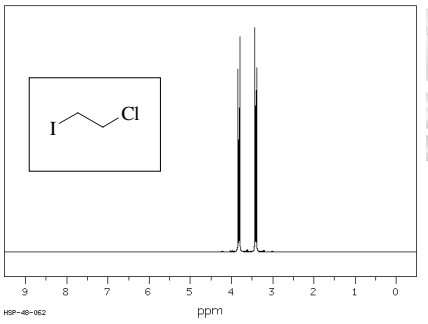
^{1}H NMR Spectrum of 1-Nitropropane



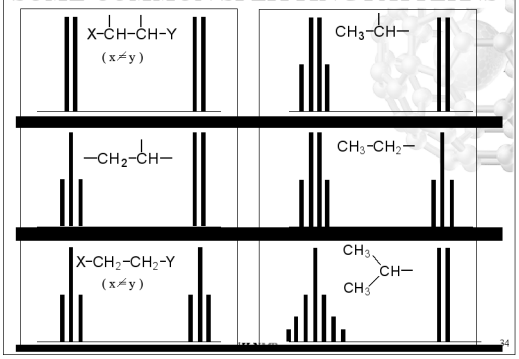
^{1}H NMR Spectrum of 1,2-dichloroethane



^{1}H NMR Spectrum of 1-chloro-2-iodoethane

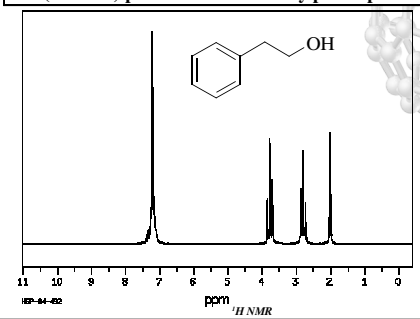


SOME COMMON SPLITTING PATTERNS



^{1}H NMR Spectrum of 2-phenyl ethanol

OH (and NH) protons do not usually participate in splitting

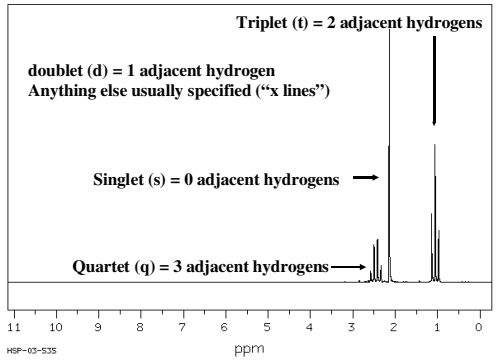


INTENSITIES OF MULTIPLET PEAKS

PASCAL'S TRIANGLE

The interior entries are the sums of the two numbers immediately above.

1	**singlet**
1 1	**doublet**
1 2 1	**triplet**
1 3 3 1	**quartet**
1 4 6 4 1	**quintet**
1 5 10 10 5 1	**sextet**
1 6 15 20 15 6 1	**septet**
1 7 21 35 35 21 7 1	**octet**



SUMMARY

TYPES OF INFORMATION FROM ^{1}H NMR SPECTRA

1. Each different type of hydrogen gives a peak or group of peaks (multiplet).

2. The chemical shift (δ, in ppm) gives a clue as to the type of hydrogen generating the peak (alkane, alkene, benzene, aldehyde, etc.)

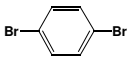
3. The integral gives the relative numbers of each type of hydrogen.

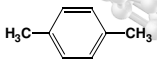
4. Spin-spin splitting gives the number of hydrogens on adjacent carbons.

Use the following symbols to predict what splitting, if any, occurs in each of the following compounds: *s* singlet, *d* doublet, *t* triplet, *q* quartet and *m* multiplet.

A) $(CH_3)_3C\text{-}O\text{-}CH_3$ $Br\text{-}CH_2CH_2CH_2\text{-}Br$

$(CH_3)_2CH\text{-}O\text{-}CH_3$ $Br\text{-}CH_2CH_2\text{-}Br$

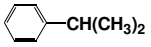




B) Predict the splitting pattern for each type of proton set.

C) Predict the splitting pattern for the red set protons.

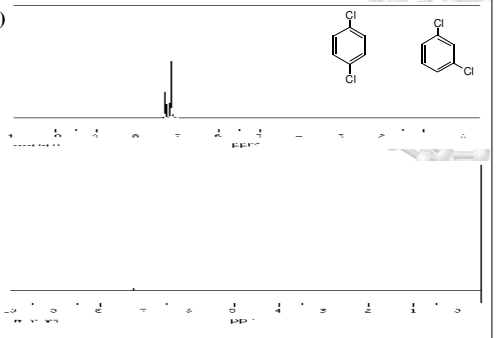
$(H_3C)_3C\text{–}O\text{–}CH_2\text{-}CH_3$ $CH_3O\text{–}CH_2\text{–}N(CH_3)_2$



$(CH_3CH_2O)_2CHCH_3$

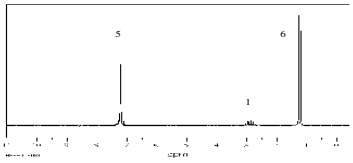
Practice Problems **I. Match the compound with its spectrum.**

A)



II. Draw the structure of the compound based on its ¹H NMR spectrum:

A)



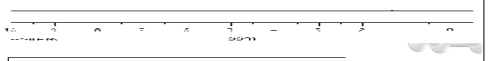
integral values shown above peak sets

a hydrocarbon with molecular formula C_9H_{12}

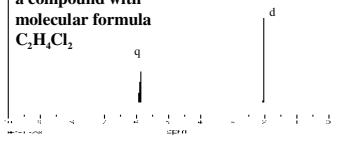
B) **an ester with molecular formula $C_4H_8O_2$**

II. Draw the structure of the compound based on its ^{1}H NMR spectrum:

C) **an ether with molecular formula $C_5H_{12}O$**



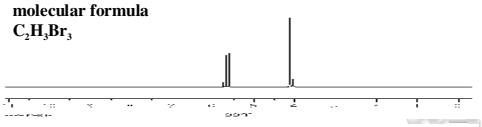
D) **a compound with molecular formula $C_2H_4Cl_2$**



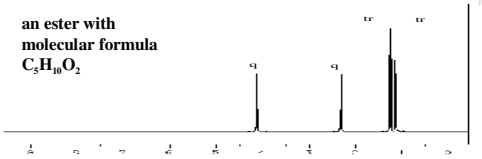
multiplicities are given next to peak sets

II. Draw the structure of the compound based on its ^{1}H NMR spectrum:

E) **a compound with molecular formula $C_2H_3Br_3$**

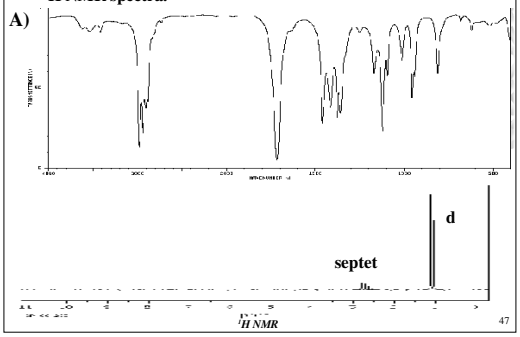


F) **an ester with molecular formula $C_5H_{10}O_2$**

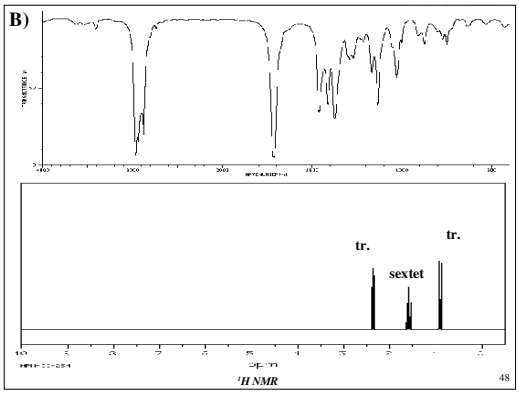


- **The following four unknowns have molecular formula $C_7H_{14}O$. Deduce the structure of each unknown based on their IR and ^{1}H NMR spectra.**

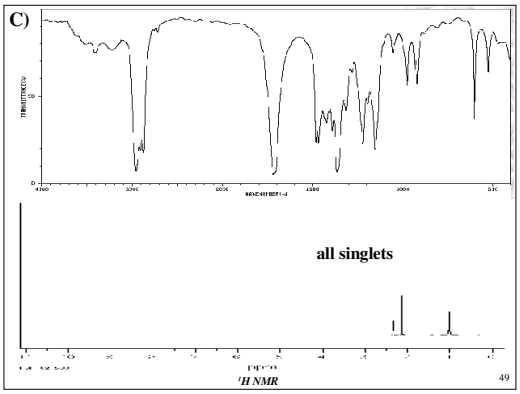
A)



B)



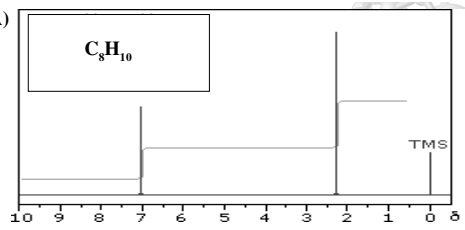
C)



all singlets

- Determine the structure of based on the ¹H NMR spectrum.

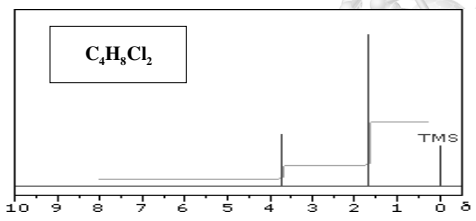
A) C_8H_{10}



integration heights: 18 mm
27 mm

- Determine the structure of based on the ¹H NMR spectrum.

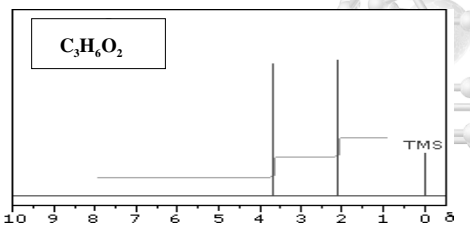
B) $C_4H_8Cl_2$



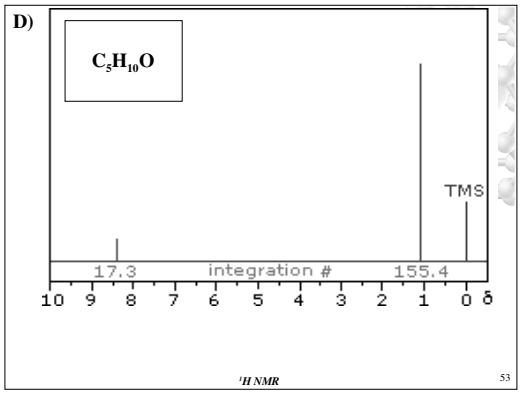
integration heights: 8 mm
25 mm

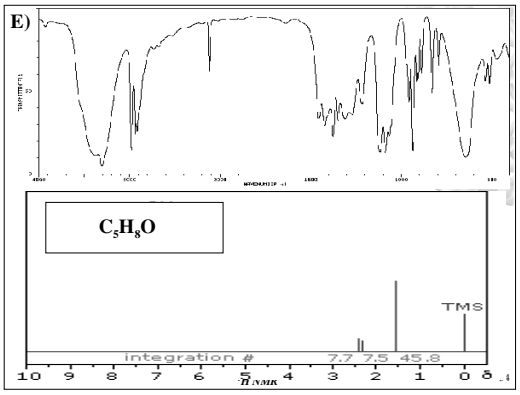
- Determine the structure of based on the ¹H NMR spectrum.

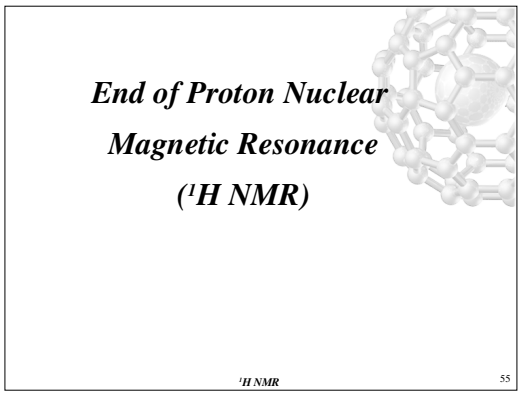
C) $C_3H_6O_2$



integration heights: 14 mm
15 mm


D)
$C_5H_{10}O$
TMS
17.3
integration #
155.4
10 9 8 7 6 5 4 3 2 1 0 δ
^1H NMR
53


E)
C_5H_8O
TMS
integration #
7.7 7.5 45.8
10 9 8 7 6 5 4 3 2 1 0 δ
^1H NMR


End of Proton Nuclear Magnetic Resonance (^1H NMR)
^1H NMR
55