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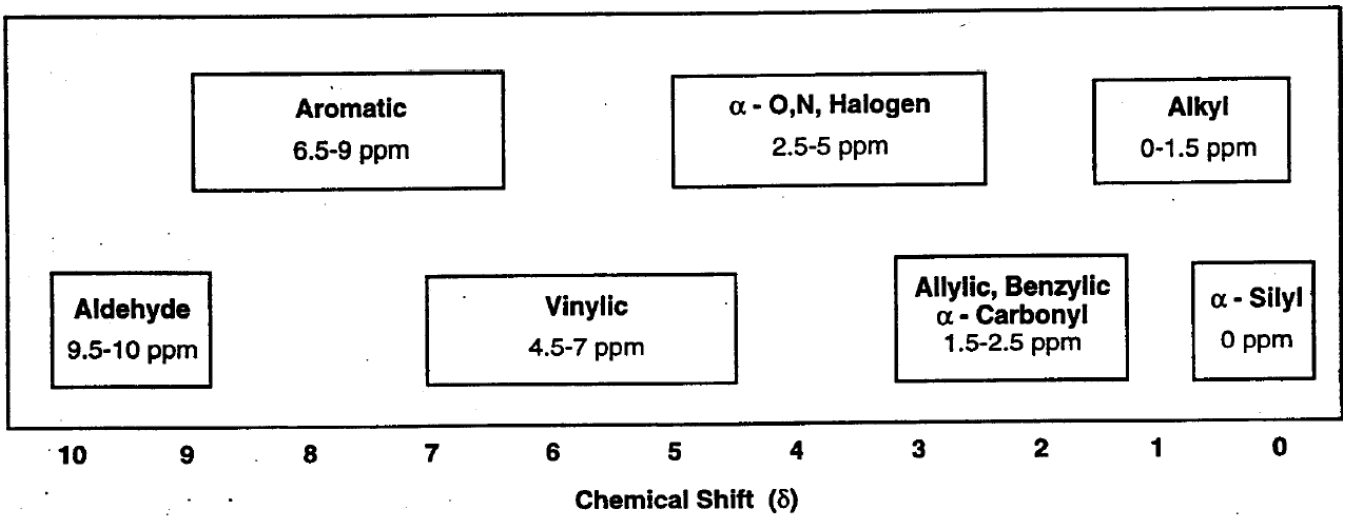
Massachusetts Institute of Technology
Organic Chemistry 5.13

September 19, 2003
Prof. Timothy F. Jamison

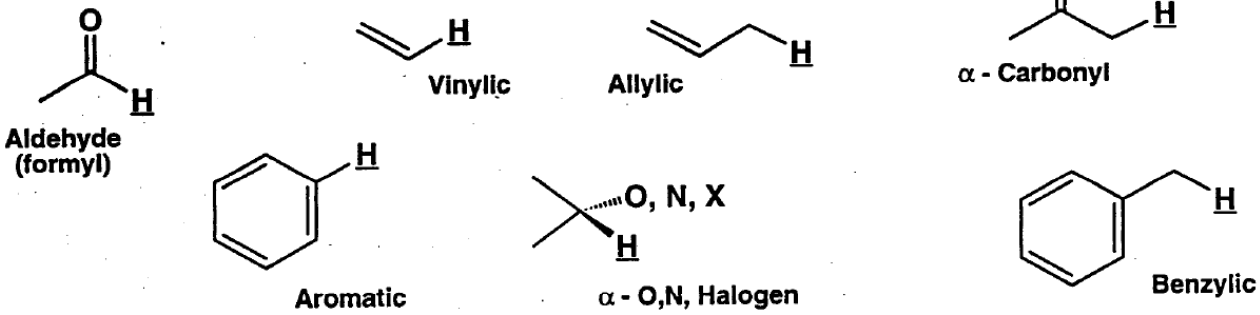
Notes for Lecture #7

^{1}H NMR Spectroscopy – Chemical Shift

Regions of the ^{1}H NMR Spectrum

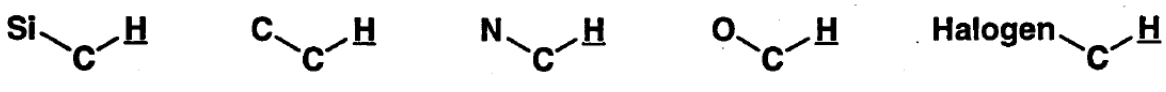


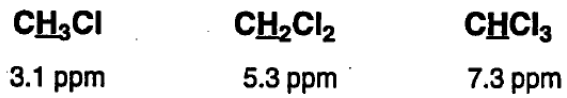
Definitions



Diamagnetic Shielding

Can we rationalize the following trends?





^{1}H NMR Spectra: Tables of Reference

Average Chemical Shifts (δ) of α-Hydrogens in Substituted Alkanes*

X	CH_3X	RCH_2X	R_2CHX
H	0.233	0.9	1.25
CH_3 or CH_2	0.9	1.25	1.5
F	4.26	4.4	—
Cl	3.05	3.4	4.0
Br	2.68	3.3	4.1
I	2.16	3.2	4.2
OH	3.47	3.6	3.6
OR	3.3	3.4	—
OAr	3.7	3.9	—
OCOR	3.6	4.1	5.0
OCOAr	3.8	4.2	5.1
SH	2.44	2.7	—
SR	2.1	2.5	—
SOR	2.5	—	2.8
SO_2R	2.8	2.9	3.1
NR_2	2.2	2.6	2.9
NR-Ar	2.9	—	—
NCOR	2.8	—	3.2
NO_2	4.28	4.4	4.7
CHO	2.20	2.3	2.4
COR	2.1	2.4	2.5
COAr	2.6	3.0	3.4
COOH	2.07	2.3	2.6
COOR	2.1	2.3	2.6
$CONH_2$	2.02	2.2	—
$CR{=}CRCR^1$	2.0-1.6	2.3	2.6
Phenyl	2.3	2.7	2.9
Aryl §	3.0-2.5	—	—
C≡CR	2.0	—	—
C≡CN	2.0	2.3	2.7

* The tabulated values are average values for compounds that do not contain another functional group within two carbon atoms from the indicated hydrogens.

§ Includes polycyclic and many heterocyclic aromatics.

Chemical Shifts of Hydrogens Bonded to Unsaturated Centers

Type	Unconjugated	Conjugated*
$R_2C{=}CH_2$	4.6-5.0	5.4-7.0
$R_2C{=}CHR$	5.0-5.7	5.7-7.3
Aromatic	6.5-8.3	-----
Nonbenzenoid aromatic	6.2-9.0	-----
Acetylenic	2.3-2.7	2.7-3.2
Aldehydic	9.5-9.8	9.5-10.1
R_2NCHO	7.9-8.1	-----
ROCHO	8.0-8.2	-----

* The position depends on the type of functional group in conjugation with the unsaturated group.

Chemical Shifts of Hydrogen Bonded to Oxygen, Nitrogen, and Sulfur

Functional Group		Chemical Shift, δ	
OH	Alcohols	0.5 0.5-5	(Monomeric) (Associated)
	Phenols	4.5 4.5-8	(Monomeric) (Associated)
	Enols	15.5	
	RCO_2H	9-12	(Dimeric)
	H-bonded to C=O	13-16	
NH_2	Alkylamine	0.6-1.6	
	Arylamine	2.7-4.0	
	Amide	7.8	
NH	Alkylamine	0.3-0.5	
	Arylamine	2.7-2.8	
R_3NH^+	Ammonium salts	7.1-7.7	(in CF_3COOH)
SH	Aliphatic	1.3-1.7	
	Aromatic	2.5-4	