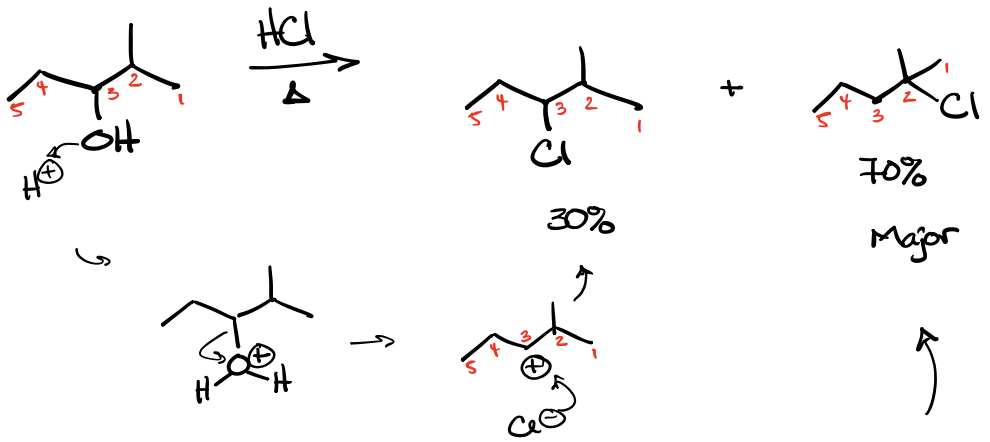
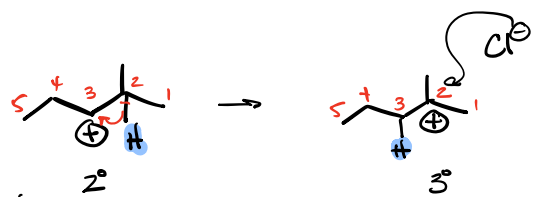
S_N1 ⇒ Carbocation intermediate

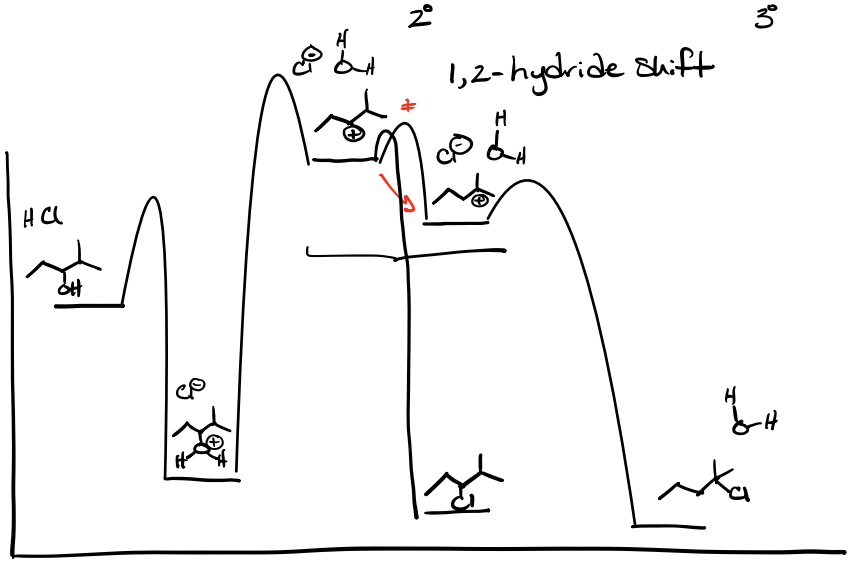
Rate $3° >> 2° > 1°$ Substrate

allylic $>$ $3° >> 2° > 1°$

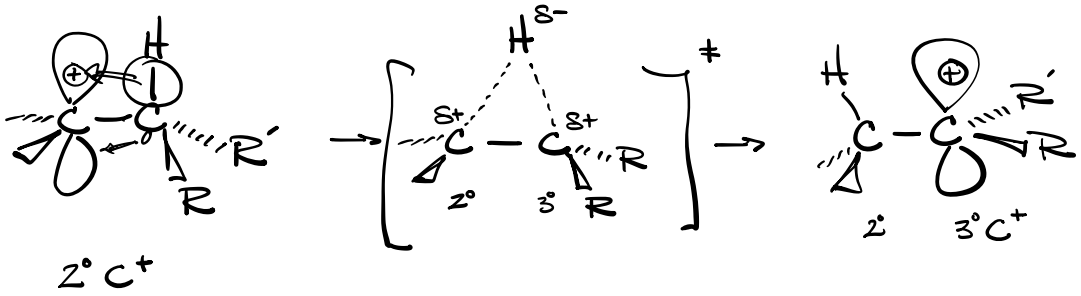
watch out for all of the stability factors!



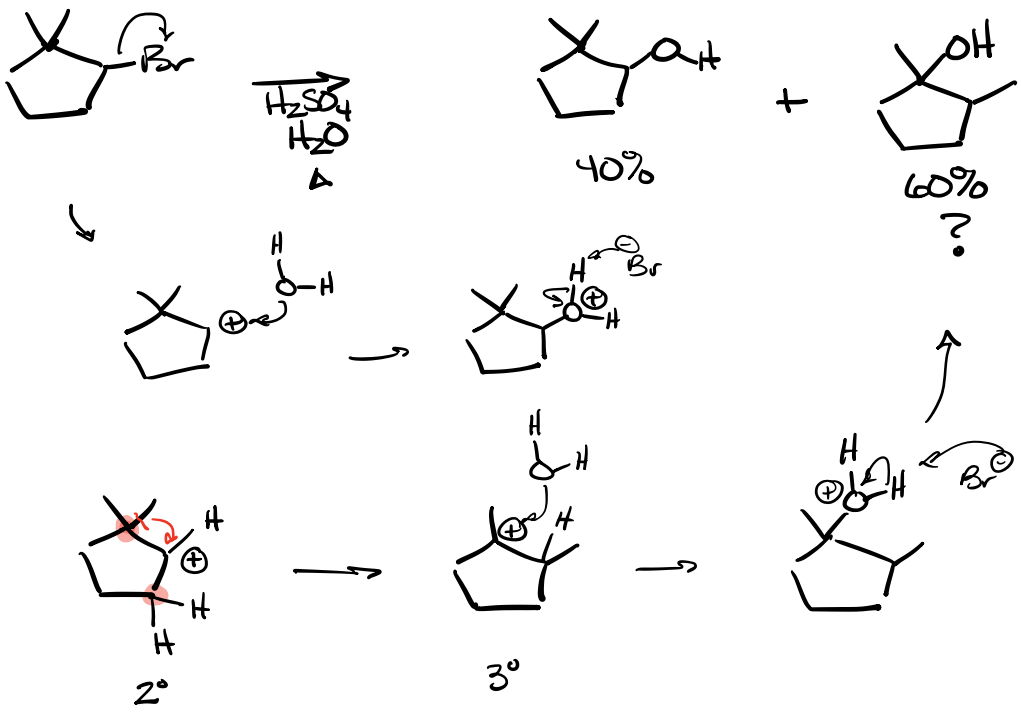




1,2- hydride shift Mechanism

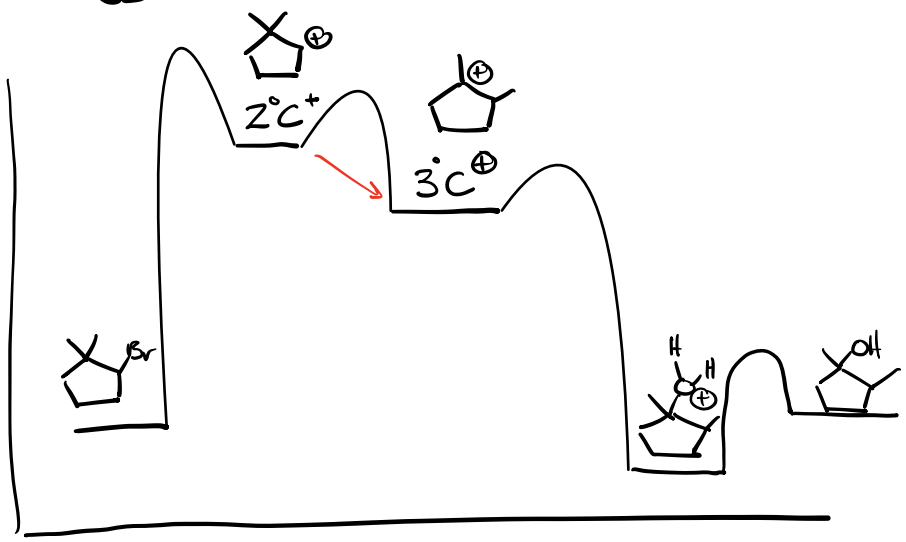


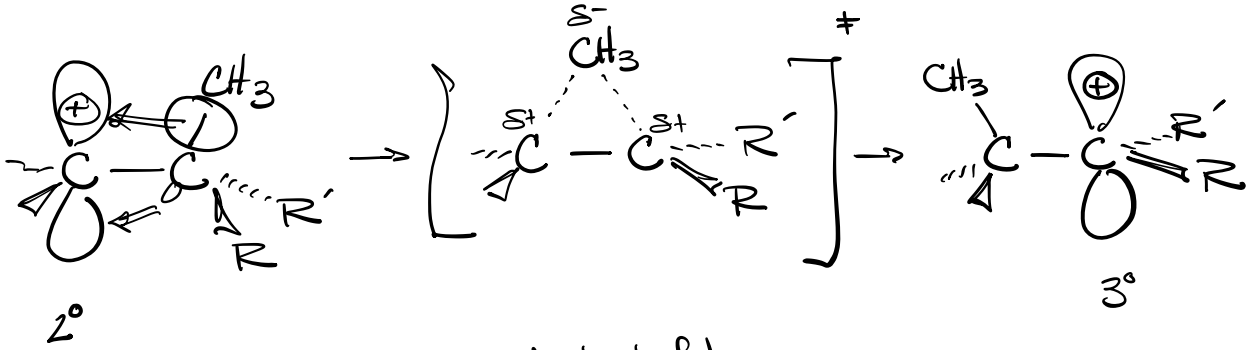
only see 1,2- hydride shift
& only see one shift, no multiple shifts
& only shifts towards more stable C+



1,2-Alkyl Shift

Energy Diagram 1,2-Alkyl Shift



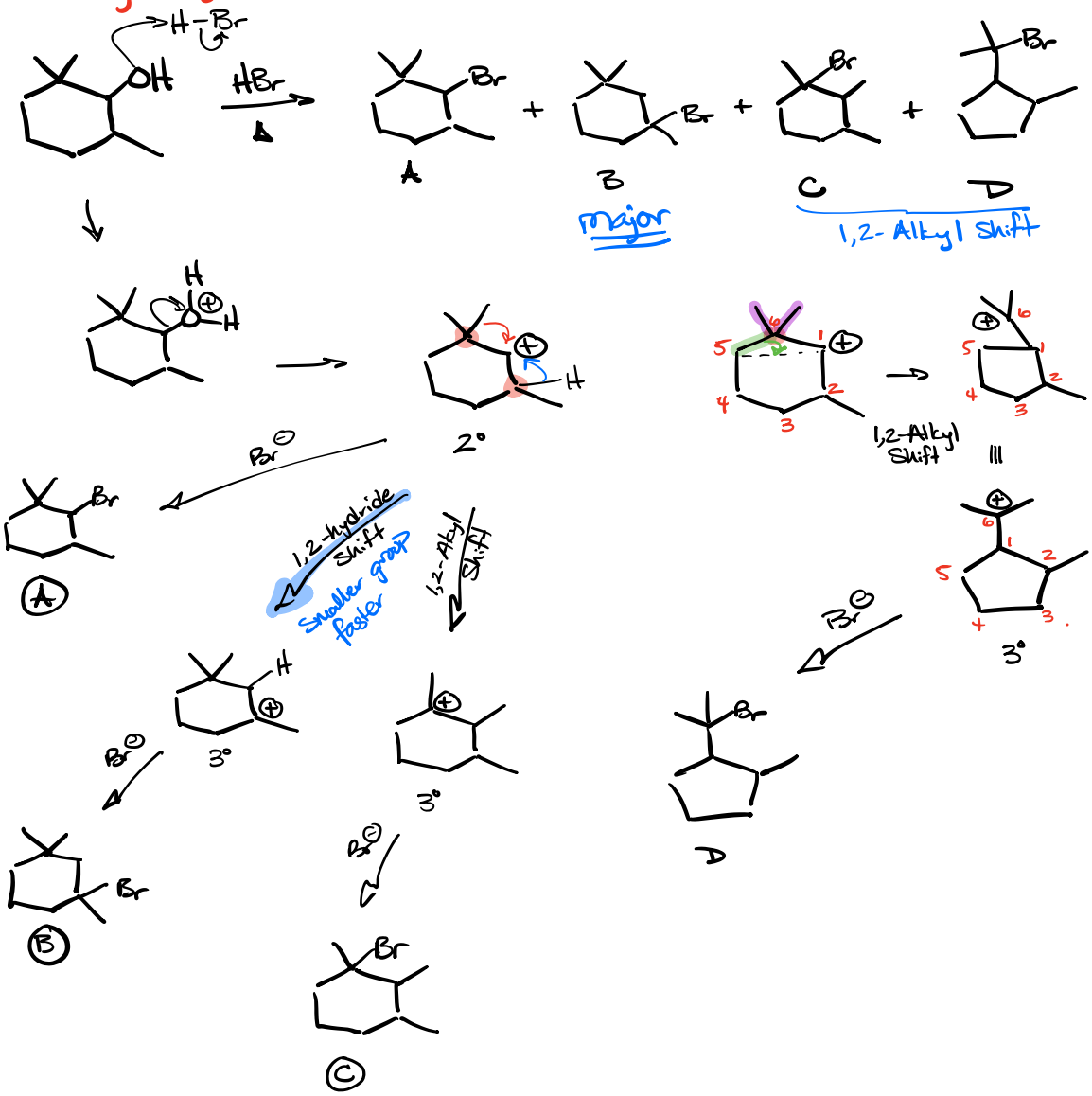


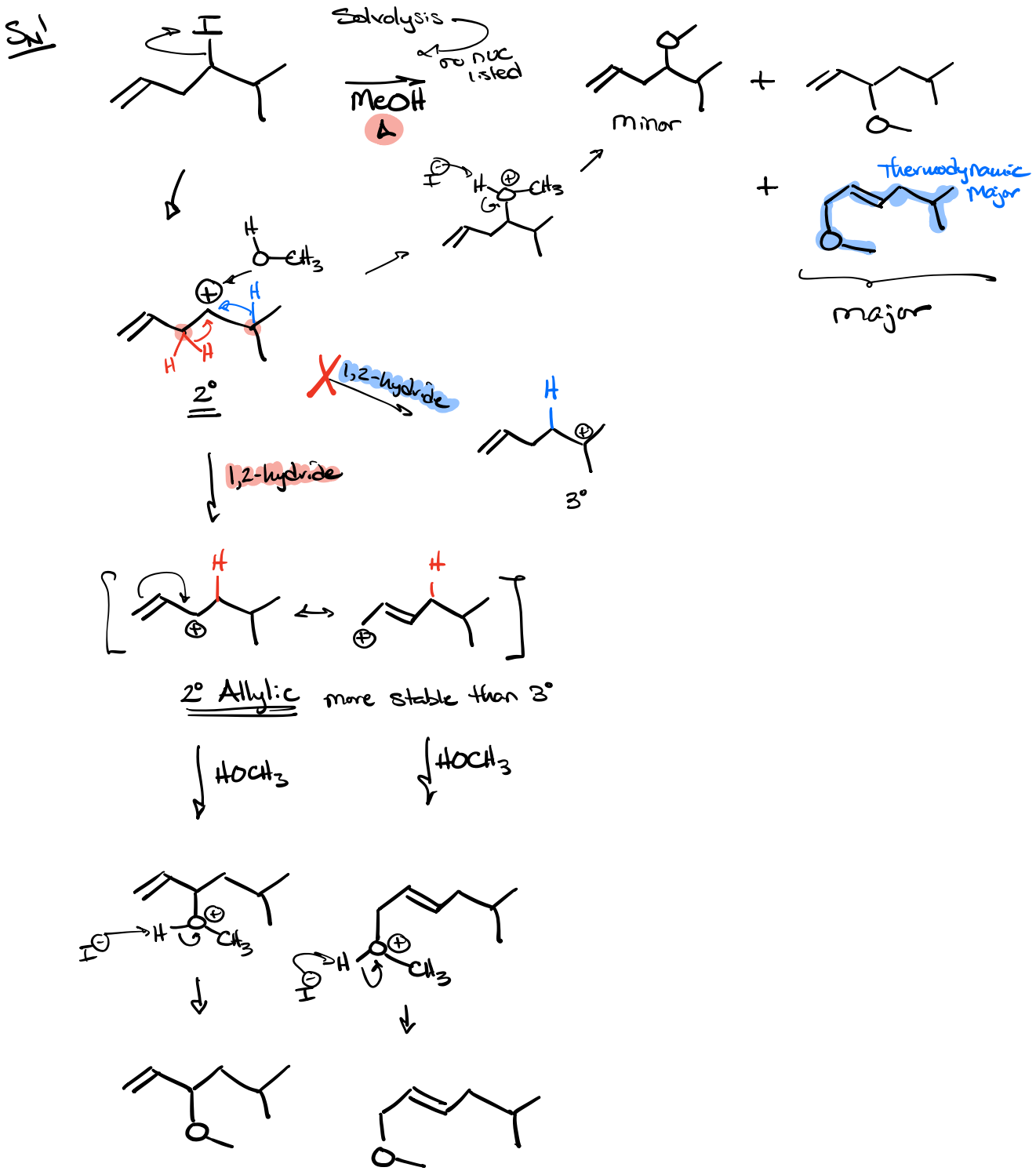
1,2-Alkyl Shift

Alkyl Shifts & Hydride Shifts

* only shift towards more stable C+
* only single shift allowed

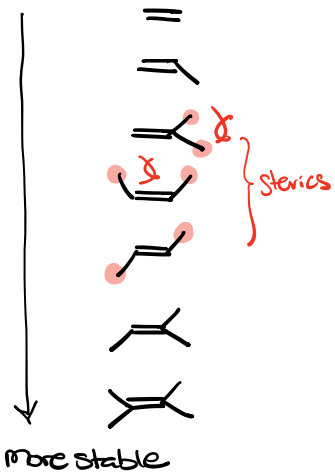
SN1



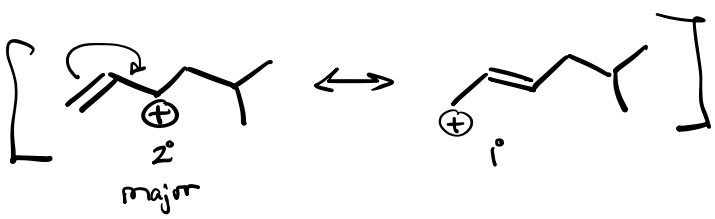

SN1
Solvolysis
no nuc listed
MeOH
A
minor
+
+
Thermodynamic Major
major
2°
1,2-hydride
3°
1,2-hydride
2° Allylic more stable than 3°
HOCH3
HOCH3

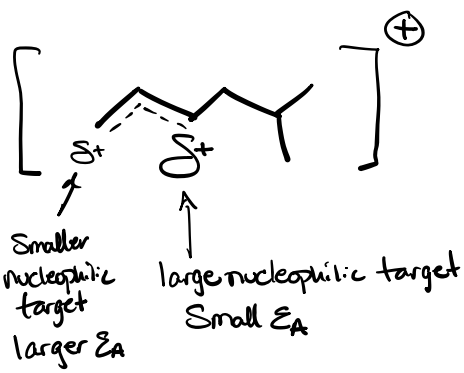
1st factor

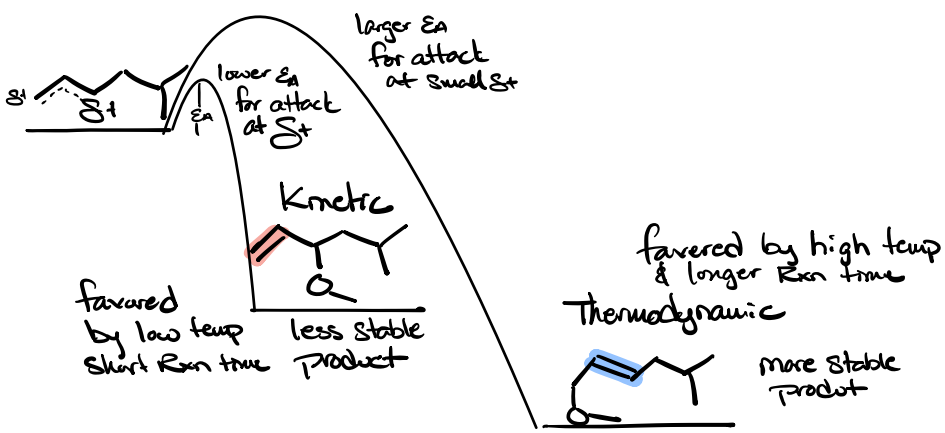
Stability of double bonds (Alkenes)

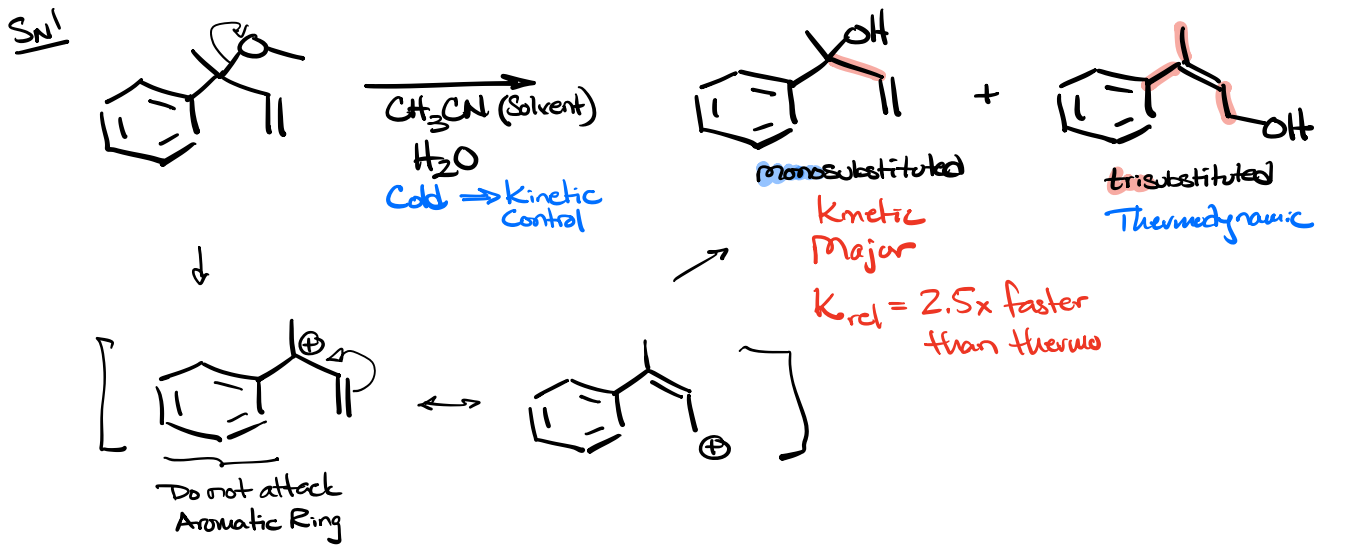


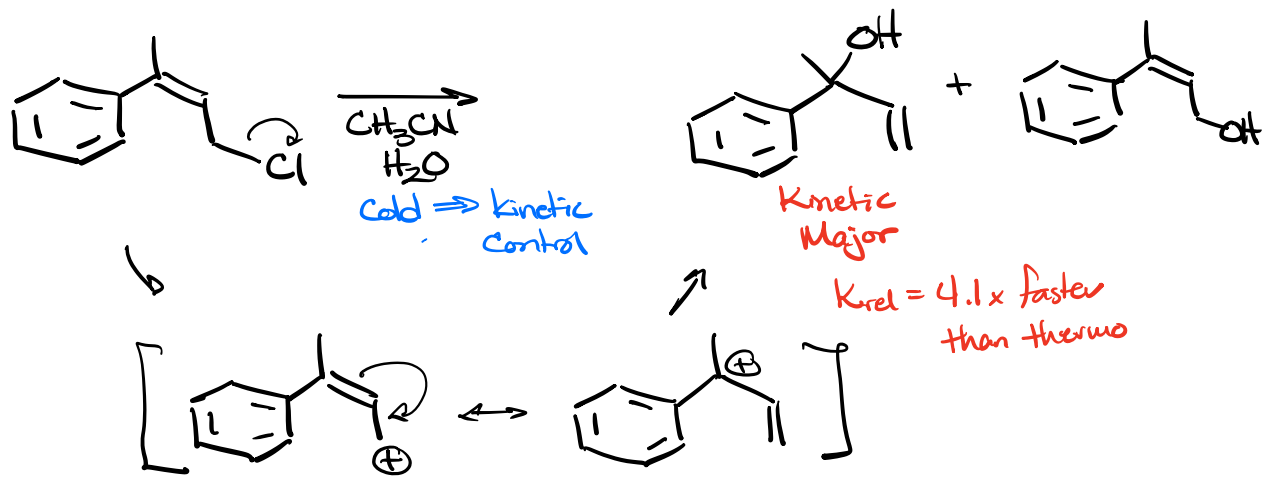
2nd factor



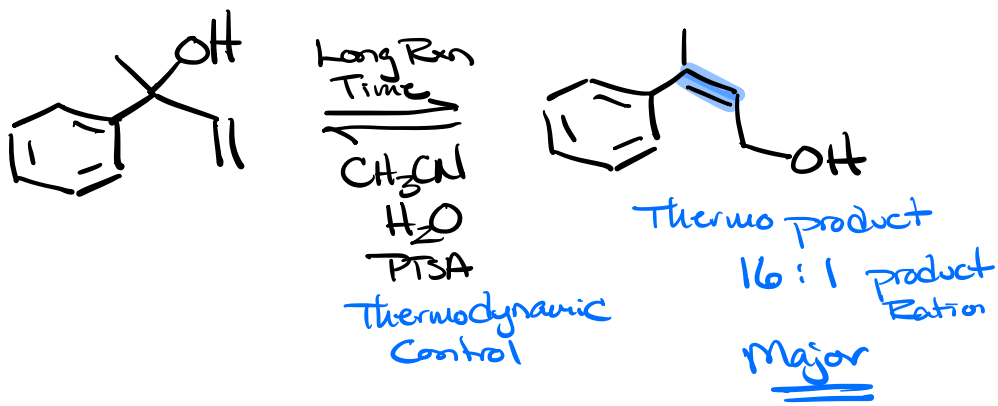




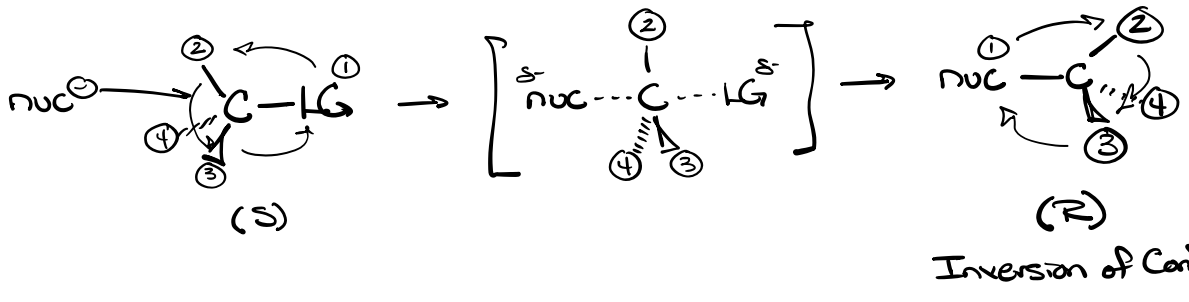




JOC 2002, 67, 182-187



S_N2 Stereochemistry



S_N1 Stereochemistry