Special Topic Day

Requests for

- Fragmentation in Mass Spec & Calc Loss
- More Challenging NMR

Mass Spec - Fragmentation Patterns

Table

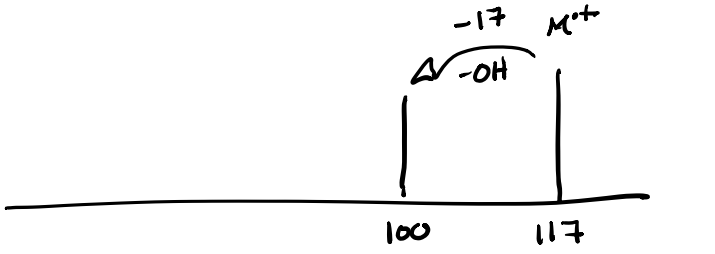
m/z	observed or loss group
15	CH_3
17	OH
28	CO
⋮	

Ex

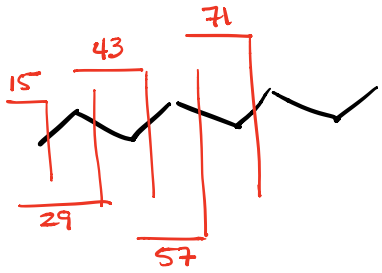
$\oplus CH_3$ observable

15

Loss



Alkanes



$-CH_2-$ = 14

Alkyl trend m/z 15, 29, 43, 57, $57+(14)_n$

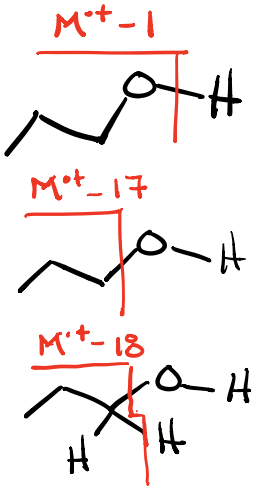
Alcohols

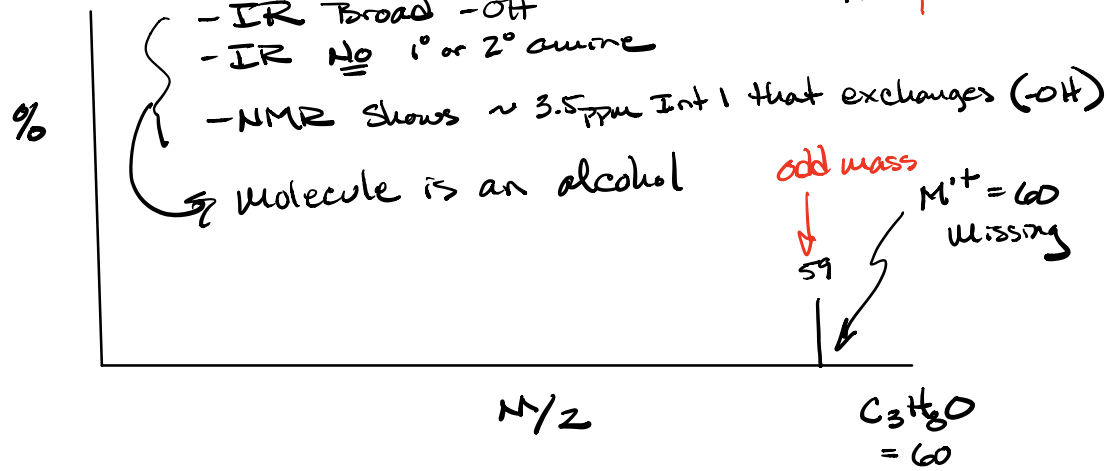
⇒ Frequently missing $M^{\cdot+}$

Loss of 1 amu H^+

Loss of 17 amu ^-OH

Loss of 18 amu H_2O

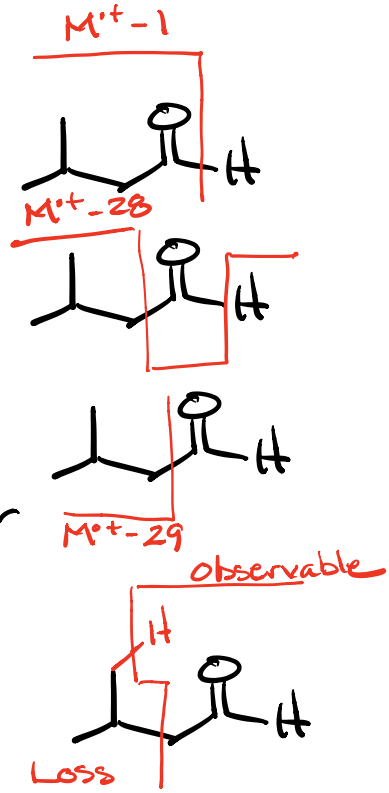




Aldehydes

- Loss of 1 amu
- Loss of 28 CO
- Loss of 29 HCO

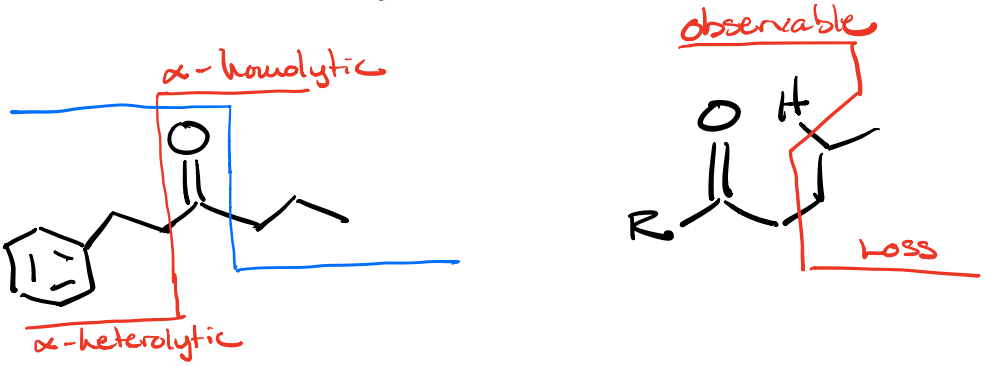
McLafferty Common for longer chains



Ketones

α-Cleavage (both homo & heterolytic)
* 4 different Cleavages possible

McLafferty Common



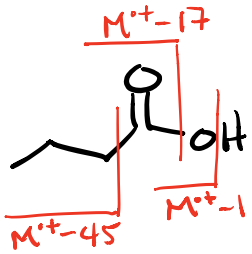
Carboxylic Acids

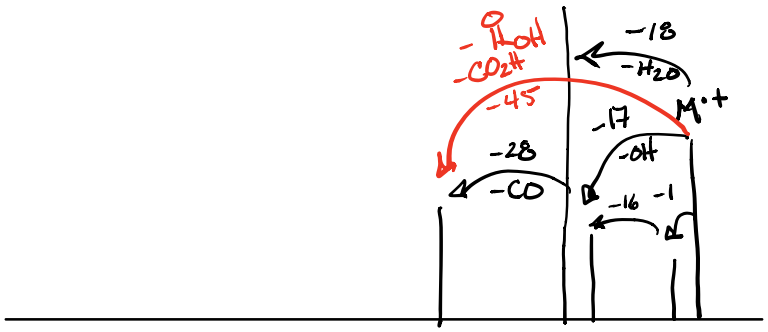
Loss of 1 amu H

Loss of 17 amu OH

Loss of 28 amu CO

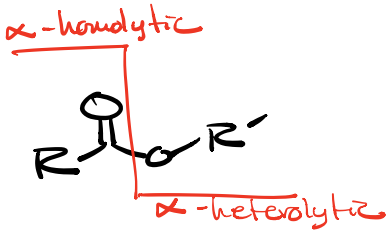
Loss of 18 amu H_2O



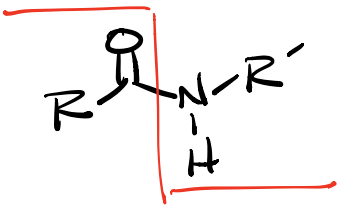


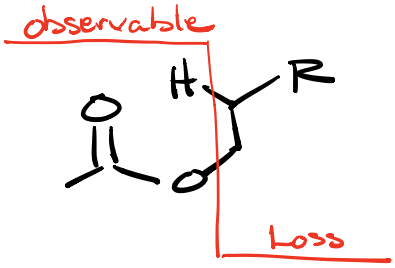
Ester & Amides ← add M°+

α-Cleavage



Mclafferty Common

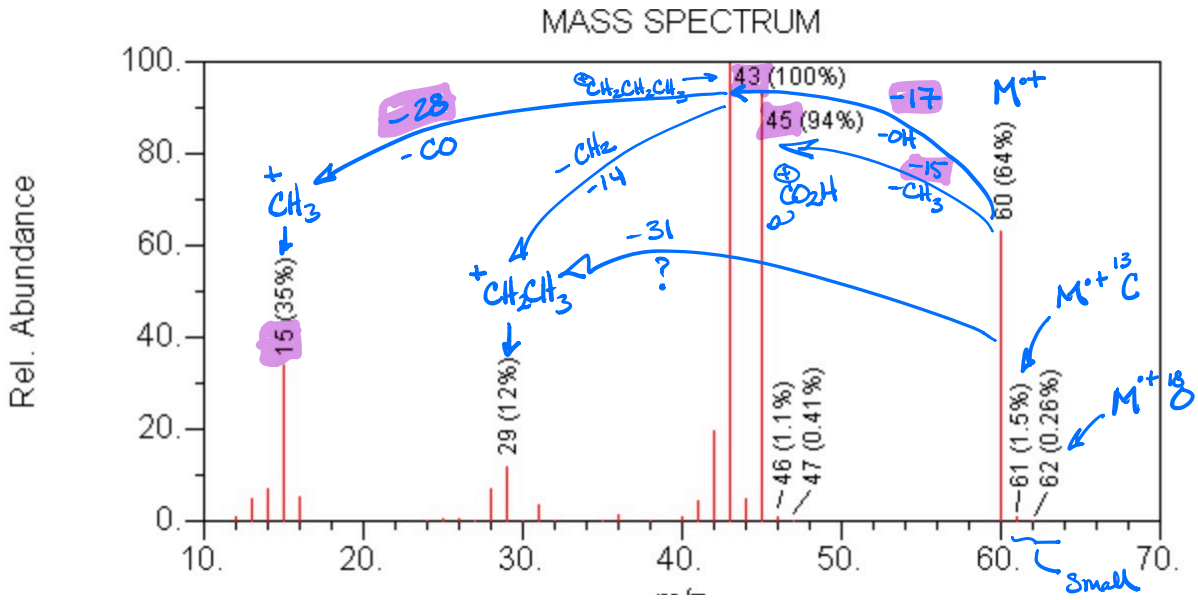




Aromatics

→ M°+ = Base

Fragment @ 77 = 



Primary Job

$M^{+} = 60$

Rule 13

$$4 \overline{)60} \quad -52 \quad 8$$

$C_4H_{4+8} = C_4H_{12}$

$C_4H_{12} \xrightarrow[+O]{-CH_4} C_3H_8O \xrightarrow[+O]{-CH_4} C_2H_4O_2$

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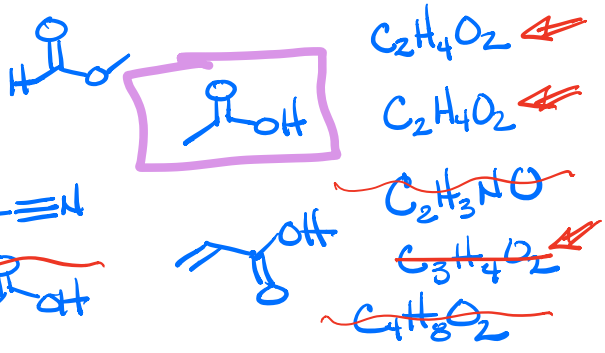
a) methyl formate 60

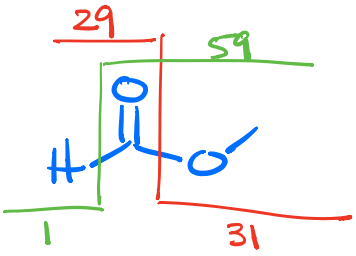
b) acetic acid 60

c) ~~hydroxy acetonitrile 57~~

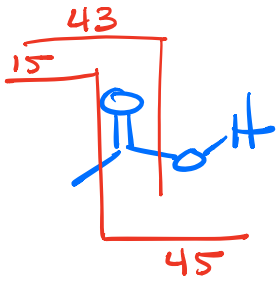
d) ~~2-propenoic acid 60~~

e) ~~butanoic acid 72~~



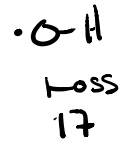


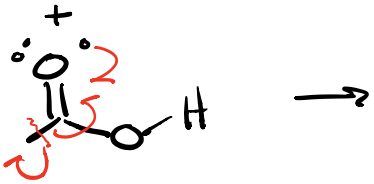
α-cleavage



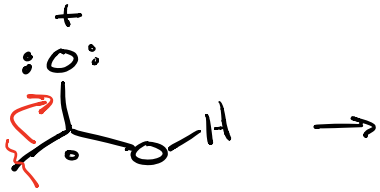
α-cleavage

m/z
43

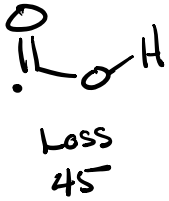


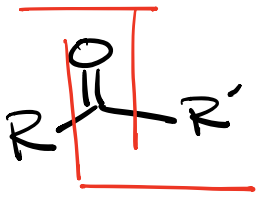


m/z
45



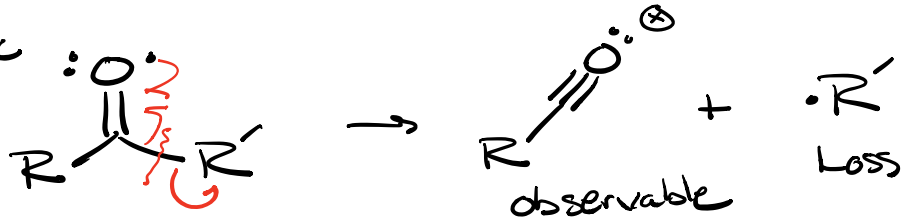
m/z
15

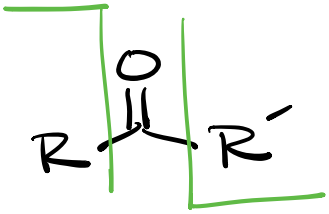




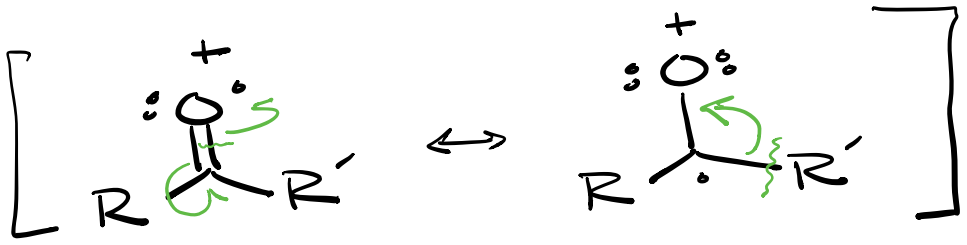
two homolytic α's

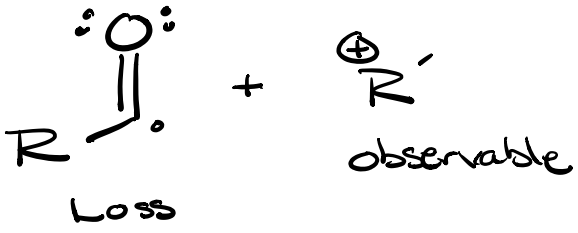
homolytic



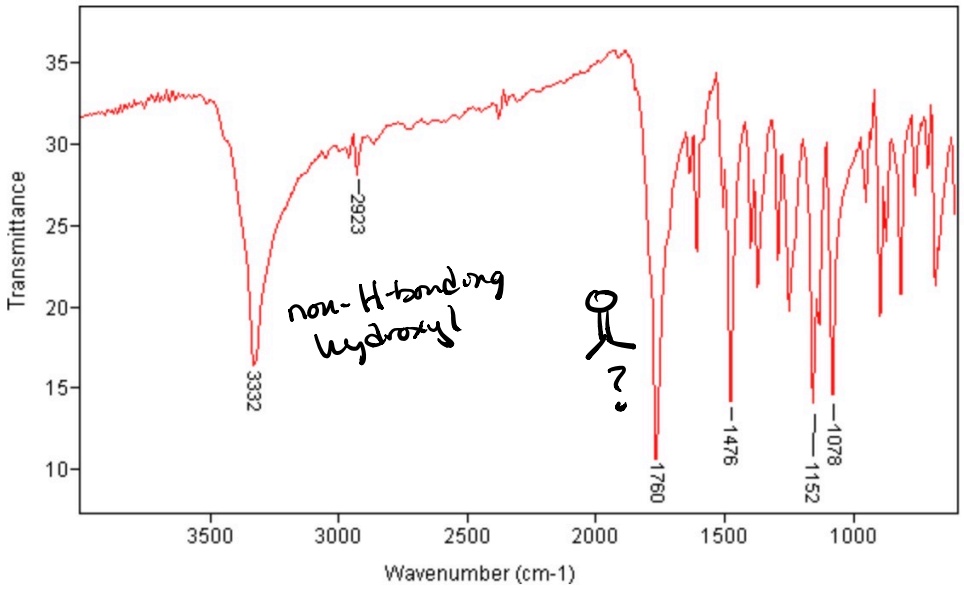


two heterolytic α's





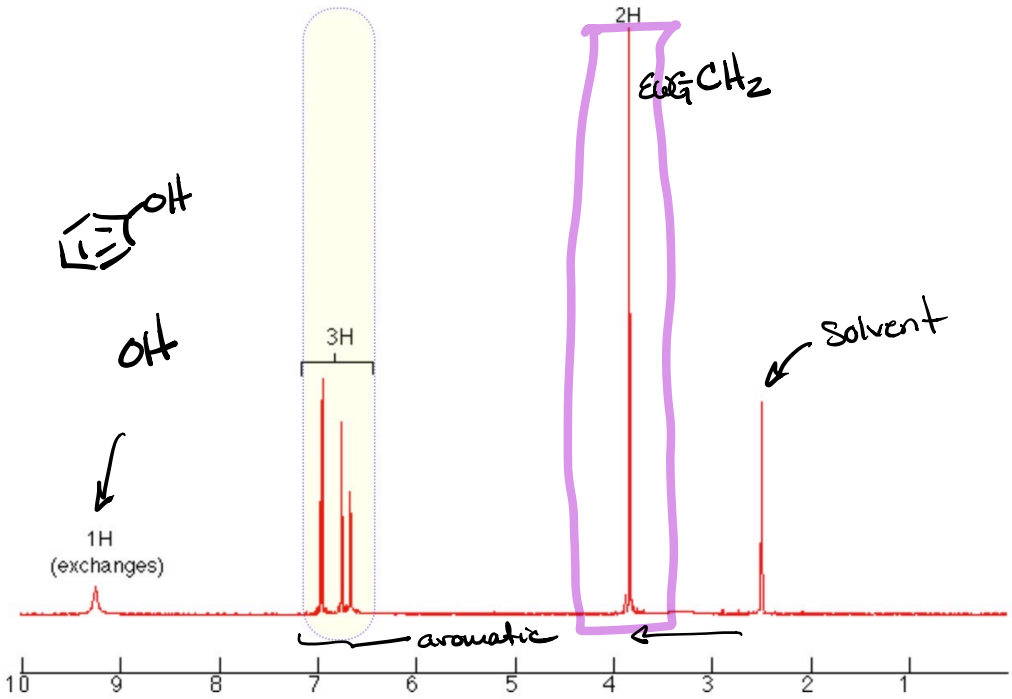
Problem 51 - IR spectrum



$C_8H_6O_3$ ⇒

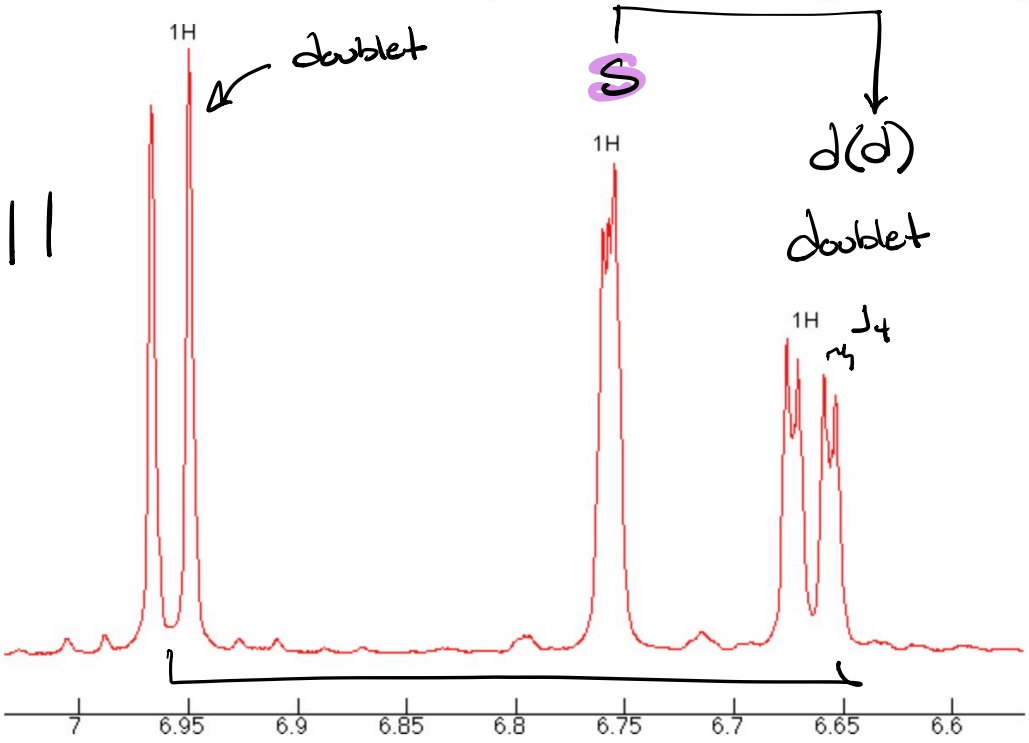
18
6
2|12
6 units

Problem 51 - ^{1}H NMR spectrum (DMSO-d_6, 500 MHz)



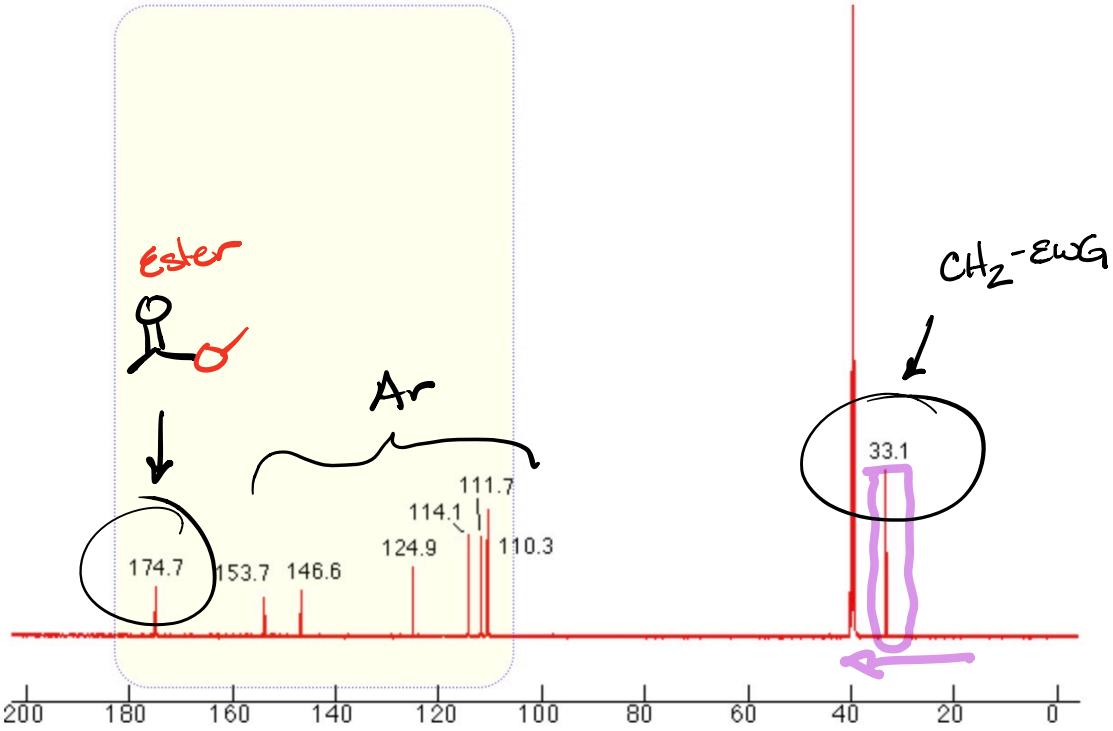
Click on the highlighted area to zoom. Click again to zoom back out.

Problem 51 - ^{1}H NMR spectrum (DMSO-d_6, 500 MHz)



Click on the highlighted area to zoom. Click again to zoom back out.

Problem 51 - ^{13}C NMR spectrum (DMSO-d_6, 125 MHz)



Click on the highlighted area to zoom. Click again to zoom back out.

8 Environments

$C_8H_6O_3$

} no symmetry

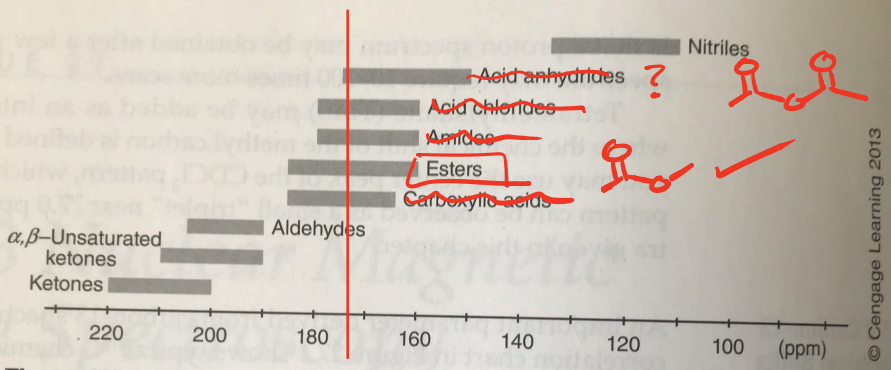


Figure 27.2
A ^{13}C correlation chart for carbonyl and nitrile functional groups.

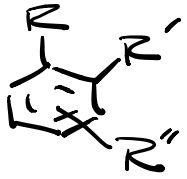
Electronegativity, hybridization, and anisotropy all affect ^{13}C chemical shifts in nearly the same fashion as they affect ^{1}H chemical shifts; however ^{13}C chemical shifts are about 20 times larger. Electronegativity (see Section 26.7) produces the same deshielding effect in carbon NMR as in proton NMR—the electronegative element produces a large downfield shift. The shift is greater for a ^{13}C atom than for a proton because the electronegative atom is directly attached to the ^{13}C atom and the effect occurs through only a single bond, C—X. With protons, the electro-

$C_8H_6O_3$ 6 units of unsat

IR - sharp -OH (phenol)

 ⇒ check cm^{-1} ⇒  ester

^1H NMR -

3 Ar protons  tri substituted

phenol 9.5 ppm exchanges $R = OH$

CH_2 - EWG

⇒ No CH_3's

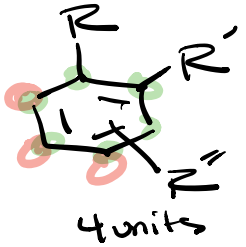
^{13}C NMR

8 environments ⇒ no symmetry

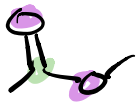
6 Ar

1 aliphatic CH_2 - EWG

1 174 ppm ⇒  ester



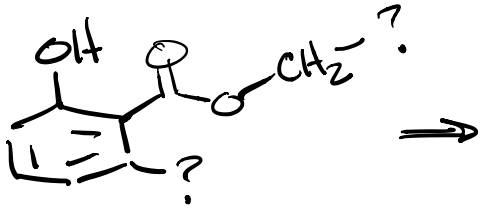
4 units

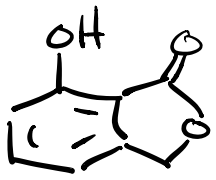


CH_2 Ar-OH

1 unit = 5 units

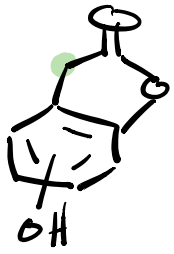
$C_8H_6O_3$ units of unsat 6

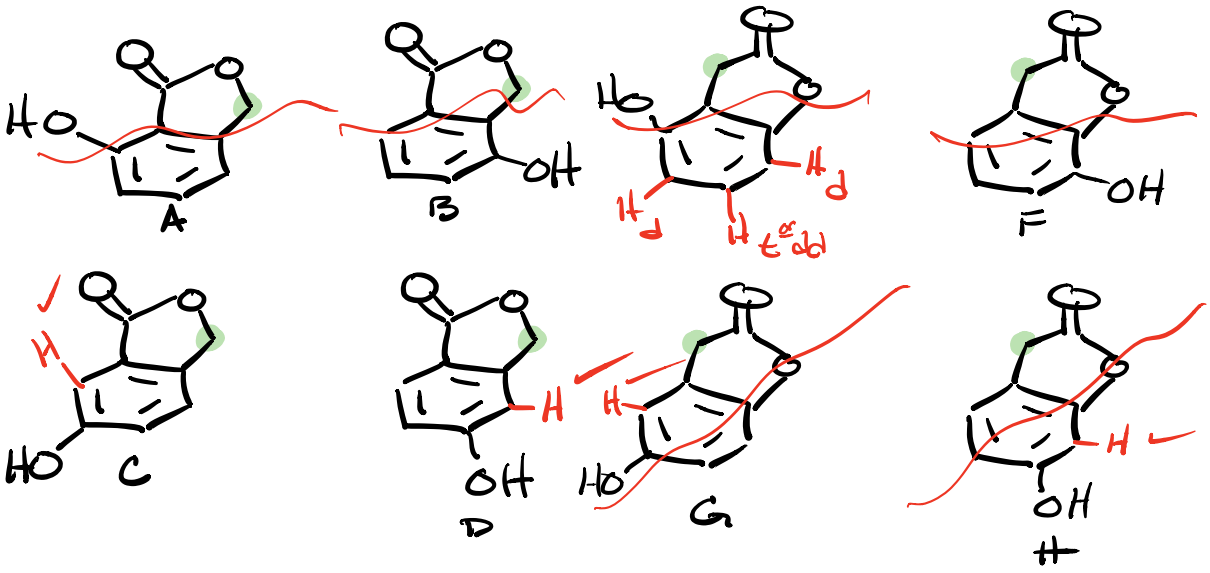




$C_8H_6O_3$ 6 units unsat

or





types of protons. For the beginner, it is often difficult to memorize a large body of numbers relating to chemical shifts and proton types. However, this needs to be done only approximately. It is more important to "get a feel" for the regions and the types of protons than to know a string of actual numbers. To do this, study Figure 26.7 carefully.

The values of chemical shift given in Figure 26.7 and in Table 26.1 can be easily understood in terms of two factors: local diamagnetic shielding and anisotropy. These two factors are discussed in Sections 26.7 and 26.8.

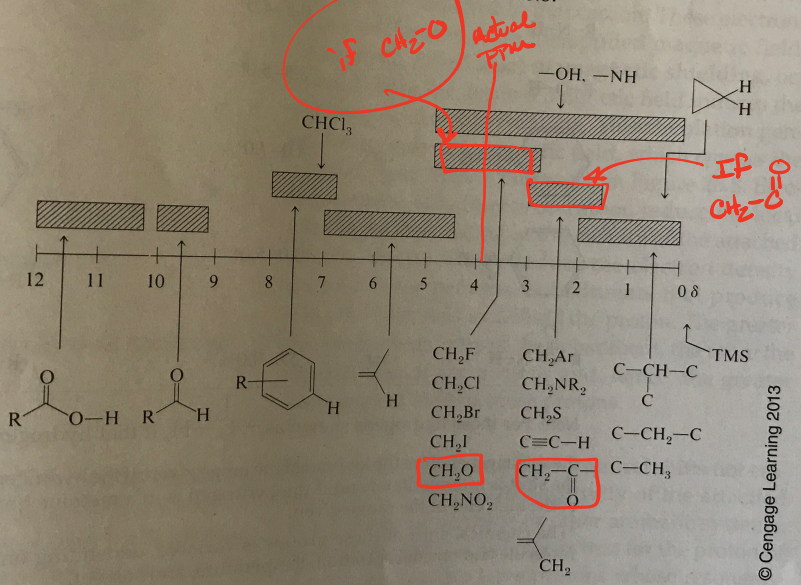


Figure 26.7
A simplified correlation chart for proton chemical shift values.

onstrates the effect of electronegative atoms (40–80 ppm). The next section of the chart demalkene and aromatic-ring carbon atoms (100–175 ppm). Finally, the fourth section contains carbonyl carbons, which appear at the lowest field values (155–220 ppm).

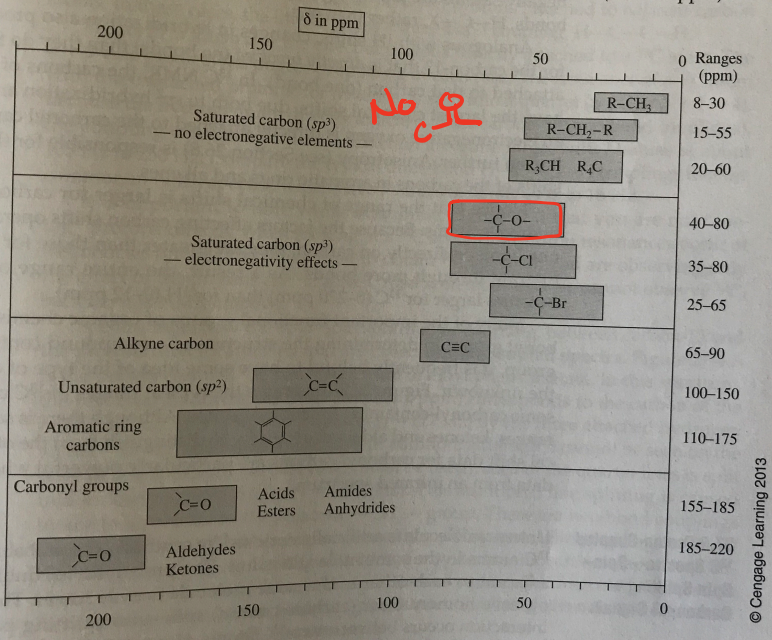
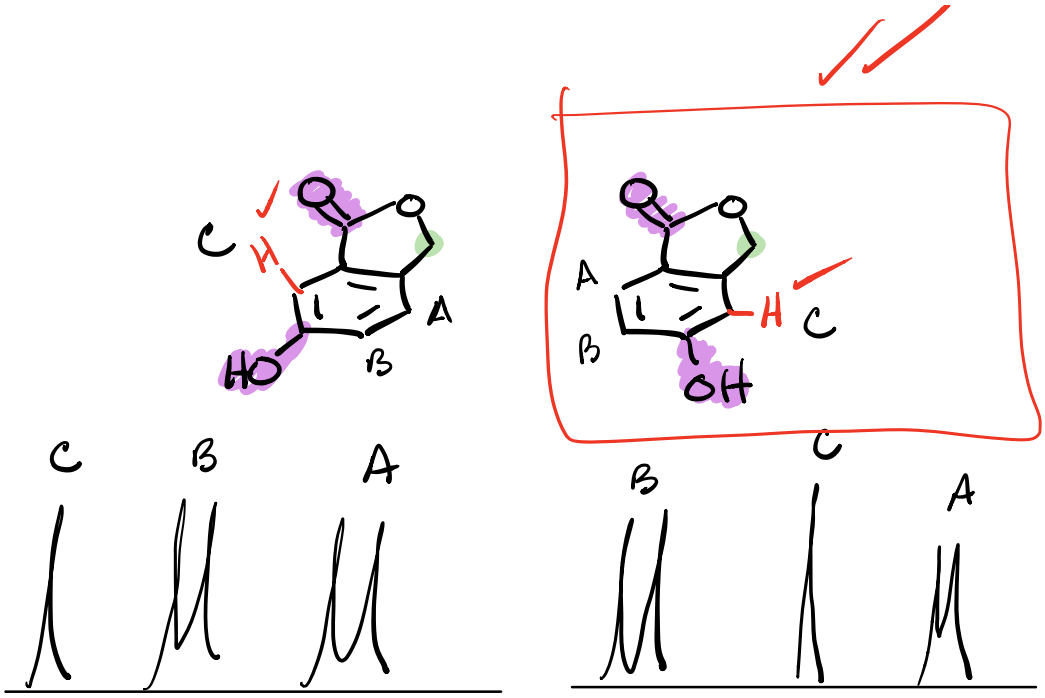


Figure 27.1
for ^{13}C chemical shifts (chemical shifts are listed in parts per million


C
H
A
HO
B
A
B
H
C
OH
C
B
A
B
C
A