NMR SPECTROSCOPY DIFFER FROM" IR" SPECTROSCOPY:

PART TWO

1. The energy needed for NMR is much smaller than that required for IR Spectroscopy.
2. Time scales of the two techniques are quite different.

(NMR about 10^{-3} second, while IR about 10^{-13} second)

The position on the chart at which a nucleus absorbs is called its **chemical shift**. The chemical shift of TMS is set as the zero point, and other absorptions normally occur downfield, to the left on the chart. NMR charts are calibrated using an arbitrary scale called the **delta (δ) scale**, where 1 δ equals 1 part per

1δ = 1 ppm

ppm (part of the million) of the operating frequency of the instrument. e.g. if we use spectrometer operating at

200 MHz, 1 δ would be 1 millionth of 200,000,000 Hz, or 200 Hz. If we were measuring the spectrum using a 500 MHz instrument, 1 δ = 500 Hz. The following equation can be used for any absorption:

$$\delta = \frac{\text{Observed chemical shift (number of Hz away from TMS)}}{\text{Spectrometer frequency in MHz}}$$

Although this method of calibrating NMR charts may seem complex, there's a good reason for it. As we saw earlier, the rf frequency required to bring a given nucleus into resonance depends on the spectrometer's magnetic field strength. But because there are many different kinds of spectrometers with many different magnetic field strengths available, chemical shifts given in frequency units (Hz) vary from one instrument to another. Thus, a resonance that occurs at 120 Hz downfield from TMS on one spectrometer might occur at 600 Hz downfield from TMS on another spectrometer with a more powerful magnet.

By using a system of measurement in which NMR absorptions are expressed in relative terms (parts per million relative to spectrometer frequency) rather than absolute terms (Hz), it's possible to compare spectra obtained on different instruments. *The chemical shift of an NMR absorption in δ units is constant, regardless of the operating frequency of the spectrometer.* A ^1H nucleus that absorbs at 2.0 δ on a 200 MHz instrument also absorbs at 2.0 δ on a 500 MHz instrument.

The range in which most NMR absorptions occur is quite narrow. Almost all ^1H NMR absorptions occur 0 to 10 δ downfield from the proton absorption of TMS,

Thus there is a considerable accidental overlap of non equivalent signal will occur.

The advantages of using an instrument with higher field strength (say, 500 MHz) rather than lower field strength (200 MHz) is that different NMR absorptions are more widely separated at the higher field strength. The chances that two signals will accidentally overlap are therefore lessened, and interpretation of spectra becomes easier. For example, two signals that are only 20 Hz apart at 200 MHz (0.1 ppm) are 50 Hz apart at 500 MHz (still 0.1 ppm).

DIAMAGNETIC ANISOTROPY:

- It means that shielding and deshielding depend on the orientation of the molecule with respect to applied magnetic field. For example:
  1. The NMR peak of the proton of acetylene is found further to the right than electronegativity would predict, (peak = 1.8 **δ**) more shielded than ethylene protons (peak = 5.25 **δ**).

- Note: electron with drawing effect = SP > SP^2 > SP^3

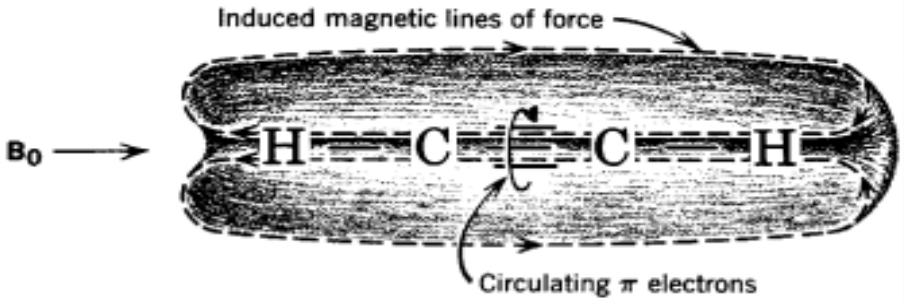


FIGURE 4.16. Shielding of alkyne protons.

2. Unexpected deshielding position of the aldehydic proton. (9.7- 10)

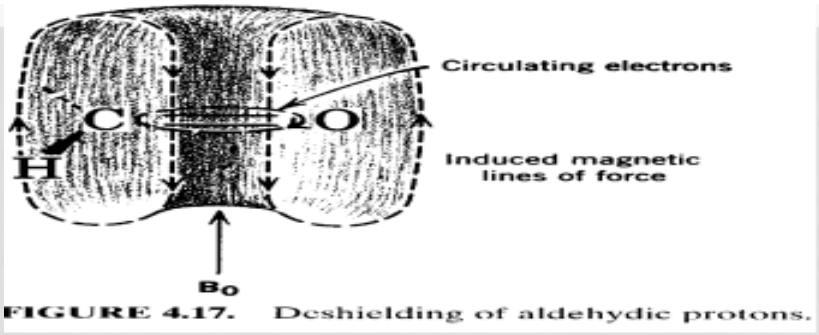


FIGURE 4.17. Deshielding of aldehydic protons.

3. Large deshielding of alkene protons.

4. Large deshielding of benzene ring protons, which is called "ring current effect" (6.5_ 8).

Note: a proton held directly above or below the aromatic ring is shielded.

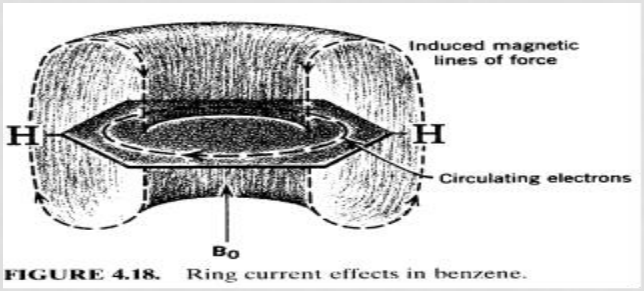
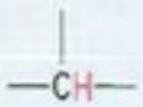
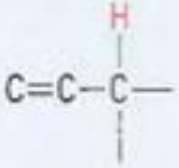
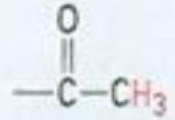
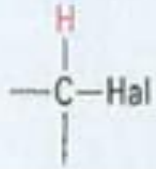
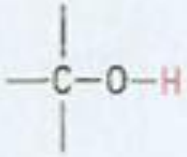
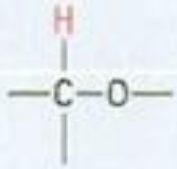
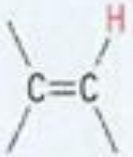
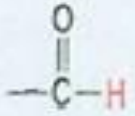
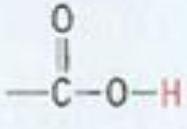


FIGURE 4.18. Ring current effects in benzene.

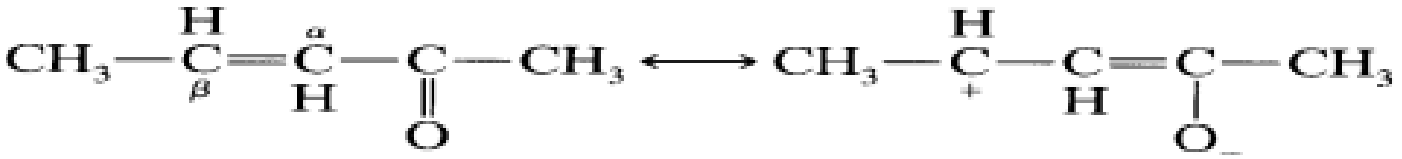
Table 13.3 Correlation of ^1H Chemical Shift with Environment

Type of hydrogen		Chemical shift (δ)
Reference	$Si(CH_3)_4$	0
Alkyl (primary)	$-CH_3$	0.7–1.3
Alkyl (secondary)	$-CH_2-$	1.2–1.6
Alkyl (tertiary)		1.4–1.8
Allylic		1.6–2.2
Methyl ketone		2.0–2.4
Aromatic methyl	$Ar-CH_3$	2.4–2.7
Alkynyl	$-C\equiv C-H$	2.5–3.0
Alkyl halide		2.5–4.0

Type of hydrogen		Chemical shift (δ)
Alcohol		2.5–5.0
Alcohol, ether		3.3–4.5
Vinylic		4.5–6.5
Aryl	$Ar-H$	
Aldehyde		9.7–10.0
Carboxylic acid		11.0–12.0

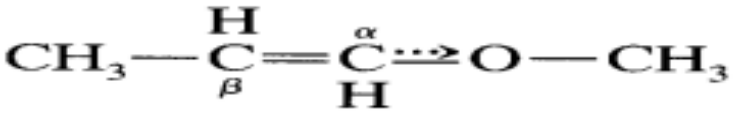
RATIONALIZATION AND PREDICTION OF APPROXIMATE CHEMICAL SHIFT DEPENDING ON INDUCTIVE EFFECT & DIAMAGNETIC ANISOTROPY

1. In an α,β-unsaturated ketone, resonance deshields the β-proton;



α-proton = $\delta \sim 6.2$
β-proton = $\delta \sim 6.8$

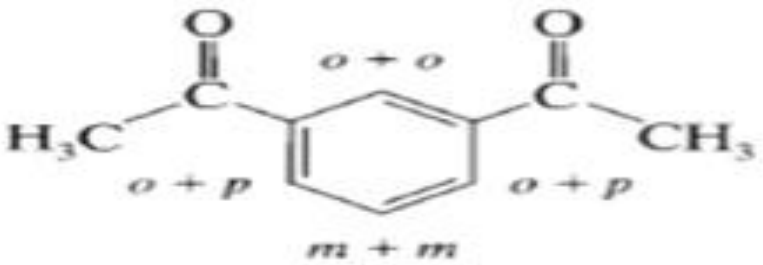
2. In a substituted vinyl ether, the oxygen atom deshields the α-proton by an inductive effect and shields the β-proton by resonance.



α-proton = $\delta \sim 6.2$
β-proton = $\delta \sim 4.6$

3. The shifts of protons *ortho*, *meta*, or *para* to a substituent on an aromatic ring are correlated with electron densities and with the effects of electrophilic reagents (Appendix Chart D.1). For example, the *ortho* and *para* protons of phenol are shielded because of the higher electron density that also accounts for the predominance of *ortho* and *para* substitution by electrophilic reagents. Conversely, the *ortho* and *para* protons of nitrobenzene are deshielded, the *ortho* protons more so (see Figure 3.23).

Since chemical shift increments are approximately additive, it is possible to calculate the ring proton shifts in polysubstituted benzene rings from the monosubstituted values in Appendix Chart D.1. The chemical shift increments for the ring protons of *m*-diacetylbenzene:



SOLVENT SELECTION:

- Characteristic of the ideal solvent:
- 1. should contain no protons
- 2. inert
- 3. low boiling
- 4. inexpensive
- 5. Deuterated solvents are necessary for modern instruments because they depend on a deuterium signal to lock or stabilize the B° field of the magnet.
- Solvent used in NMR spectroscopy:
- 1. CCl_4: because a/ it is contain no hydrogen.
- b/ good solvent for many organic compounds.
- c/ cheap and readily available.
- 2. $CDCl_3$

INFORMATION OBTAINED FROM NMR SPECTRA:

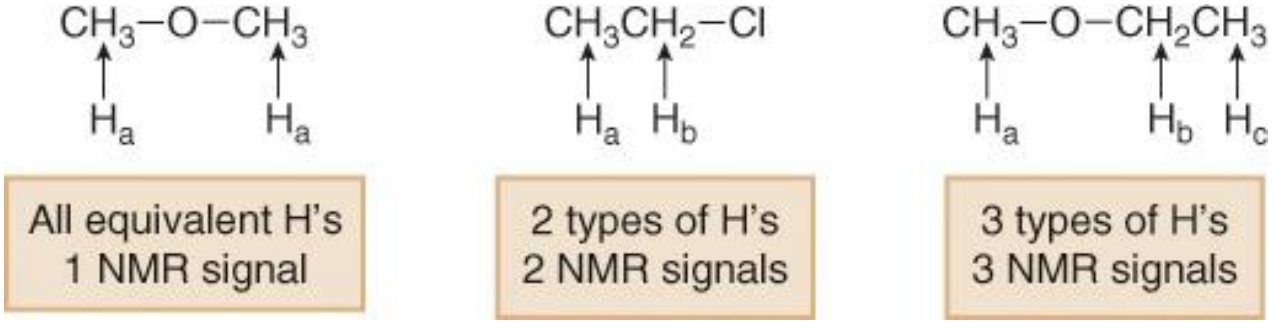
- 1. Number of signal: → number of sets of chemically equivalent protons.
- The equivalence or non-equivalence of two protons can be determined by seeing whether the same or different structures would result, if some group X were substituted for one of protons.
- If the protons are chemically equivalent → same product will be formed regardless of which protons is replaced, if the protons are chemically non equivalent → different product.
- e.g. 2,3- dimethyl butene →
- all 12 protons are equivalent $(CH3)_2C = C(CH3)_2$ → 4 methyl are equivalent

e.g. 2- methyl ,2-butene → are not equivalent

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Number of Signals

- The number of NMR signals equals the number of different types of protons in a compound.
- Protons in different environments give different NMR signals.
- Equivalent protons give the same NMR signal.

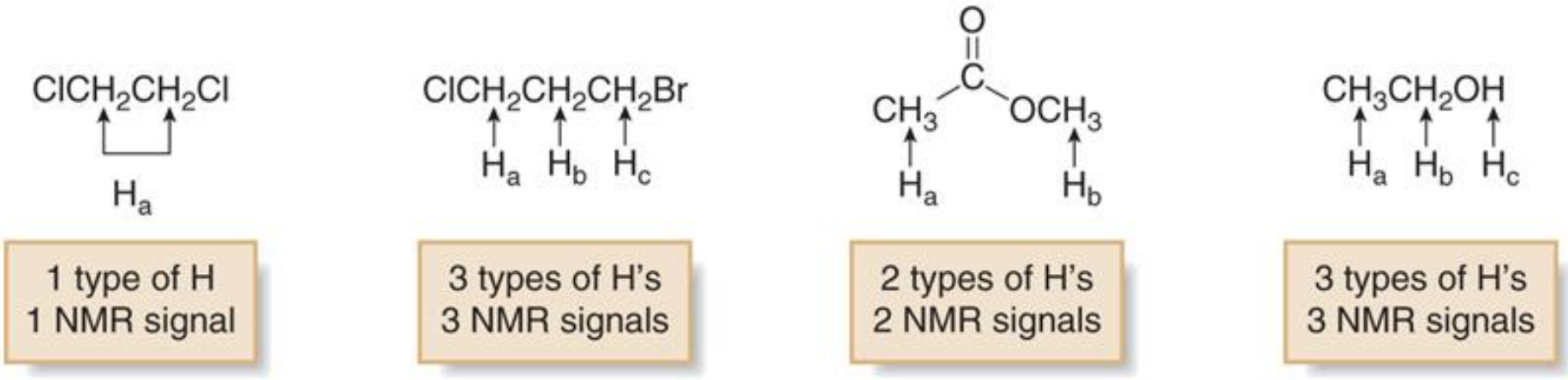


- To determine equivalent protons in cycloalkanes and alkenes, always draw all bonds to hydrogen.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Number of Signals

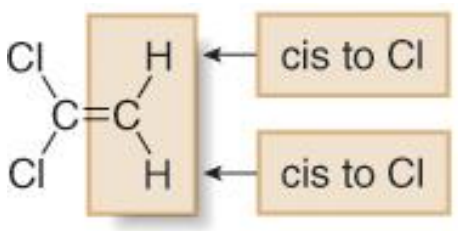
Figure 14.2
The number of ^{1}H NMR signals of some representative organic compounds



Nuclear Magnetic Resonance Spectroscopy

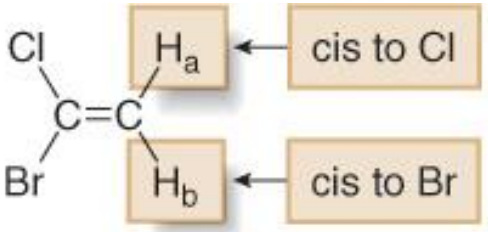
^{1}H NMR—Number of Signals

- **In comparing two H atoms on a ring or double bond, two protons are equivalent only if they are cis (or trans) to the same groups.**



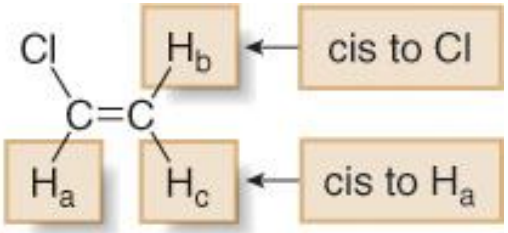
1,1-dichloroethylene

1 type of H
1 NMR signal



1-bromo-1-chloroethylene

2 types of H's
2 NMR signals

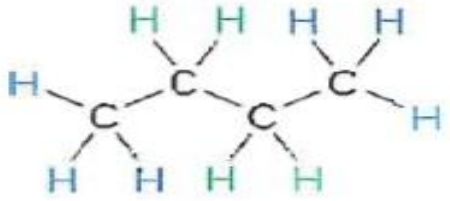


chloroethylene

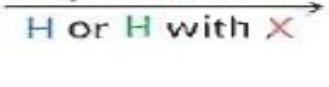
3 types of H's
3 NMR signals

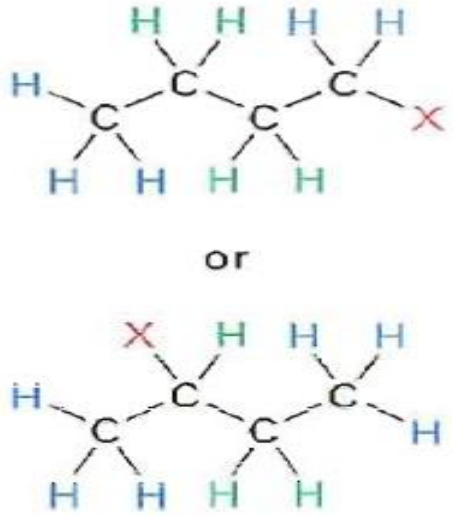
- To predict the number of signals, must determine how many sets of protons are in unique environments:

One possibility is that the protons are chemically unrelated and thus non-equivalent. If so, the products formed on replacement of H by X would be different constitutional isomers. In butane, for instance, the $-CH_3$ protons are



The $-CH_2-$ and $-CH_3$ hydrogens are unrelated and have different NMR absorptions.





The two replacement products are constitutional isomers.

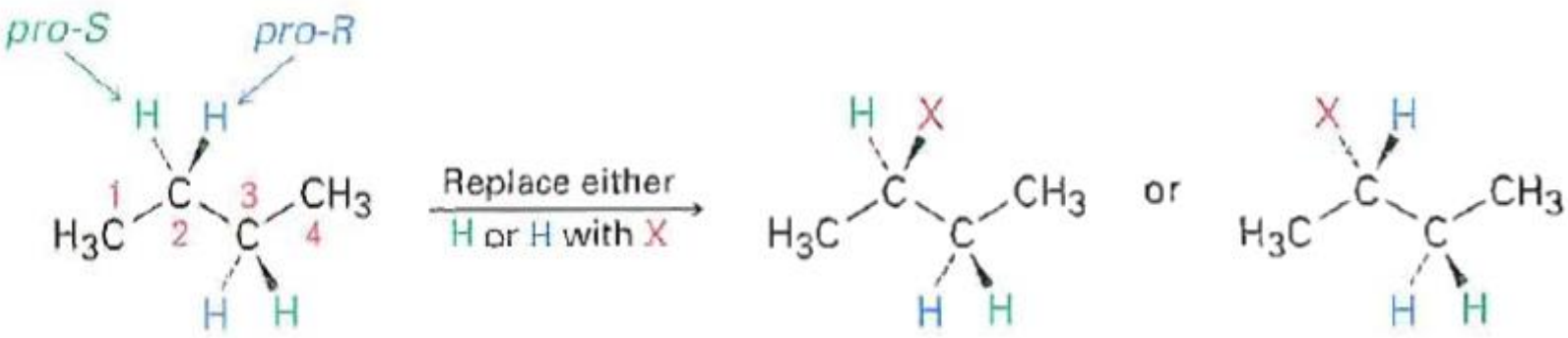
- 2. Homotopic Hydrogens (equivalent)
- Hydrogens are chemically equivalent or homotopic if replacing each in turn by the same group would lead to an identical compound.

The 6 $-CH_3$ hydrogens are *homotopic* and have the same NMR absorptions.

Only one replacement product is possible.

- # 3. EnantiotopicHydrogens

If replacement of each of two hydrogens by some group leads to enantiomers, those hydrogens are enantiotopic

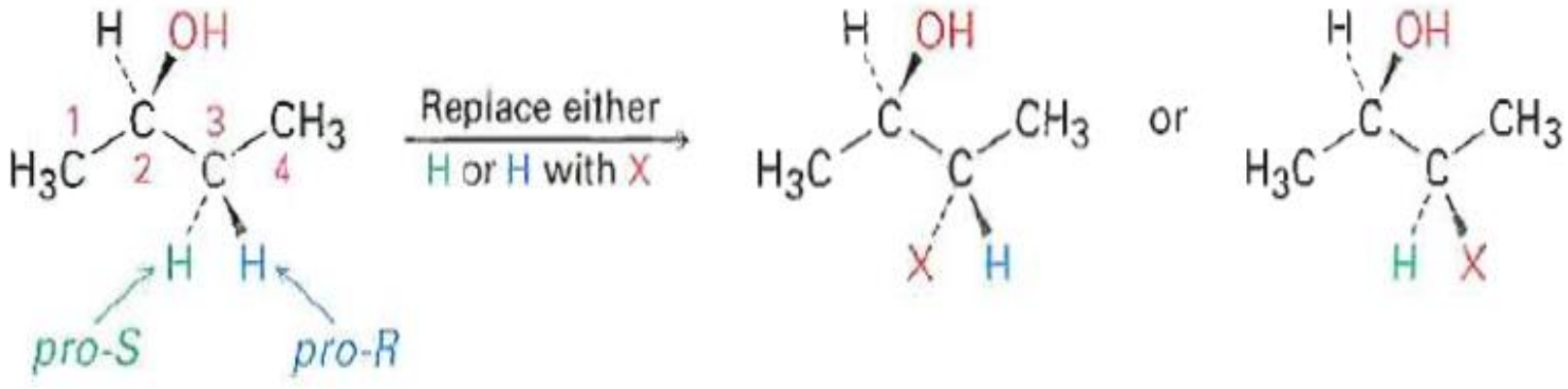


The two hydrogens on C2 (and the two hydrogens on C3) are *enantiotopic* and have the same NMR absorption.

The two possible replacement products are enantiomers.

- # 4. Diastereotopic Hydrogens

- **If replacement of each of two hydrogens by some group leads to diastereomers, the hydrogens are diastereotopic**
- **H Diastereotopic hydrogens have different chemical shifts and will give different signals**

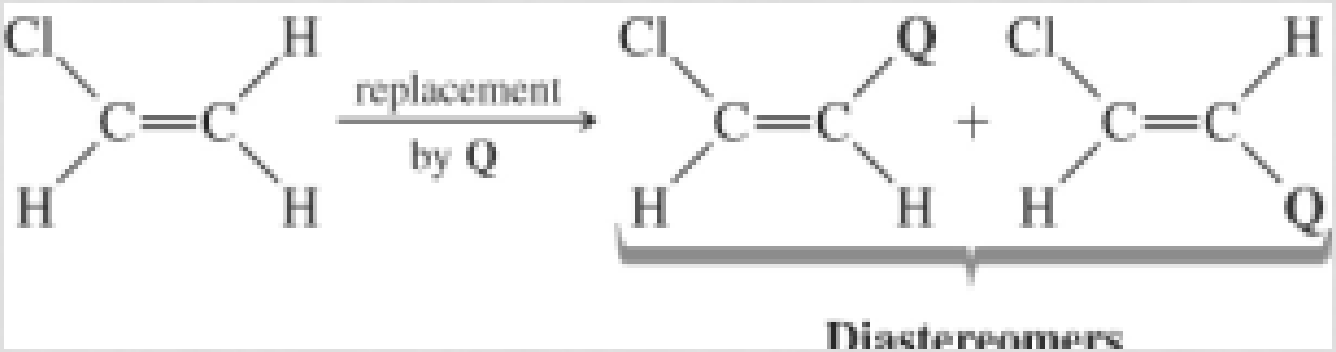


The two hydrogens on C3 are *diastereotopic* and have different NMR absorptions.

The two possible replacement products are diastereomers.

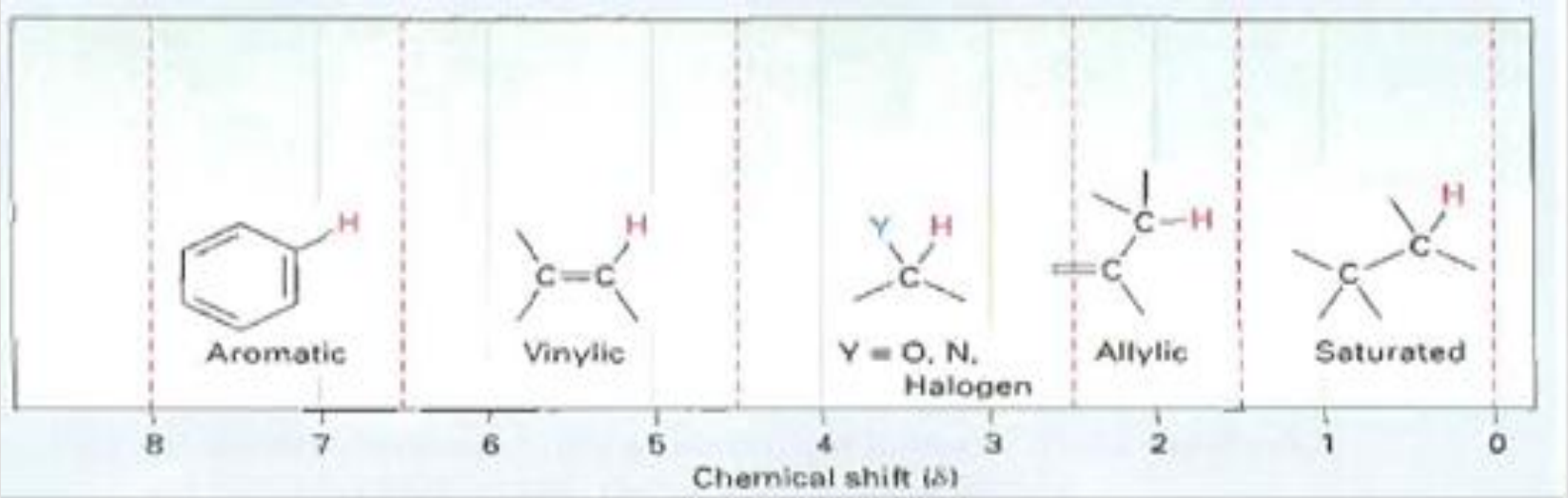
- The protons on a CH_2 group are usually diastereotopic if:

- On an unsymmetrical double bond
- t On opposite sides of a substituted ring
- t There is a chiral center in the molecule



- 2. the position of the signals (chemical shift in H-NMR Spectroscopy)

We said previously that differences in chemical shifts are caused by the small local magnetic fields of electrons surrounding the different nuclei. Nuclei that are more strongly shielded by electrons require a higher applied field to bring them into resonance and therefore absorb on the right side of the NMR chart. Nuclei that are less strongly shielded need a lower applied field for resonance and therefore absorb on the left of the NMR chart.



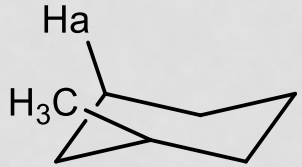
FACTORS EFFECTING CHEMICAL SHIFT:

1. inductive effect:

Table 13.3 shows the correlation of ^1H chemical shift with electronic environment in more detail. In general, protons bonded to saturated, sp^3-hybridized carbons absorb at higher fields, whereas protons bonded to sp^2-hybridized carbons absorb at lower fields. Protons on carbons that are bonded to electronegative atoms, such as N, O, or halogen, also absorb at lower fields.

2. anisotropic effect

3. vanderwaals deshielding: proton (a) is not effected by proton (b), but if we substituted proton (b) by CH3 → repulsive because of steric effect with the proton (a) → deshielding → down field.



- 4. Hydrogen bonding:

They cause decrease the density around the hydrogen → deshielded by inductive effect.

The intensity of intermolecular hydrogen bonding depending on:

- The concentration: increase concentration → increase H-bonding → increase deshielding.
- The temperature: increase temperature → breakdown the H-bonding → high field.
- The purity.
- Polarity of the solvent: the solvent should be deuterated ($CDCl_3$) and also should not polar.

- Intramolecular H - bonds are less affected by their environment than are intermolecular H - bonds.