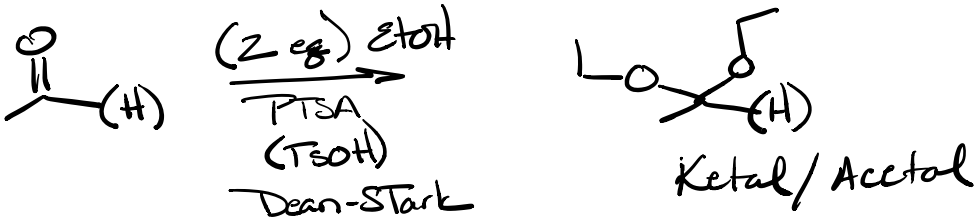
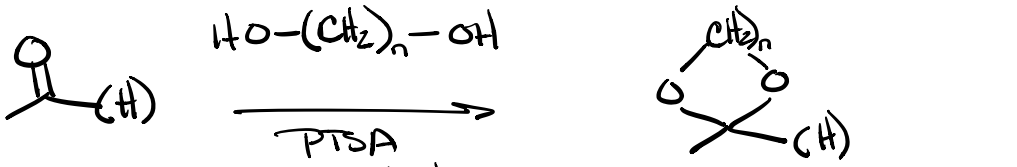
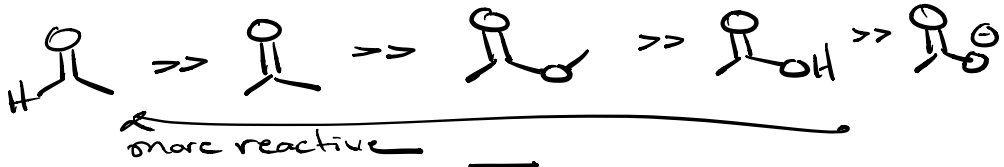
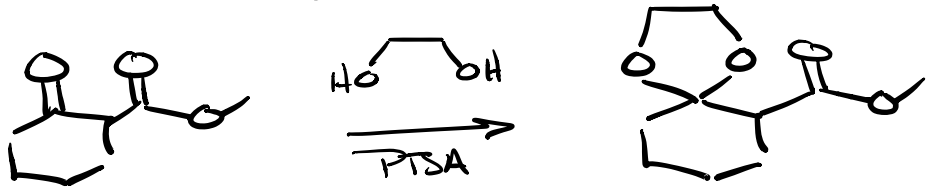


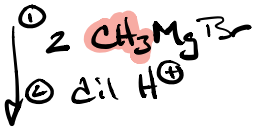


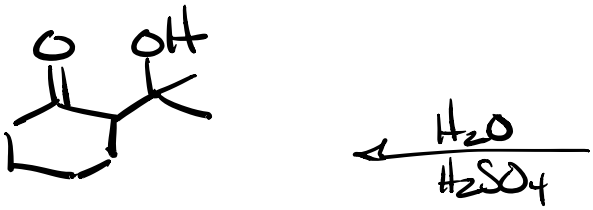
more robust
⇒ Harder to cleave
used as protecting groups

Ex

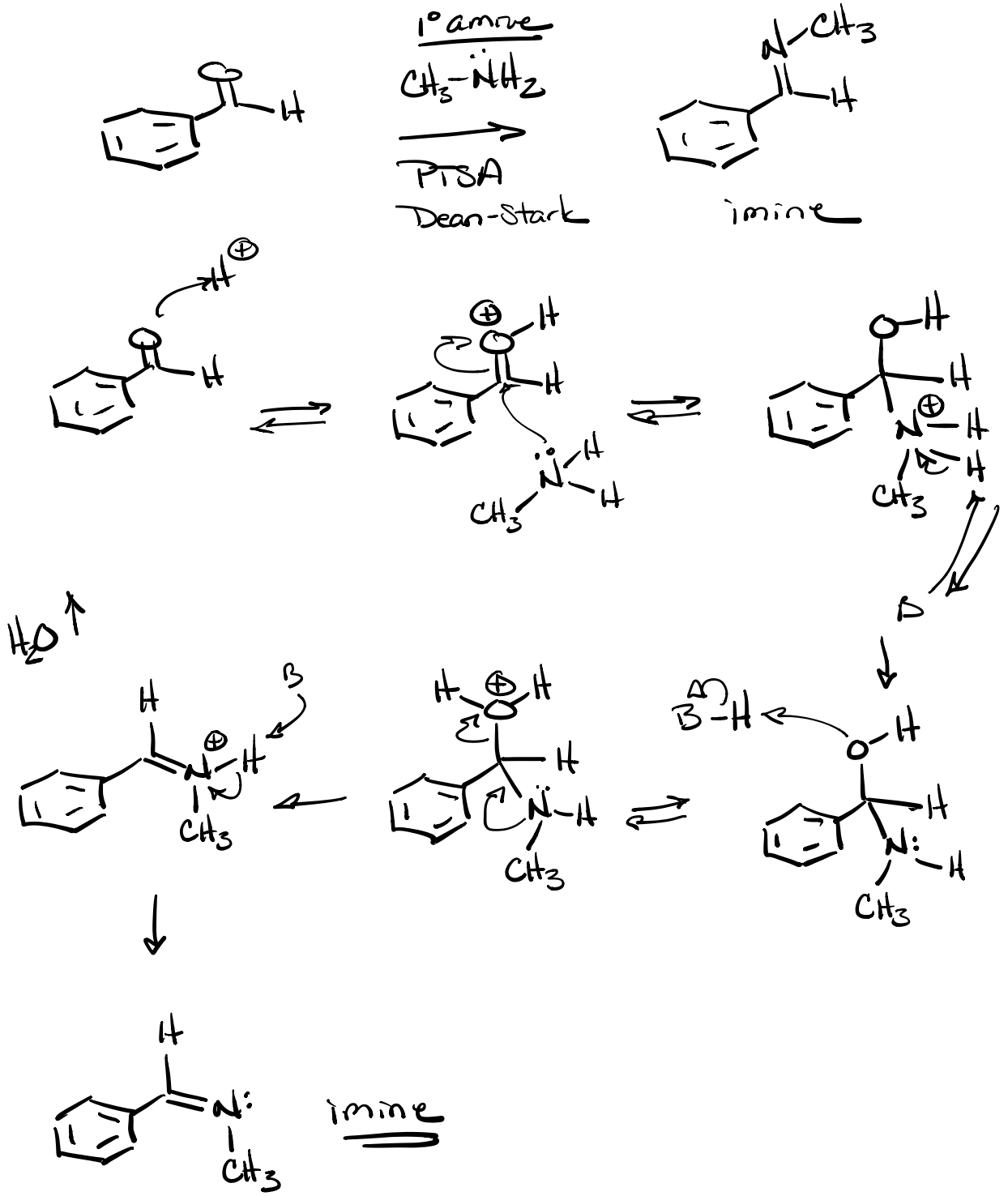


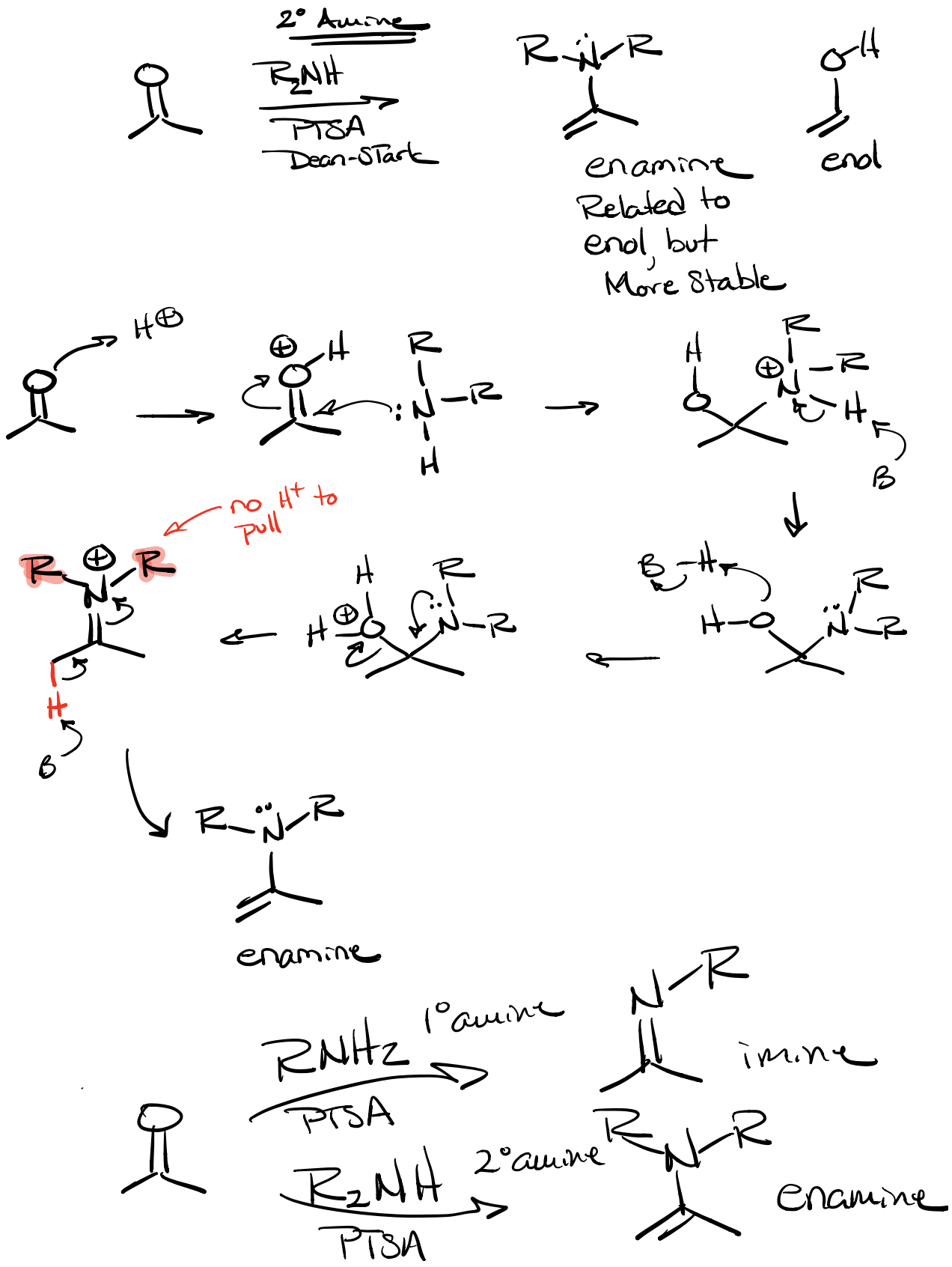




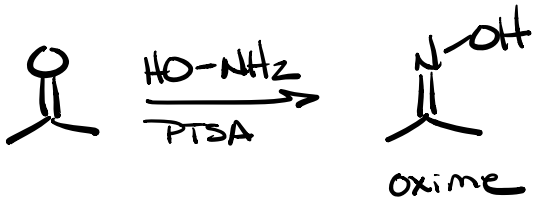


Nitrogen Nucleophiles

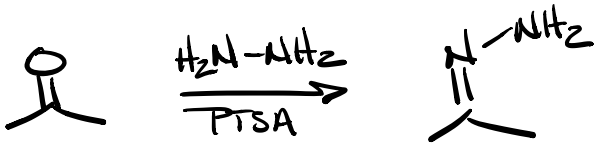



2° Amine
R2NH
PTSA
Dean-Stark
enamine
Related to
enol, but
More Stable
enol
no H+ to pull
enamine
RNH2
1°amine
PTSA
R2NH
2°amine
PTSA
imine
enamine

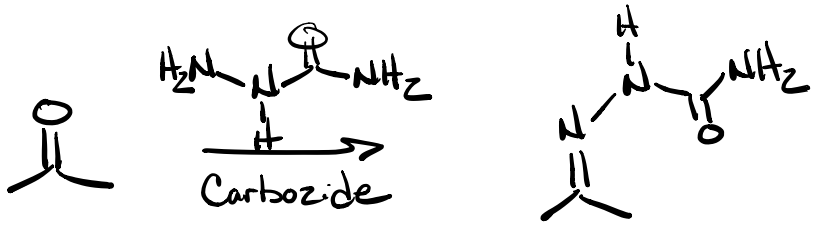
imine & enamine are very similar to other functional groups.



oxime

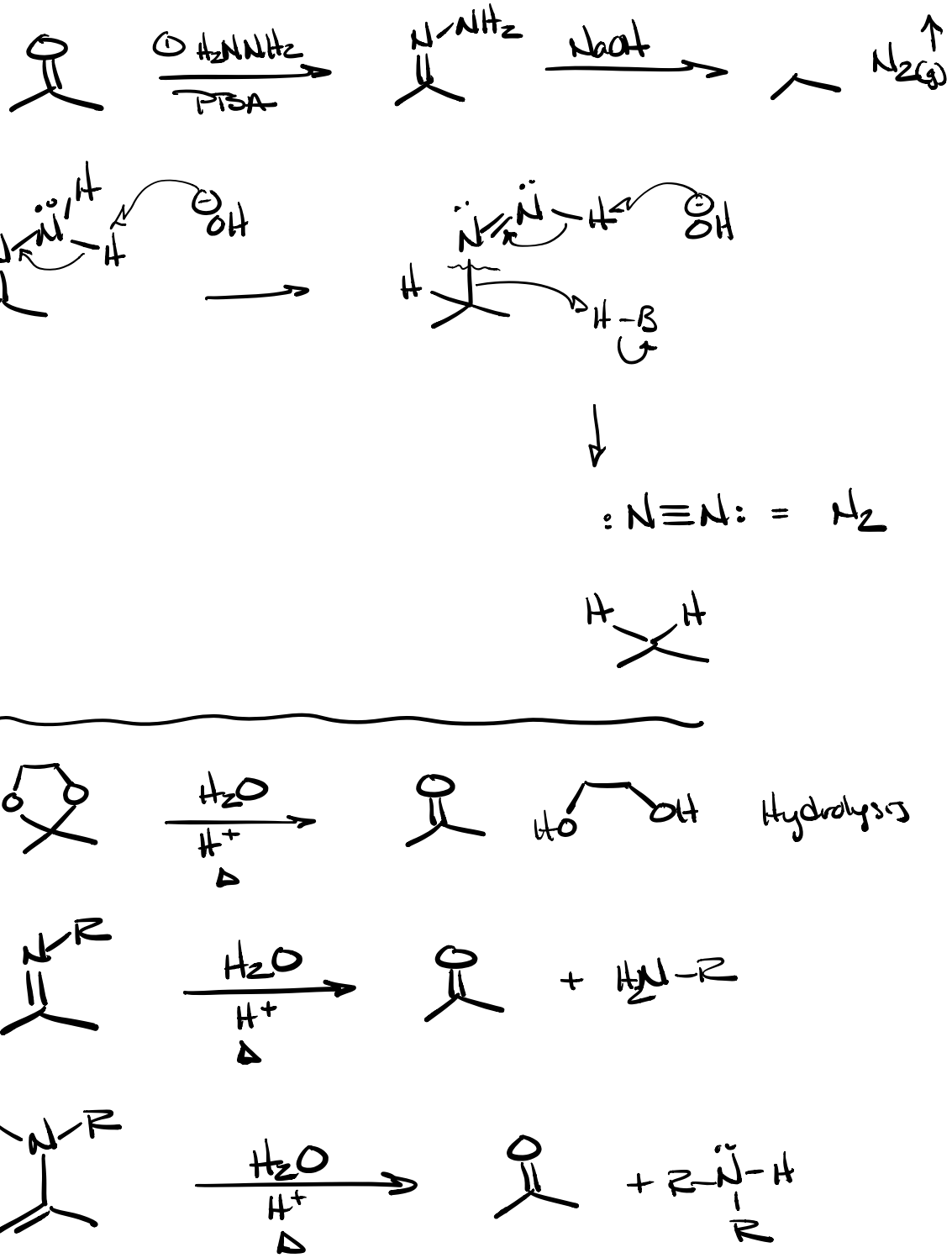


hydrazone

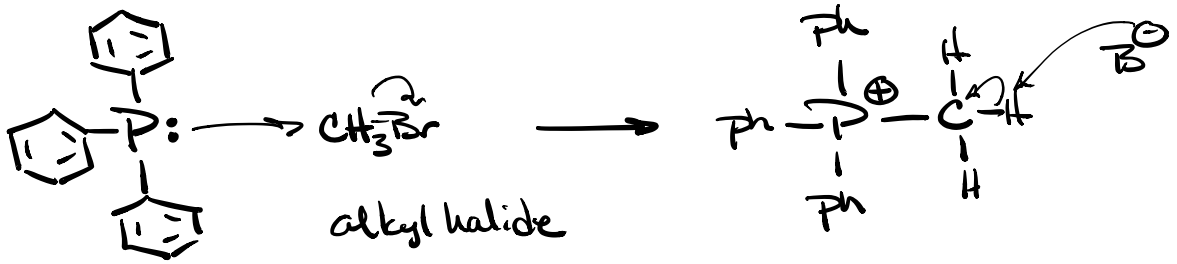


Carbazone

Wolff - Kisner Reduction



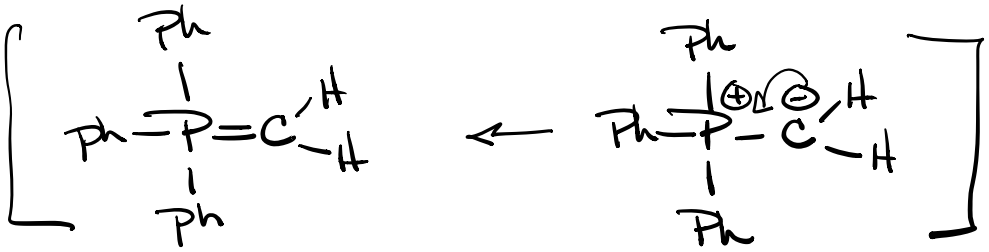
Wittig Rxn (Pronounced Vittig)



alkyl halide

Super organic soluble nucleophile

strong base LDA or KO^tBu



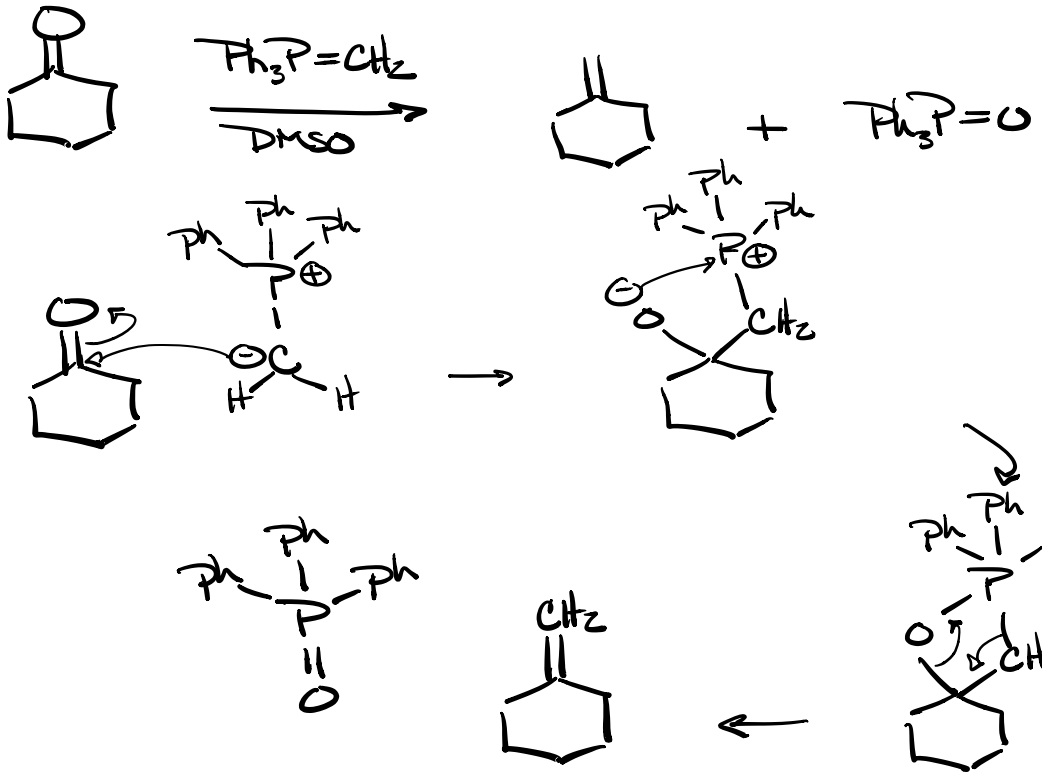
Major Resonance Contributor

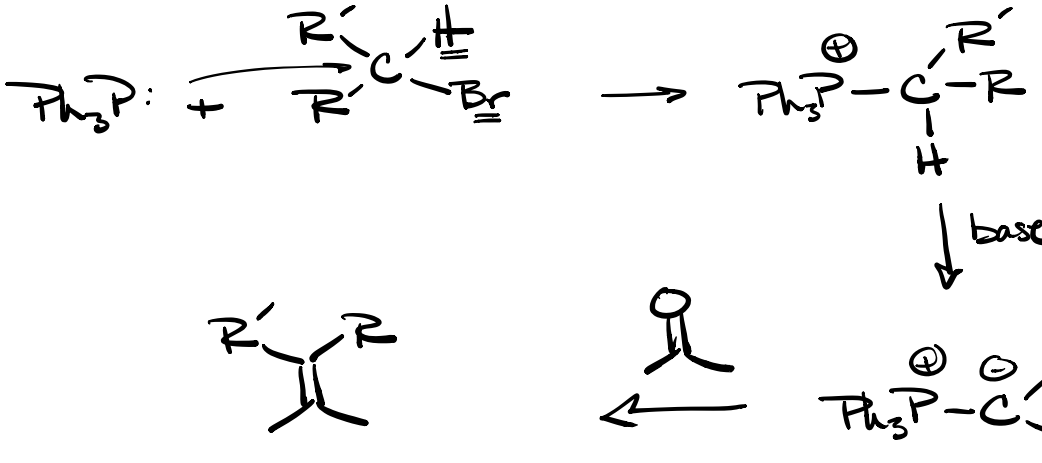
sp^3d

Wittig Reagent

Ylide

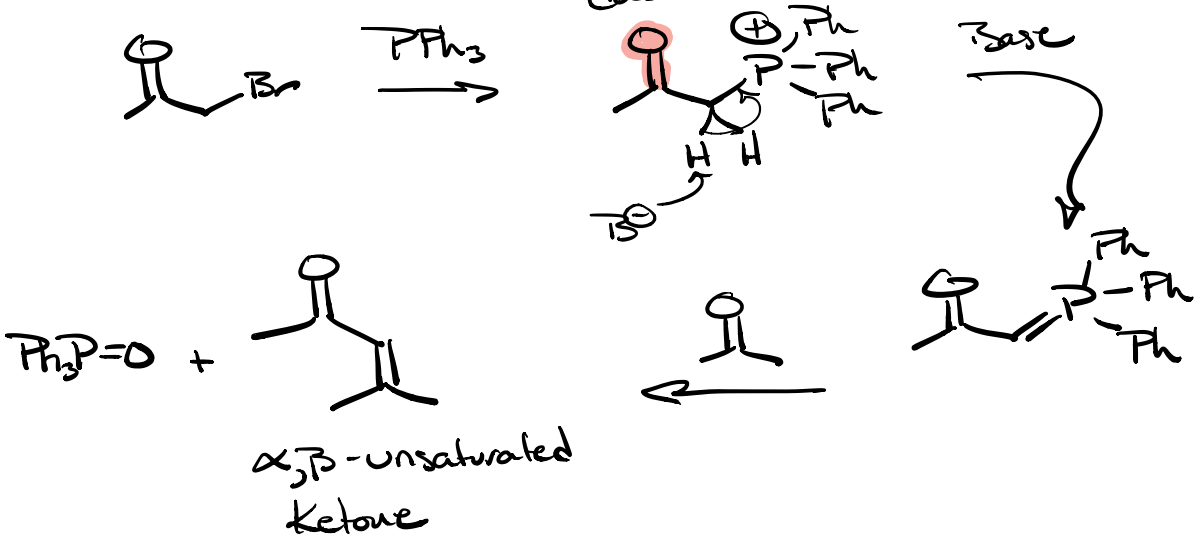
But Reacts as a Carbon nucleophile

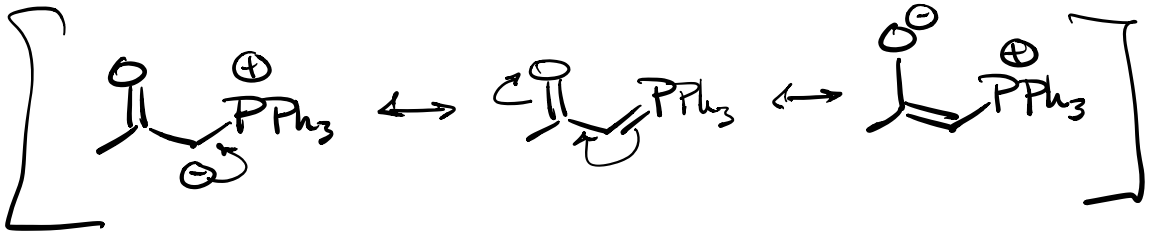

Ph3P=CH2
DMSO
+
Ph3P=O
Ph
Ph
Ph
P
O
H
H
CH2
CH2


Ph3P:
+
R'
R'
H
Br
Ph3P
R'
R
H
base
R'
R
R'
R

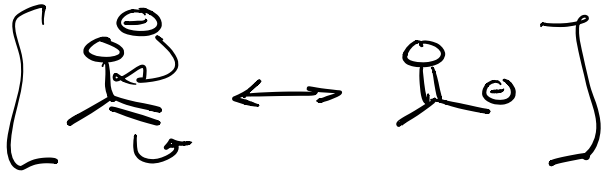
Tolerates carbonyls α to Wittig

doesn't need PG!





what about



as nucleophile

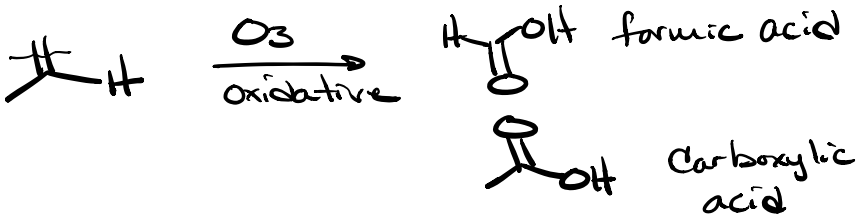
Enolate

Concludes Chapter 19

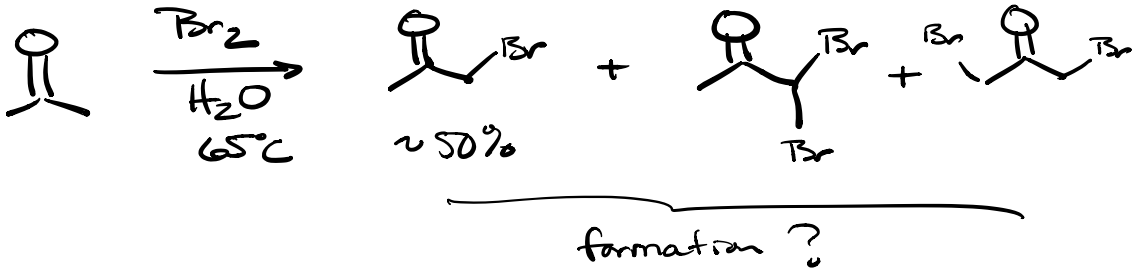
Chapter 20 Carboxylic acids

⟹ formation of Carboxylic acids

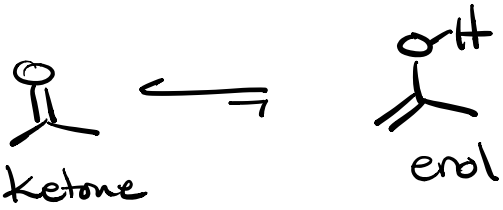
Ex

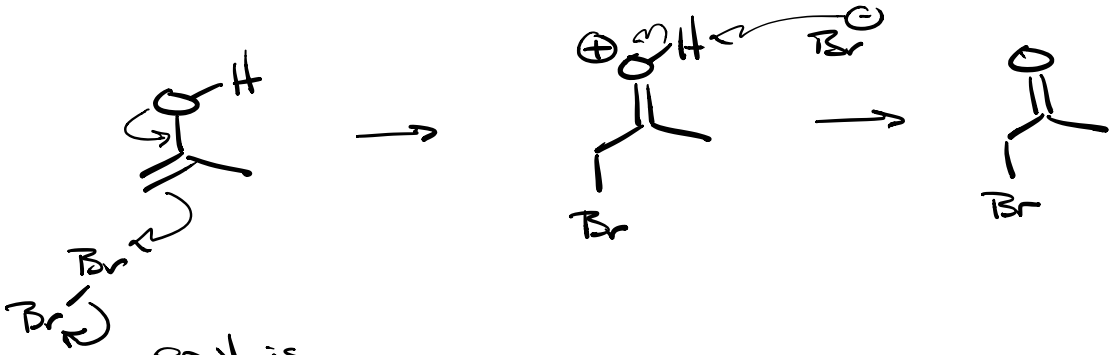


Chapter 21

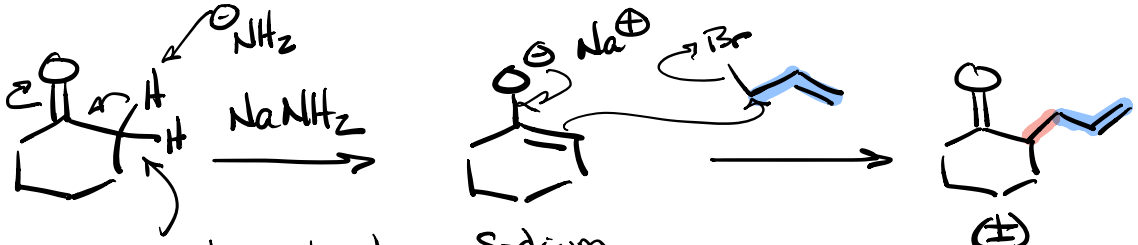


Enol/keto tautomerism



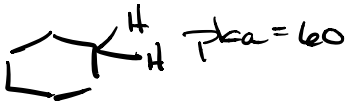


enol is a nucleophile

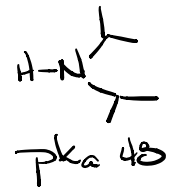


α-to carbonyl H's are acidic

pka ~ 26

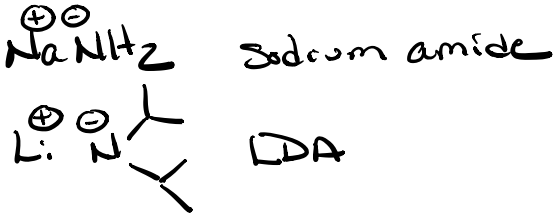


Two main strong bases are



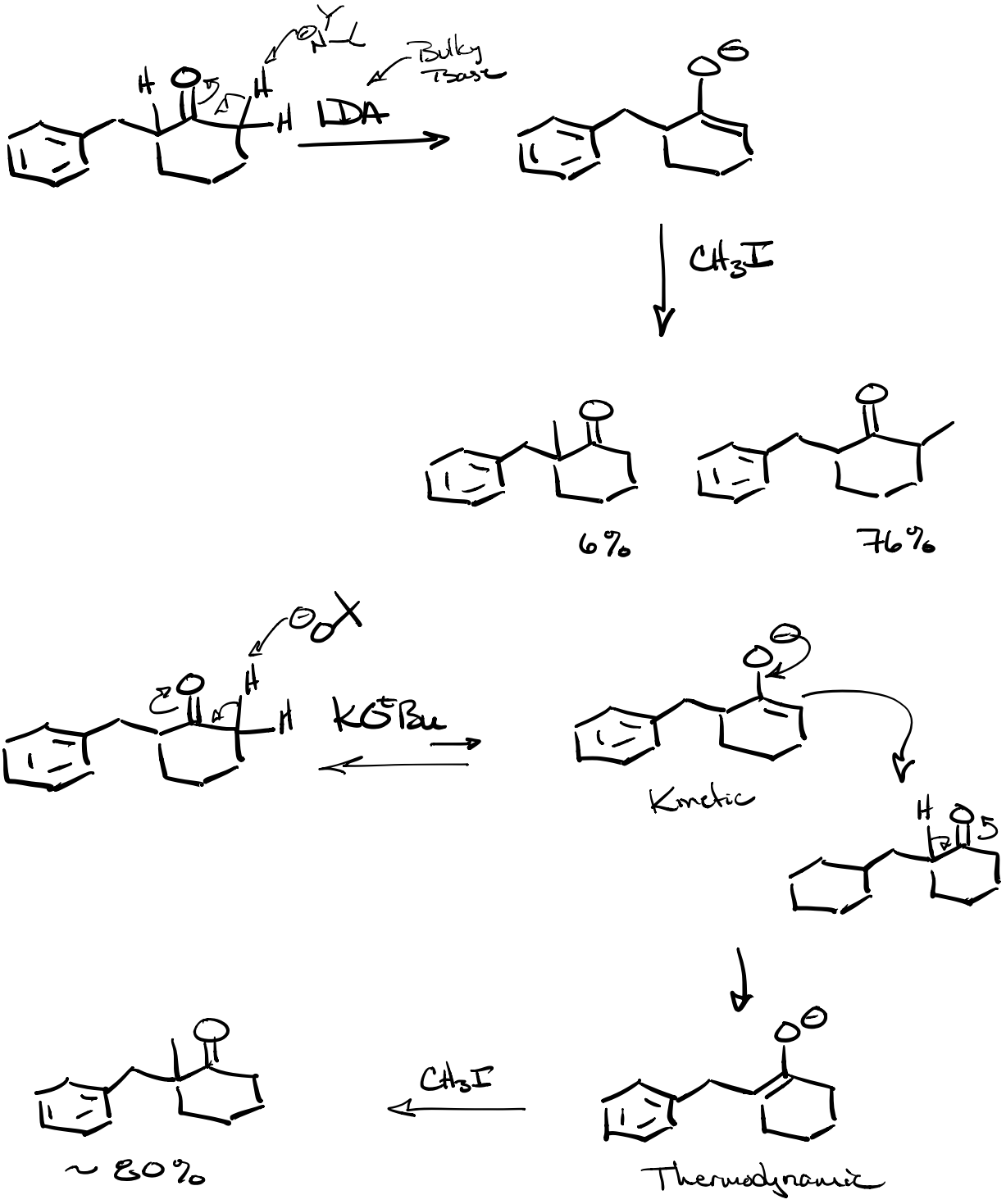
pka 43

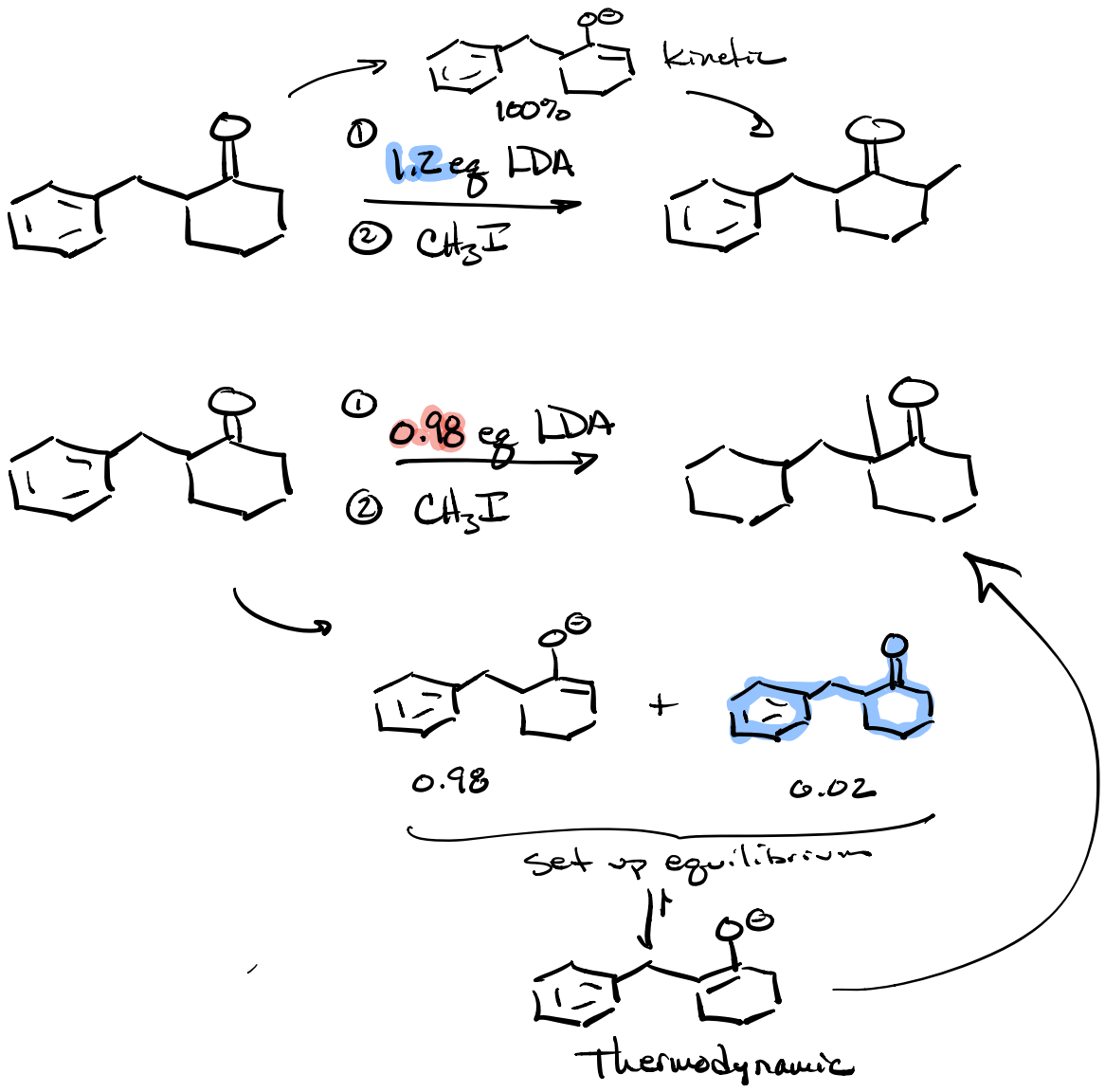
pka 48

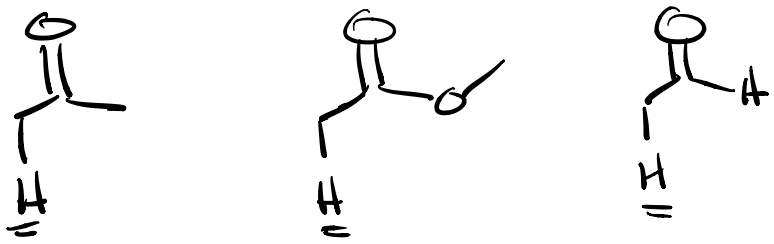


Sodium amide

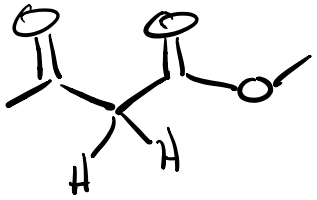
LDA


Bulky Base
LDA
CH_3I
6%
76%
KO^{t}Bu
Kinetic
Thermodynamic
CH_3I
~ 80%

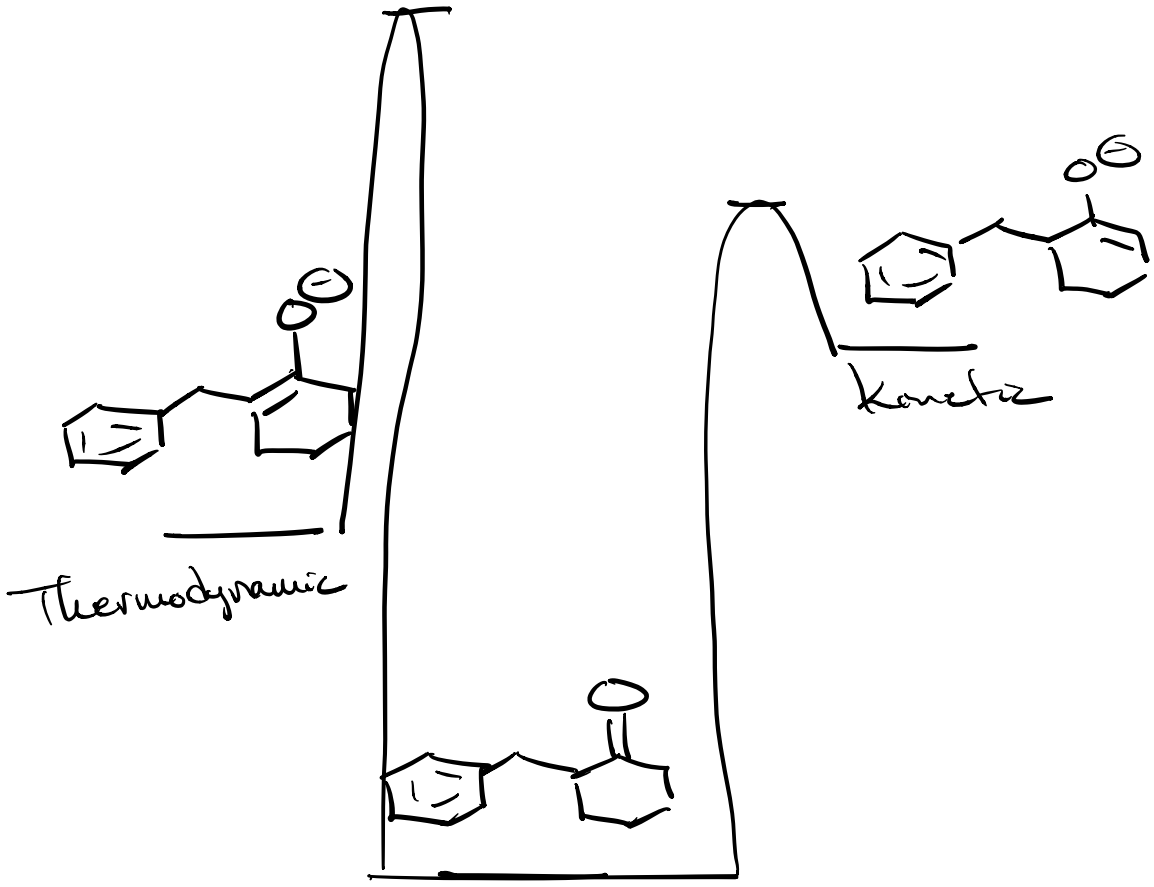

kinetic
100%
① 1.2 eq LDA
② CH_3I
① 0.98 eq LDA
② CH_3I
0.98
0.02
set up equilibrium
thermodynamic



~26 pKa



pKa ~ 12


Thermodynamic
Kinetic