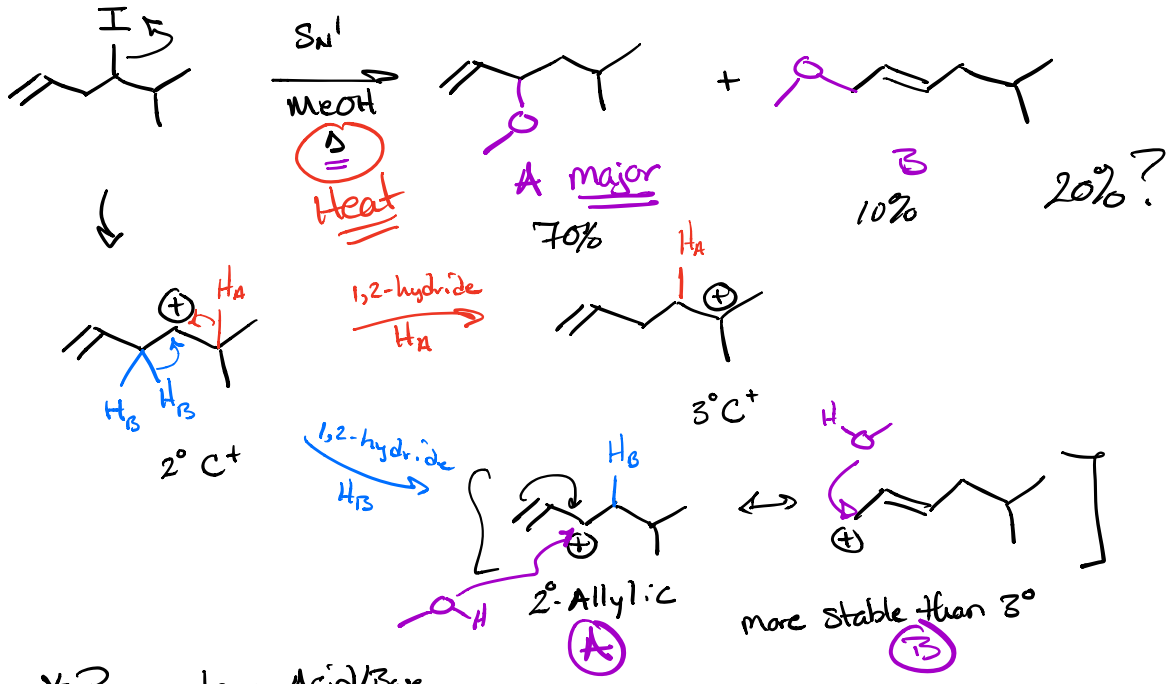
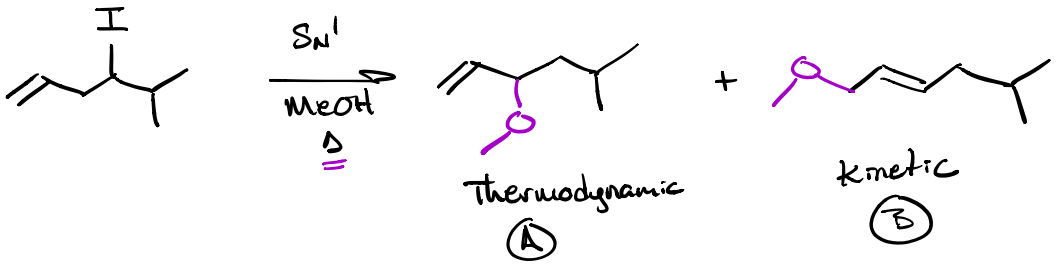


* Reminder Acid/Base

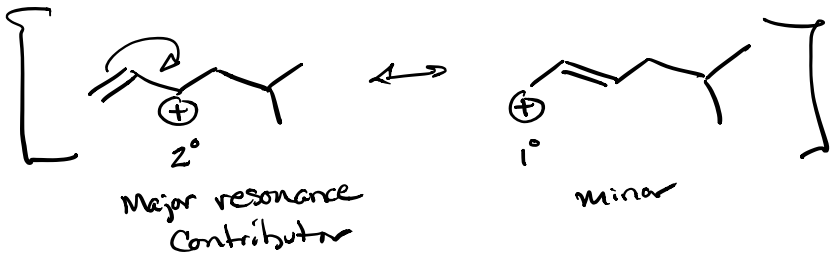
⇒ Resonance 15-20 pka units

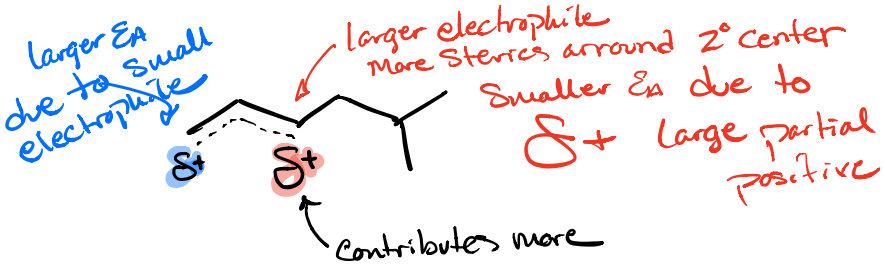
Induction 0.2-2 pka units

Closer look @ Rxn

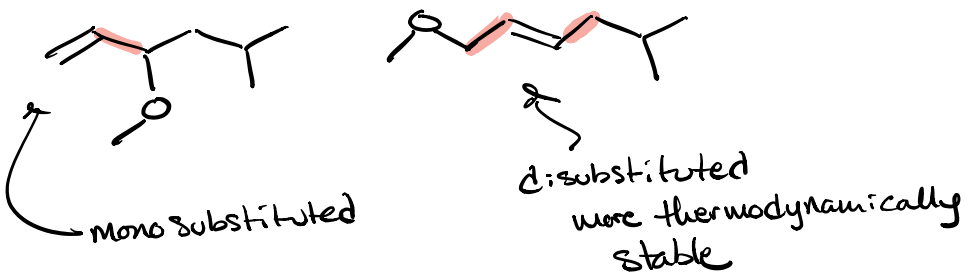


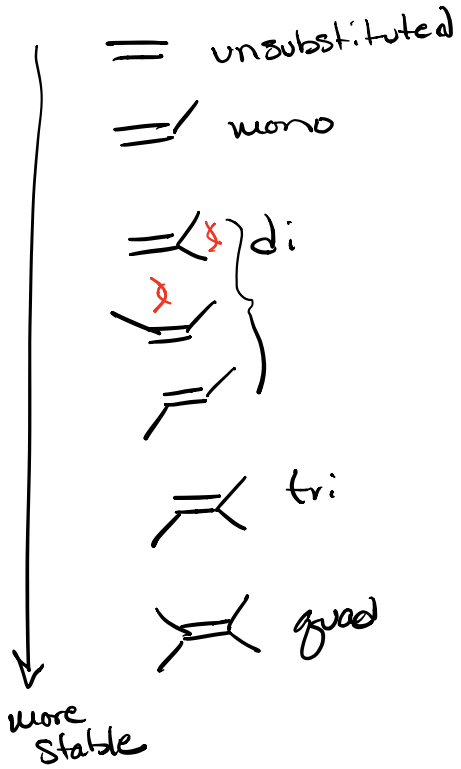
Carbocation



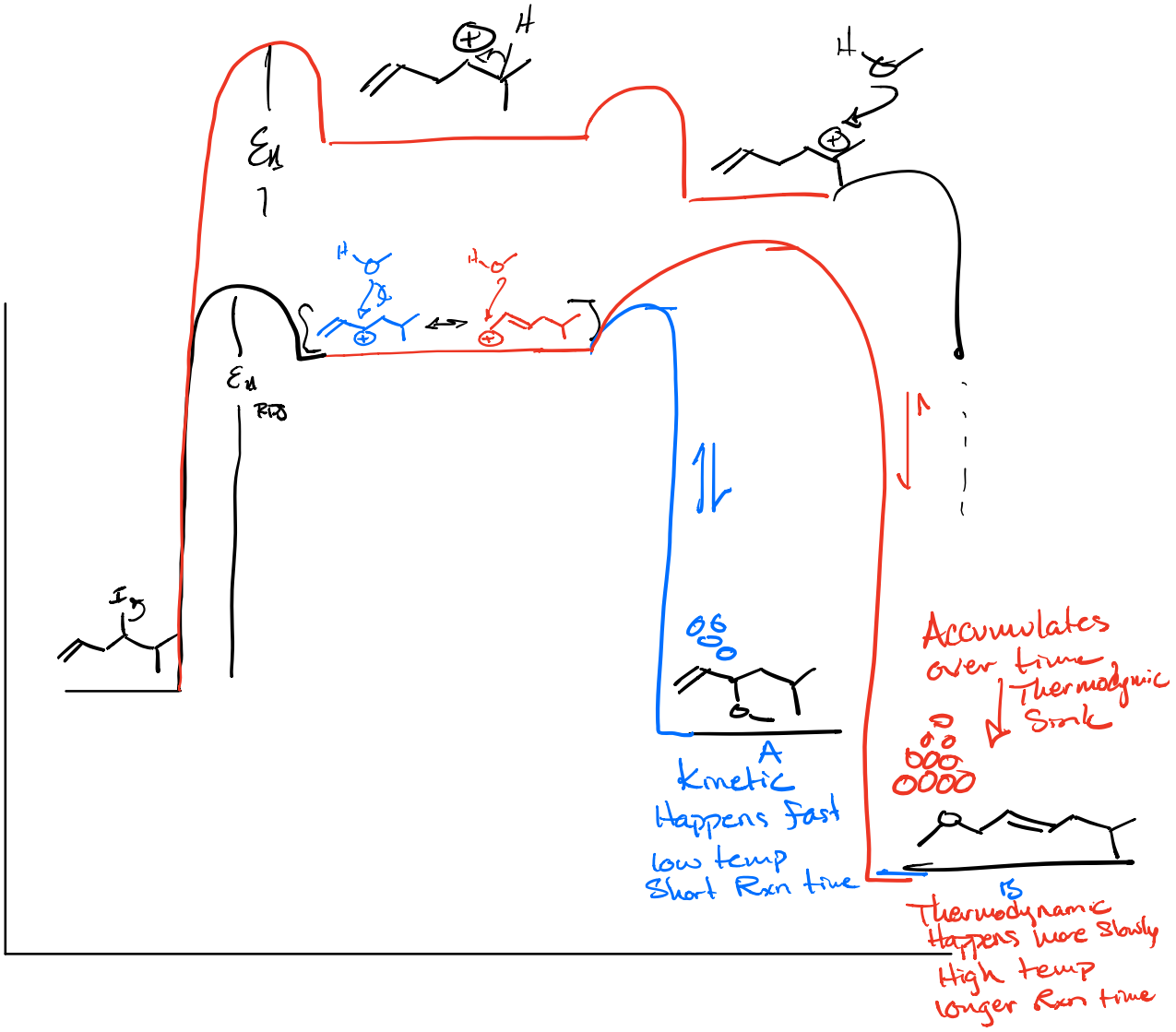

larger Ea due to small electrophile
larger electrophile
More Sterics arround 2° center
Smaller Ea due to
δ+ Large partial positive
δ+
δ+
contributes more

Products

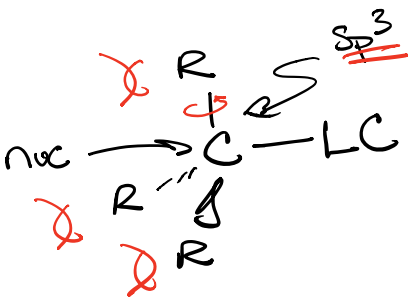

monosubstituted
disubstituted
more thermodynamically stable

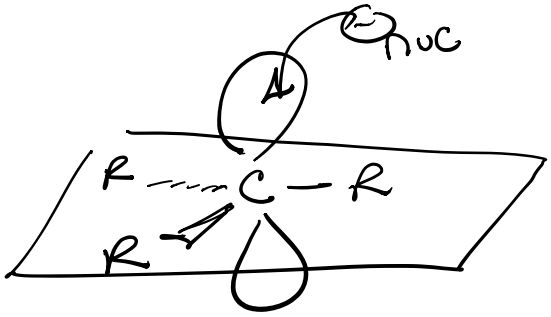

unsubstituted
mono
di
tri
quad
more stable


endo


Accumulates over time
Thermodynamic Sink
A
Kinetic
Happens fast
low temp
Short Rxn time
B
Thermodynamic
Happens more slowly
High temp
Longer Rxn time

Sterics



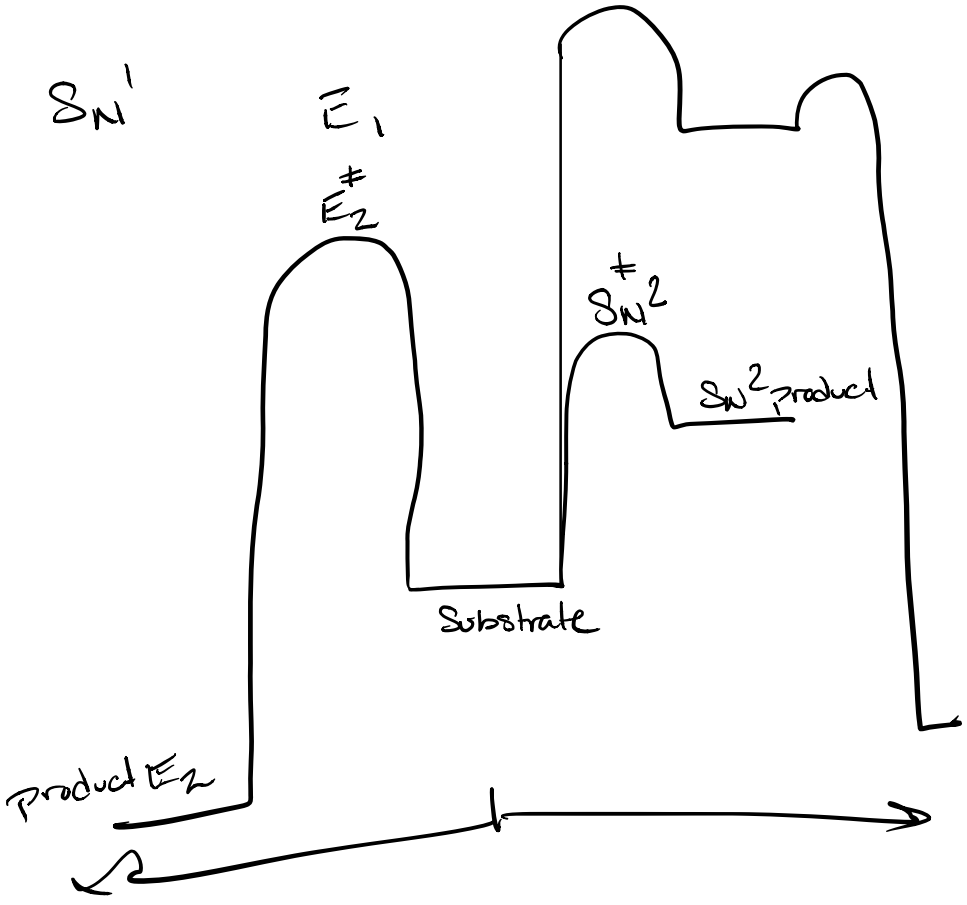


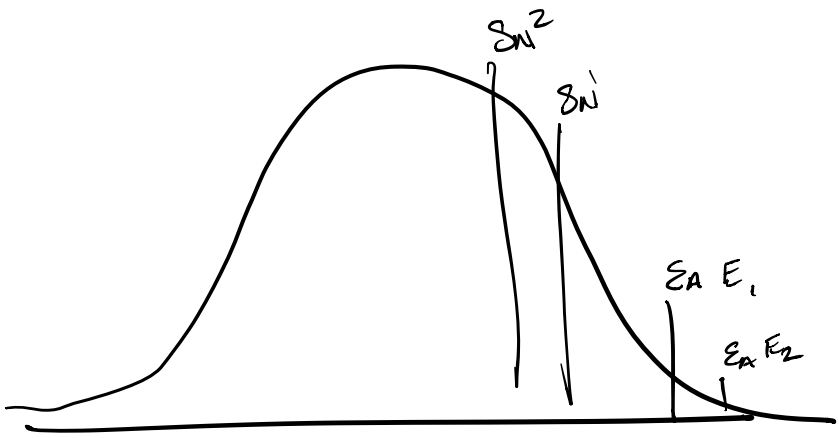
sp^2 flat

trigonal planar

S_N2 E_2

S_N1 E_1

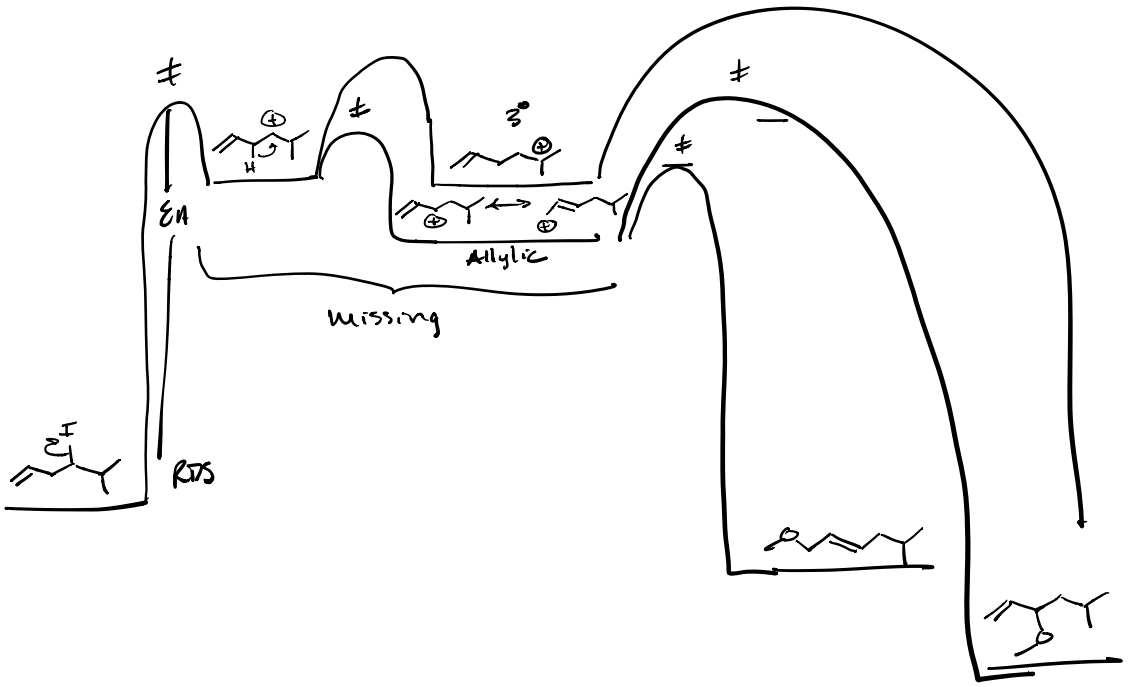


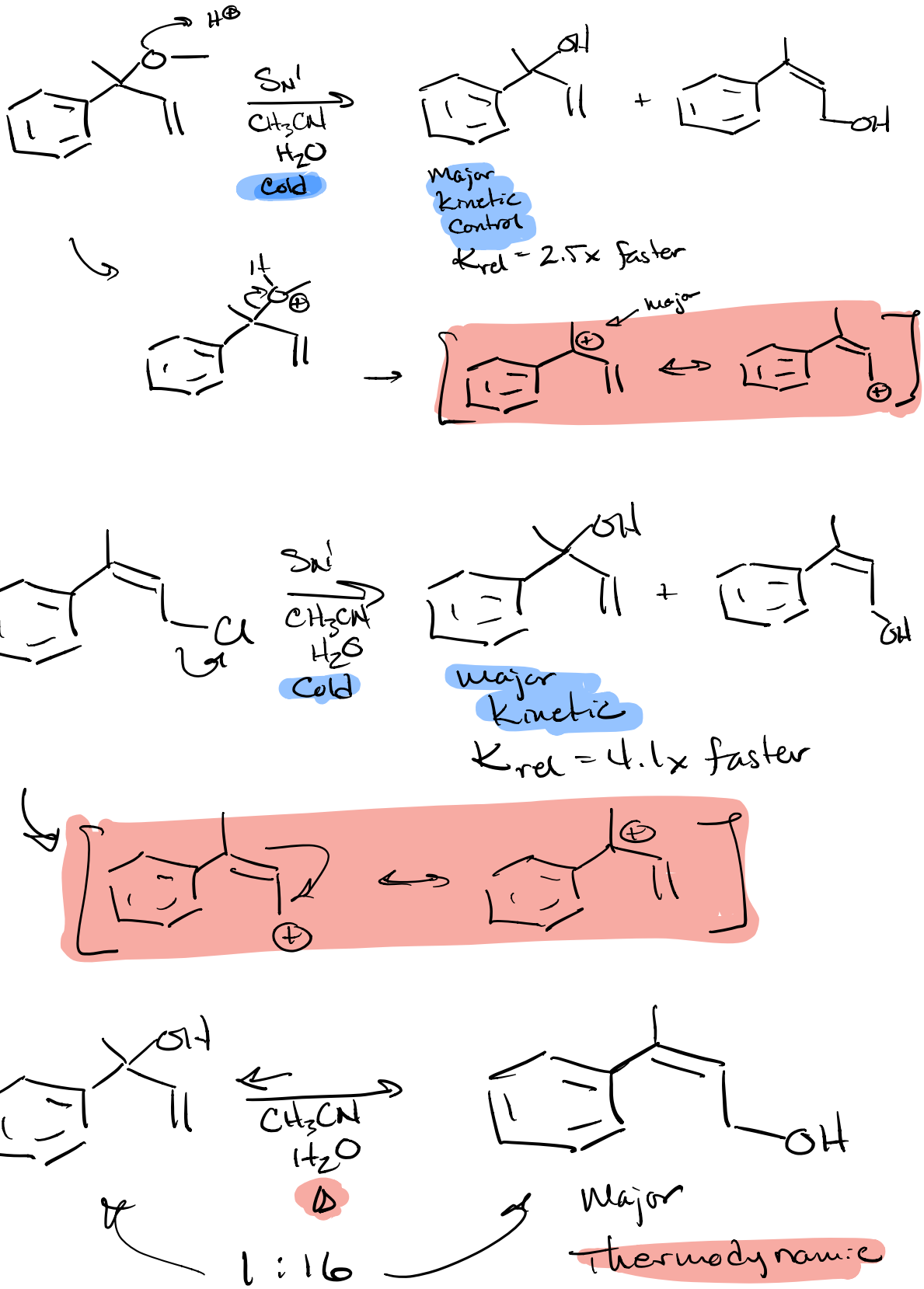


$\triangle$ = Reflux

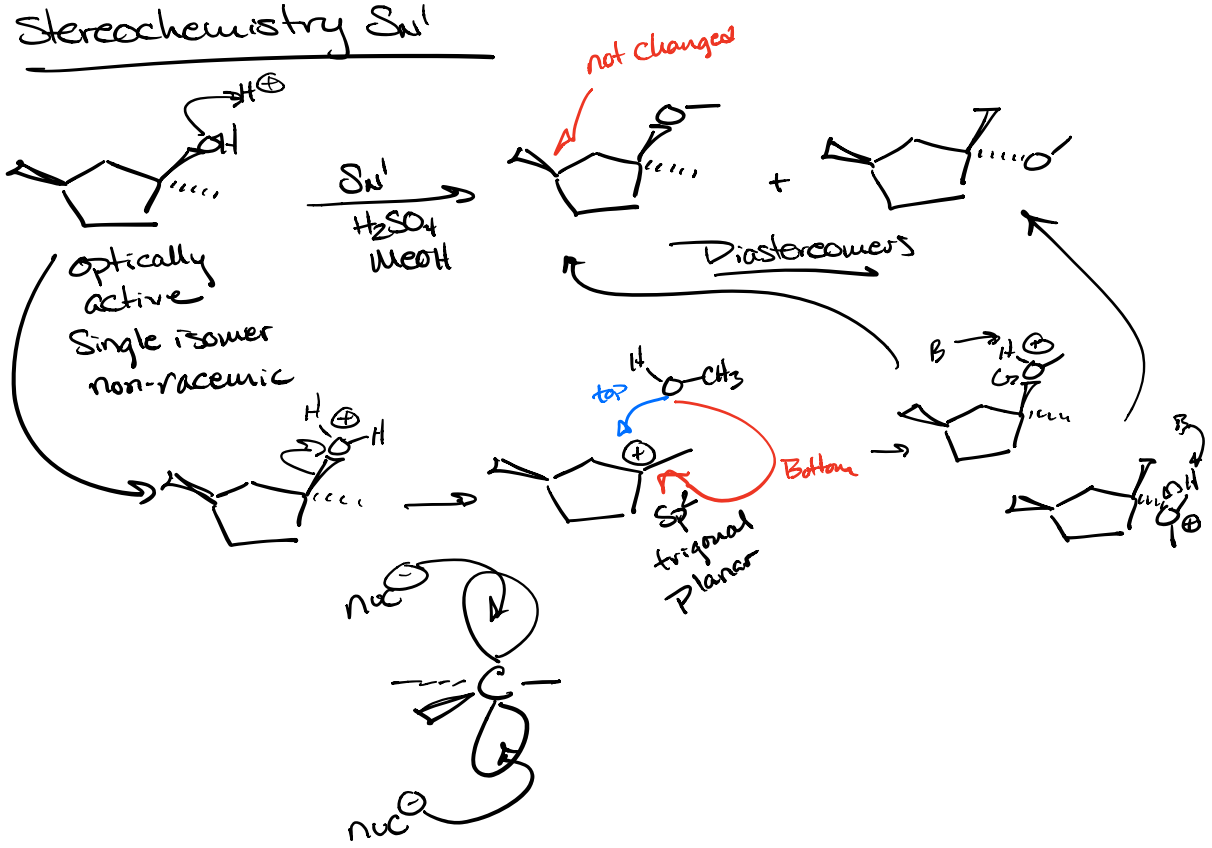
MeOH Bp 65°C

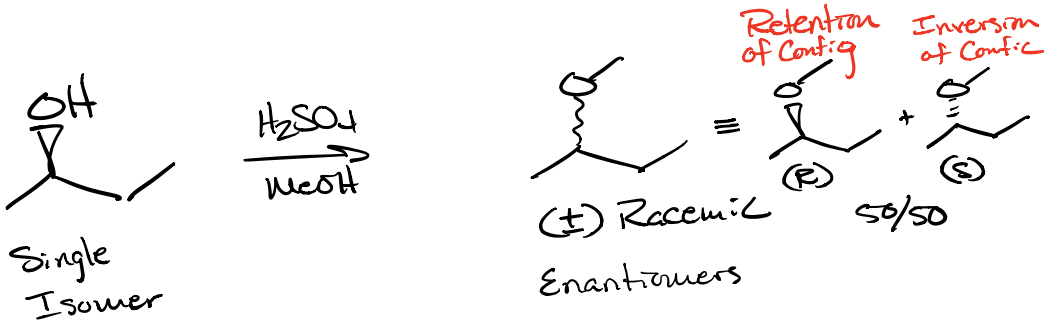
EtOH Bp 78°C


EA
Allylic
Missing
RDS


H⊕
SN1
CH3CN
H2O
Cold
OH
+
OH
Major
Kinetic
Control
Krel = 2.5x faster
major
SN1
CH3CN
H2O
Cold
Cl
OH
+
OH
Major
Kinetic
Krel = 4.1x faster
OH
CH3CN
H2O
Δ
1 : 16
OH
Major
thermodynamic

Stereochemistry S_N1





S_N2 Governed by Sterics of Substrate

Rate = 1° > 2° >> 3° $R = k[R\text{-}LG][nuc]$

Bimolecular & Concerted (single step)

Inversion of Configuration

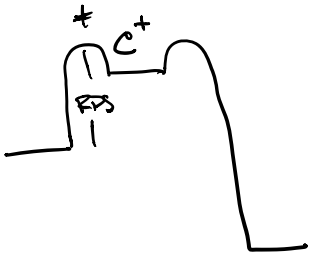
S_N1 Governed by electronics (C^+ stability ⇒ not sterics)

Rate = 3° > 2° >> 1°

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

Stepwise Rxn

Racemic products



① Substrate 1° 2° 3°

SN2 SN1

② LG Better LG → SN1

nucleophile Better nucleophile ⇒ SN2 $R-\ddot{O}^{\ominus}$ > R-OH

③ Solvent polar aprotic SN1 ≠ polar non-polar SN2 ≠ non-polar

④ Temperature High temp SN1

low temp SN2