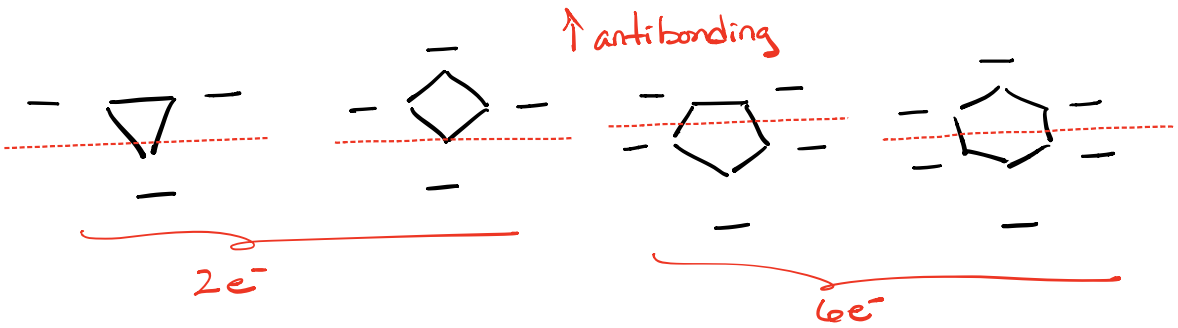
Material Since Spectroscopy Exam

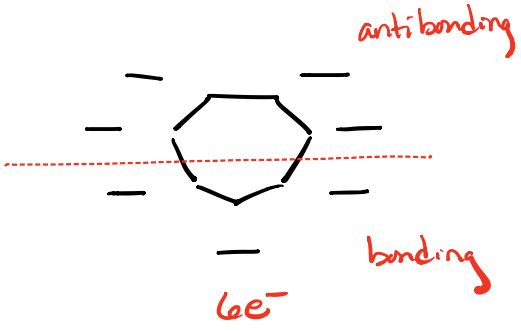
Aromaticity

- what makes something aromatic
  - Ring
  - flat
  - fully conjugated
  - $4n+2\ \pi e^-$ | $n = 0, 1, 2, \cdots$

Frost's Circle should show all bonding orbital full & anti bonding empty



n	4n+2
0	2
1	6
2	10



- Reactions of aromatic Systems

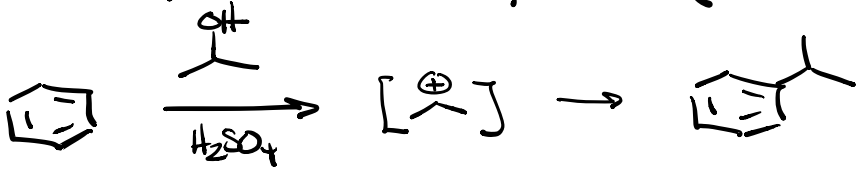
Electrophilic Aromatic Substitution

EDG - Activating & ortho/para directors

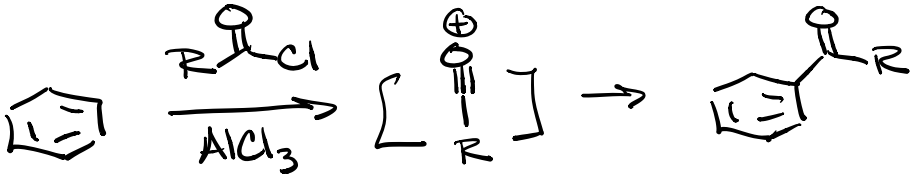
$-\ddot{X}$ ($-\ddot{O}R$, $-\ddot{N}R_2$)

EWG - Deactivating & meta directors

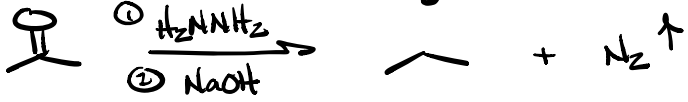
- Alkylations & Acylations (Friedle Crafts)



Any way to create Carbocation



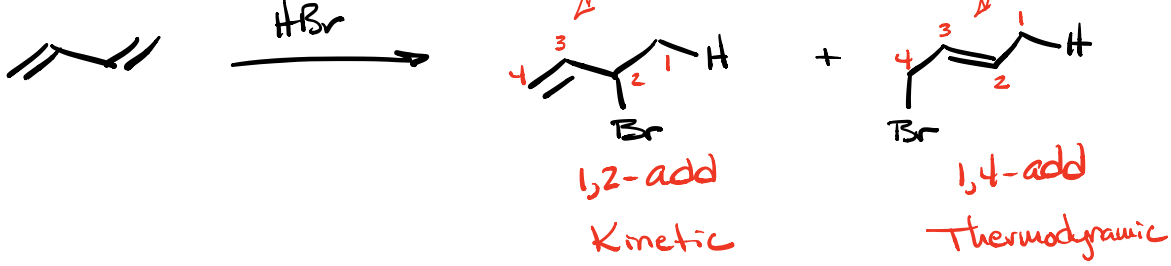
Two reactions to remove Carbonyls:

Wolff Kishner 

Clemenson 

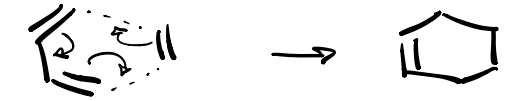
Diene Systems

- Electrophilic Addition Rxns

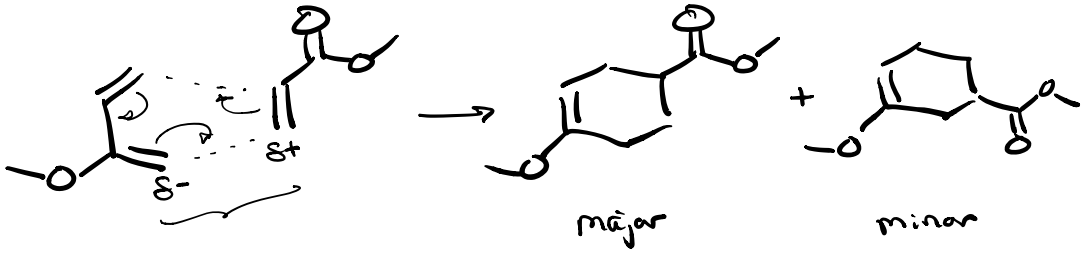


- Diels-Alder Rxns

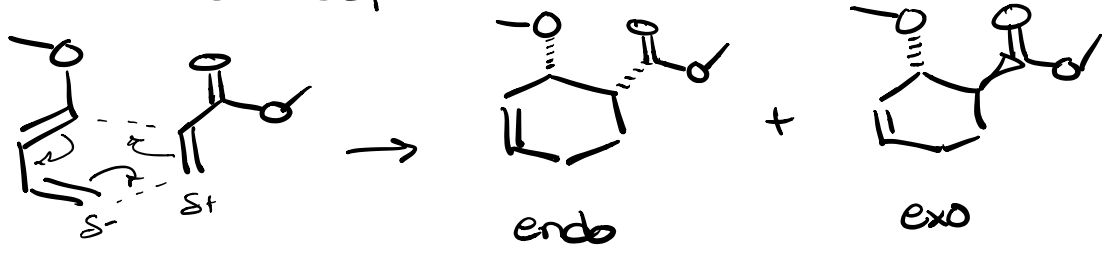
- Concerted



- Regiospecific



- Stereospecific



HOMO ψ_2 LUMO ψ_3

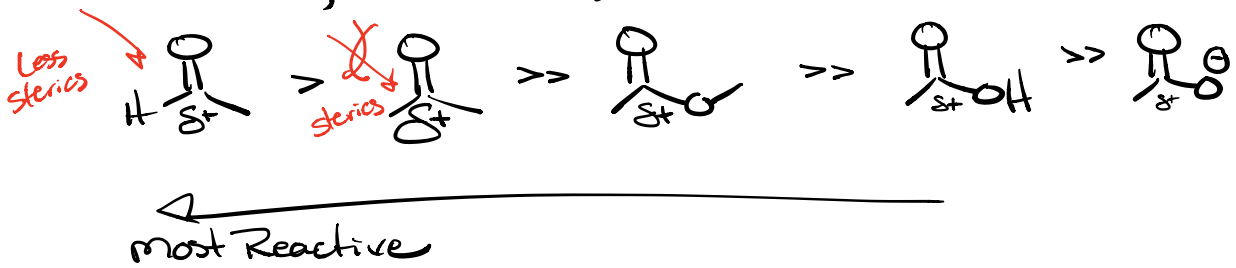
Major

3 orbital overlaps
$\Rightarrow$ lower E_A

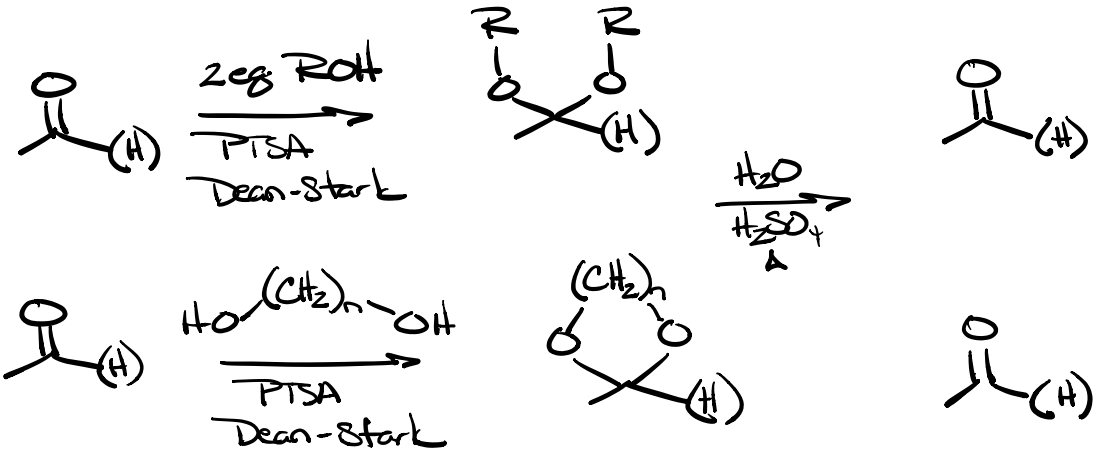
2 orbital overlaps

Carbonyl Chemistry

Reactivity of Carbonyl Compounds



- Acetals & ketals

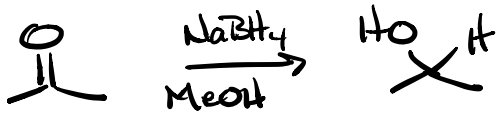


used to make products that are acetals or ketals, Carbohydrate chemistry, as protecting groups.

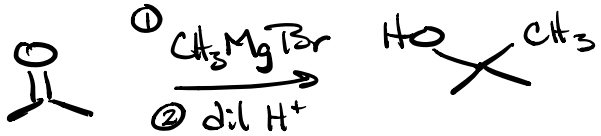
Most other reactions were review

oxidations

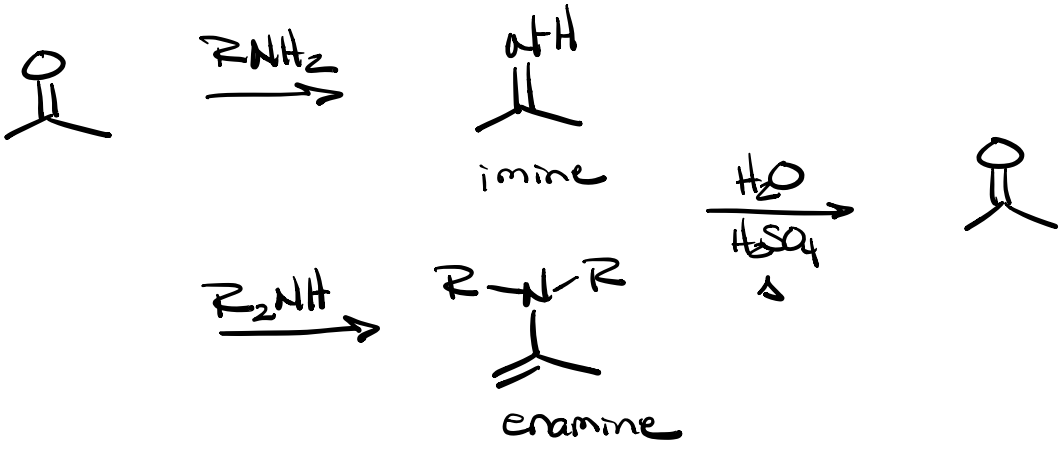
Reductions



Alkylations

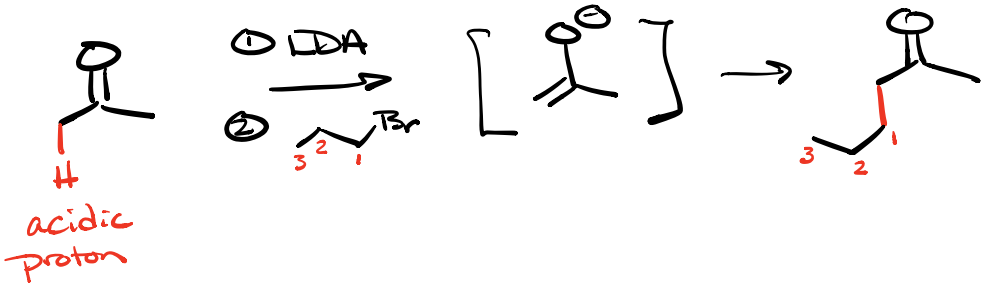


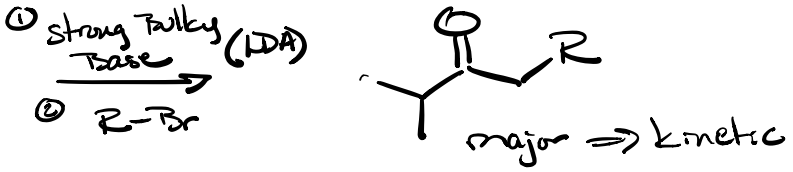
New Reactions

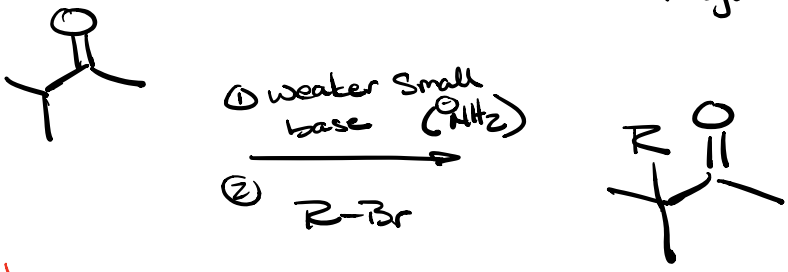


* mechanism all go through assited leaving steps
  ⇒ No S_N2 steps.

Alkylation Reactions at α position

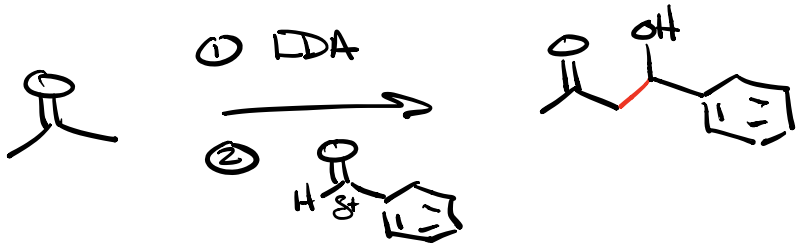


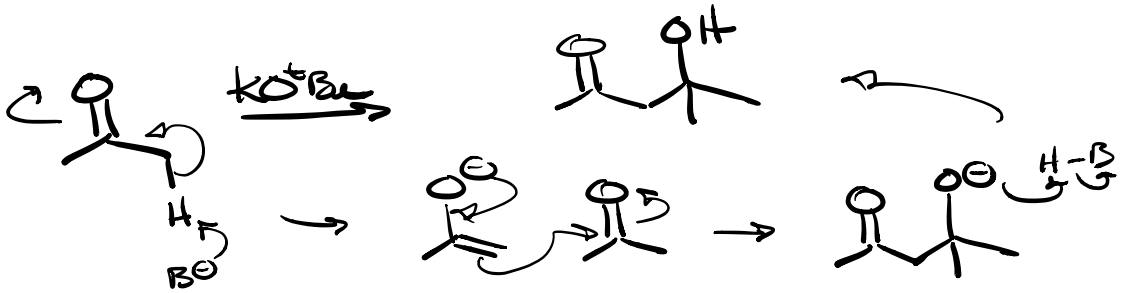


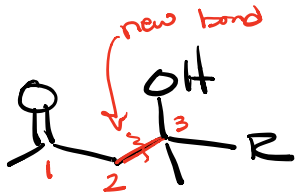


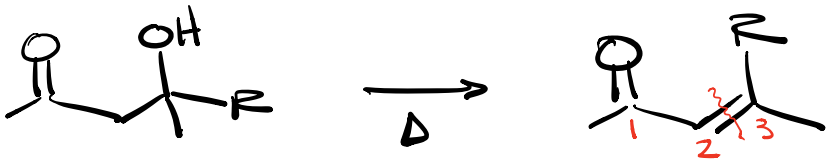
Cut Here

Aldol Reactions

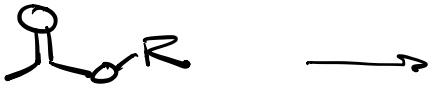




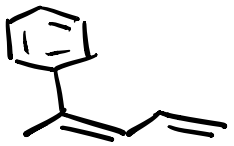




All Aldol like Reactions

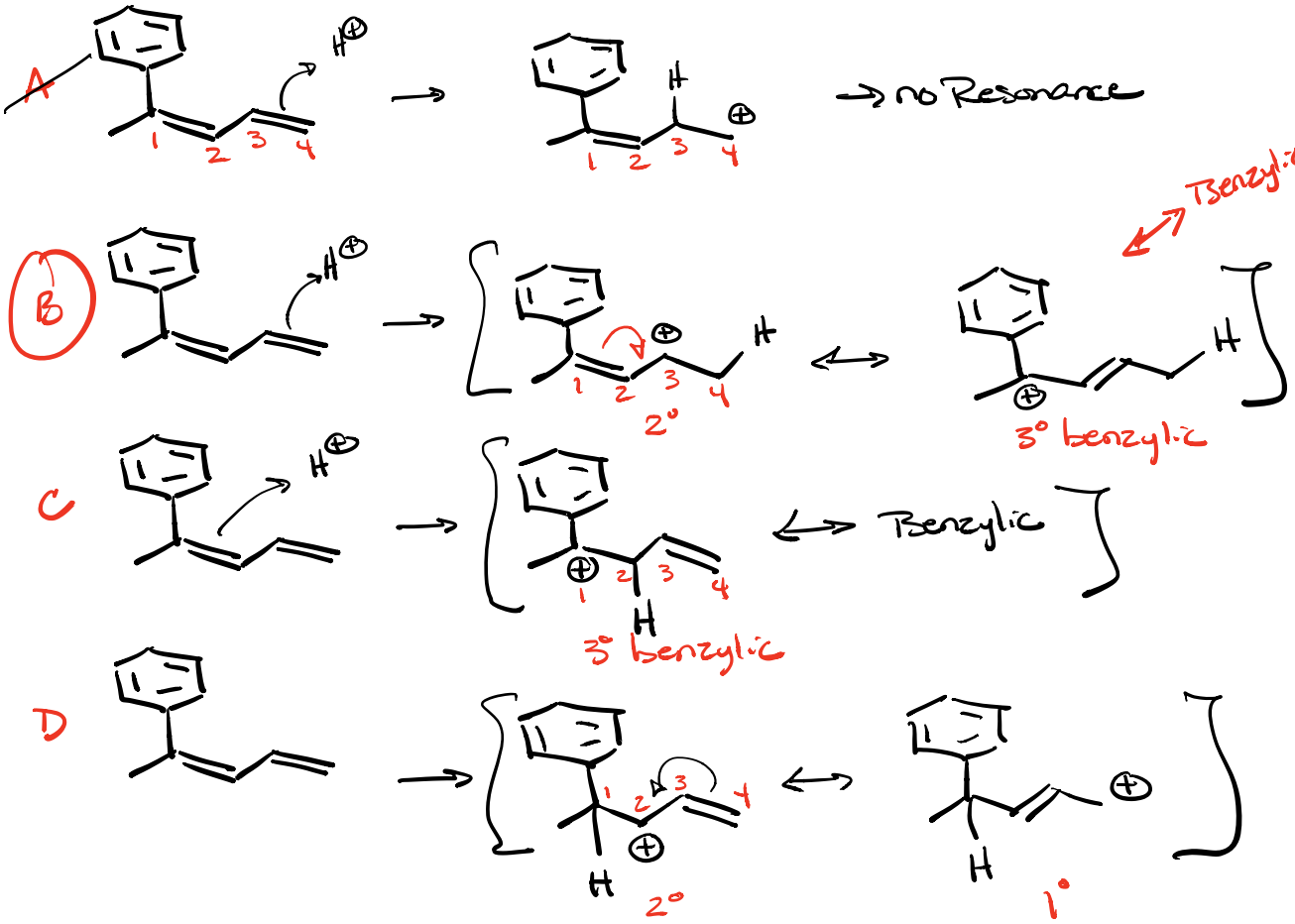


Diene & Diels-Alder Problems

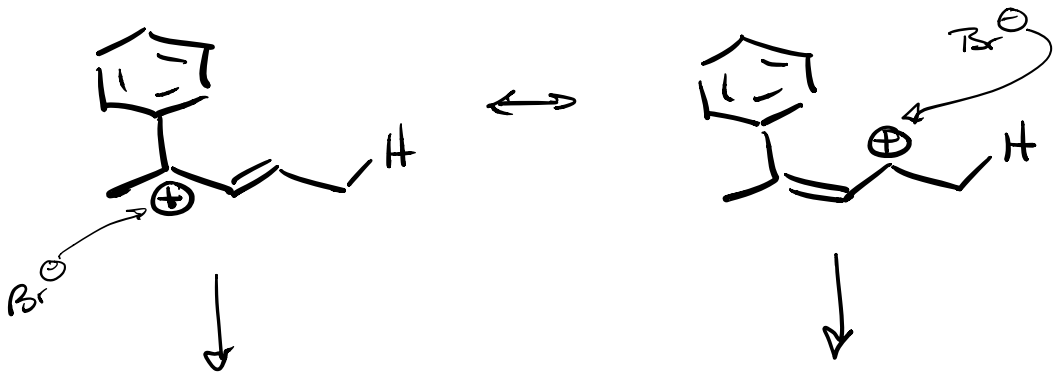


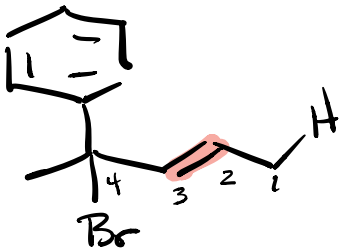
Give major product

Draw all 4 C^+



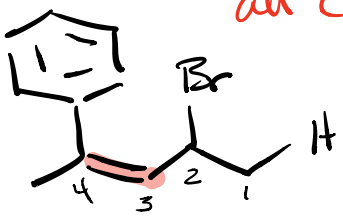
⇒ Take B and look at Resulting products



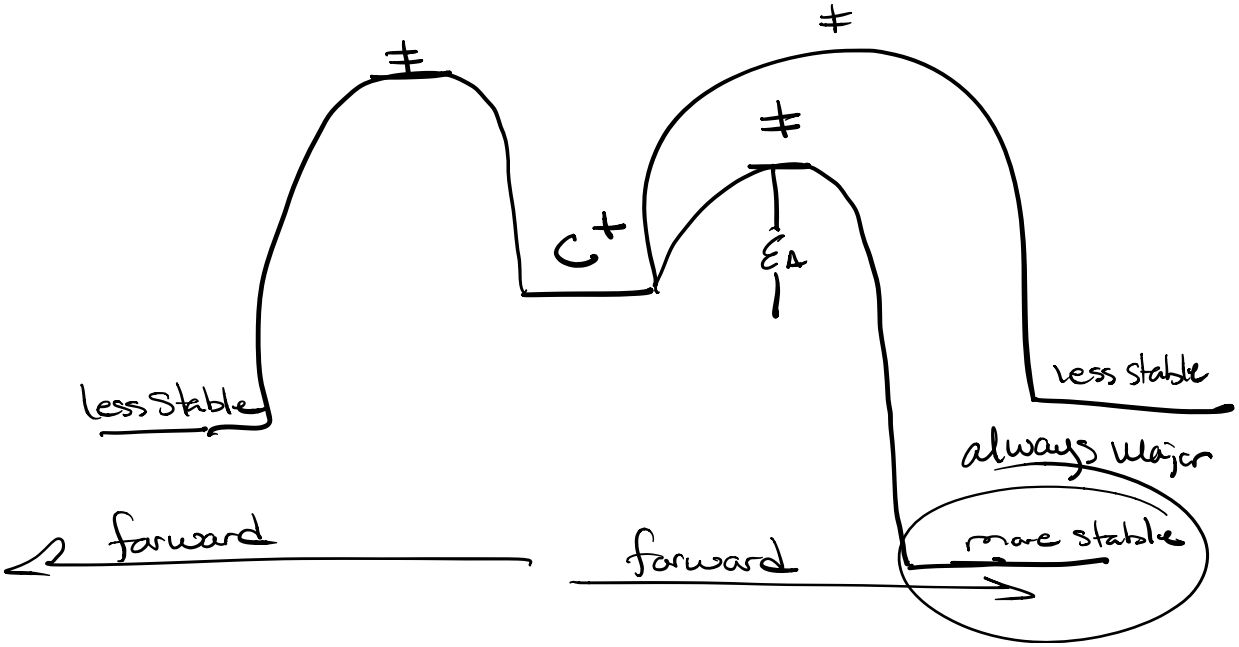


1,4-Addition more energy
Less-substituted Less Stable

Major under all Conditions



1,2-Addition Less energy
more Substituted more Stable



① Draw all 4 C^+

② Analyse Resonance

③ find most stable C^+ (Both Resonance Contributors)

④ Draw 2 products

⑤ Analyse 1,2 vs. 1,4
&
More Substituted vs. Less

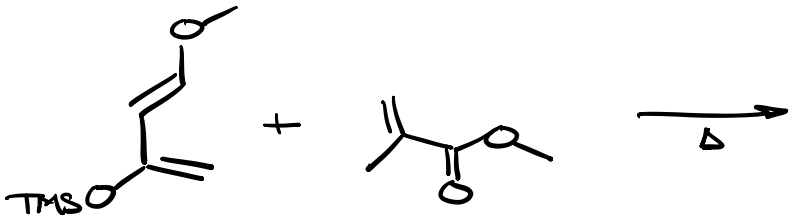
if
1,2 sub & more substituted ⇒ always Major

if
1,2 & less Sub kinetic Product
(lower temp & Short Rxn time)

vs

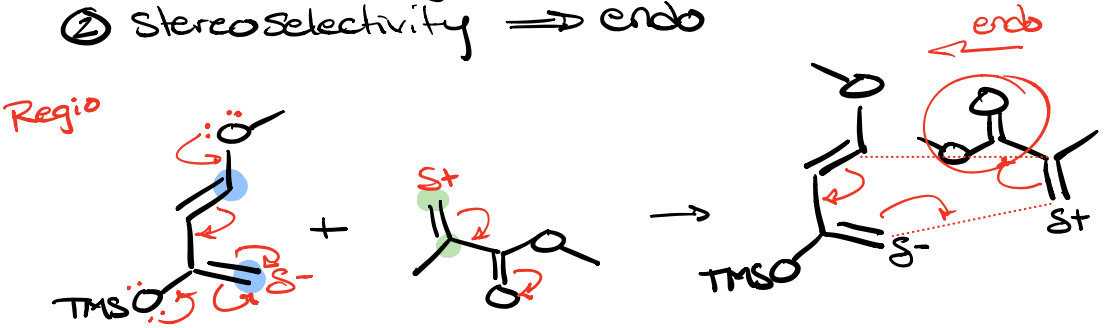
1,4 & more Sub Thermodynamic
(Higher Temp & long Rxn time)

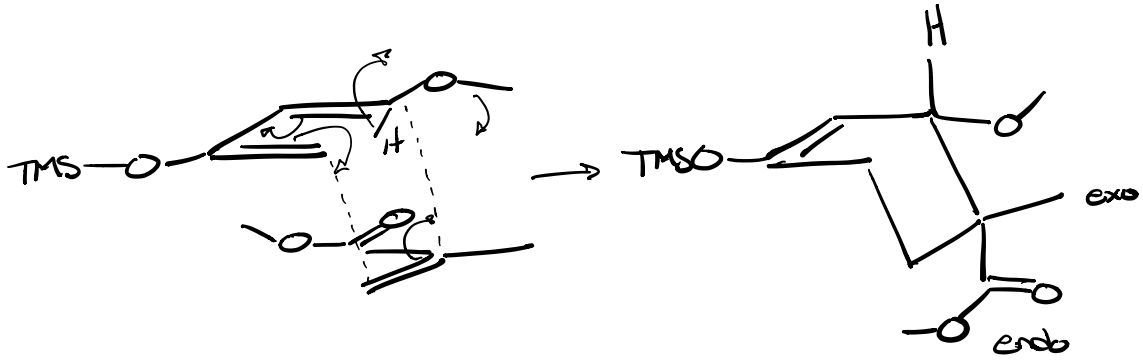
⇒ if no Rxn conditions given
⇒ assume Thermodynamic

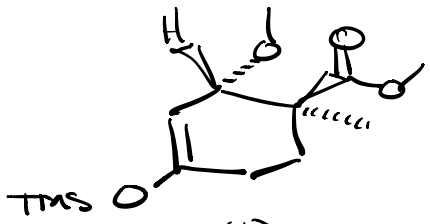


① Regioselectivity δ^+ & δ^-

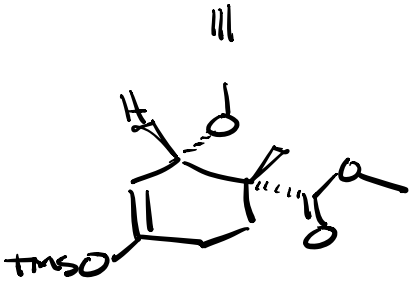
② Stereoselectivity ⟹ endo



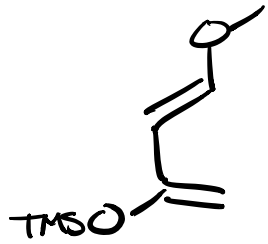




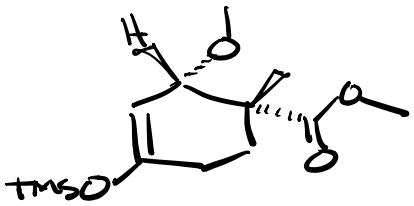
(±)
exo product



(±)
endo product
major



Danishevsky Diene



① TBAF
② dil H^+