

# More Enolates

Note Title

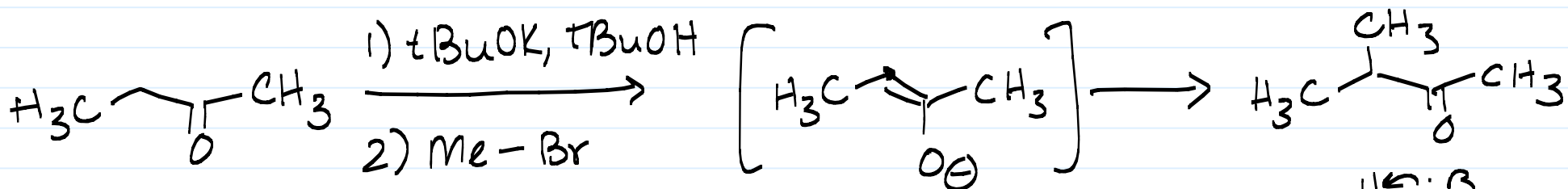
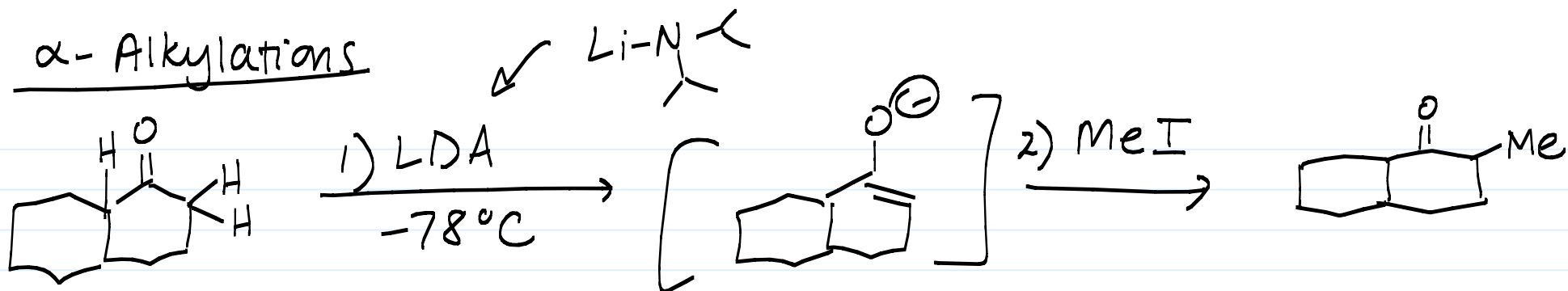
5/1/2014

Announcements: 1) Midterm 3 is SATURDAY!

- Review Session: Fri 6-8 pm

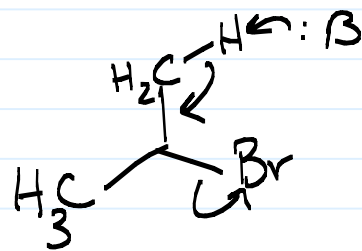
2) Music Videos due tomorrow

## $\alpha$ -Alkylations

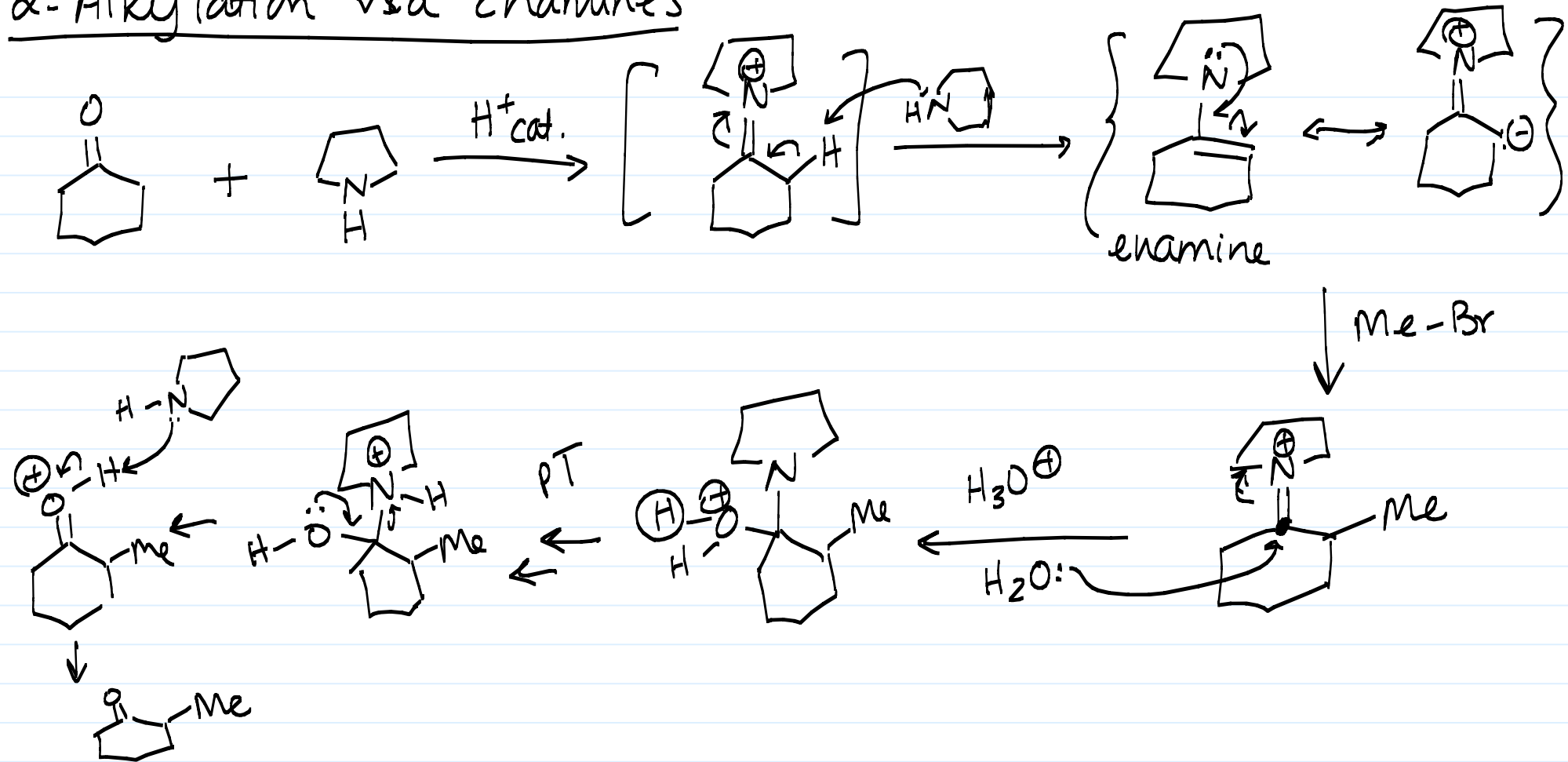


NOTE:  $\text{S}_{\text{N}}2$  rxns on electrophile  
but enolates are also basic, so watch out for  
elimination, esp w/ sterically demanding  $\text{E}^{\oplus}$  +  $2^{\circ}$   $\text{E}^{\oplus}$

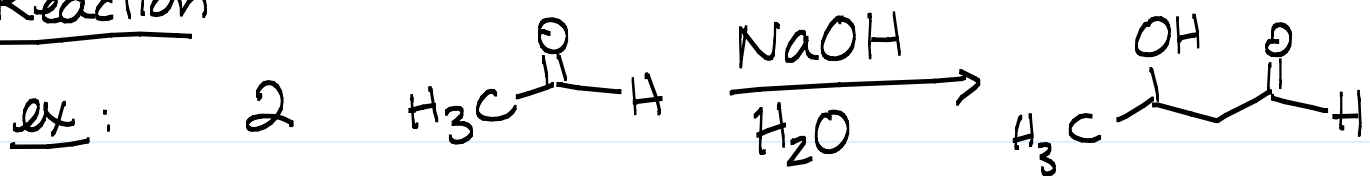
Good Electrophiles: MeI, EtBr, BnBr,  $=\text{C}=\text{C}(\text{Cl})$ , etc...



# $\alpha$ -Alkylation via Enamines

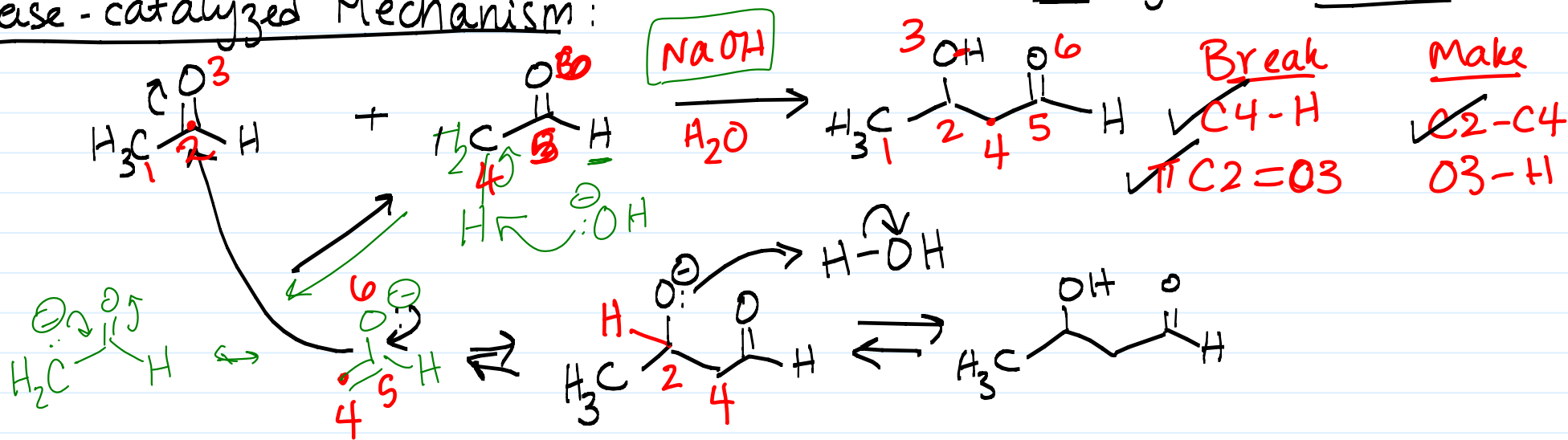


# Aldol Reaction

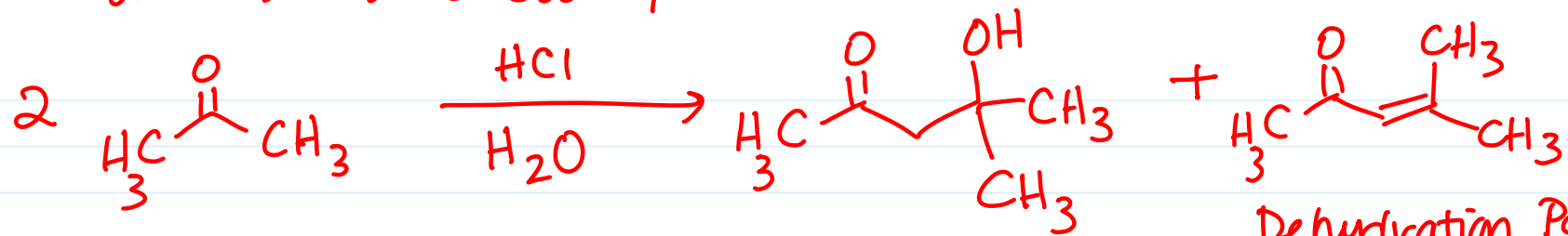


aldol product  
↓  
aldehyde → alcohol

## Base-catalyzed Mechanism:

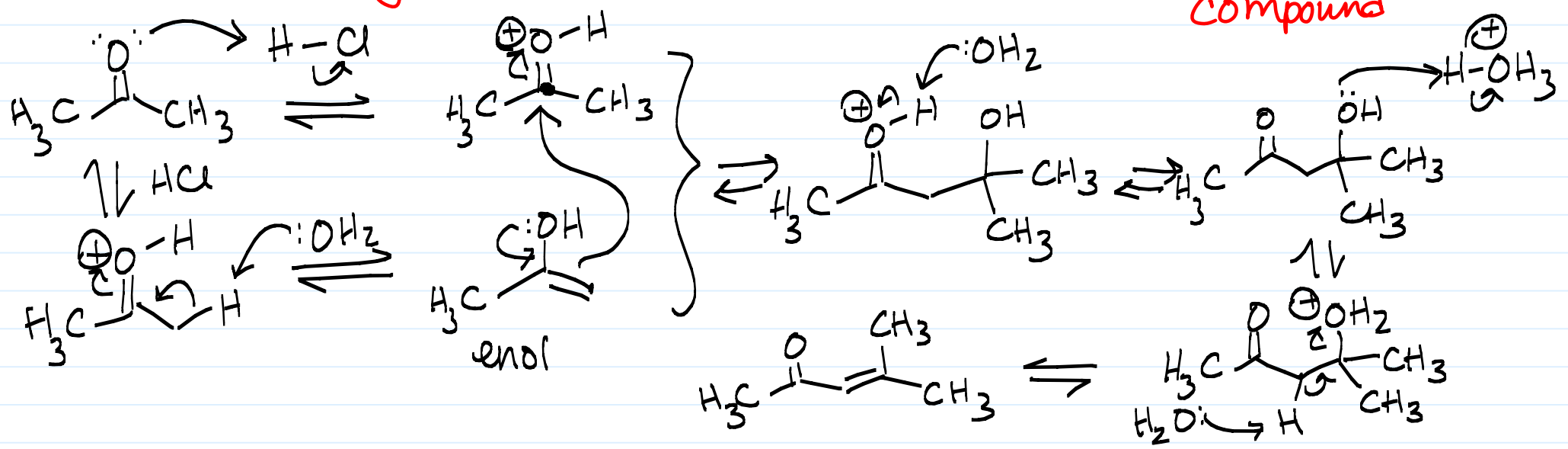


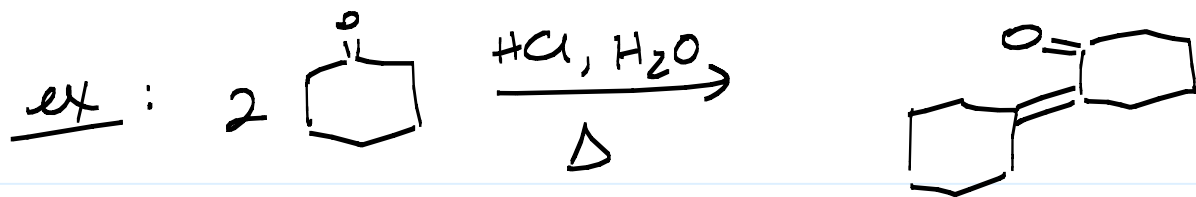
Can also be acid-catalyzed!



Dehydration Prod.  
 $\alpha,\beta$ -unsaturated carbonyl  
 Compound

\* To favor dehydration: heat + acid.

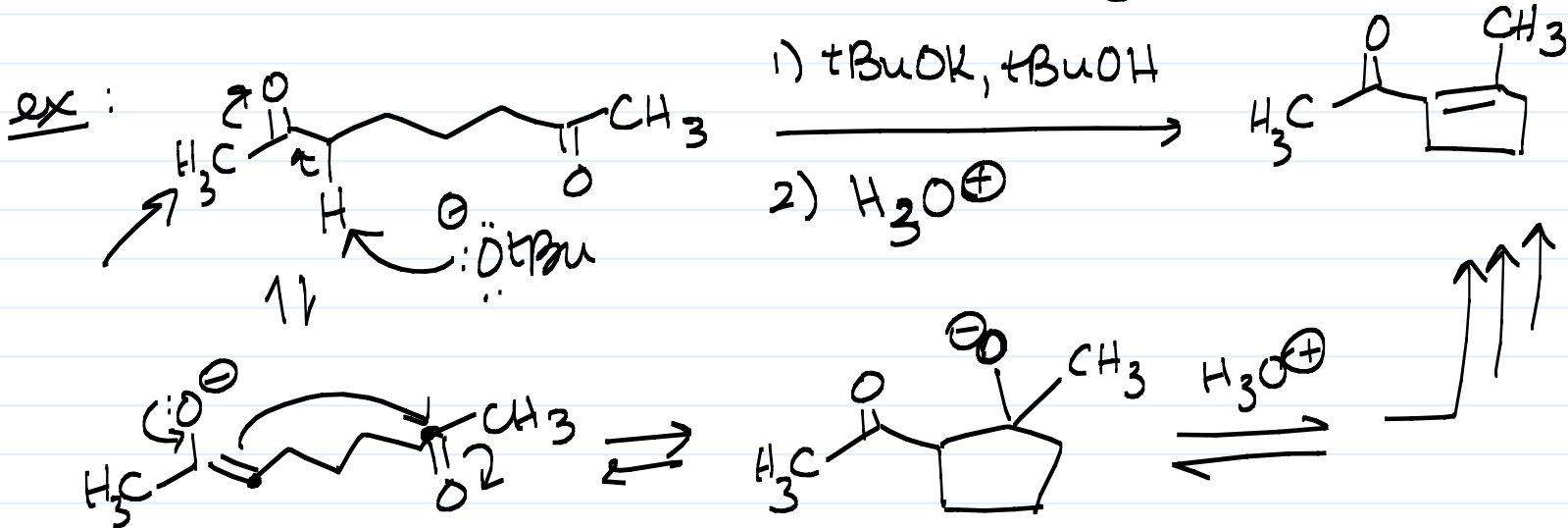




Mech?

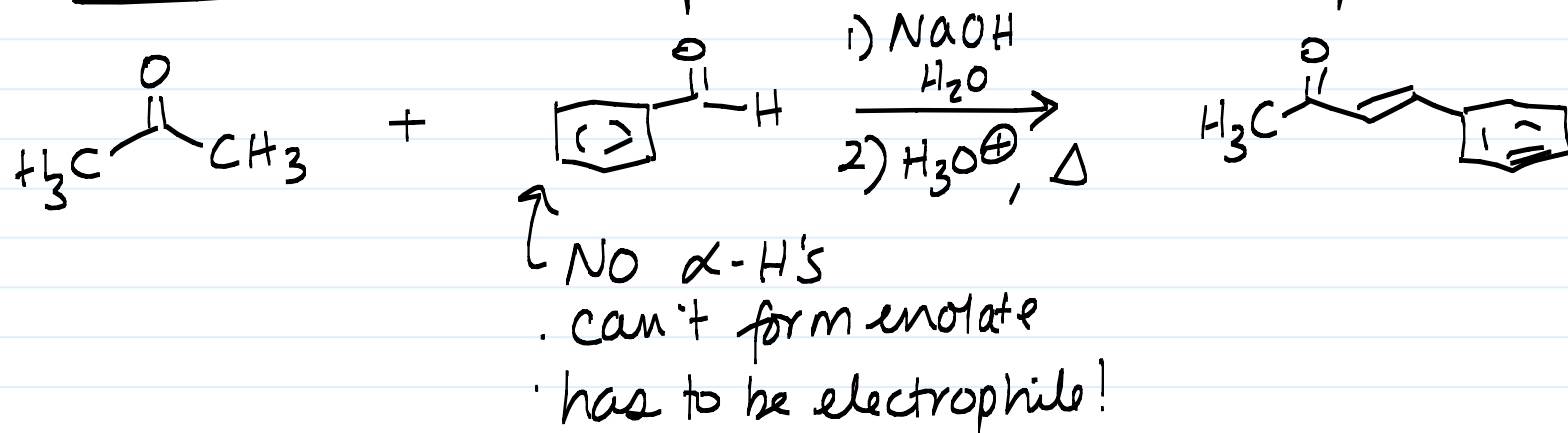
# Intramolecular Aldol (Acid or Base Catalyzed)

- favored if 5- or 6-membered ring is formed.



Aldol Cross Coupling: 2 different carbonyls  
→ you have to be strategic!

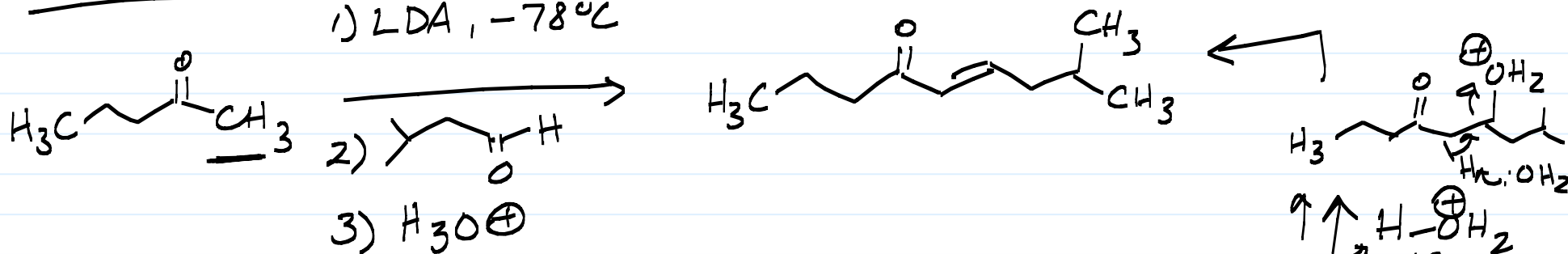
Method 1: Force 1 partner to be electrophile:





Method 2: Form kinetic enolate 1<sup>st</sup>

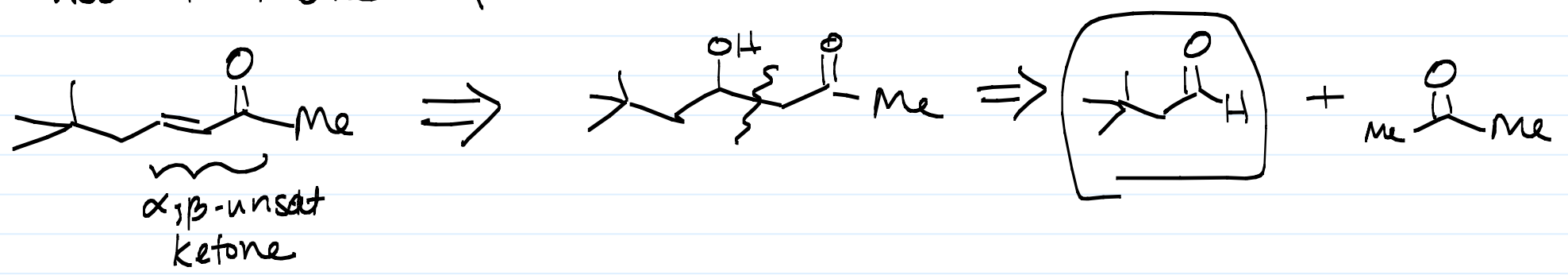
1) LDA, -78°C



# Side note: Retrosynthetic Analysis

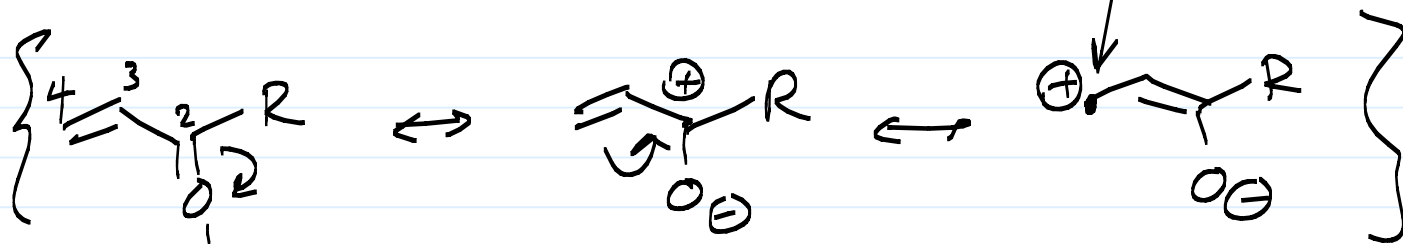
Think backwards...

How to make CC(C)C=CC(=O)C?



Forward Direction?

# Reactions of $\alpha,\beta$ -unsat. Carbonyls



Michael Rxn: enolate +  $\alpha,\beta$ -unsat. carbonyl

