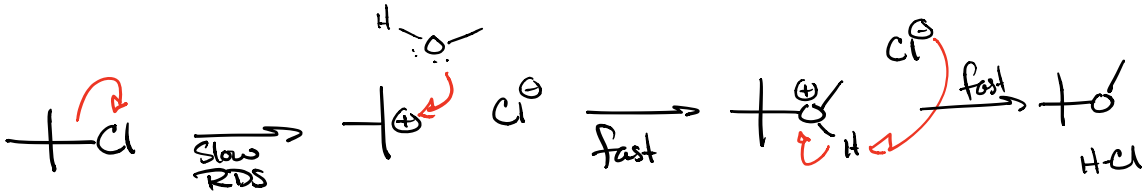
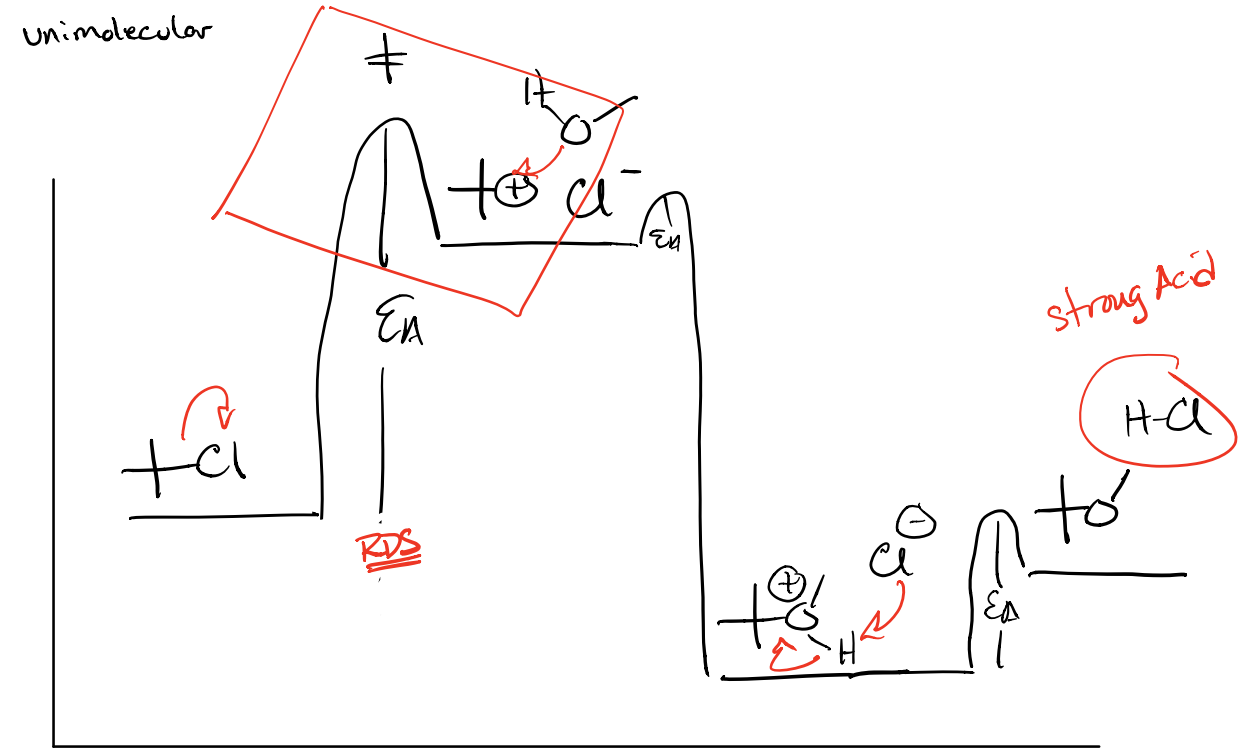
Solvolysis — Replacement of LG by solvent



Dissociation & Carbocation formation unimolecular

nucleophilic attack

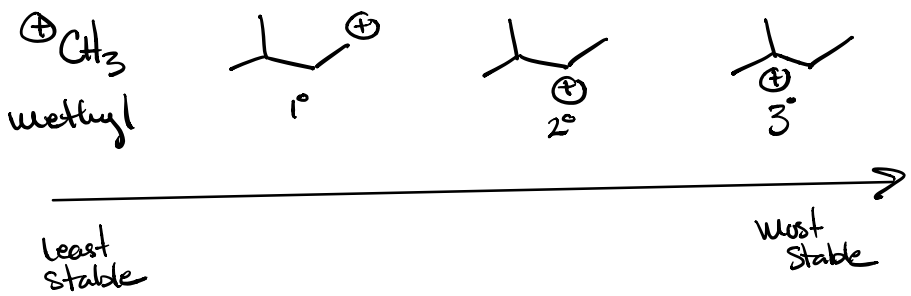
Proton transfer



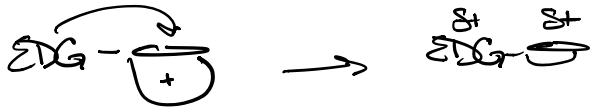
$\neq_{RDS}$ $\left[\; \overset{\delta+}{\text{---}} \cdots Cl^{\delta-} \; \right]^{\neq}$ Carbocation Like

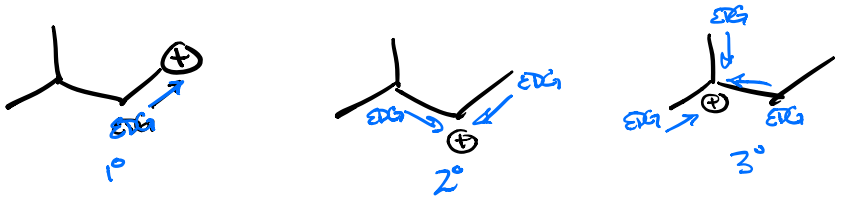
to understand S_N1 you must understand C^+

Carbocation Stability



Why? ⟹ Remember that alkyl group EDG?

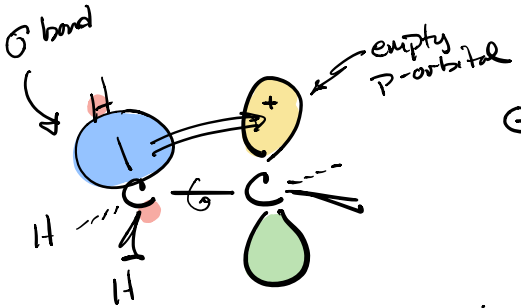




Why is an alky group EDG?

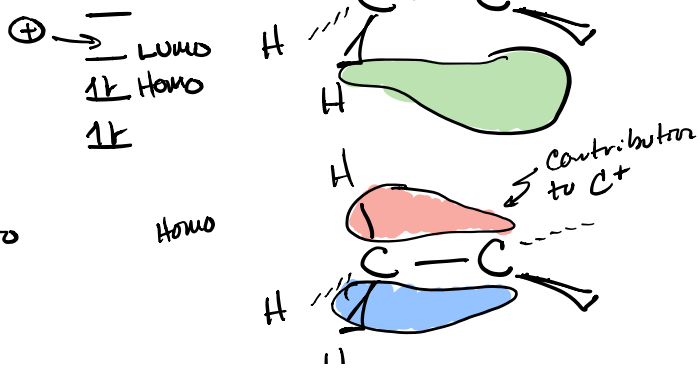
Induction

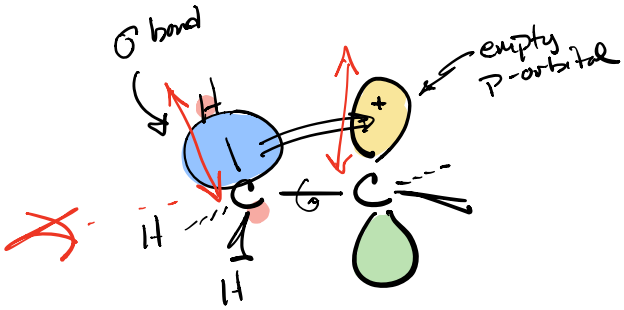
Hyperconjugation
(Natural bonding theory)
Localized bonds

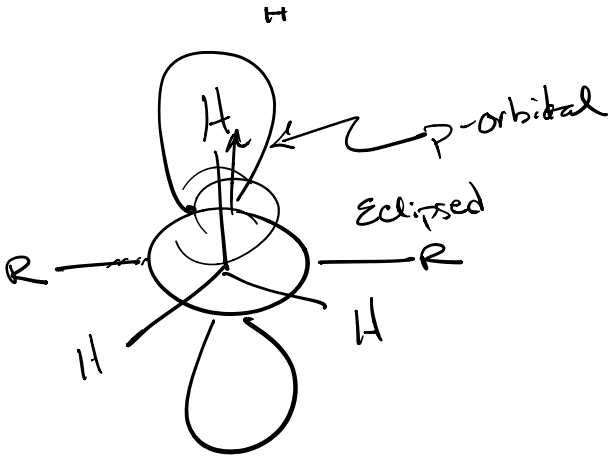


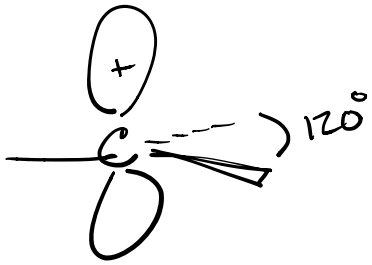
σ- dumps e⁻ density into empty p-orbital
Back bonding

Molecular Orbital Theory
Molecular Orbitals



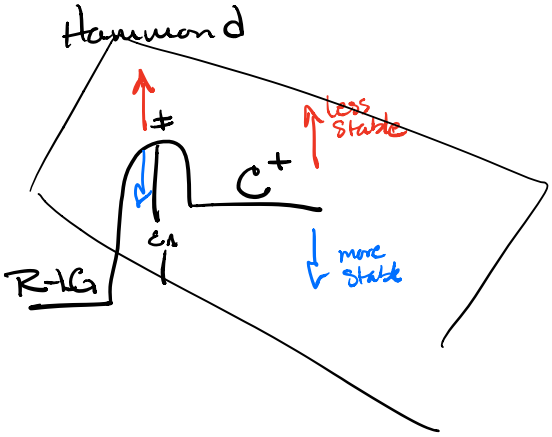






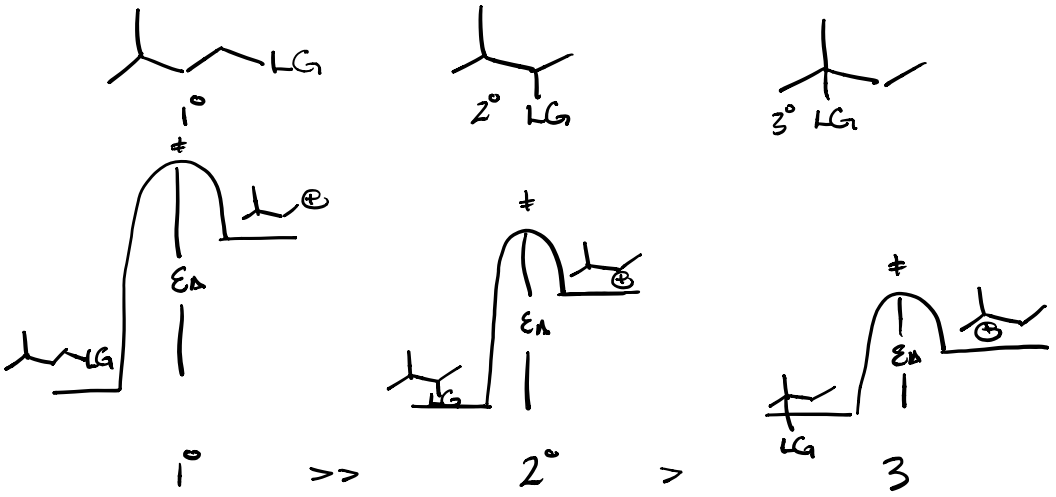
sp^2

Trigonal planar



≠ Energy is linked to C^+ energy

$\neq \propto C^+$



1° >> 2° > 3

$$\text{Rate} = k[\text{R-LG}]$$

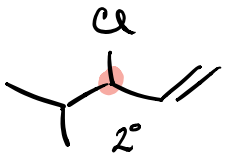
$$k \propto E_A$$

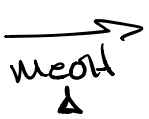
$$k = k_0 e^{-(\Delta G^{\ddagger}/RT)}$$

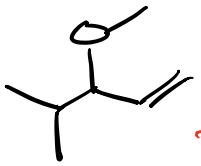
$$k = k_0 e^{-(E_A/RT)}$$

$\Delta G^{\ddagger} = E_A$

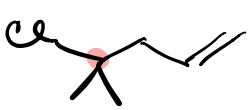
Which Rxn faster ?

A) 

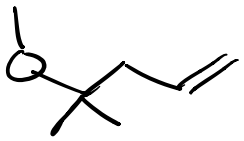




faster
Due to Resonance

B) 

3°

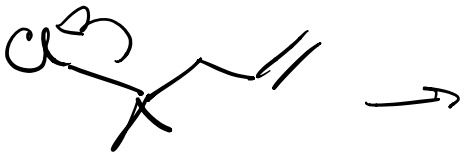
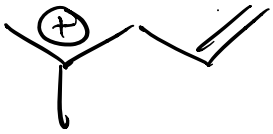



Don't look at Substrate ⇒ look at resulting C+

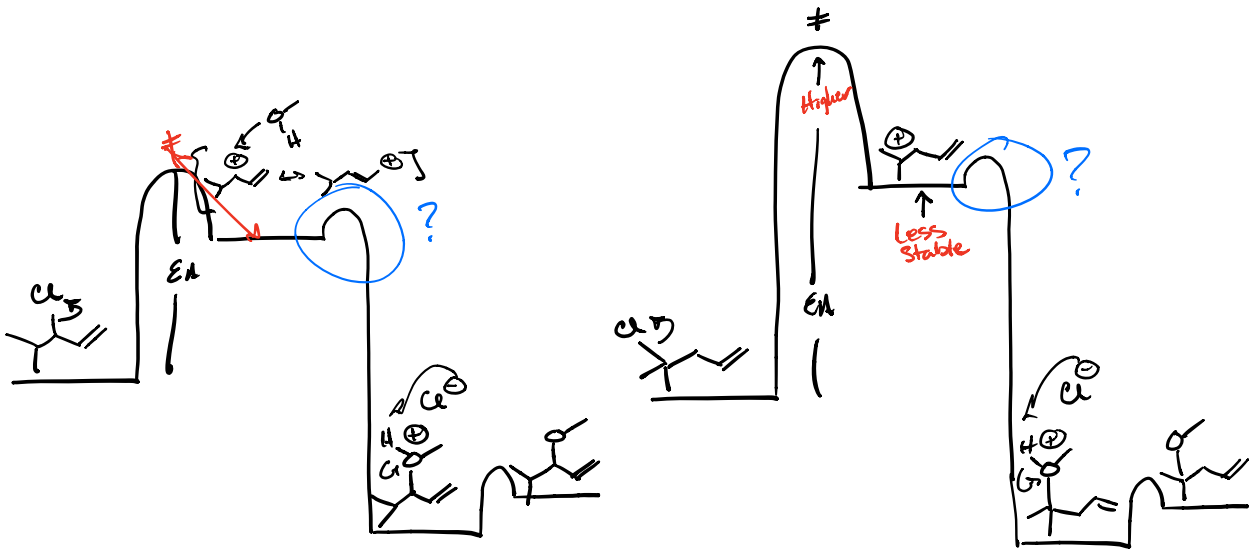
2° C+ ⇒ Allyl: C

faster

more stable C+ & EA for formation

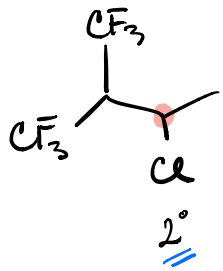



3° no Resonance



Which Rxn is faster?

A)

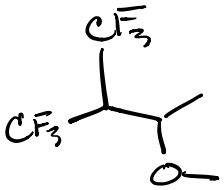


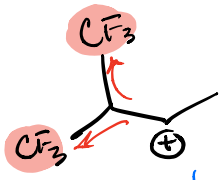
2°

Faster

MeOH

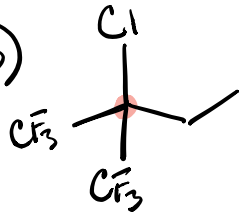
Δ





2° more stable farther from the EWG CF_3's
⇒ lower E_A
⇒ faster

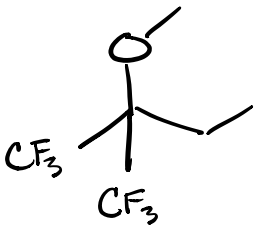
B)

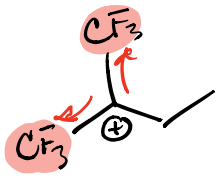


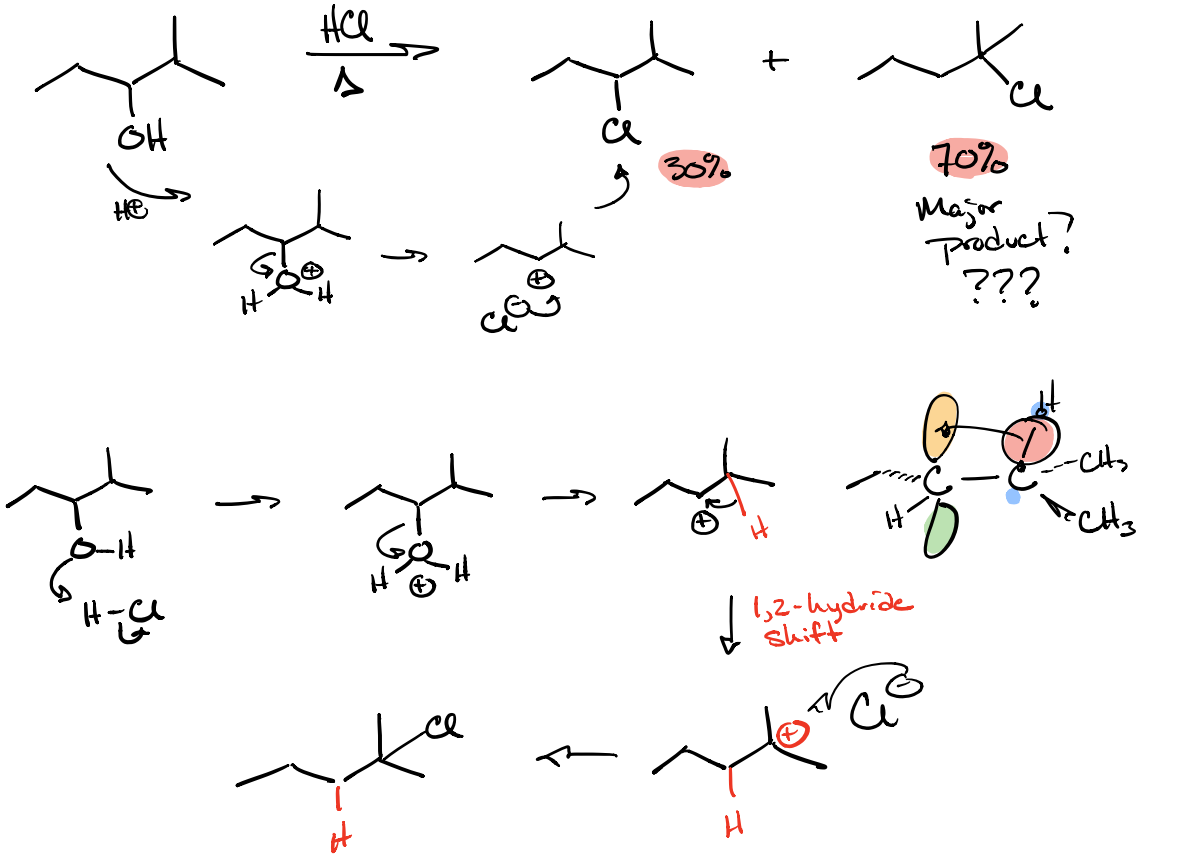
3°

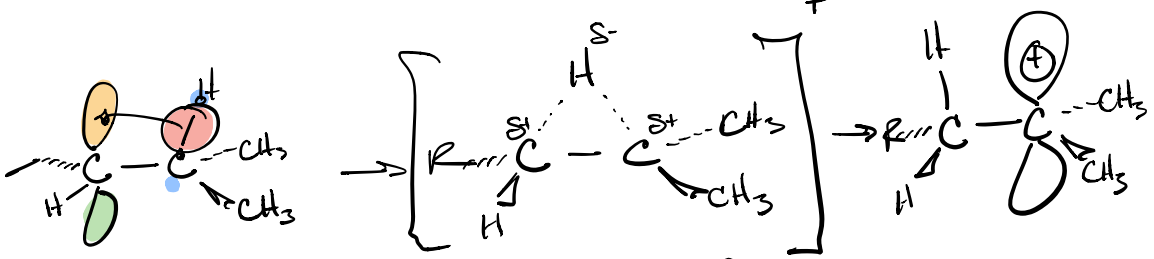
MeOH

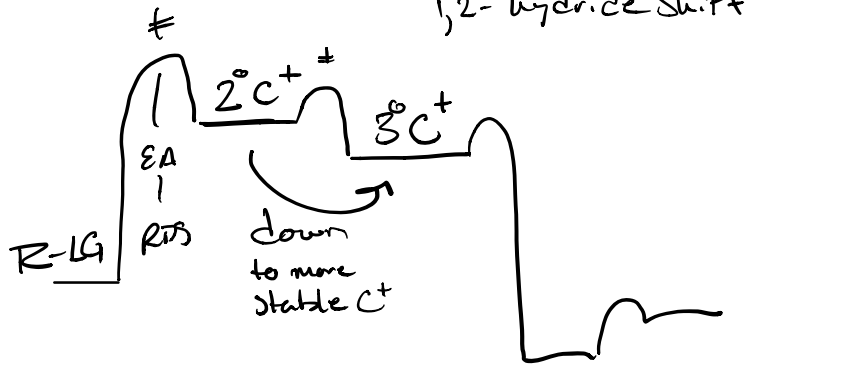
Δ

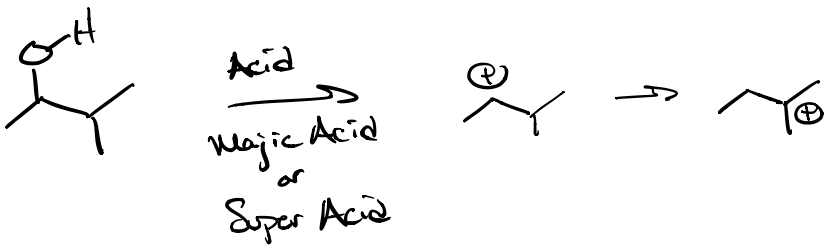




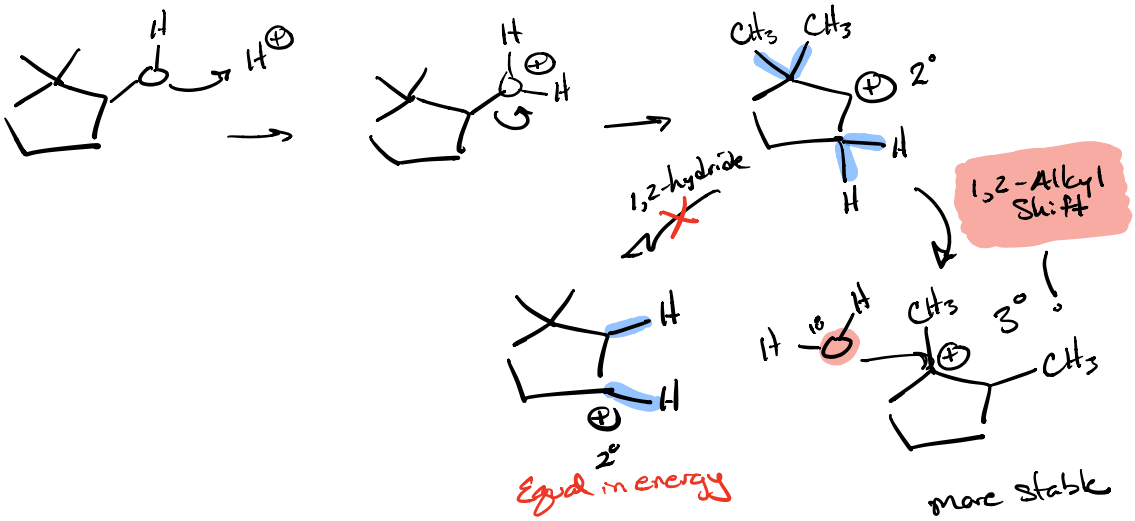

HCl
Δ
OH
H⊕
30%
70%
Major Product?
???
1,2-hydride shift

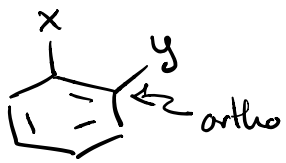

1,2-hydride Shift

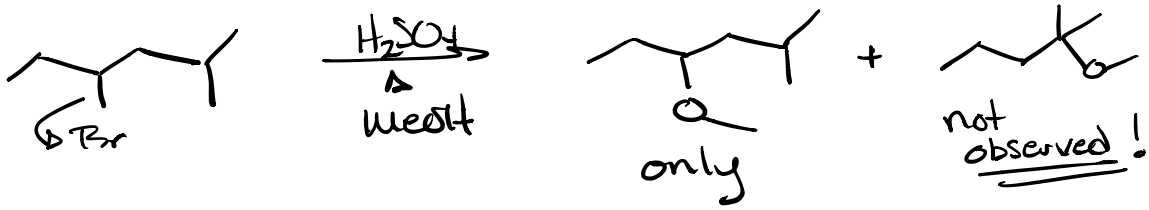

2° C+
3° C+
EA
RDS
R-LG
down to more stable C+

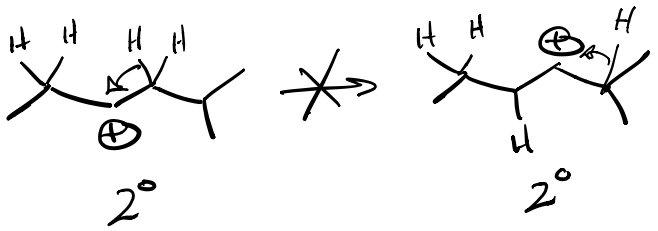

Acid
Magic Acid
or
Super Acid

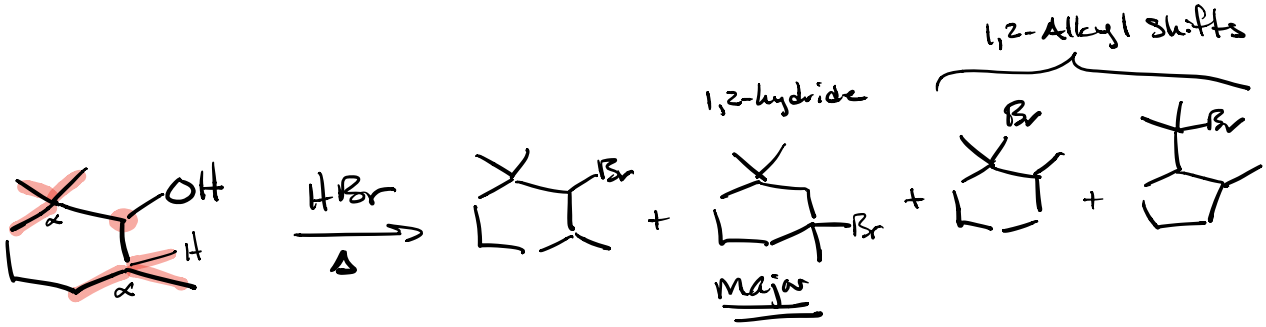

OH
H2SO4
H2O18
Δ
OH18
40%
+
OH18
60%


H
H⊕
H
H
2°
CH3
CH3
1,2-hydride
1,2-Alkyl Shift
H
H
2°
Equal in energy
H
CH3
3°
CH3
more stable
B
H
CH3
CH3
CH3
OH18
H

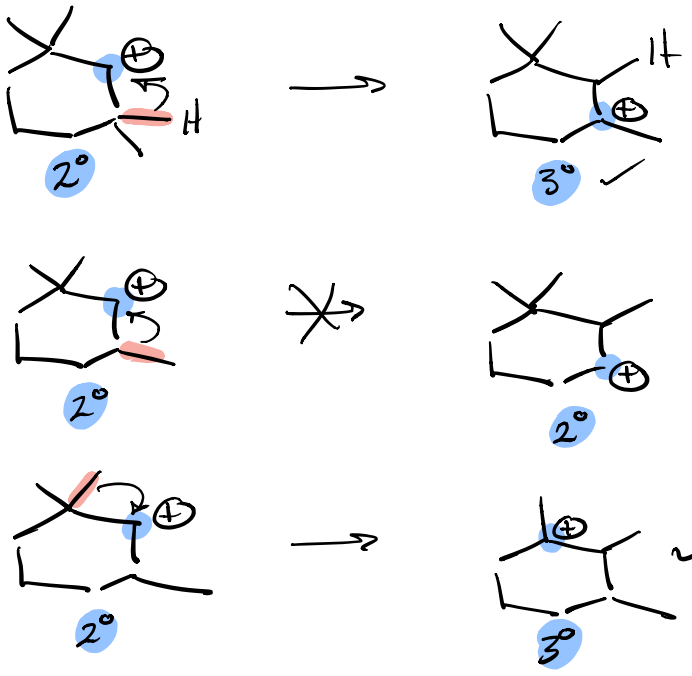

X
Y
ortho

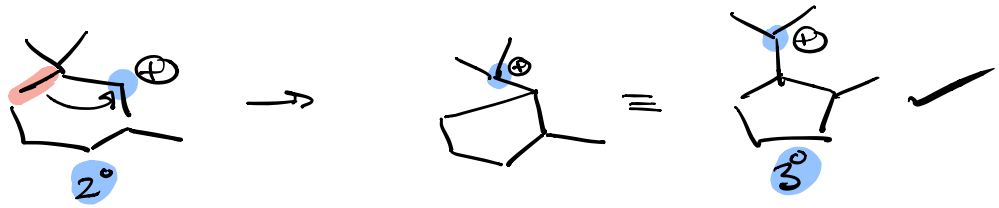


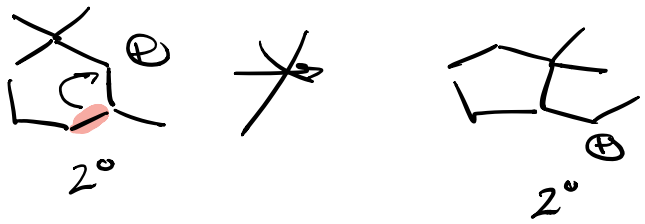


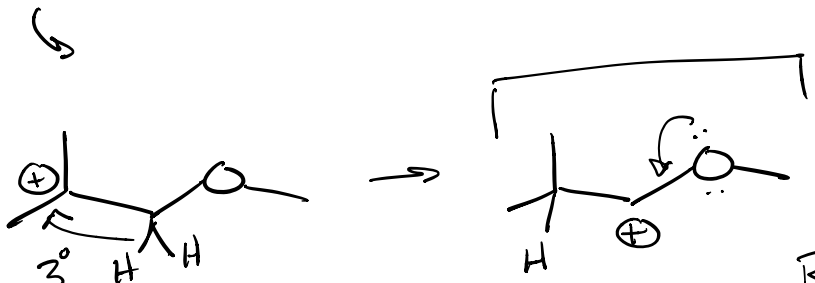


How many products?

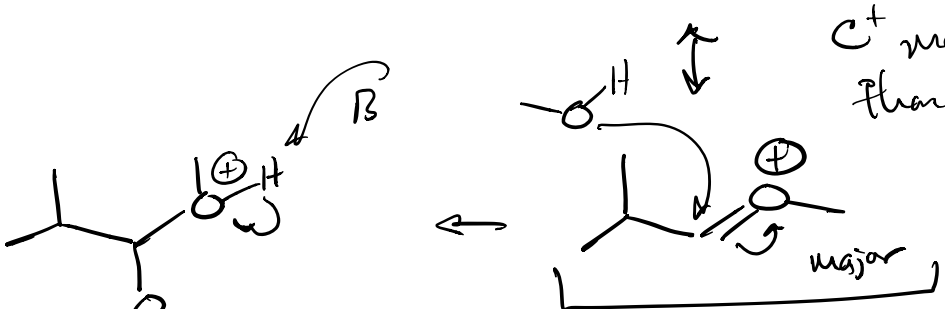




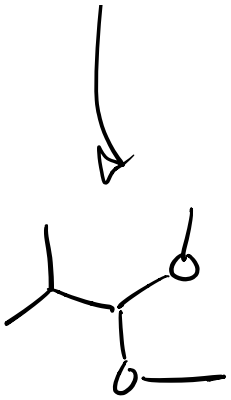


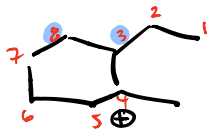


Resonance makes 2° C^+ more stable than 3°



1





↑ EN/hybridization pka 20-30

Resonance	10-15	←
Size	5-10	
Induction	0.2-1	←