

Today

Chap 17 Reactions at the α -C of a Carbonyl

Sections 17.2, 17.3: Keto-Enol
Tautomerization

Section 17.1 The Acidity of α -Hs

Second Class from Today

Benzene and Aromaticity 8.1, 8.2, 8.16 - 8.18

Electrophilic Aromatic Substitution
8.16 - 8.21, 18.1 -18.8

Next Class

Alkylation of the α -C of a Carbonyl
Section 17.6, 17.7

Benzene and Aromaticity 8.1, 8.2, 8.16 - 8.18

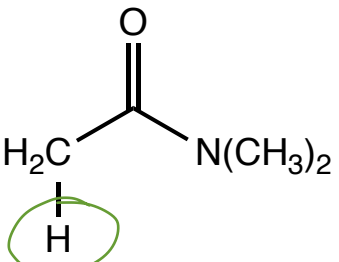
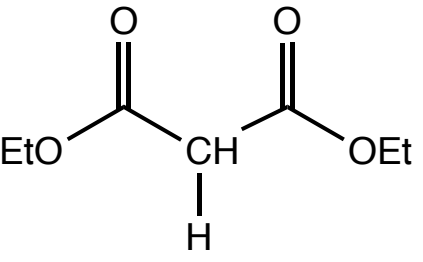
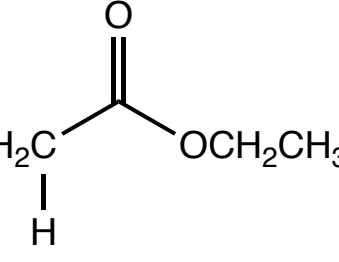
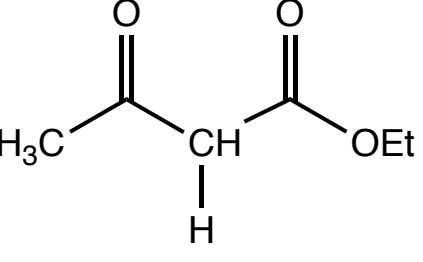
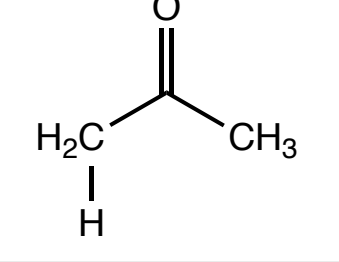
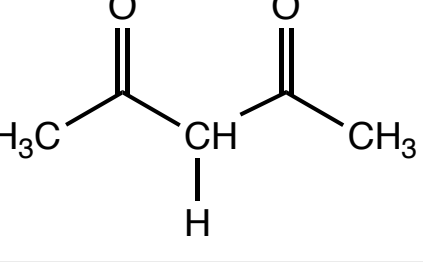
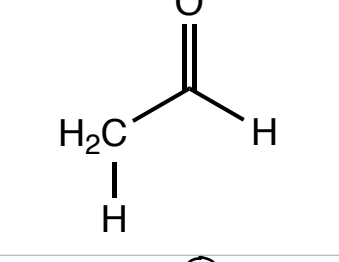
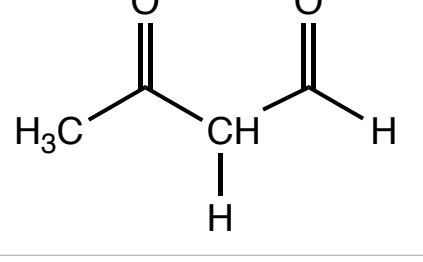
Third Class from Today

Electrophilic Aromatic Substitution
8.16 - 8.21, 18.1 -18.8

On a separate piece of paper rework test 2 and hand in on Friday, April 14

Acidic α -Hydrogens

Section 17.1

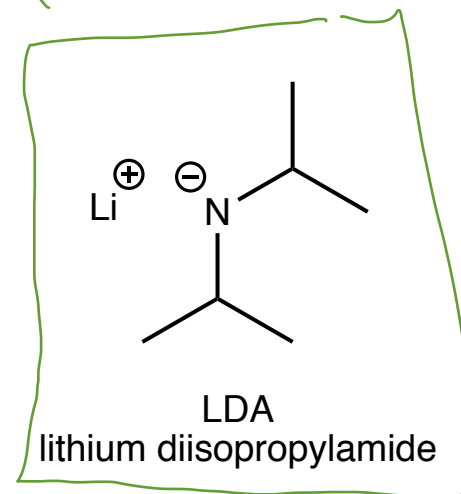
	pK _a		pK _a
	30		13.3
	25		10.7
	20		8.9
	17		5.9

CH₃CH₂-H pK_a = 50

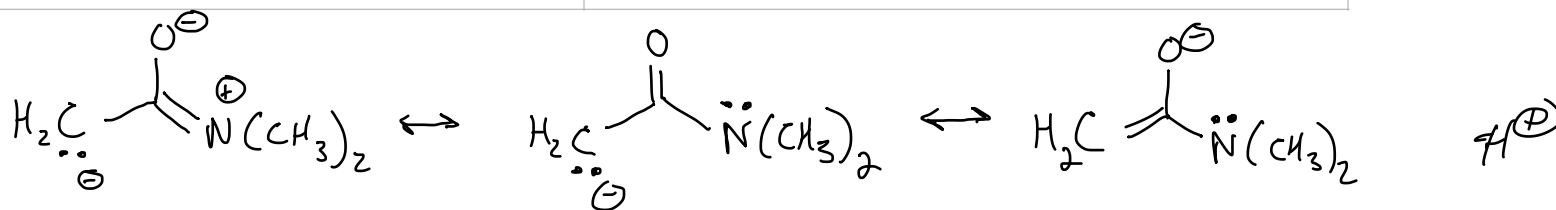
CH₃CH₂O-H pK_a = 16

CH₃C(O)O-H pK_a = 4.75

a very strong base ... not as strong as butyl lithium but safer.

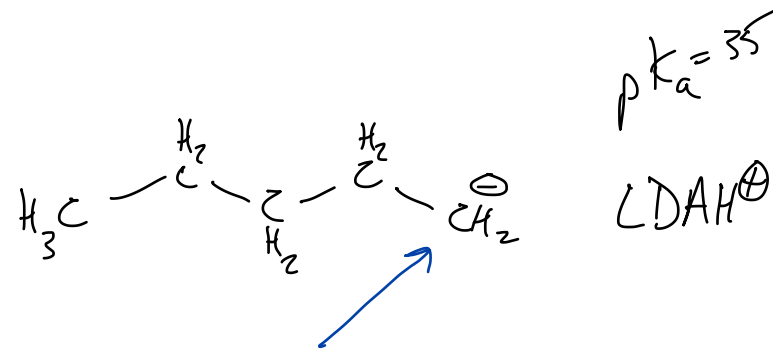
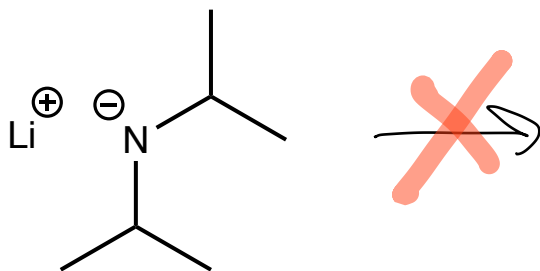
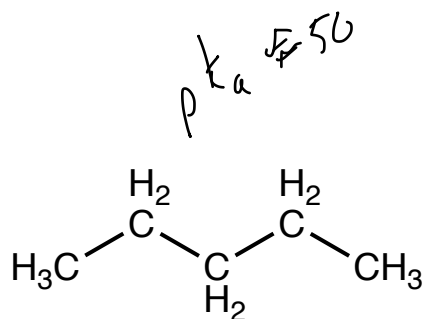


pK_a LDAH⁺ = 35

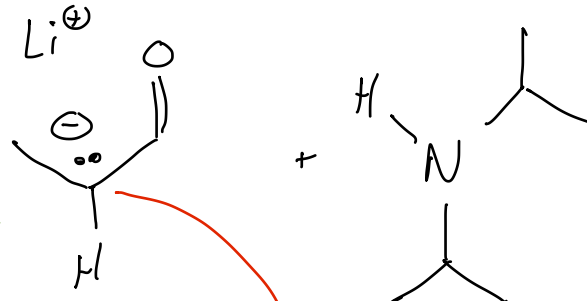
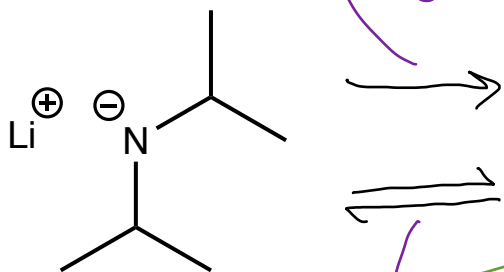
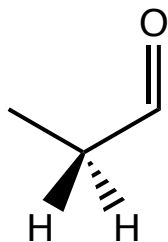


Acidic α -Hydrogens

Section 17.1



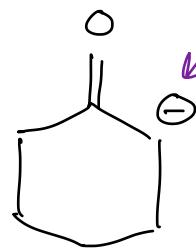
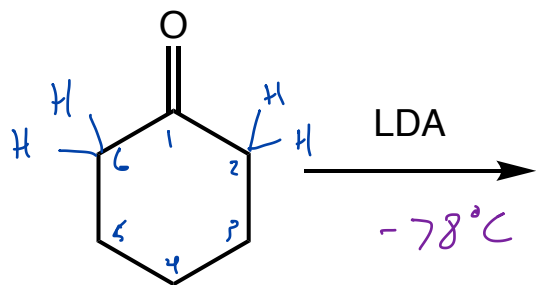
LDA is not strong enough a base to deprotonate an alkane and form an unstabilized carbanion



this is called an enolate
 it's an α -enolate (used for anions)
 enol



Reactions at the α -Carbon - Forming a Carbanion

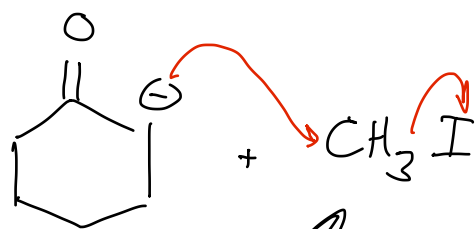


lp e⁻'s on C are more reactive than lp e⁻'s on O
LDAH⁺

nucleophilic C atom

because of the symmetry of the molecule

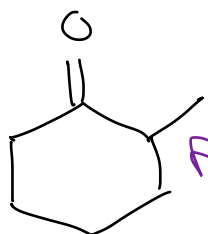
deprotonation will occur at C₂ or C₆... but it doesn't matter which one



iodomethane

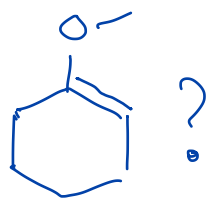
excellent S_N2 substrate

-78°C



Li⁺ + I⁻

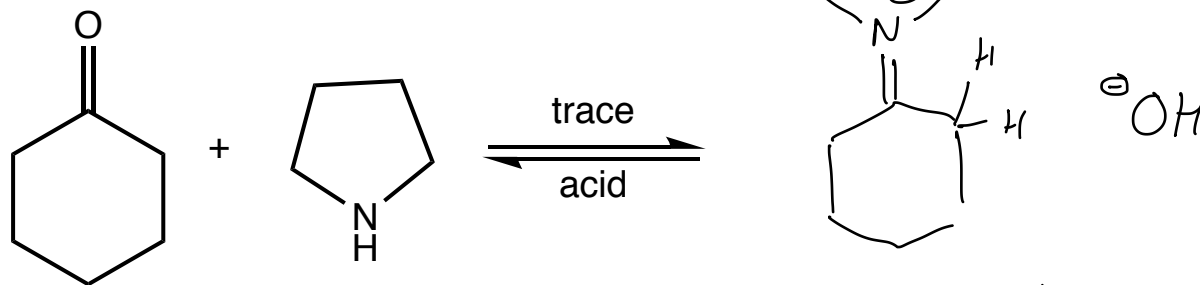
this α -C has been alkylated



C=O double bond is lower in E than C=C double bond

Reactions at the α -Carbon - An Alternate Method for Alkylation

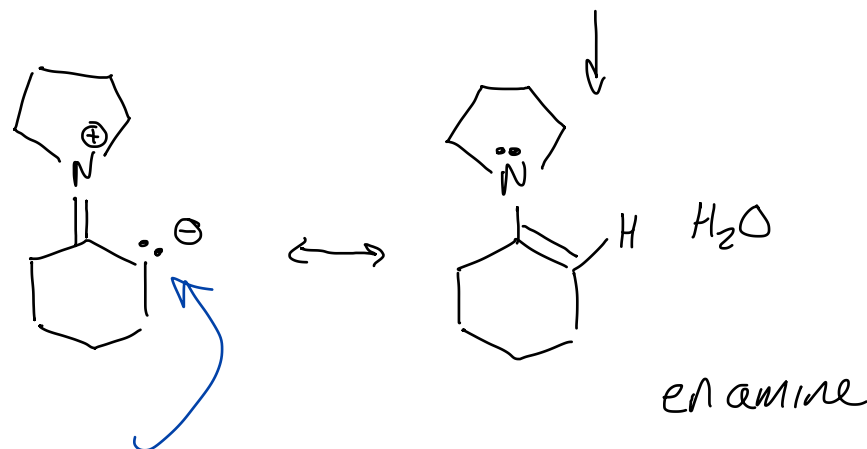
Section 17.8



Why might you want to use pyrrolidine instead of triethylamine?

not as strong base
crazy strong base
a little safer

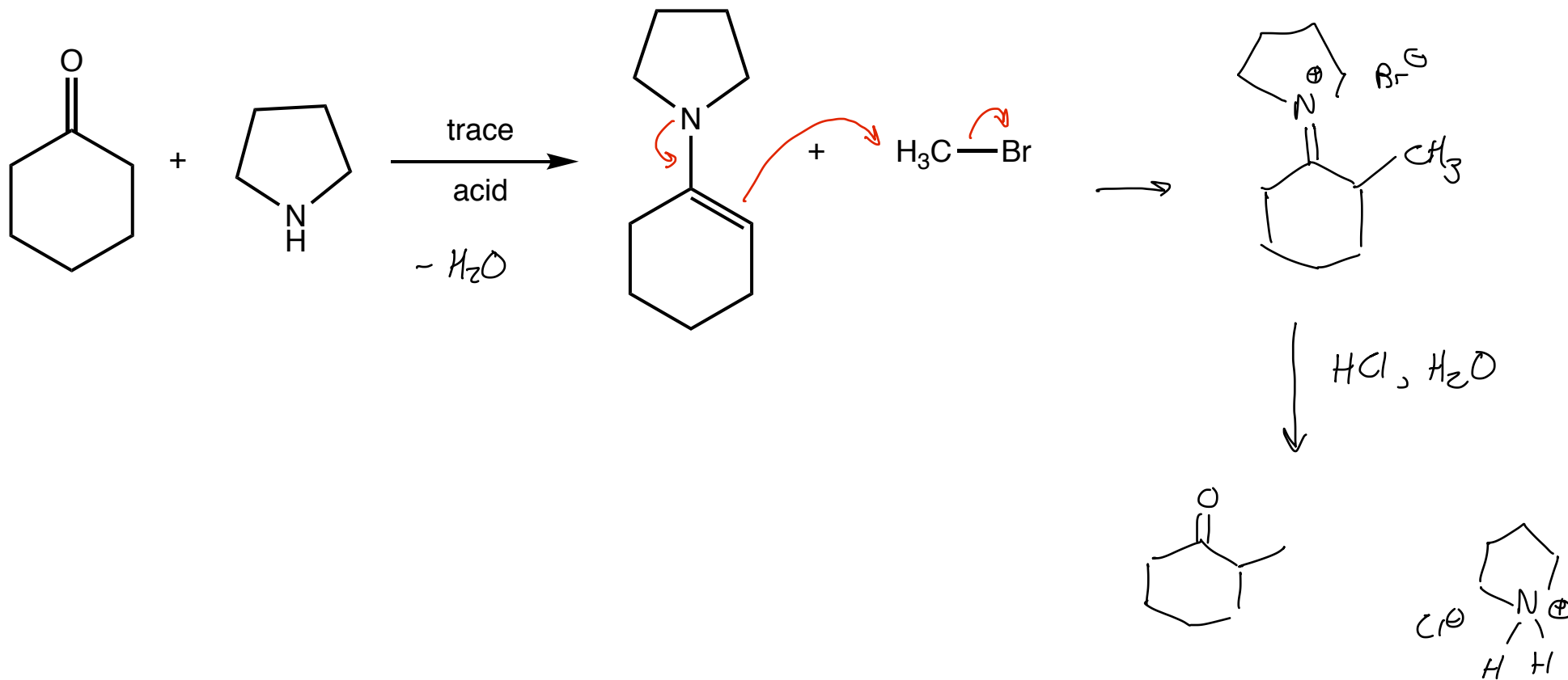
the triethylamine would need to be removed so it doesn't react with electrophile

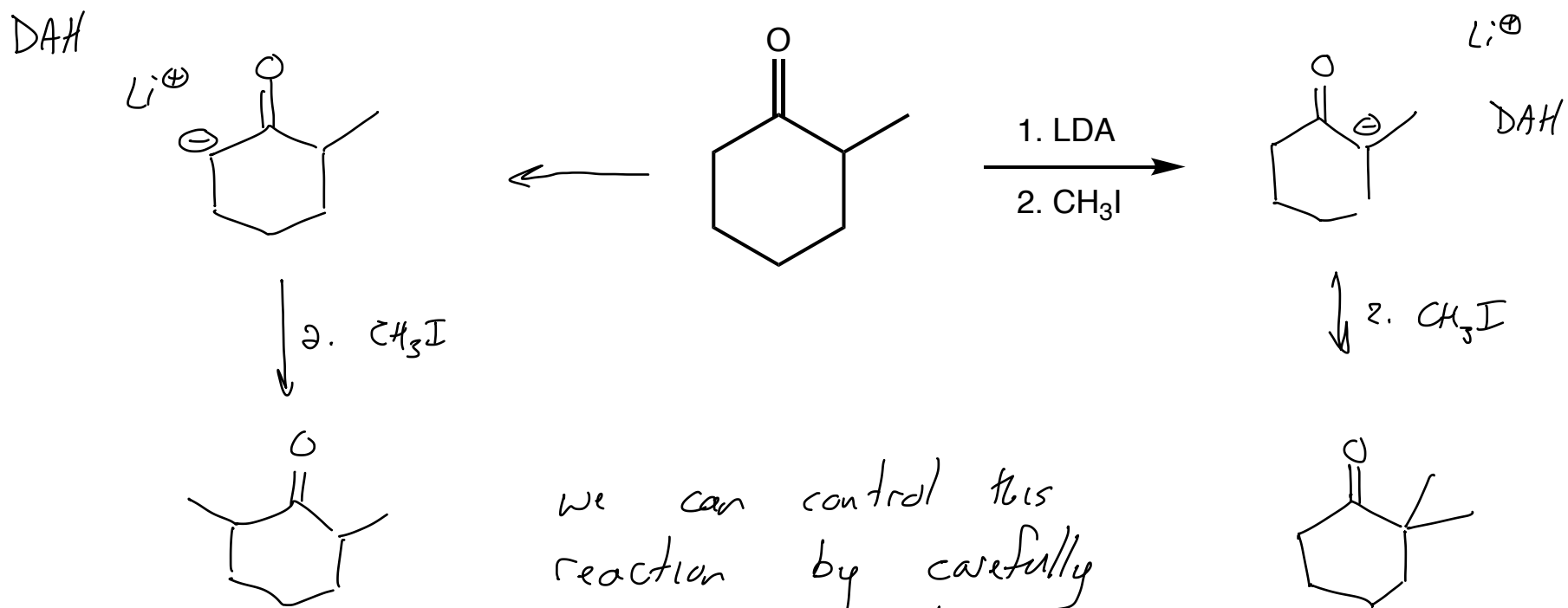


Making enamines is another way to make the α -C nucleophilic

Reactions at the α -Carbon - An Alternate Method for Alkylation

Section 17.8





we can control this reaction by carefully controlling the temp...

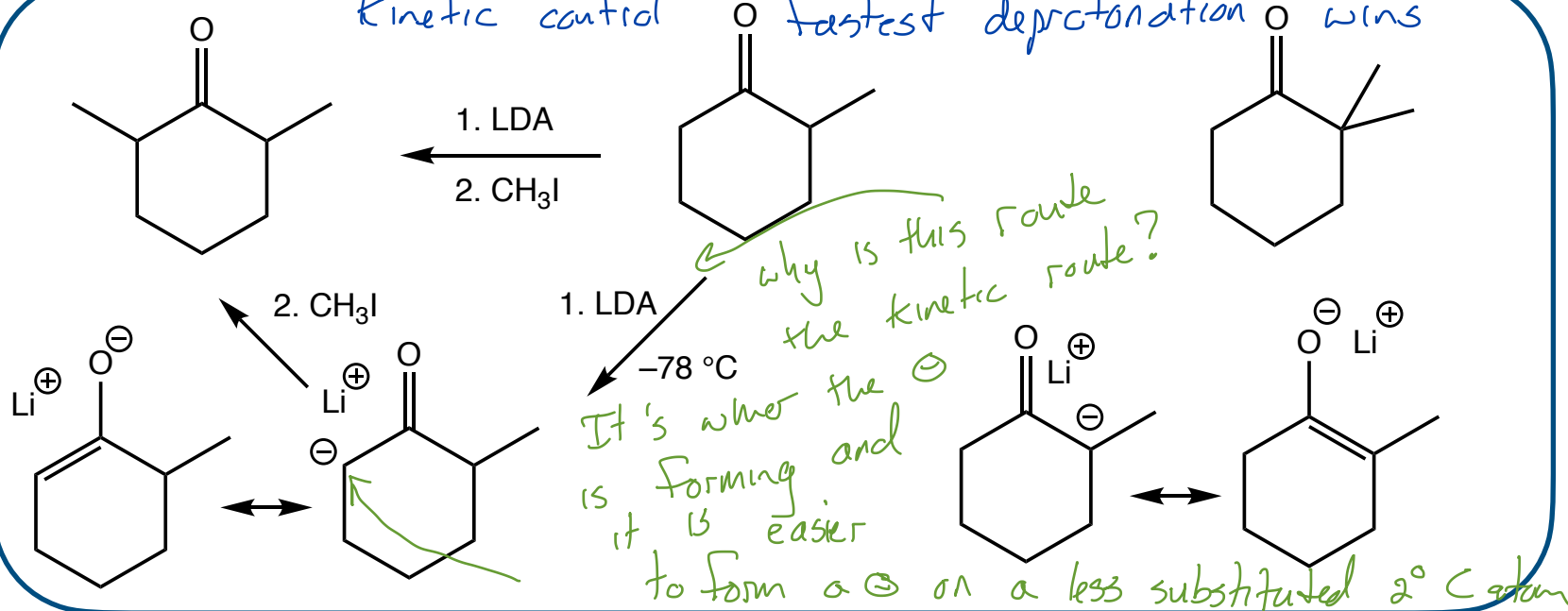
we are choosing between the kinetic product product that forms fastest and the thermodynamic product the product that is more stable

Kinetic vs Thermodynamic Control

Section 17.7

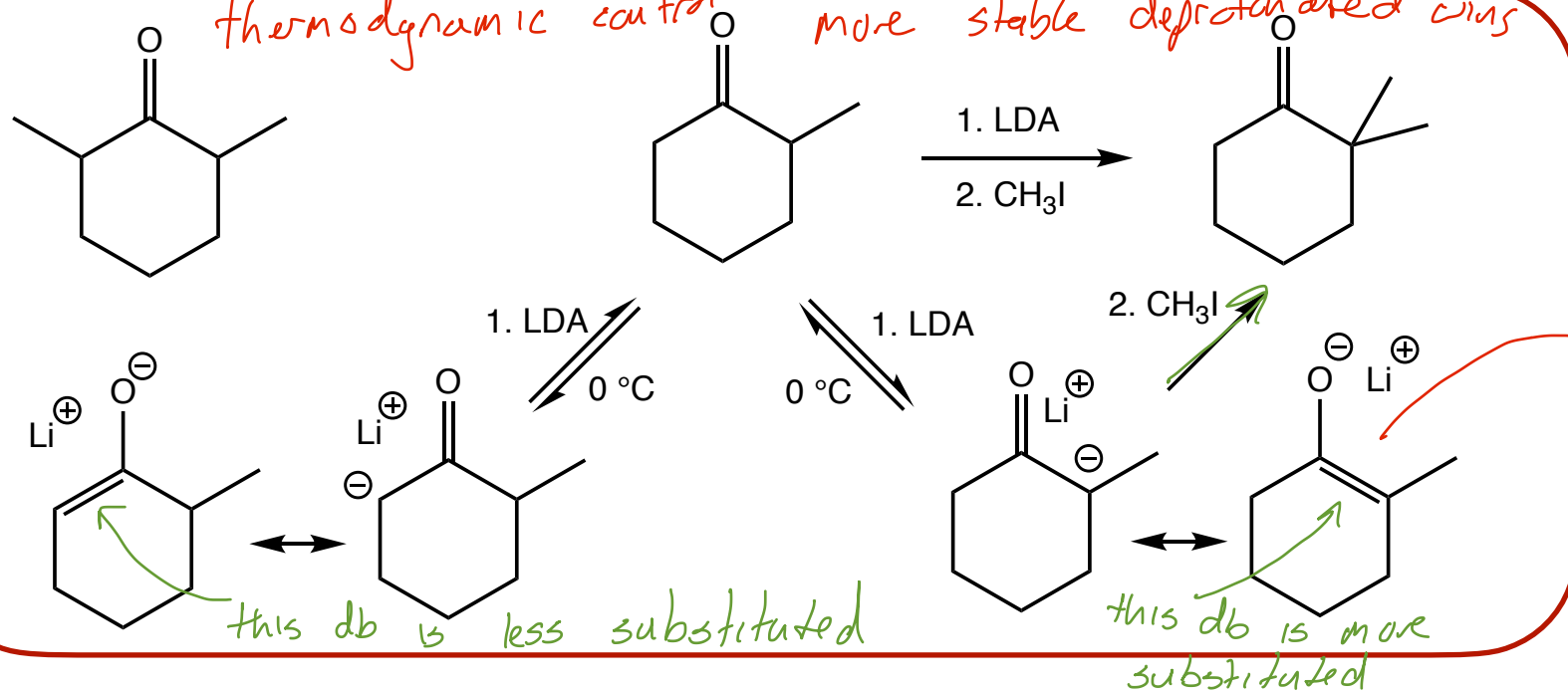
kinetic control

fastest deprotonation wins



carbanions are destabilized by the increased e^- density around more substituted C atoms
 C^\ominus stability order
 $1^\circ > 2^\circ > 3^\circ$

thermodynamic control more stable deprotonated wins



just enough E to get an equilibrium going
the concentration of these lower E molecules will grow over time