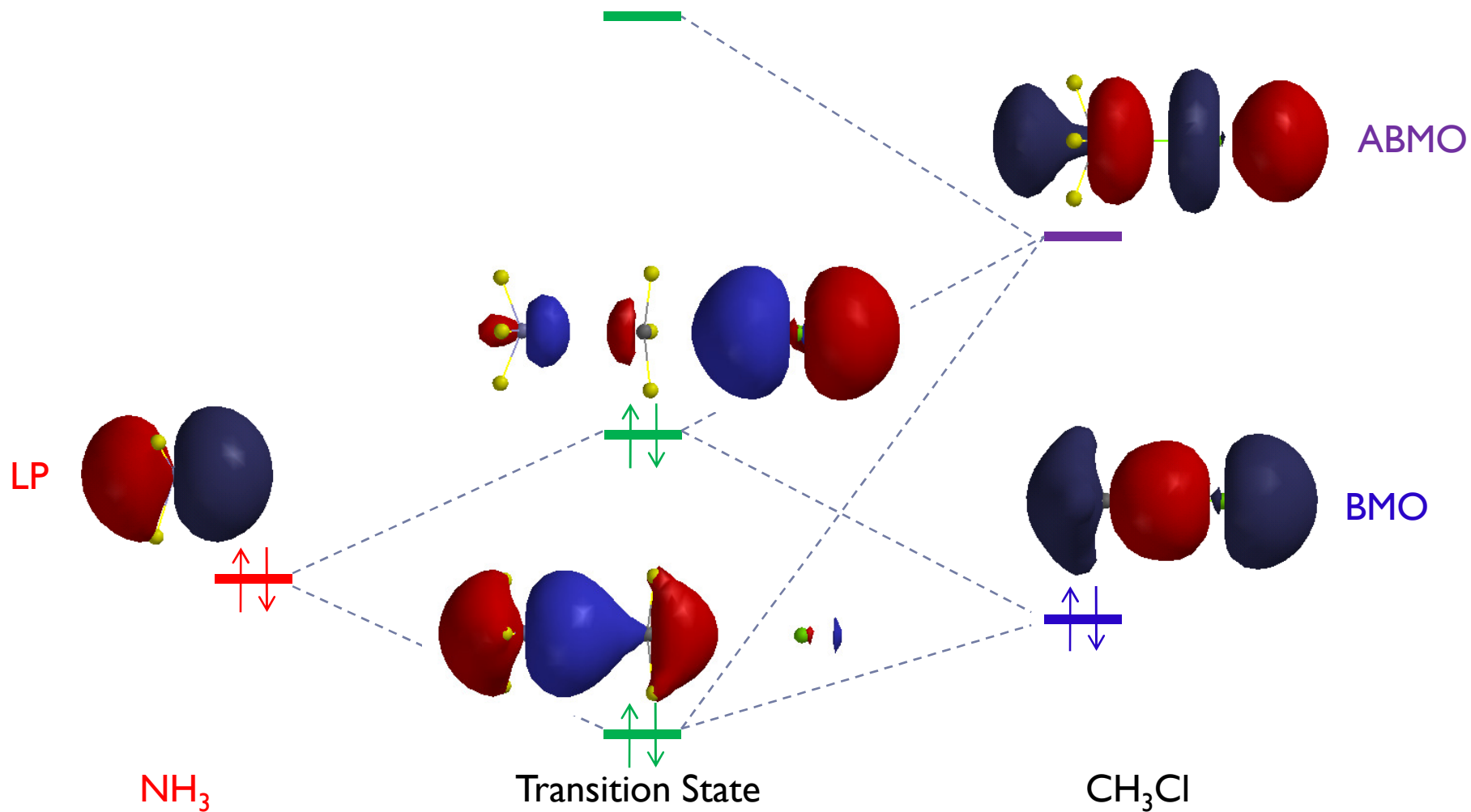


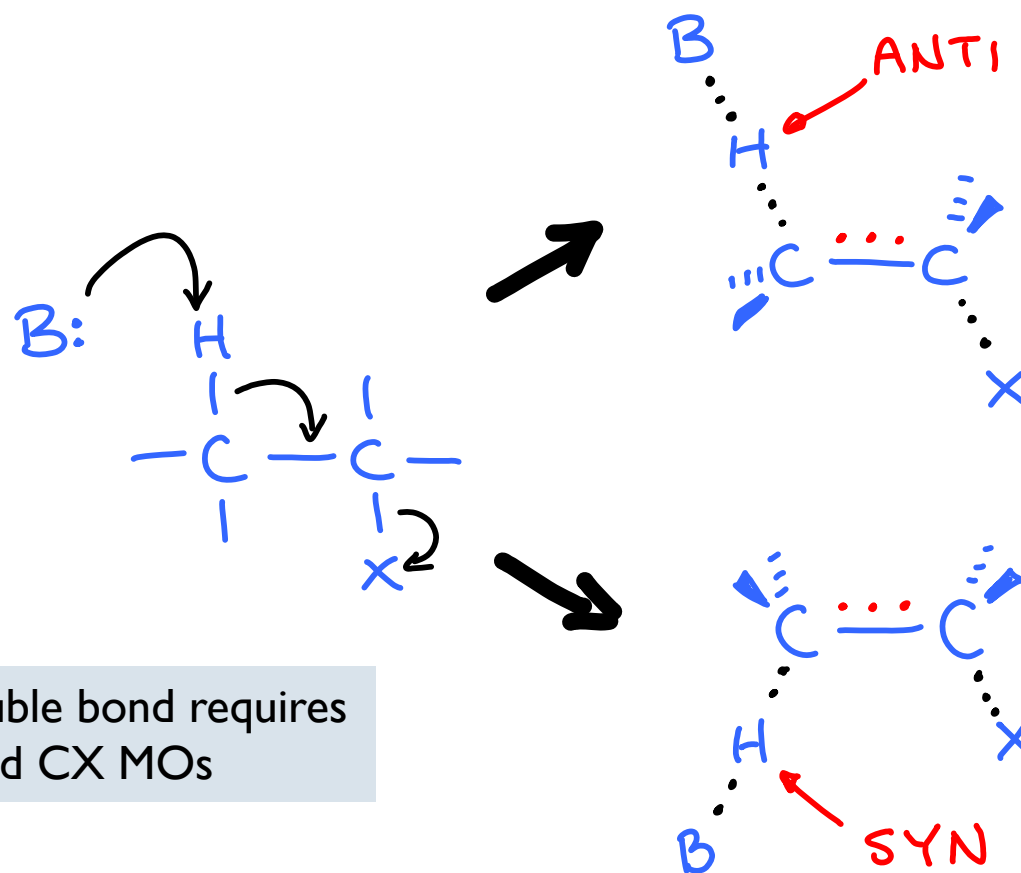
Class #25, W, Nov 3, 2010

Stereoelectronics wrap-up, Electron-donating groups

Delocalized bonds require delocalized MOs

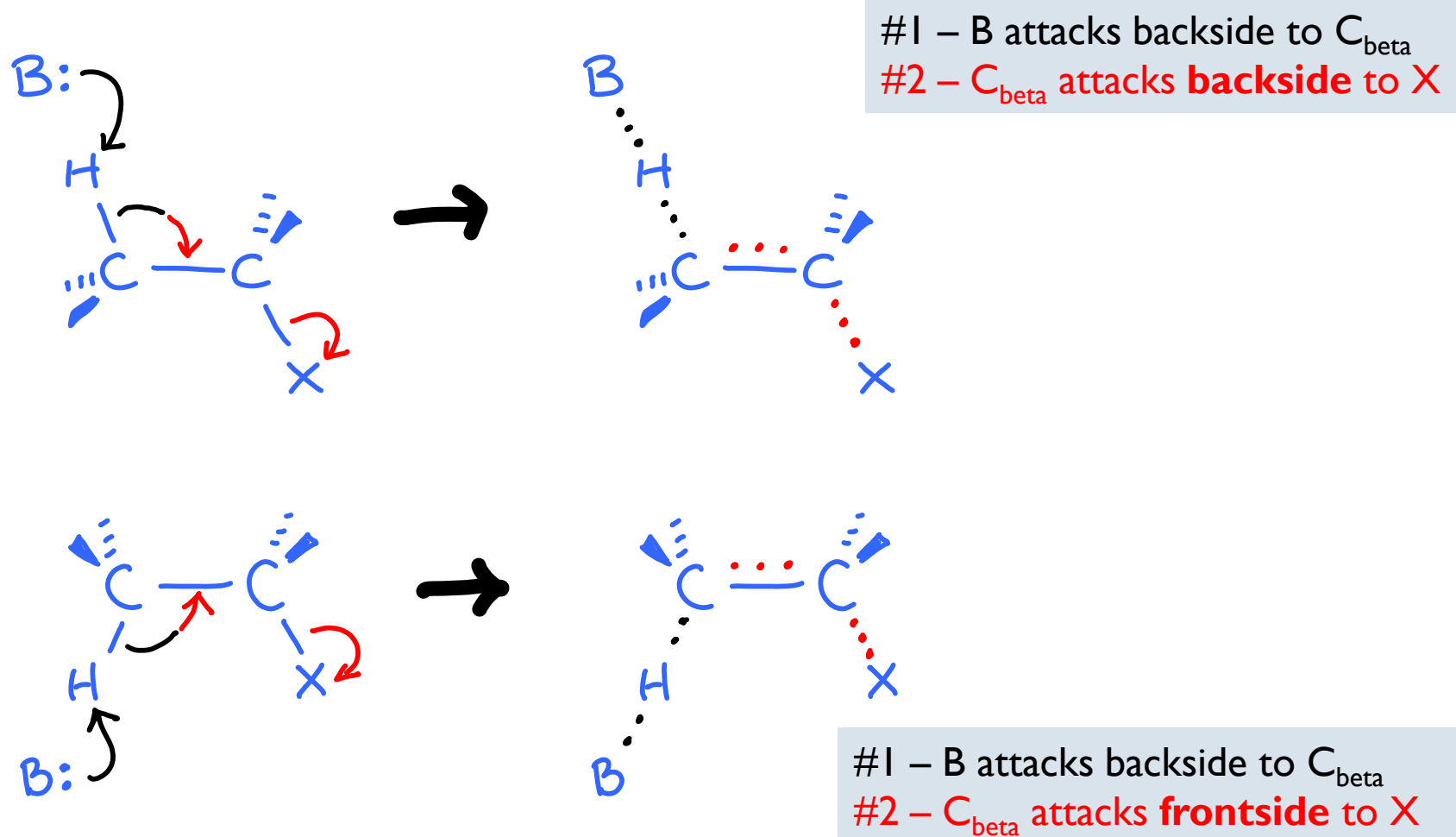


E2 Stereochemistry



Formation of CC double bond requires **PI overlap** of CH and CX MOs

Treat 3 electron pairs as TWO electron pair displacements

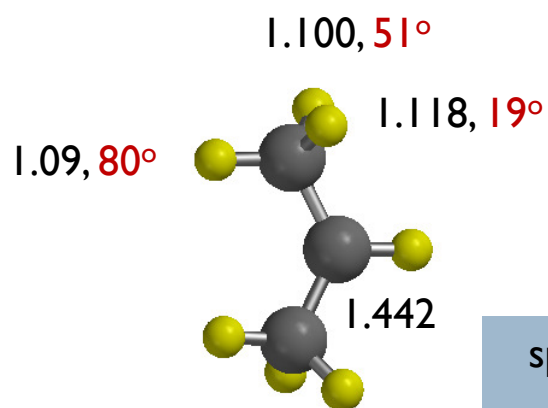


Alkyl groups stabilize carbocations (C⁺)

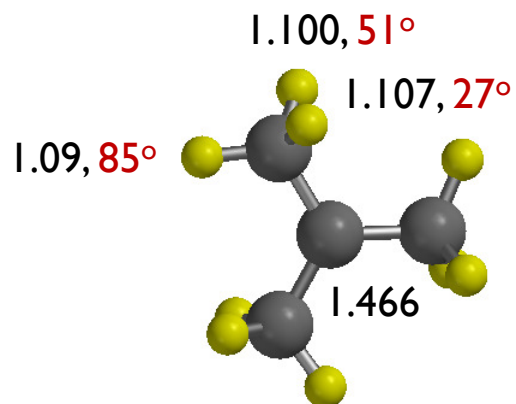
Ionization Rxn	ΔE_{aq} (kJ/mol)	ΔE_{gas} (kJ/mol)
$\text{H}_3\text{C}\text{Cl} \rightarrow \text{H}_3\text{C}^+ + \text{Cl}^-$	336	987
$\text{CH}_3\text{C}\text{H}_2\text{Cl} \rightarrow \text{CH}_3\text{C}^+\text{H}_2 + \text{Cl}^-$	220	824
$(\text{CH}_3)_2\text{C}\text{HCl} \rightarrow (\text{CH}_3)_2\text{C}^+\text{H} + \text{Cl}^-$	162	734
$(\text{CH}_3)_3\text{C}\text{Cl} \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{Cl}^-$	113	682

smaller range
same trend as gas

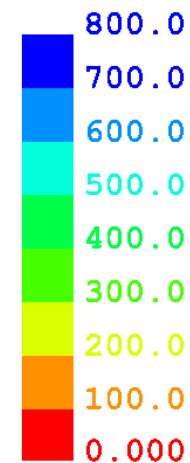
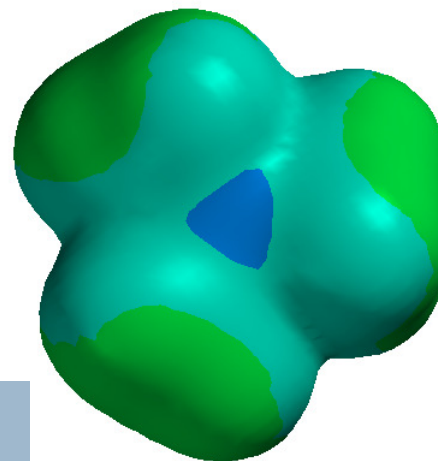
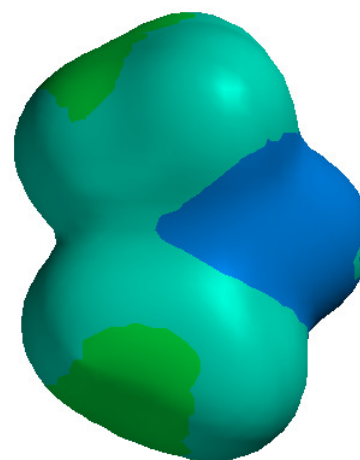
CH₃ is changed by bonding to C⁺



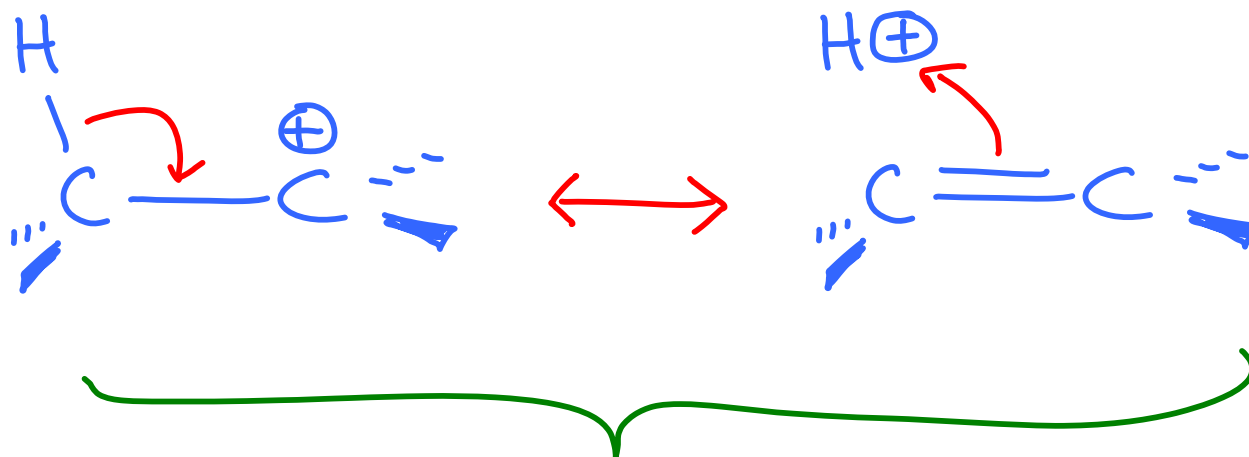
sp³-sp² CC usually 1.49
CC shortened
certain CH lengthened



CH₃ more e-rich
& C⁺ more e-rich too



Hyperconjugation

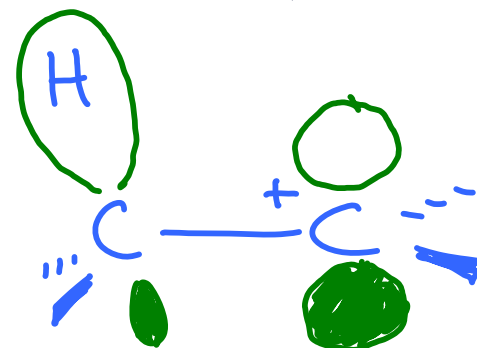
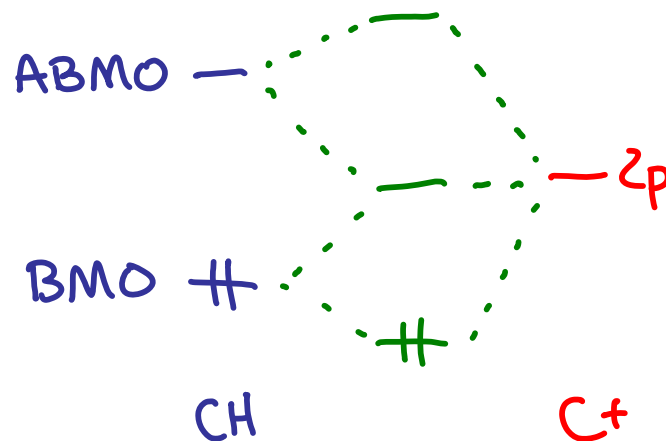
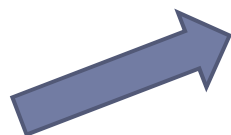
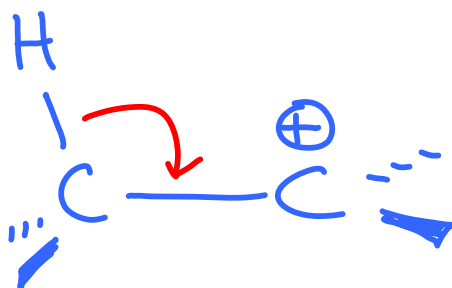


- longer C-H
 - H more acidic
 - shorter C-C
-
- A diagram showing partial charges (δ⁺) on the hydrogen and the carbocation center, with a dashed line representing the interaction between them. The C-H bond is shown as longer and the C-C bond as shorter.

Atoms don't move,
only electrons.

MO Model of Hyperconjugation

- ▶ Resonance hybrid – 3 atoms with partial bonds
 - ▶ S_N2 TS – 4 electrons
 - ▶ Hyperconjugation – 2 electrons



- CH BMO/ABMO
- C+ 2p AO

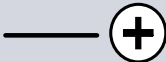
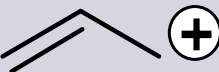

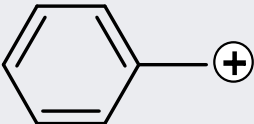
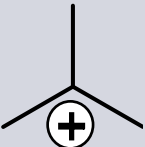
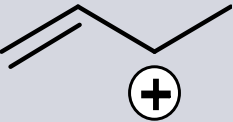
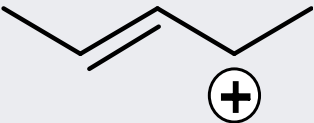
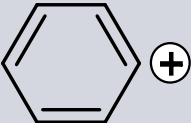
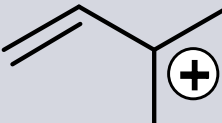
2 electrons delocalized over 3 atoms
 π overlap explains CH orientation

Take-home electron-sharing lessons

- ▶ Replacing *alpha* H with CH₃ makes RX → R⁺ X⁻ easier
 - ▶ **no rxn** H₃CX or RCH₂X
 - ▶ Only R₂CHX and R₃CX

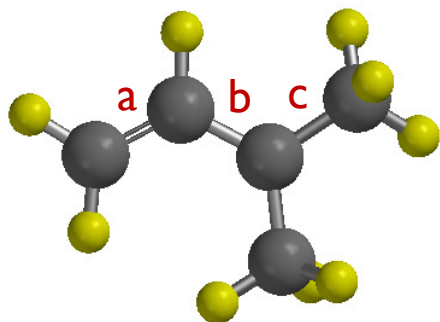
- ▶ Electron donation from R (hyperconjugation)
 - ▶ R₂CH⁺ – larger xfer from each R, but only two R
 - ▶ R₃C⁺ – smaller xfer from each R, but three R

1 “vinyl” \approx 2 “alkyl”

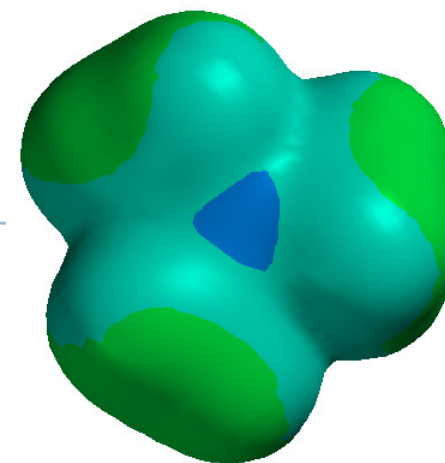
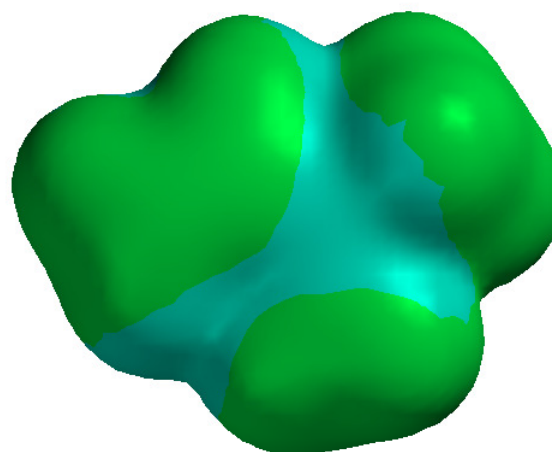
R+	ΔE (kJ/mol)	R+	ΔE (kJ/mol)
	220		155
	162		129
	113		107
			76
	330		79

What Do “Conjugated” Carbocations Look Like?

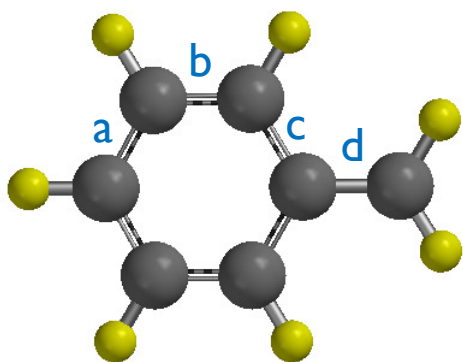
▶ 1,1-dimethylallyl



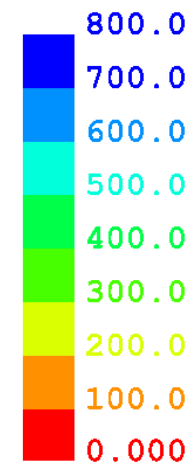
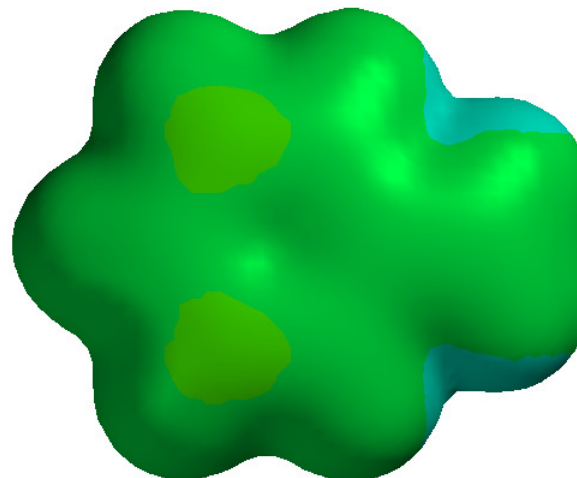
a 1.36
b 1.42
c 1.48



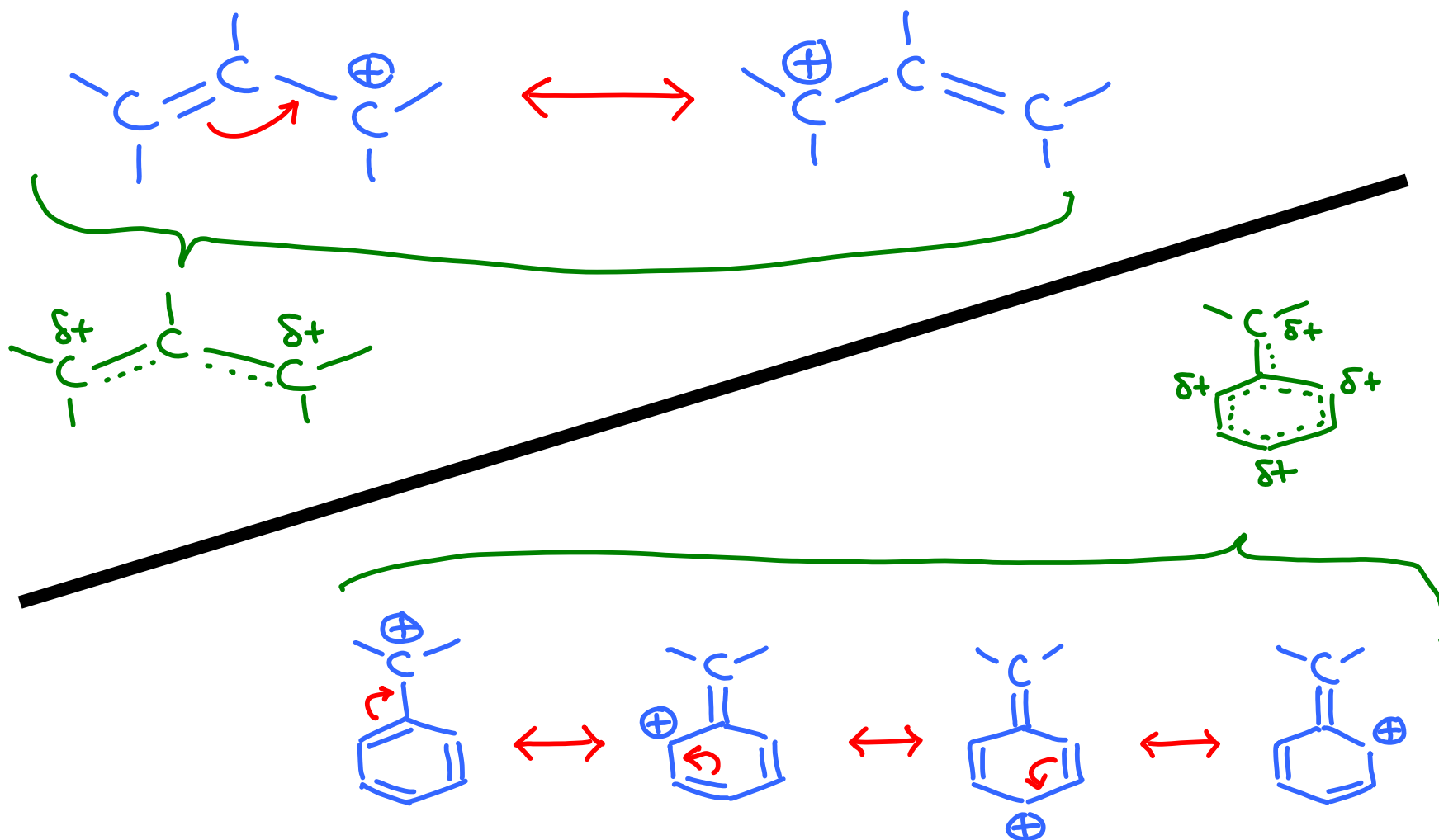
▶ Benzyl



a 1.41
b 1.38
c 1.44
d 1.37

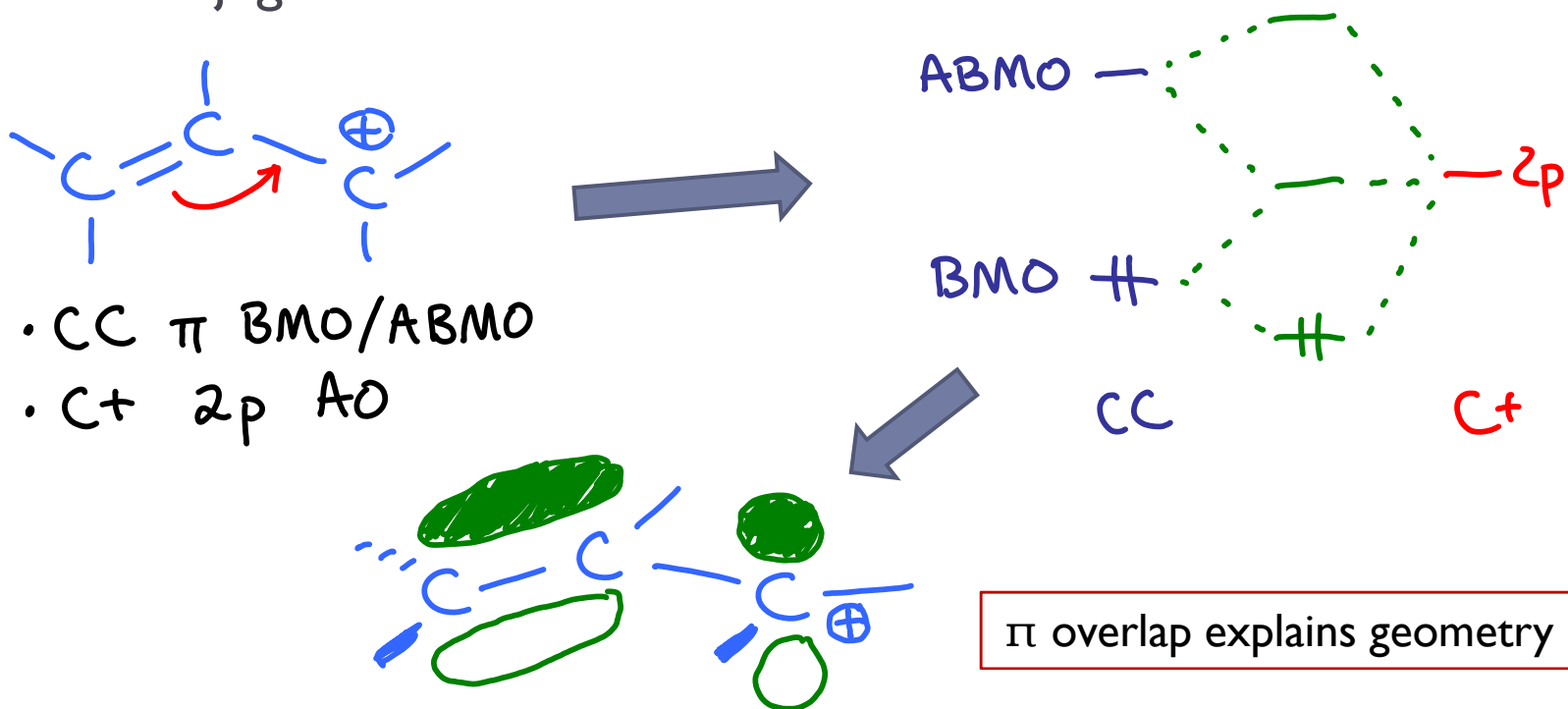


Conjugated Carbocations



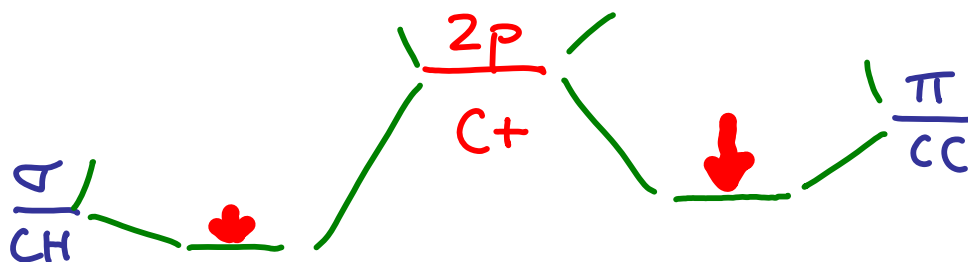
MO Model of Conjugation (Allyl Cation)

- ▶ Resonance hybrid – 3 atoms with partial bonds
 - ▶ S_N2 TS – 4 electrons
 - ▶ Hyperconjugation – 2 electrons from σ bond
 - ▶ Conjugation – 2 electrons from π bond



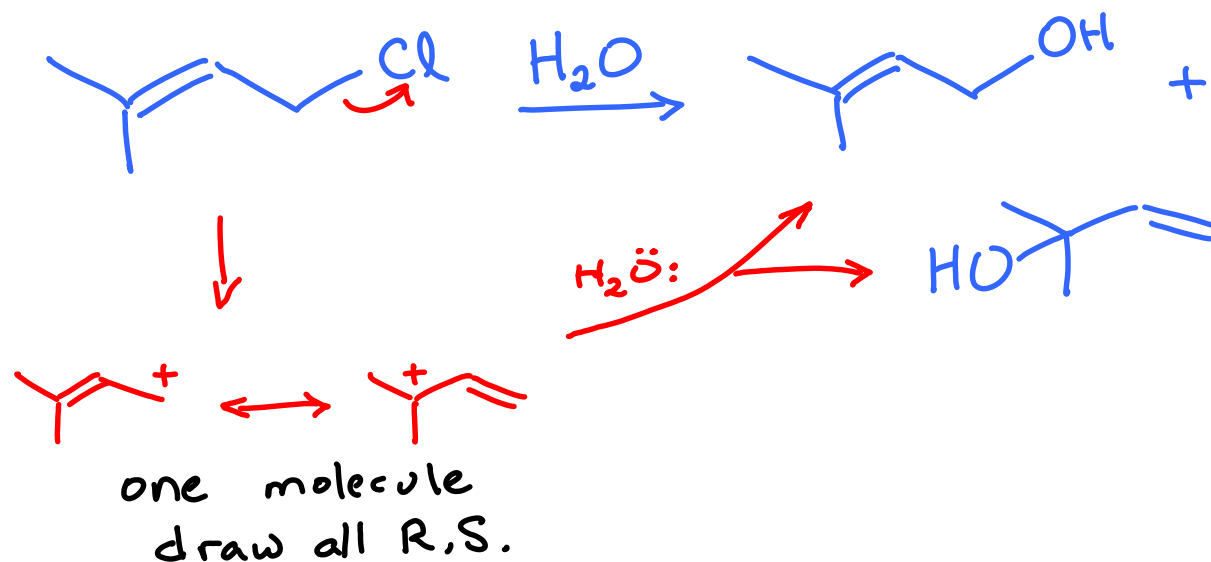
Take-home MO lessons

- ▶ Replacing *alpha* H with Z makes $RX \rightarrow R^+ X^-$ easier
 - ▶ Z = CH_3 or *alkyl* (hyperconjugation) **small** effect
 - ▶ Z = $C=C$ or *aryl* (conjugation) **large** effect
- ▶ Effect depends on orbital mixing
 - ▶ C+ 2p **closer in energy** to CC π MO than CH σ MO
 - ▶ C+ 2p **overlaps better with** CC π MO than CH σ MO

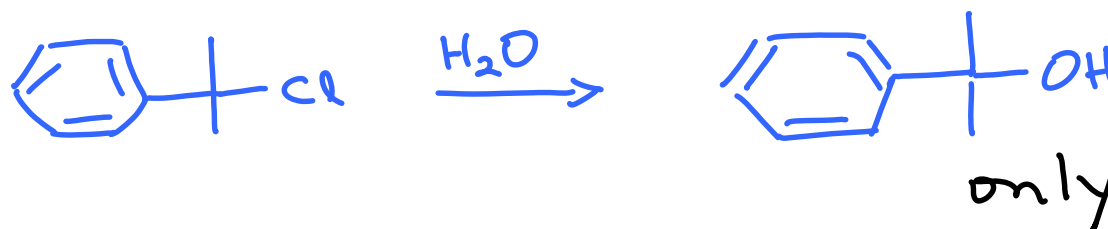


Chemical Rxns Involving Conjugated Carbocations Tend Towards S_N1 Pathway

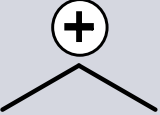
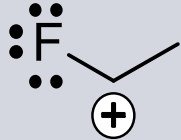
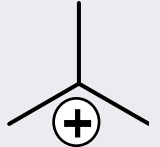
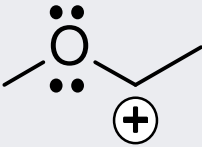
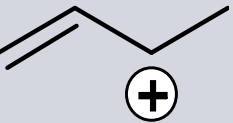
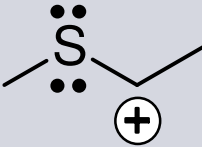
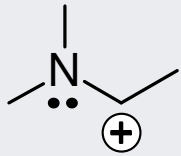
▶ Allyl inversion



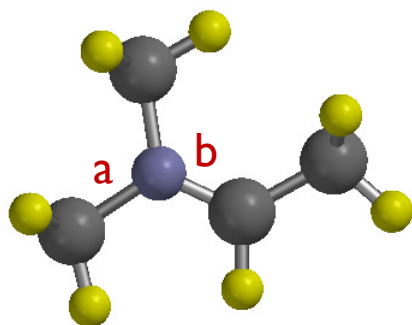
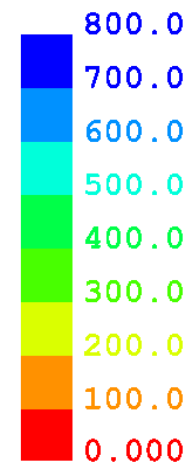
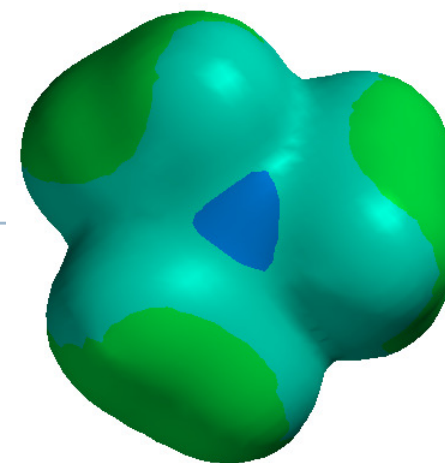
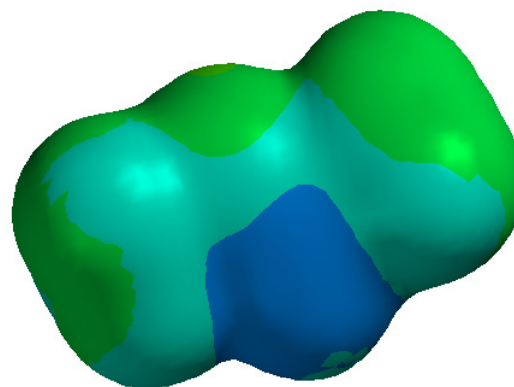
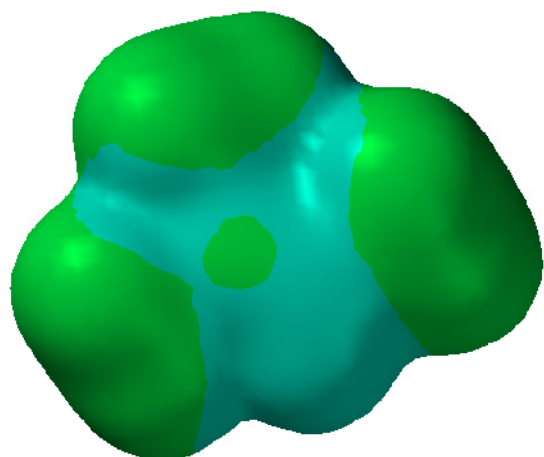
▶ Benzyl reactant → Benzyl product (preserve benzene)



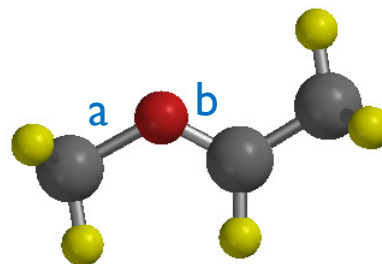
“Right” Heteroatom Better than “Vinyl”

R+	ΔE_{aq} (kJ/mol)	R+	ΔE_{aq} (kJ/mol)
	162		183
	113		77
	107		71
			-17

What Do Heteroatom-Substituted Carbocations Look Like?



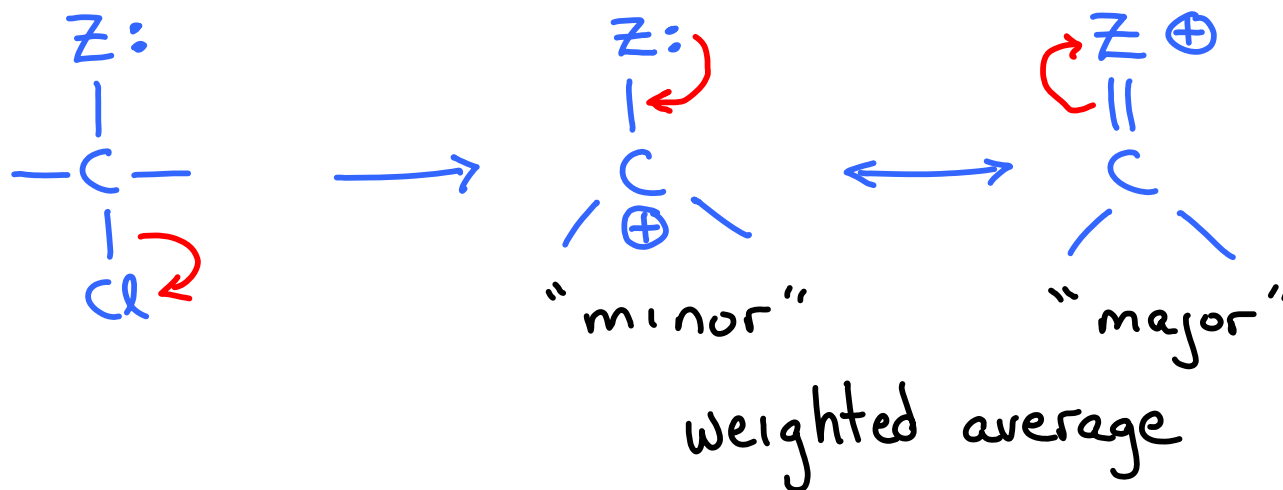
a 1.48
b 1.29



a 1.48
b 1.26

Electron-sharing in N/O/S-substituted C⁺

▶ Resonance



▶ MO

