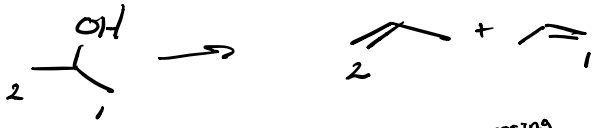
Elimination Rxns

E_1 Elimination 1st order

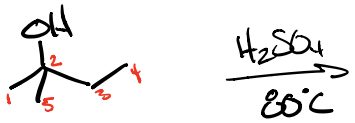
E_2 Elimination 2nd Order

dehydration Rxn
both regio & stereoselective

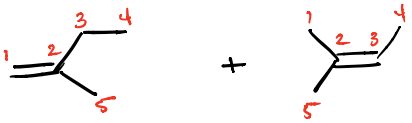
Stereoselective  vs 

regioselective 

Regioselective

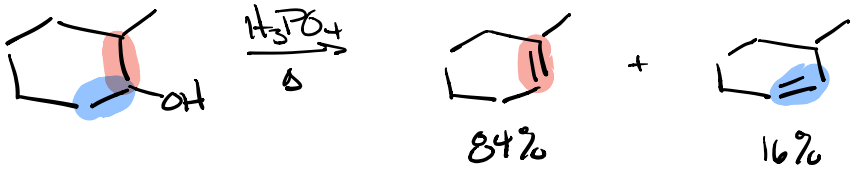


3° alcohol



10% disubstituted

90% more substituted tri sub

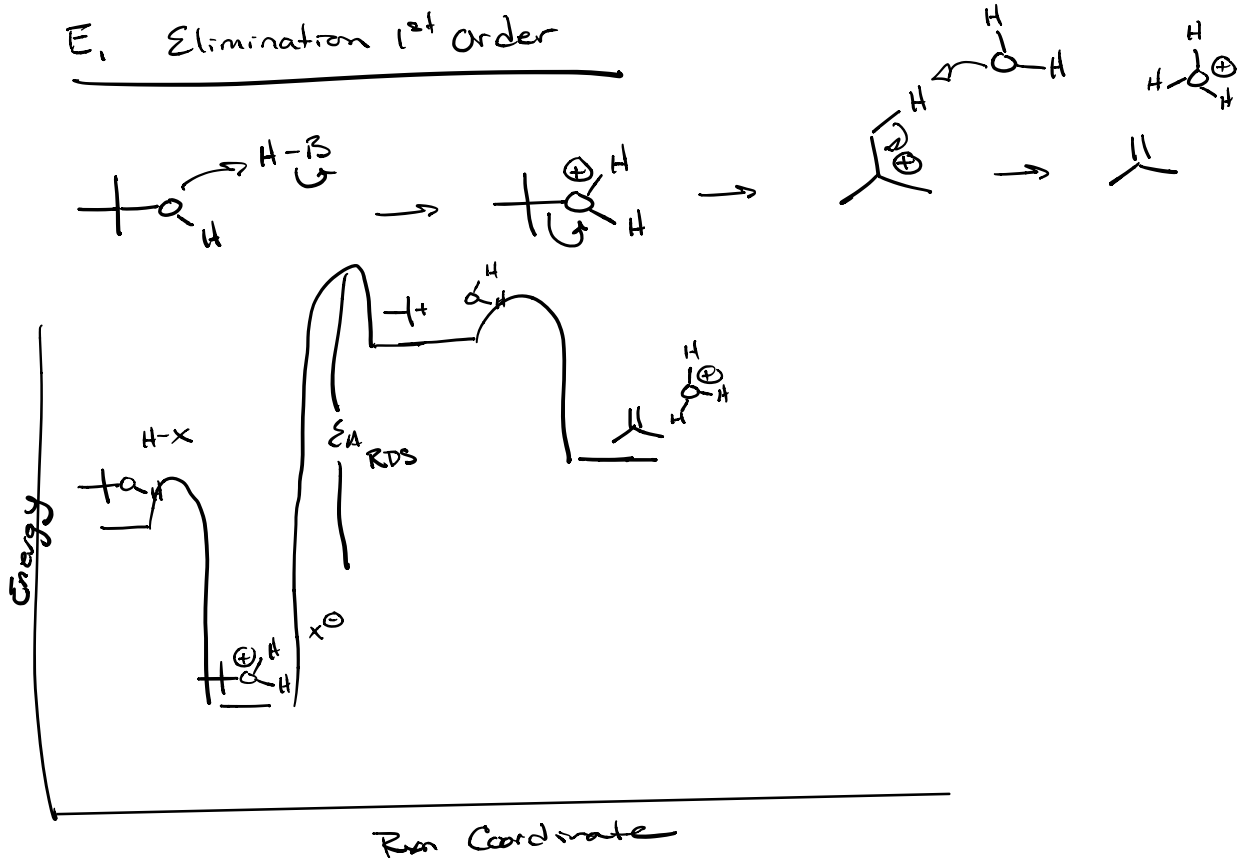


84%

16%

Zaitsev's Rule (1875 Alexander Zaitsev)

E_1 Elimination 1st order



$$\text{Rate} = k[\text{R-LG}] \Rightarrow \text{Identical } S_N1$$

Same factors apply as for S_N1

Rate $3^\circ > 2^\circ > 1^\circ$

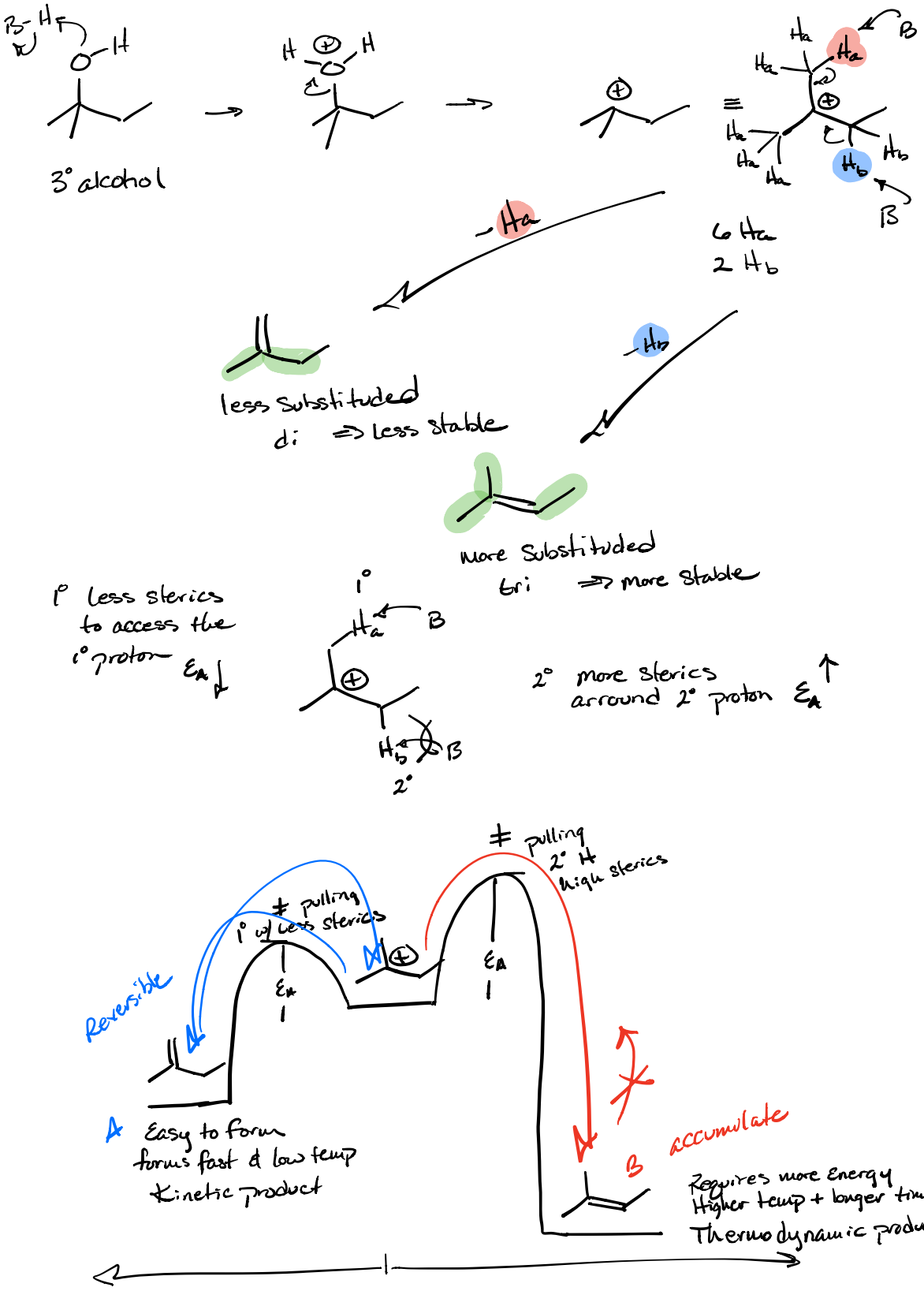
Substrate

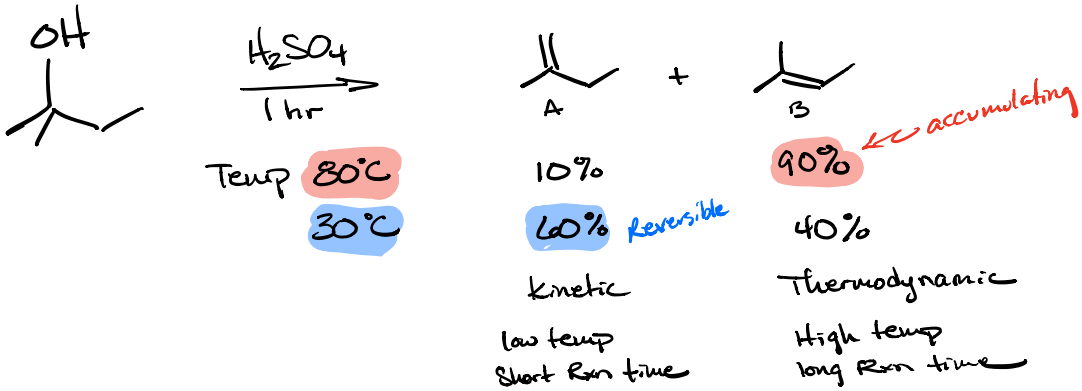
R-LG

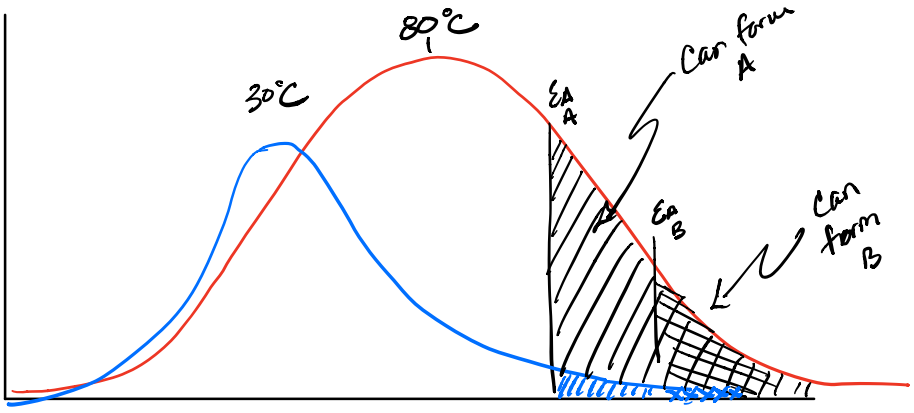
$$HI > HBr > HCl >> HF$$

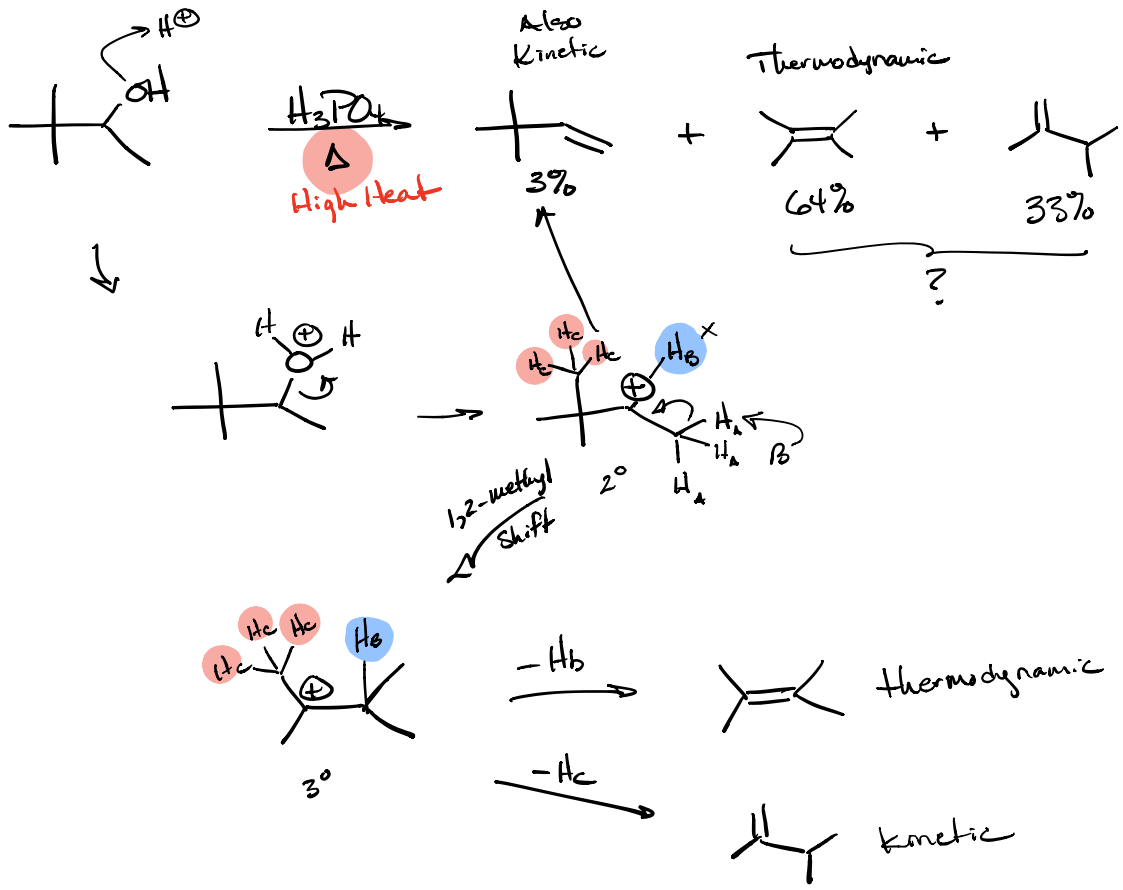
Stronger acid

$$\text{Rate} = k[R\text{-}\overset{\oplus}{C}\overset{H}{\underset{H}{}}]$$

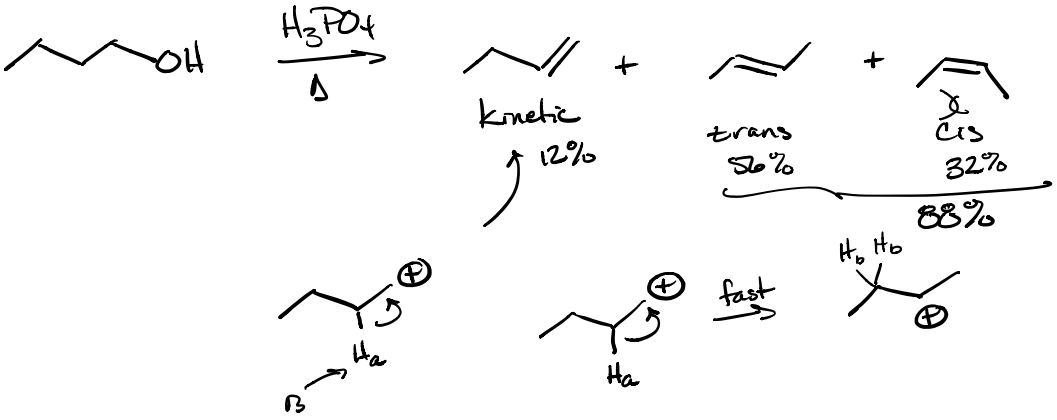

3° alcohol
6 Ha
2 Hb
less Substituded
di ⇒ less stable
More Substituded
tri ⇒ more stable
1° less sterics to access the 1° proton
2° more sterics arround 2° proton
1°
2°
≠ pulling 1° w/ Less sterics
≠ pulling 2° H high sterics
Reversible
Easy to form forms fast & low temp Kinetic product
accumulate
Requires more Energy Higher temp + longer time Thermodynamic product


OH
H_2SO_4
1 hr
A
+
B
Temp 80°C
30°C
10%
60%
Reversible
90%
accumulating
40%
Kinetic
Thermodynamic
Low temp
Short Rxn time
High temp
long Rxn time

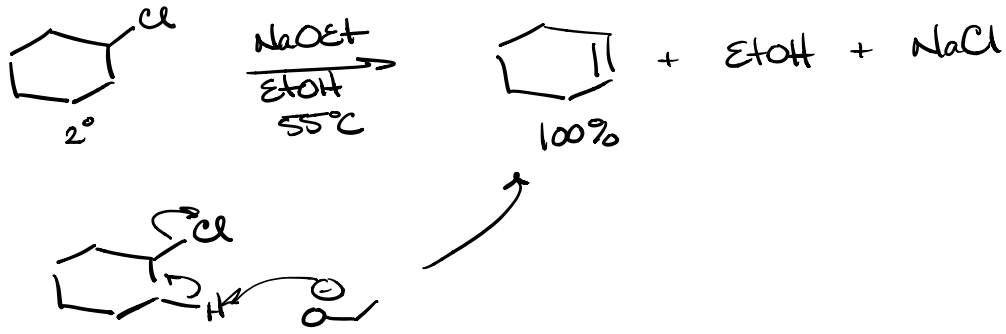

80°C
30°C
E_A A
E_A B
Can form A
Can form B

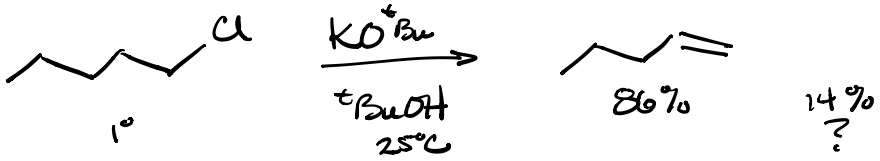


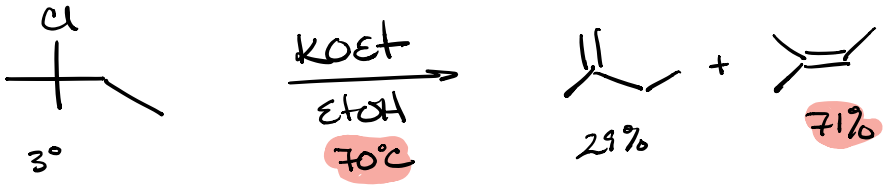
Δ = Reflux = High heat = Thermodynamic product

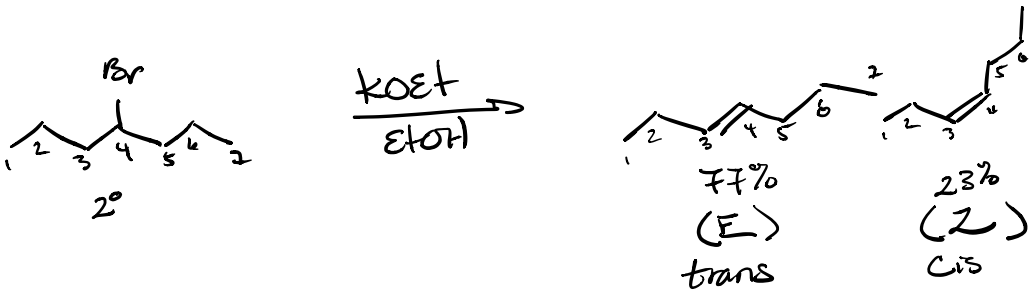


Dehydrohalogenation

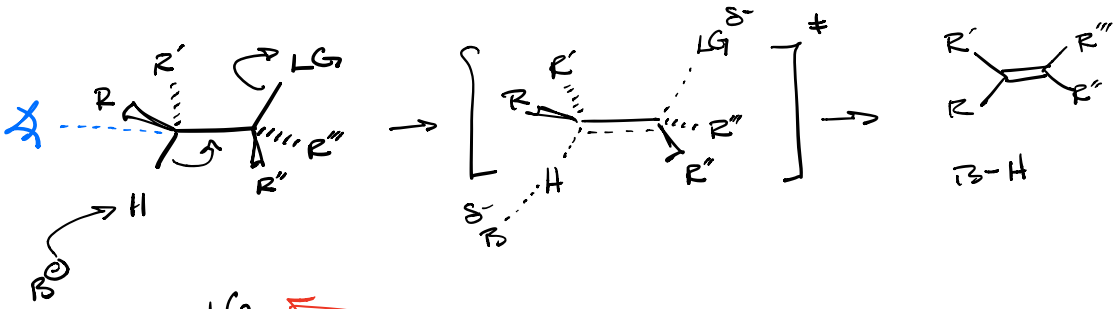


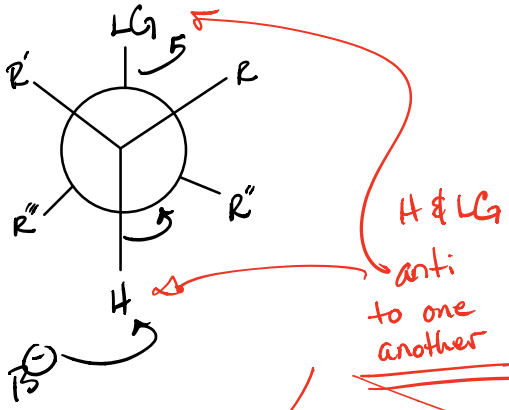


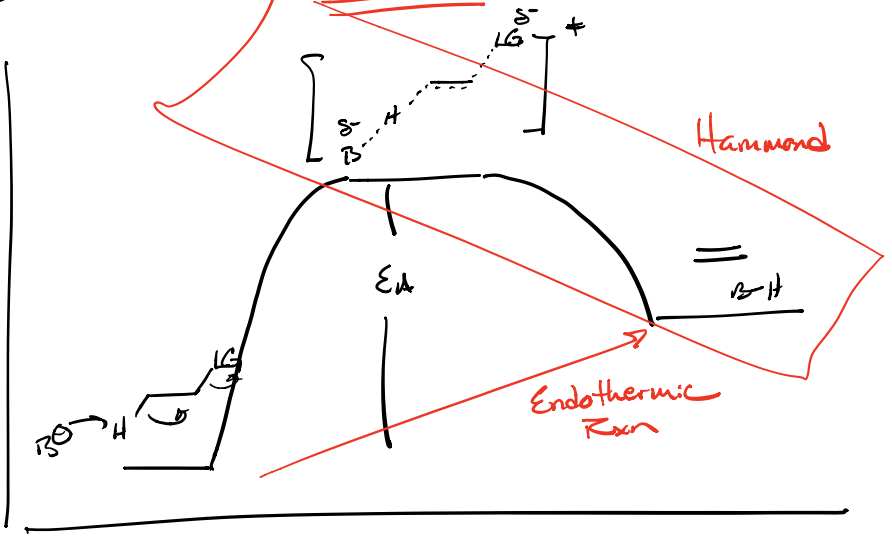




E_2 Elimination 2nd Order







Concerted = Bond breaking & Bond making Simultaneous

E_2 Rate $= k[\text{Base}][\text{R-LG}]$

S_N2 Rate $= k[\text{nuc}][\text{R-LG}]$

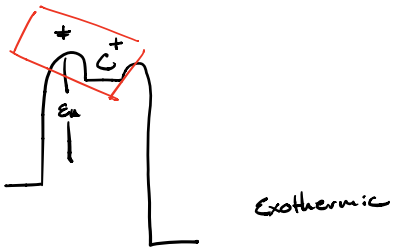
difference Base vs. Nucleophile

E_2 base

S_N2 nucleophile

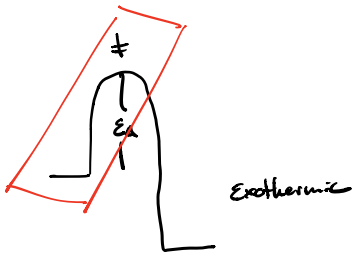
Rate $3^\circ > 2^\circ > 1^\circ$ R-LG $\Rightarrow$ ≠ product like structure of the product (stability of product) governs Rxn Rate

S_N1



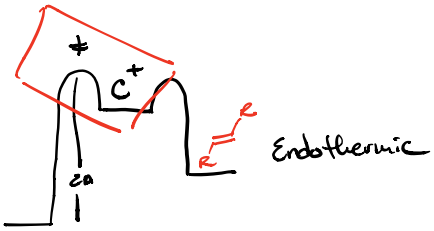
Alkyl & hydride shifts
Intermediate C^+
Stepwise

S_N2



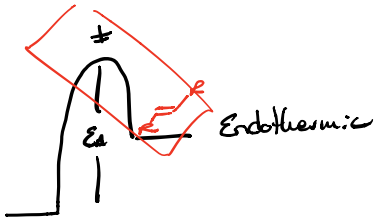
no shifts
no intermediate
Concerted

E_1



Alkyl & hydride shifts
Intermediate C^+
Stepwise

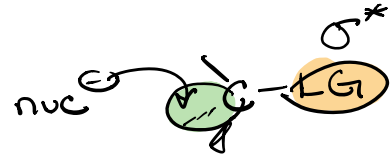
E_2



no shifts
no intermediate
Concerted

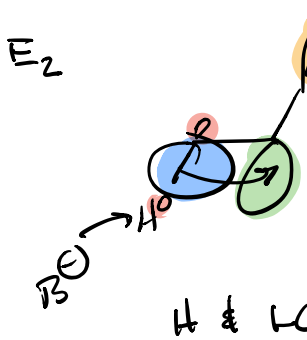
Stereoelectronic Effects

S_N2

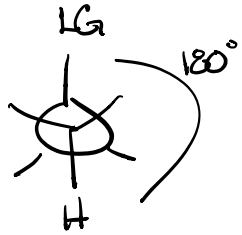


Backside attack
attack was at antibonding orbital

E_2



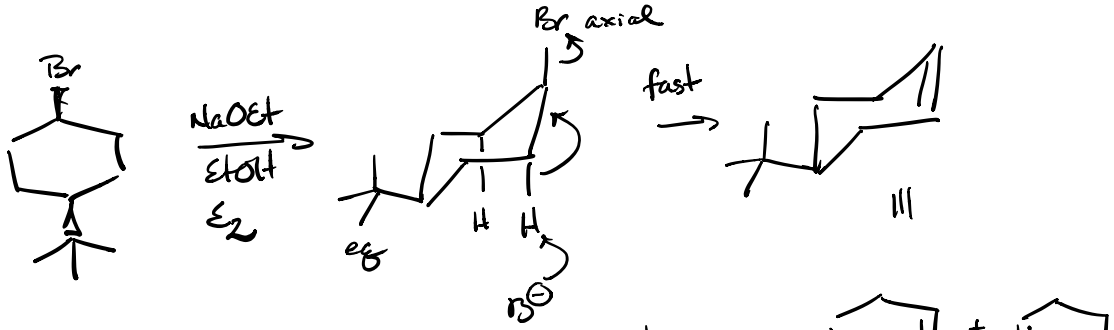
e^- dump into σ^* antibonding orbital

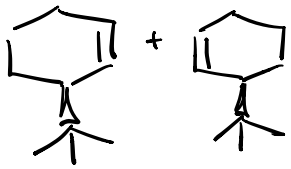


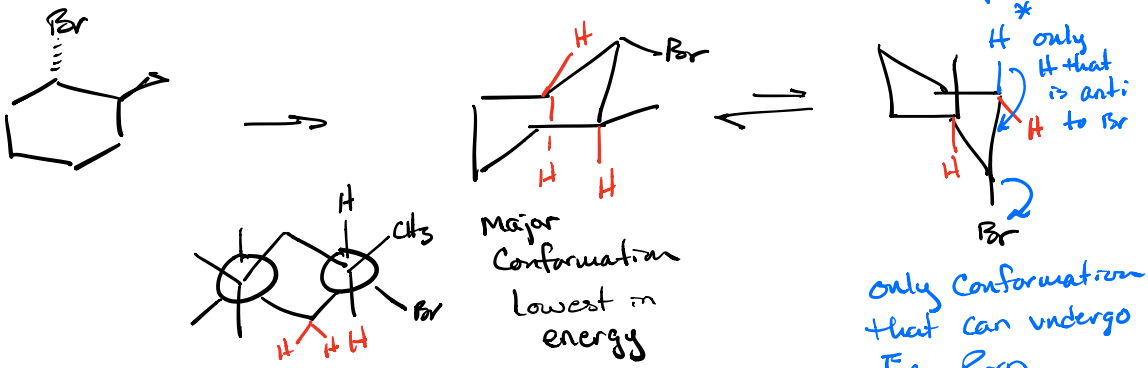
H & LG must be anti-periplanar

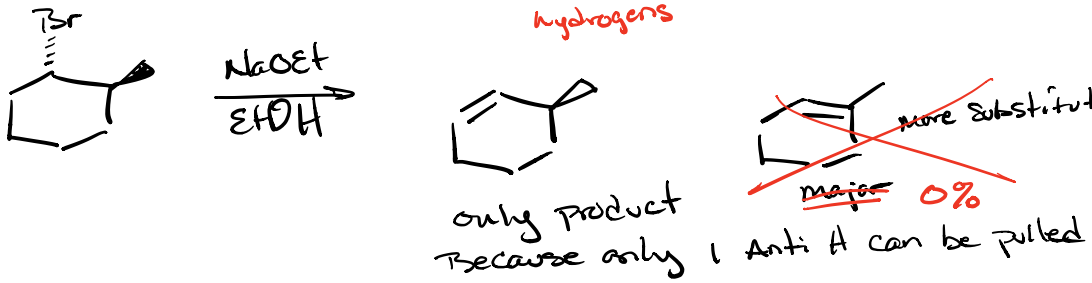
When Syn Coplanar

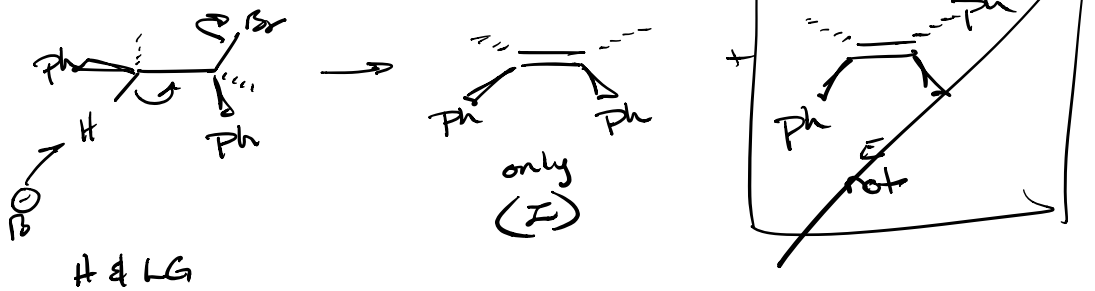
→ no Rxn or at least very very slow











H & LG
must be
anti.