Here are some things I wish I had
said when we were talking about
substitution and elimination reactions:

Good leaving group →

Nucleophiles → not simple to explain what
makes a good nucleophile →
the Table for reference

Table of Nucleophiles

Strong Nucleophiles
Br^-, I^-, $R-S^-$, $H-S^-$, $N\equiv C^-$, N_3^-

$R-C\equiv C^-$, $R-O^-$, $H-O^-$ **Strong Bases**

Medium Nucleophiles
$R-CO_2^-$, $R-S-H$, R_2S,
NH_3, RNH_2, R_2NH, NR_3

Weak Nucleophiles
$R-CO_2H$, $R-O-H$, H_2O **Very Weak Bases**

Special Case

Tert-Butoxide ($tBuO^-$) is a strong base, but
is not a nucleophile due to steric hindrance.

$$H_3C - \overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}} - \ddot{O}{:}^{\ominus} \quad K^{\oplus}$$
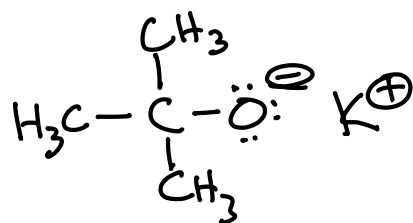
"KOtBu"
or
"$tBuO^{\ominus}$"

To understand NMR you need to know the following:

A. Physics: Moving charge generates a magnetic field, and a moving magnetic field causes charges to move in a conductor.
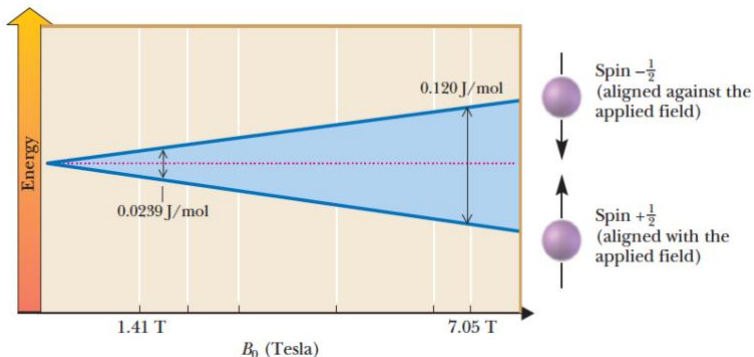
B. Atomic nuclei, like electrons, have a quantum mechanical property of "spin". Spin can be thought of as a small magnetic field around the nucleus created as if the positive charge of the nucleus were circulating.

C. NMR, nuclear magnetic resonance, is used to assign structures of organic molecules.

D. We care about the nuclei ^1H and ^{13}C since these are commonly found in organic molecules and they have spin quantum numbers of 1/2.

E. Nuclei with spin quantum number 1/2 are quantized in one of two orientations, "+1/2" (lower energy) or "-1/2"(higher energy) in the presence of an external magnetic field, that is, with and against the external field, respectively.

F. **The difference in energy between the +1/2 and -1/2 nuclear spin states is proportional to the strength of the magnetic field felt by the nucleus.**

Energy

0.120 J/mol

0.0239 J/mol

1.41 T   7.05 T

B_0 (Tesla)

Spin $-\frac{1}{2}$
(aligned against the applied field)

Spin $+\frac{1}{2}$
(aligned with the applied field)

G. Electron density is induced to circulate in a strong external magnetic field, which in turn produces a magnetic field that opposes the external magnetic field. This **shields** nuclei from the external magnetic field. The greater the electron density around a nucleus, the more shielded it is, and the lower the energy (frequency) of electromagnetic radiation required to flip its nuclear spin.

H. In the classic ^1H-NMR experiment, the molecule of interest is placed in solvent (the solvent has deuterium atoms in place of H atoms so the solvent molecules will not show up in the spectra, see R.) then is put in a spinning tube in a very strong magnetic field. The sample is exposed to radiofrequency irradiation and if it is of exactly the right frequency energy is absorbed and spins flip from +1/2 to -1/2 (come into resonance). The absorbed energy is plotted in the spectra.

I. All ^1H-NMR spectra are recorded as **chemical shift (∂, delta)** in the units of **ppm** (parts per million). Shielding magnetic field effects are around 1 millionth as large as the external magnetic field in which the sample is placed. Tetramethylsilane (TMS, $(CH_3)_4Si$)) is placed in the sample as a standard and assigned the value of 0.0 ppm. ***Warning the NMR scale is plotted "backwards", with <u>higher values to the left</u>!!***

NMR experiment →

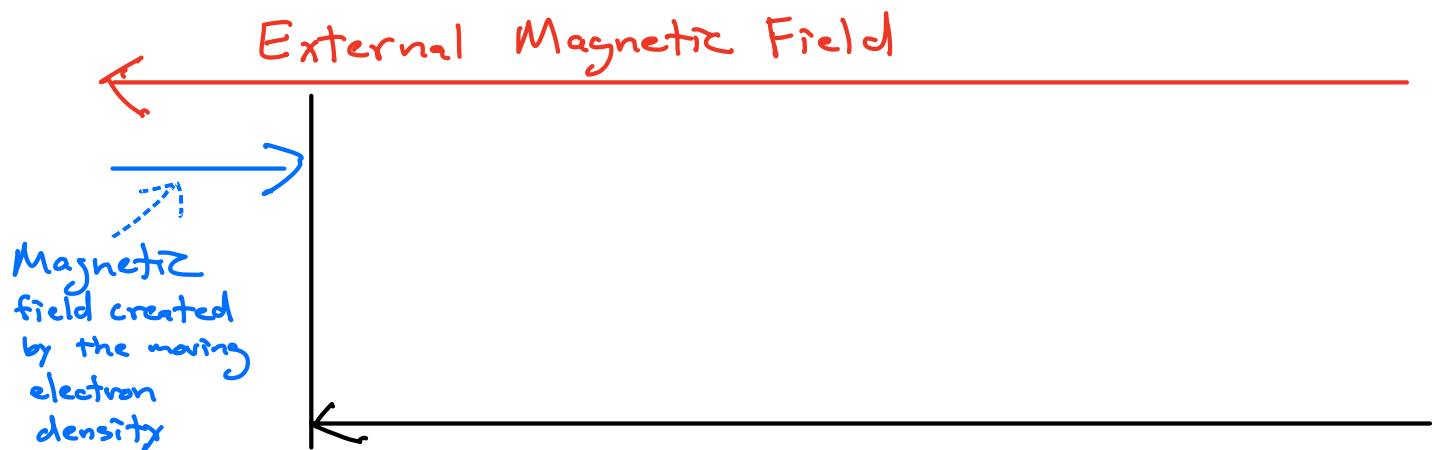$\downarrow$ $-\frac{1}{2}$

$\uparrow$ $+\frac{1}{2}$

The ^1H nucleus of spin state $+\frac{1}{2}$ absorbs a quanta of energy of precisely the correct frequency and the nucleus is "excited" to the $-\frac{1}{2}$ spin state

Key Point —→

We monitor the energy that is absorbed
by the nuclear spins as they flip

Shielding →

External Magnetic Field

Magnetic field created by the moving electron density

The magnitude of the magnetic field experienced by a nucleus under the electron density.

Shielding Bottom Line $\longrightarrow$

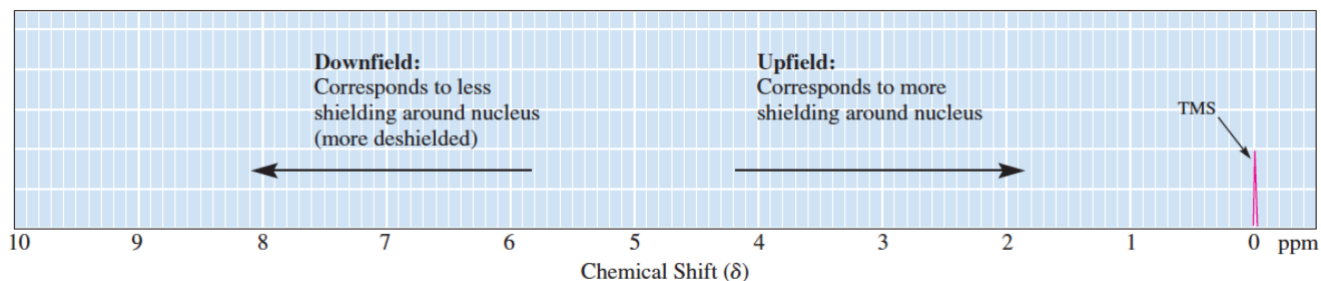$\Rightarrow$ **More electron density** generates a

so a nucleus under more electron density experiences a

$\Rightarrow$ **More electron density** around a nucleus provides   of the external magnetic field

Downfield:
Corresponds to less shielding around nucleus (more deshielded)

Upfield:
Corresponds to more shielding around nucleus

TMS

10 9 8 7 6 5 4 3 2 1 0 ppm

Chemical Shift (δ)

J. The hybridization state of carbon atoms attached to an H atom influences shielding in predictable ways by removing differing amounts of electron density around adjacent nuclei.

K. Electron density in pi bonds also has a large effect on H atom shielding because pi electrons are more free to circulate in an a magnetic field compared to electron density in sigma bonds. Geometry of the pi bond is important.

Table 13.3 The Effect of Hybridization on Chemical Shift

Type of Hydrogen (R = alkyl)	Name of Hydrogen	Chemical Shift δ
RCH_3, R_2CH_2, R_3CH	Alkyl	0.8–1.7
$R_2C=C(R)CHR_2$	Allylic	1.6–2.6
$RC\equiv CH$	Acetylenic	2.0–3.0
$R_2C=CHR$, $R_2C=CH_2$	Vinylic	4.6–5.7
$RCHO$	Aldehydic	9.5–10.1

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
		RCH_2OH	3.4-4.0
R_2NH	0.5-5.0	RCH_2Br	3.4-3.6
ROH	0.5-6.0	RCH_2Cl	3.6-3.8
RCH_3	0.8-1.0	$RCOCH_3$ (O)	3.7-3.9
RCH_2R	1.2-1.4		
R_3CH	1.4-1.7	$RCOCH_2R$ (O)	4.1-4.7
$R_2C=CRCHR_2$	1.6-2.6		
$RC≡CH$	2.0-3.0	RCH_2F	4.4-4.5
		ArOH	4.5-4.7
$RCCH_3$ (O)	2.1-2.3	$R_2C=CH_2$	4.6-5.0
		$R_2C=CHR$	5.0-5.7
$RCCH_2R$ (O)	2.2-2.6	H_2C-CH_2 (O)	3.3-4.0
$ArCH_3$	2.2-2.5		
RCH_2NR_2	2.3-2.8	RCH (O)	9.5-10.1
RCH_2I	3.1-3.3		
RCH_2OR	3.3-4.0	$RCOH$ (O)	10-13

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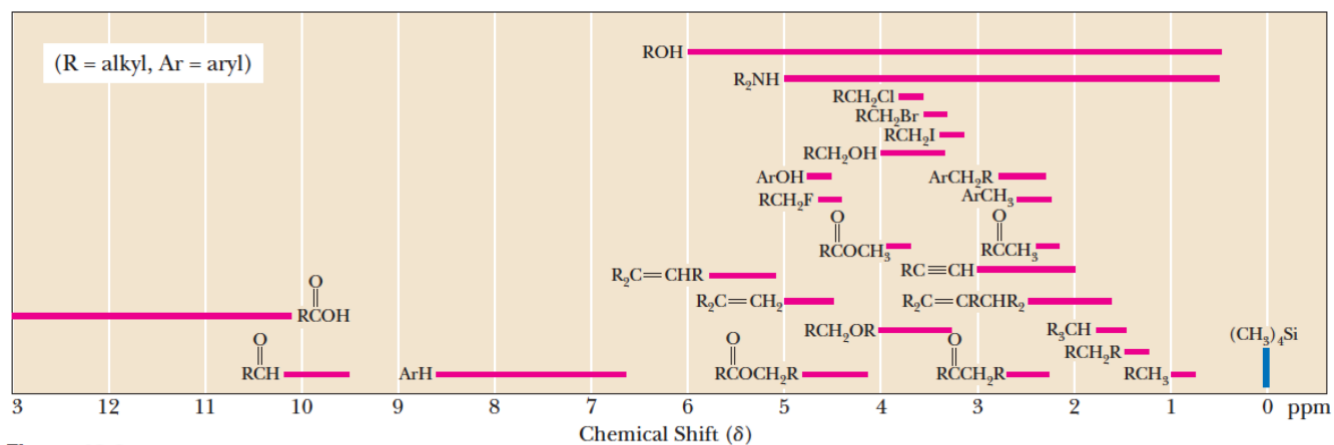

Figure 13.8
Average values of chemical shifts of representative types of hydrogens. These values are approximate. Other atoms or groups in the molecules may cause signals to appear outside of these ranges.