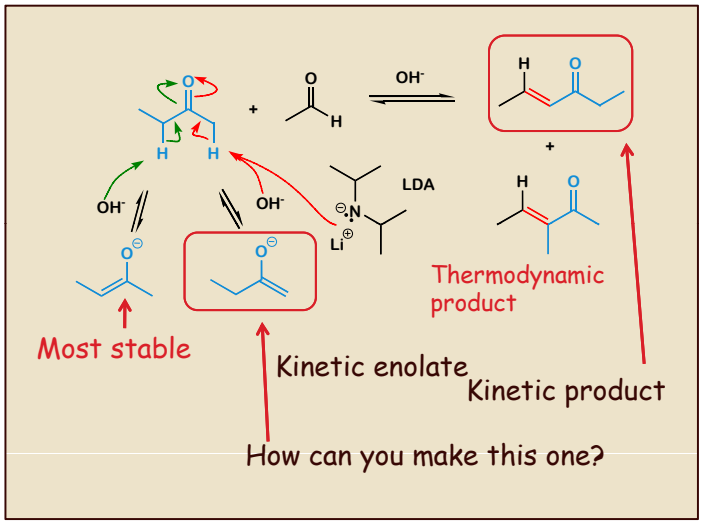
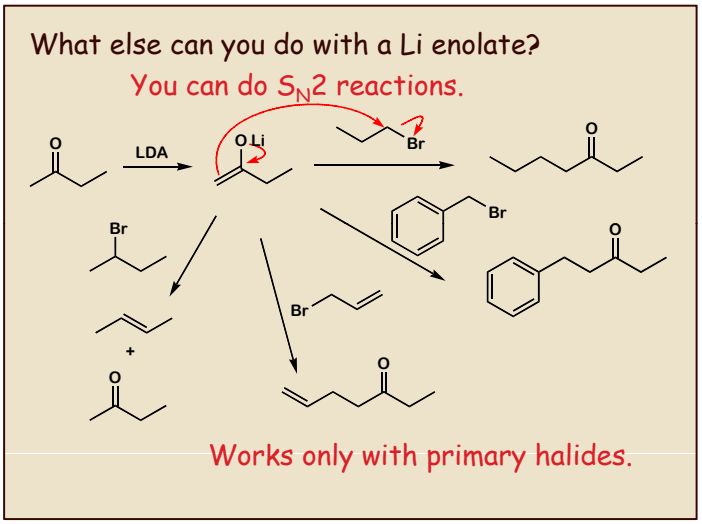
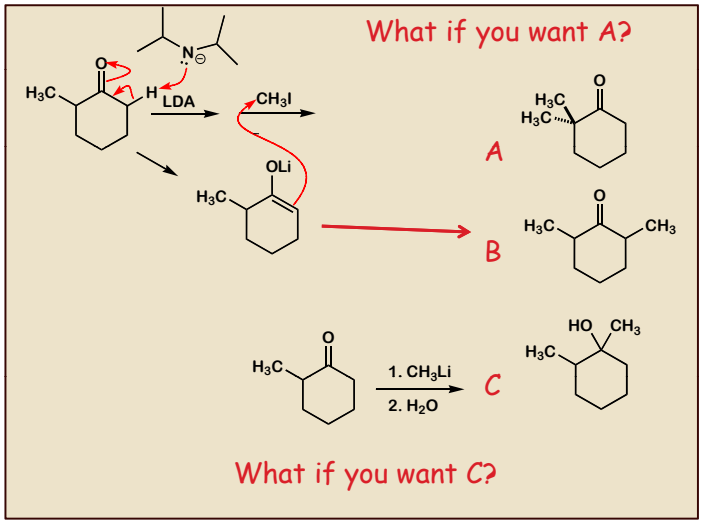
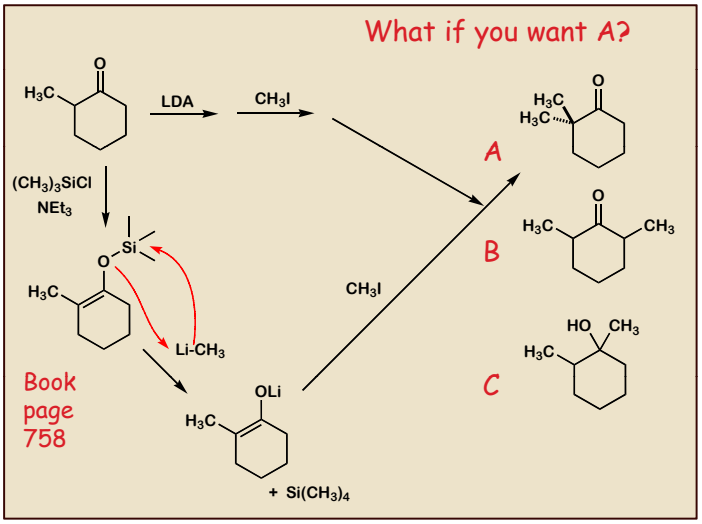
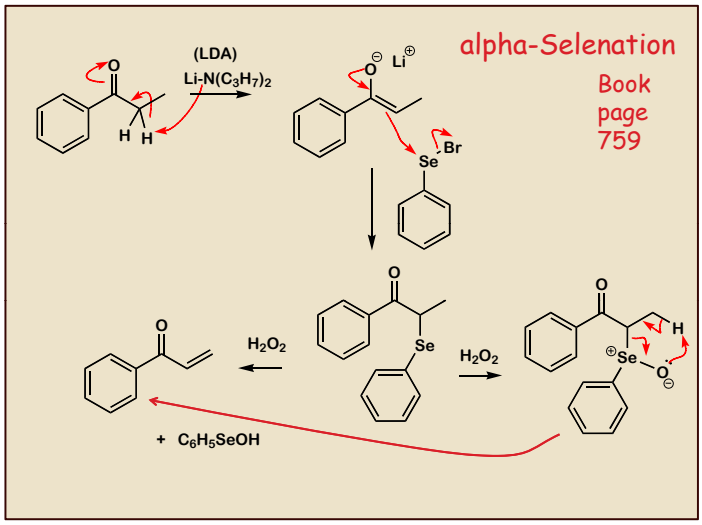
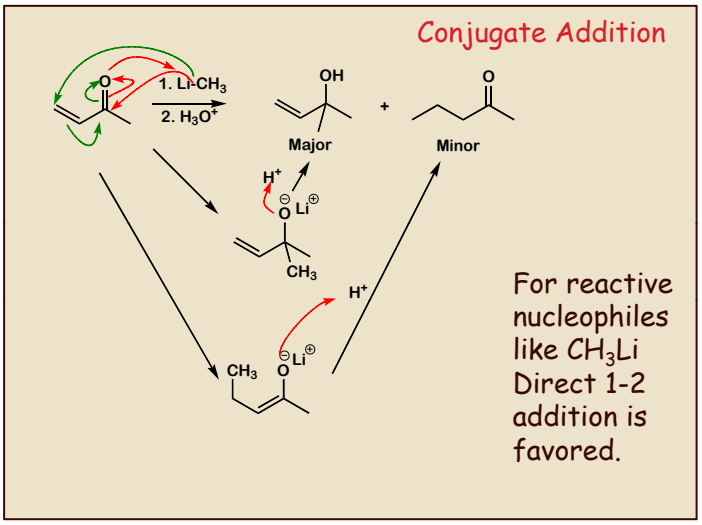

OH⁻
LDA
Thermodynamic product
Most stable
Kinetic enolate
Kinetic product
How can you make this one?


What else can you do with a Li enolate?
You can do S_N2 reactions.
LDA
Works only with primary halides.

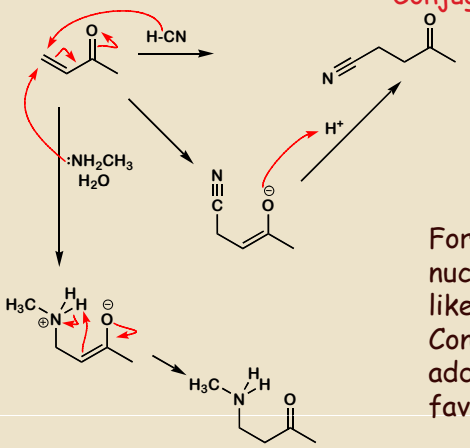

What if you want A?
LDA
CH_3I
A
B
C
1. CH_3Li
2. H_2O
What if you want C?


What if you want A?
LDA
CH_3I
$(CH_3)_3SiCl$
NEt_3
$Li\text{-}CH_3$
CH_3I
A
B
C
Book page 758
+ $Si(CH_3)_4$


alpha-Selenation
Book page 759
(LDA)
$Li\text{-}N(C_3H_7)_2$
H_2O_2
H_2O_2
+ C_6H_5SeOH

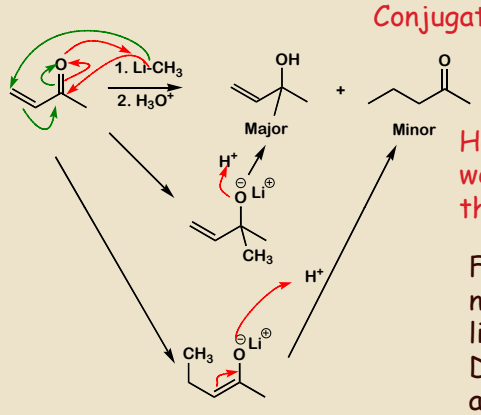

Conjugate Addition
1. $Li\text{-}CH_3$
2. H_3O^+
Major
Minor
For reactive nucleophiles like CH_3Li Direct 1-2 addition is favored.

Conjugate Addition



For weaker nucleophiles like HCN or NH_3 Conjugate 1-4 addition is favored.

Conjugate Addition



How could we improve the 1-4 yield?

For reactive nucleophiles like CH_3Li Direct 1-2 addition is favored.

We need a less reactive form of CH_3^-

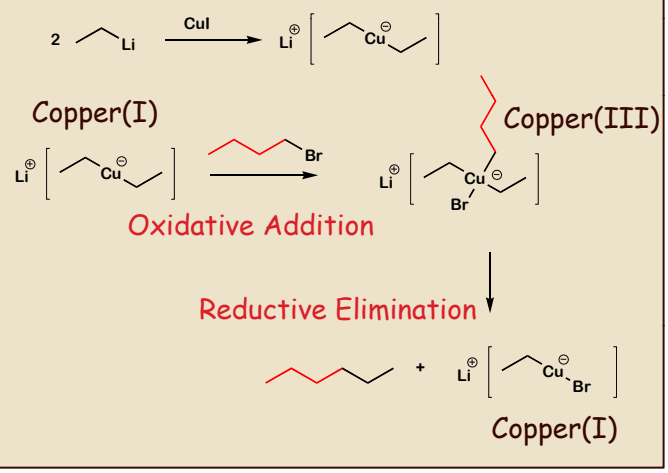
Organo Copper Chemistry

Lithium dialkylcuprates.

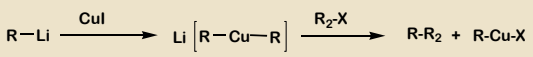
$2\ R\text{-}Li + CuI \longrightarrow Li[R\text{-}Cu\text{-}R]$

Gilman Reagents

Henry Gilman - Iowa State Univ.
"Father of
Organometallic Chemistry"



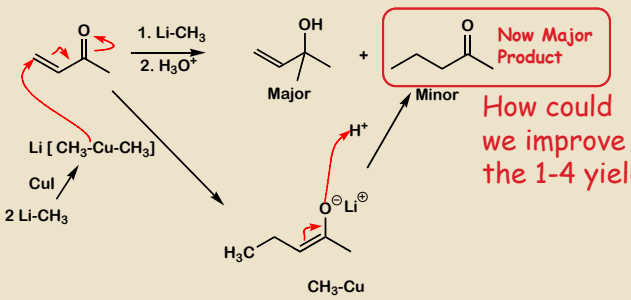
The general reaction



R- can be any alkyl group.
Problem you loose half of it.

R_2- can be an alkyl, aryl or vinyl group

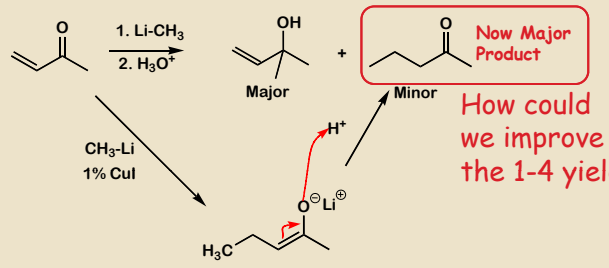
Conjugate Addition



How could we improve the 1-4 yield?

We need a less reactive form of CH_3^-

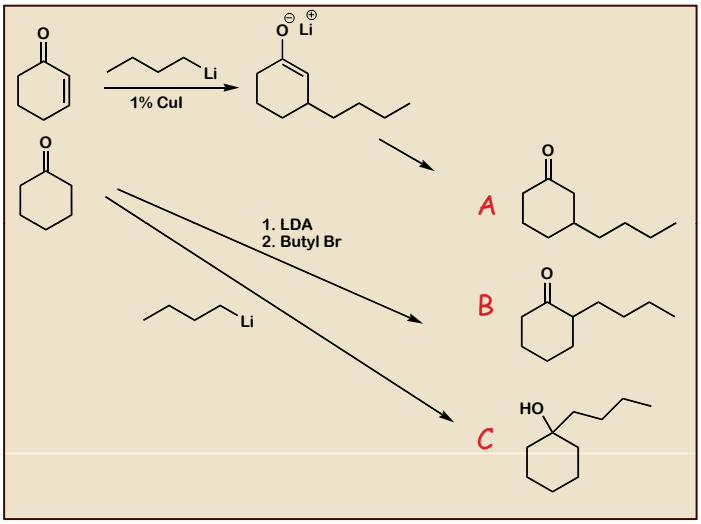
Conjugate Addition

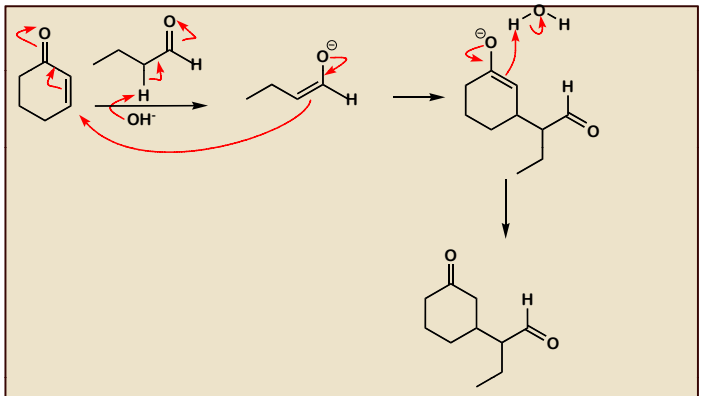


How could we improve the 1-4 yield?

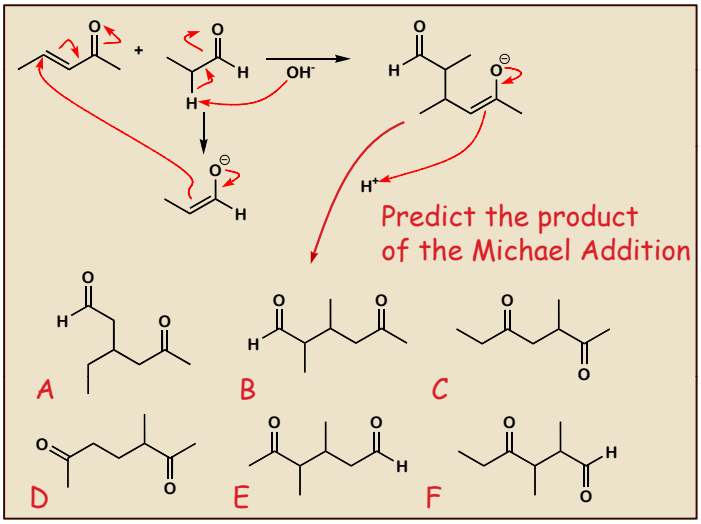
Even Better Catalytic Copper is all you need.

We need a less reactive form of CH_3^-

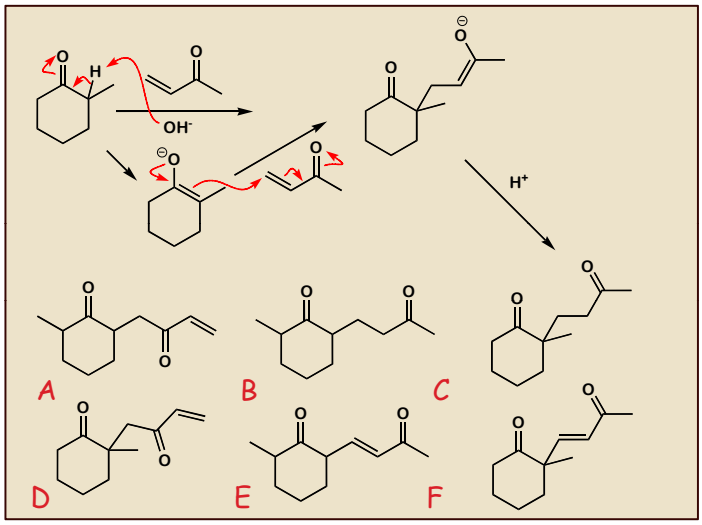


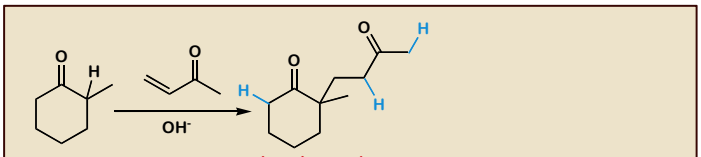


Conjugate Addition with an Enolate.
Michael Addition



Predict the product of the Michael Addition



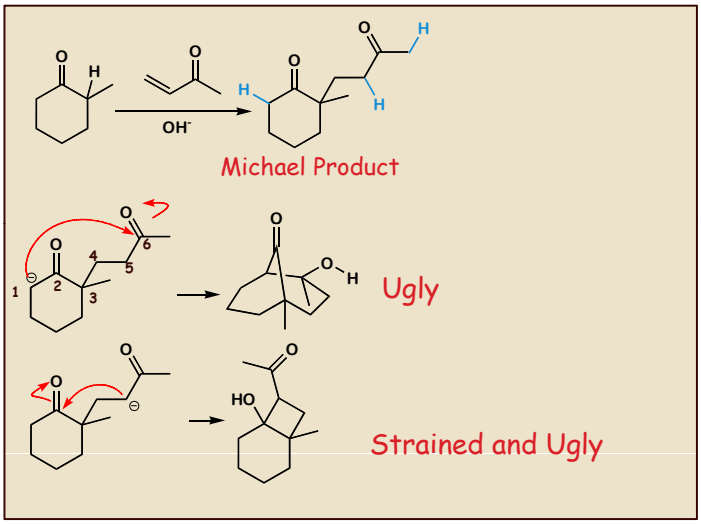


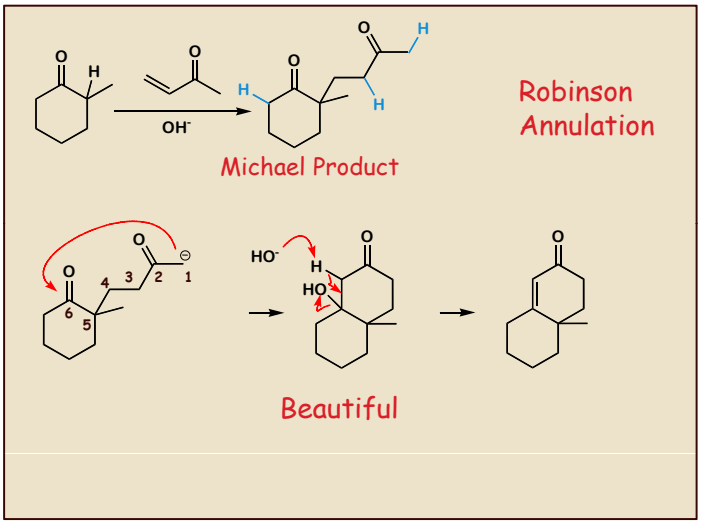
Michael Product

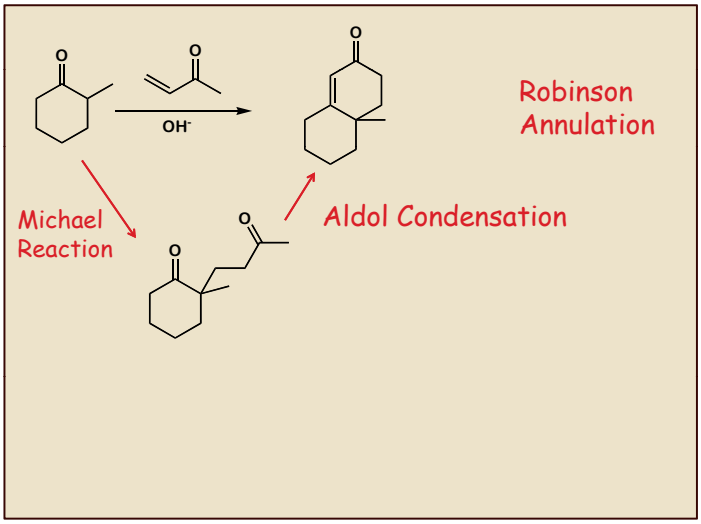
What other reaction can we do?

We still have base.

Where are the acid H atoms?


OH-
Michael Product
Ugly
Strained and Ugly


OH-
Michael Product
Robinson
Annulation
HO-
Beautiful


OH-
Robinson
Annulation
Michael
Reaction
Aldol Condensation