CHEM 222 section 01

LECTURE #06 Thurs., Sept.20, 2007

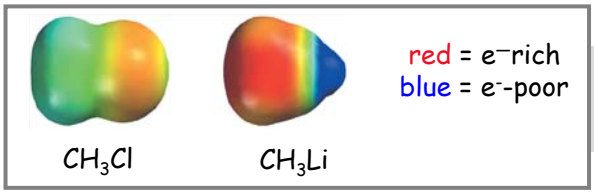
Lecture topics & readings

Today's class
- finish Ch.10: organometallics
- start Ch.12: UV/Vis spectrometry

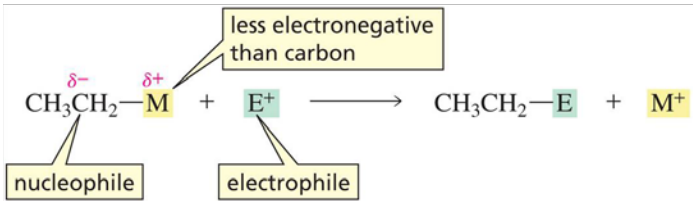
Before next class
- **practice** Ch.10 problems
- read

Next class
- finish UV/Vis & move on to IR spectrometry…

10.12-10.13 Organometallic compounds



Opposite to the usual polarity: $\delta-$ C



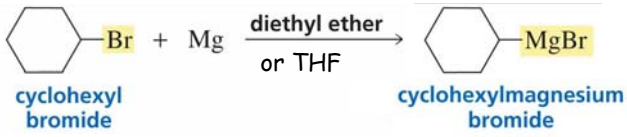
Common organometallic reagents:
- organomagnesium " Grignard" reagents: RMgBr } 10.12
- organolithium reagents: RLi } 10.12
- organocuprate "Gilman" reagents: RCuLi } 10.13

RMgBr & RLi reagents prepared via complex redox reactions

(don't need to know mechanisms for reactions on this slide)

Grignard reagents:

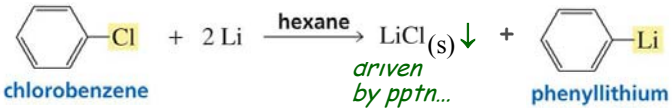
- In lab: add alkyl halide to Mg shavings in **anhydrous ether** solvent



…reacts as if it were

Organolithium reagents:

- In lab: add alkyl halide to Li dust in **anhydrous hydrocarbon** solvent



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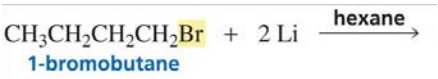

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RMgBr & RLi can <u>both</u> be prepared at sp^3 & sp^2 sites

Organometallics: "R^-" very useful for making C-C bonds

R^- = STRONG bases

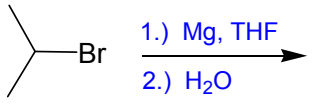
- pK_a of alkanes ~50
- can deprotonate almost anything…

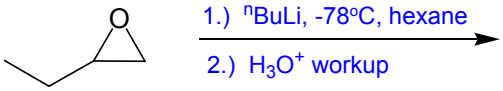
⇨ **Very strong Nu's: good for S_N of LGs**

- Plan carefully:
  1) Substrate: don't want to deprotonate
     - not alcohols …pK_a = ____ ?
     - not amines …pK_a = ____ ?
  2) Conditions:
     - solvent: anhydrous HC or ether
     - temperature: low ⇨ avoid E rxns

What should be the major product of … ?

if water gets into your rxn mixture…





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Organocuprate (Gilman) reagents (don't need to know mechanism for prep rxn)

Transmetallation rxns *aka* metal-exchange:

R-MgBr
R-Li + MX_n

R will exchange metal ions
if new M is more electronegative, *i.e.*, M_{Tr} …
⇨ new M-C bond less polar, less reactive

Preparing an organocuprate (Gilman reagent): R-Li + CuI

$$2\ CH_3Li + CuI \xrightarrow[\text{or anhydrous diethyl ether}]{\text{THF}} (CH_3)_2CuLi + LiI$$

organolithium reagent — Gilman reagent — *driven by pptn… highly insoluble.*

Using organocuprates: coupling R-Xs → more complex alkanes

$$R\text{–}X \xrightarrow[\text{hexane}]{\text{Li}} \xrightarrow[\text{THF}]{\text{CuI}} \xrightarrow{R'\text{-}X} R\text{–}R'$$

Why is this useful?

- one of Gilman reagent's R groups (both same) replaces 2nd halide's X
- works with any alkyl halides, except fluorides
- goes via a poorly understood - radical? - mechanism
  - works where S_N rxns would not work ⇨ **can "attack" sp^2 C's!**

Example:

CHARACTERIZATION METHODS - PART I
Ch.12: MS, IR spectroscopy & UV/Vis spectroscopy

Chapter Goals & hints

Learn some common tools used to elucidate structures of molecules.

- Learn the basic theory behind how spectroscopic instruments work.
- Learn to identify key spectroscopic signatures of functional groups & other structural information.

Topics Outline: *because of labs, order will not match syllabus / textbook…*

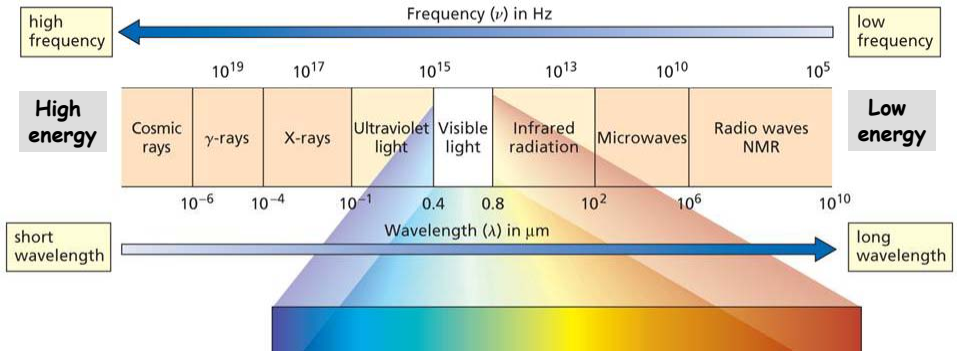
12.1-5 Mass spectrometry
Fragmentation, Isotopes, Molecular formulae, Functional groups

12.6 Spectroscopy & the electromagnetic spectrum

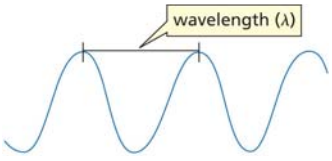
12.7-15 Infrared spectroscopy
Characteristic absorption bands due to functional groups
Absorption band intensity, position, shape, absence
Effects of resonance, EDGs, EWGs, H-bonding
Interpreting IR spectra

12.16-20 Ultraviolet/Visible spectroscopy
Beer-Lambert law, Effect of conjugation, Understanding colour
Common uses of UV/Vis spectroscopy

12.6 Spectroscopy & the electromagnetic spectrum



$$\nu = \frac{c}{\lambda}$$

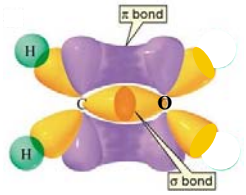


$$E = \frac{hc}{\lambda}$$

Spectroscopy
= the study of the interaction of matter & electromagnetic radiation

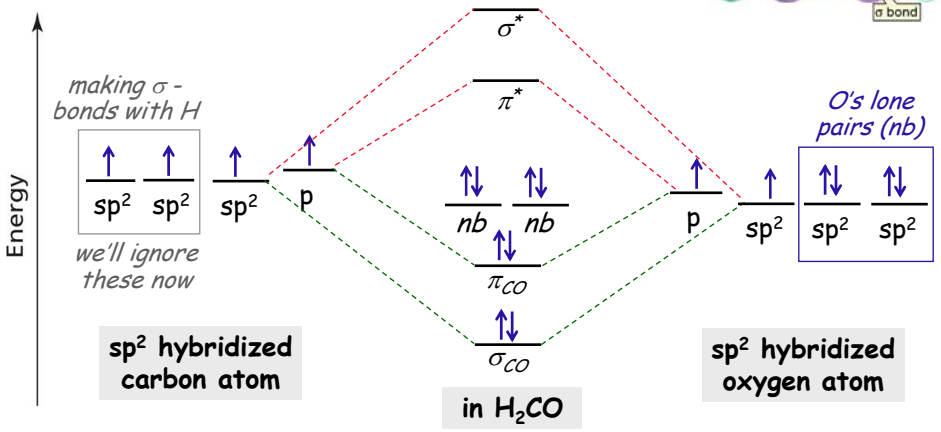
Review of molecular orbital theory (Ch.1)

FORMALDEHYDE



Overlap of atomic orbitals:

- Constructive (in-phase) ⇨ BONDING M.O.
- Destructive (out-of-phase) ⇨ ANTIBONDING M.O.

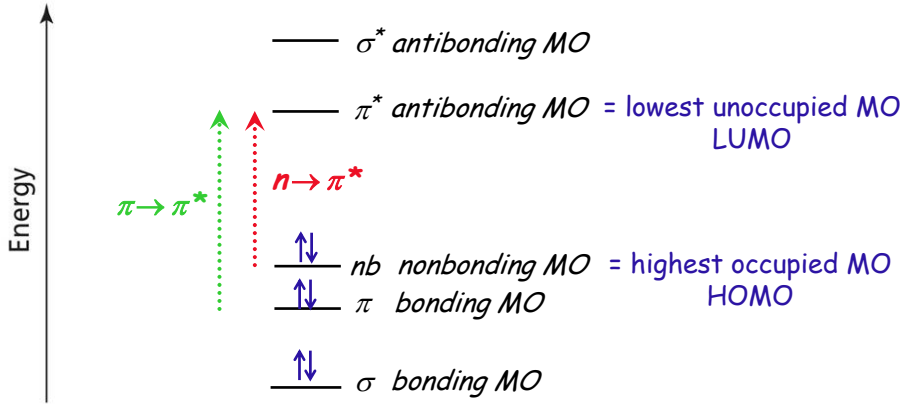


...in its GROUND STATE: e⁻s in lowest E orbitals possible

12.16 UV/Visible spectroscopy: excite molecules with light...

Absorption of UV/visible light:

- promoting an e⁻ to a higher energy level: $E_{photon} = \Delta E_{energy\ levels}$
  - UV & visible photons ⇨ sufficient E for 2 types of e⁻ transition
    ⇨ **in organic molecules with π-electrons**

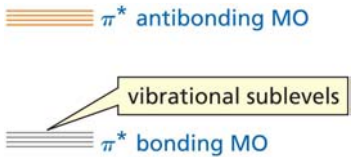


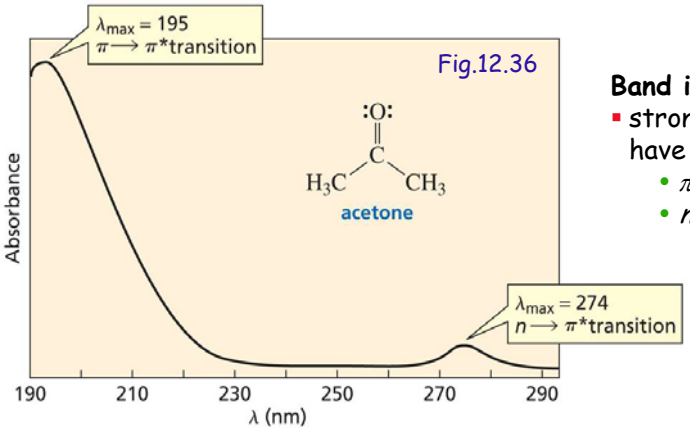
Excited molecule: relaxes (loses E) via vibrations, rotations, *etc.*

Instrument (spectrometer) measures a spectrum = How much light is absorbed at each wavelength

For molecules:

- See absorbance BANDS, not discrete line spectra

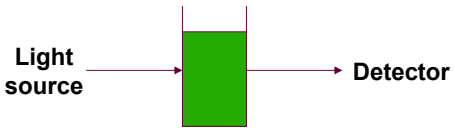


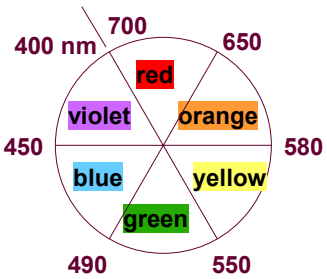


Band intensities:

- stronger if orbitals have same symmetry
  - $\pi \rightarrow \pi^*$ intense
  - $n \rightarrow \pi^*$ weaker

Absorption of visible light causes "colour"





To use colour wheel:

Find colour / wavelengths absorbed

⇨ cross pie to find colour observed

Same info: Table 12.7

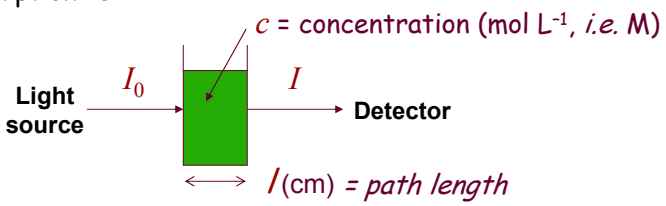
Wavelengths absorbed (nm)	Color absorbed	Color observed
380–460	blue-violet	yellow
380–500	blue	orange
440–560	blue-green	red
480–610	green	purple
540–650	orange	blue
380–420 and 610–700	purple	green

Example:

- *phenolate ion* λ_{max} = 287 nm

(12.17) Higher concentration ⇨ stronger absorbance

Intensity of absorption: I

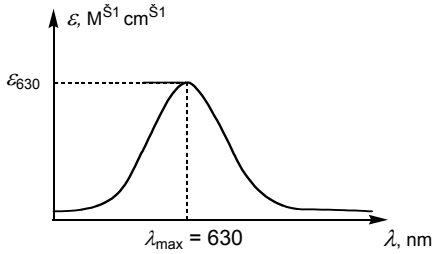


The Beer-Lambert law:

$$\log (I_o / I) = A = \varepsilon c l$$

ε = extinction coefficient ($M^{-1}cm^{-1}$)
aka molar absorptivity
characteristic of compound

A = absorbance = *the measurable*
depends on sample concentration
cell path…



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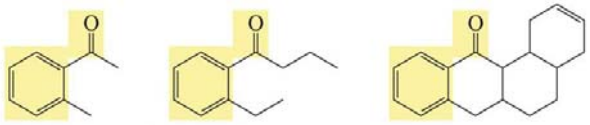
Trends in UV/Vis spectra

Organic molecules: π-e⁻ required in order to absorb UV/Vis light…

- Chromophore = part of molecule responsible for light absorption

Same chromophore
⇨ very similar λ_{max}



- Extended π-systems (aligned p-orbitals) ⇨ Lower E transitions ⇨ Longer λs absorbed

Example:

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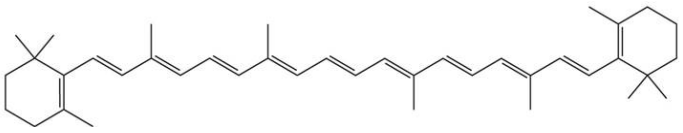
Effects of conjugation (extended π-systems)

Table 12.6

Ethylene *vs.* conjugated polyenes

Compound	λ_{max} (nm)	$\varepsilon(M^{-1}\,cm^{-1})$
$H_2C{=}CH_2$	165	15,000
	217	21,000
	256	50,000
	290	85,000
	334	125,000

β-carotene
λ_{max} = 455 nm



lycopene
λ_{max} = 474 nm