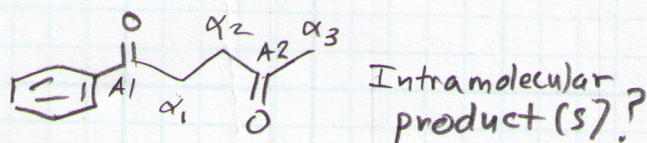


$$\Delta S^\circ \approx 0$$

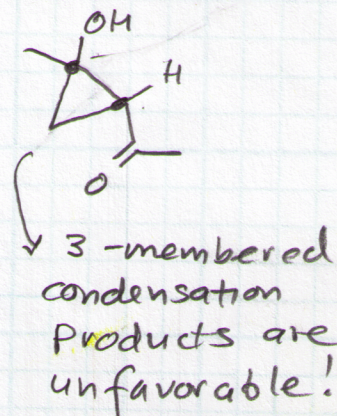
$$\Delta G^\circ = \Delta H^\circ - T \underbrace{\Delta S^\circ}_{\emptyset}$$

unimolecular  $\rightarrow$  unimol  
conversion cause  $\Delta S^\circ$  to  
not affect  $\Delta G^\circ$

Aldol condensations also occur analogously w/ ketones.  
The  $\alpha$ -H is acidic, too!



NOTE

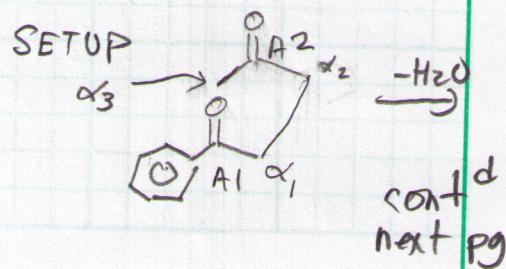


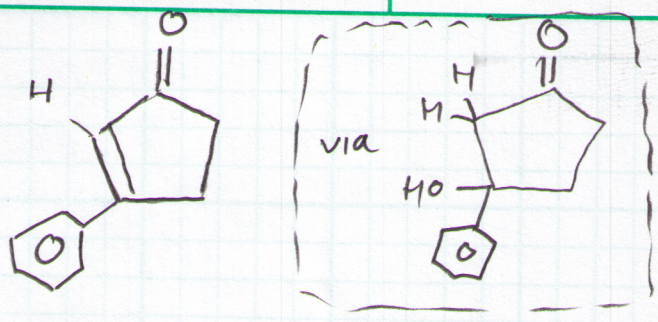
- ① ID  $\alpha$ -C
- ② Do  $\alpha$  C have  $\alpha$  H?
- ③ when  $\alpha$  H is removed to form enolate is a ring  $>$  4 atoms formed?
- ④ Yes, then that is a valid condensat<sup>n</sup> product.

Above:  $\alpha_1$  C condenses with A2  
that yields 3-atom ring  $\Rightarrow$  NOT FAVORABLE

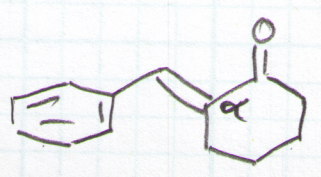
$\alpha_2$  C condenses with A1  
also yields 3-atom ring  $\Rightarrow$  NOT FAVORABLE

$\alpha_3$  condenses with A1  
yields 5-atom ring!



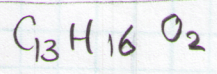
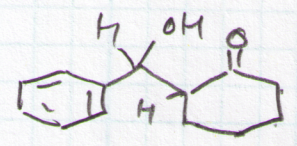
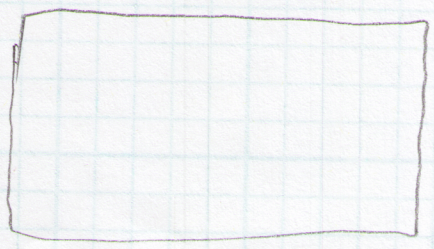


what aldehydes and/or keto compound(s) are used to make

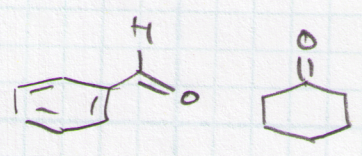
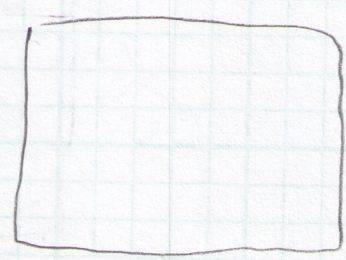


WORK BACKWARDS

⇓ THIS CAME FROM?

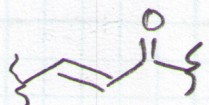


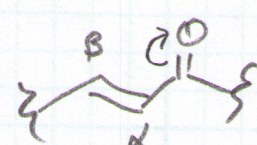
⇓ THIS CAME FROM?

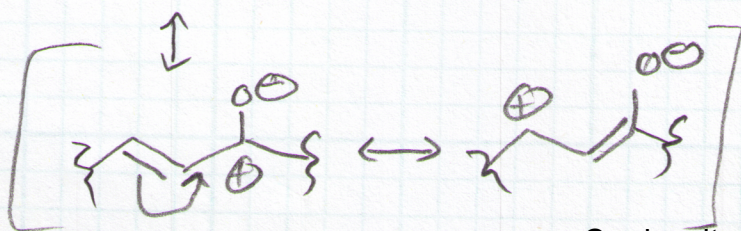


Aldehyde or  
ketone 1

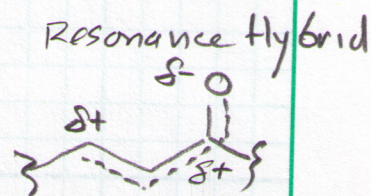
aldehyde or  
ketone ?

We have been making  condensation products after treatment of aldehydes + ketones with NaOH, Δ.

These  are α,β-unsaturated aldehydes and ketones



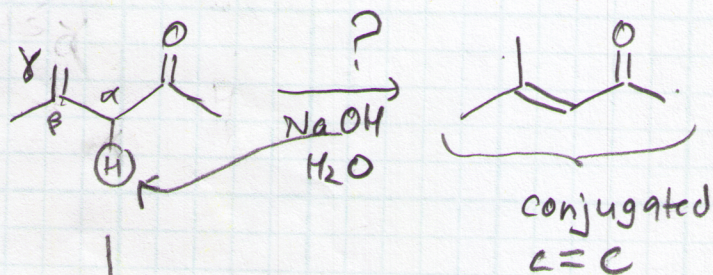
Resonance forms



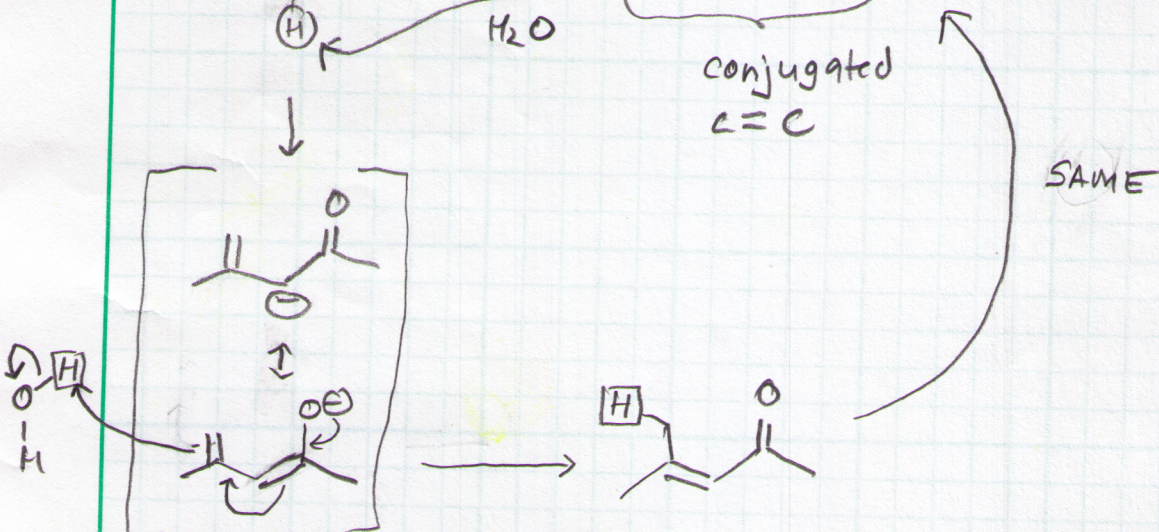
Resonance Hybrid

C+ density here is less than C+ density on carbon attached to O due to dipolar properties of C-O bond.

The C=C is conjugated with the C=O and thus resonance stabilization results.

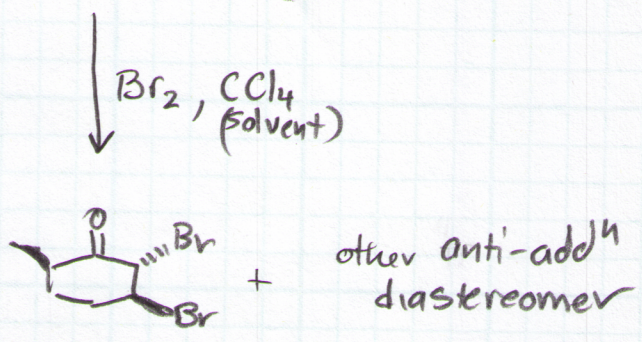
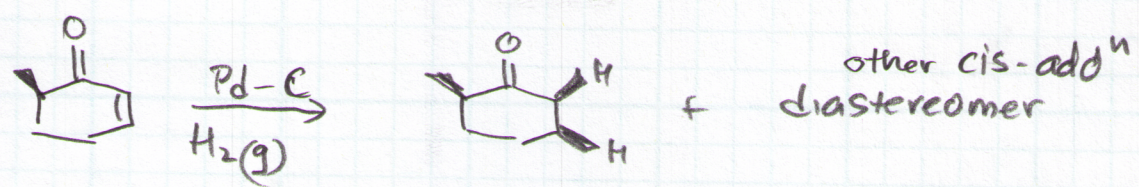


Mechanism

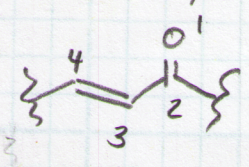


SAME

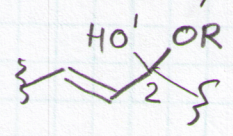
CEM 351 RXNS w/ C=C



Back to  $\alpha, \beta$ -unsaturated carbonyl cpds.

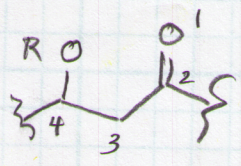


We have seen 1,2-addition rxns when acetals, hemiacetals/aminals were formed

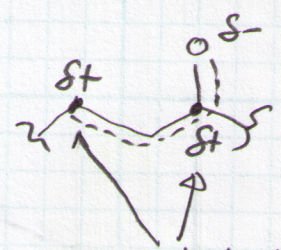


1,2-addition w/ acid or base catalysis

but can also undergo 1,4-addition reactions

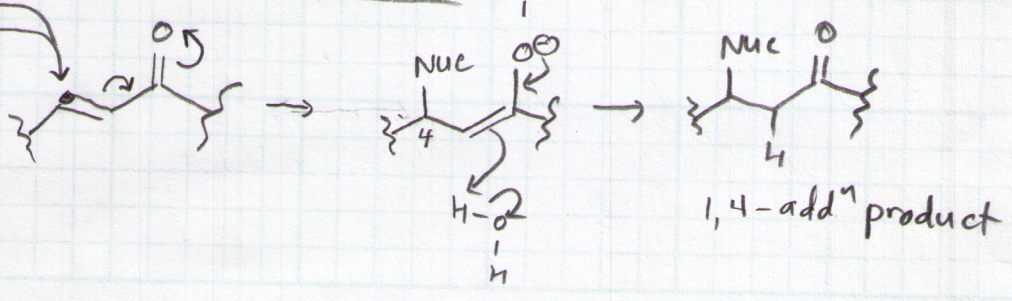


recall resonance hybrid



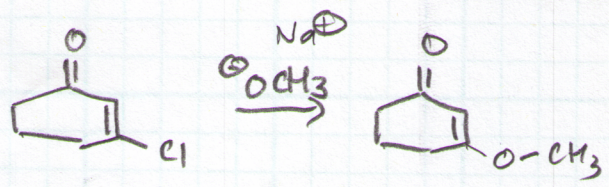
electrophilic centers

Mechanism (Michael Addition)



NuC<sup>-</sup>  
 RO<sup>-</sup>  
 R<sub>3</sub>N:  
 S<sup>-</sup>  
 O<sup>-</sup>  
 PS<sup>-</sup>  
 CN

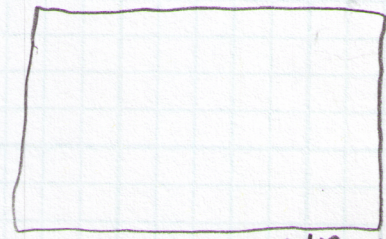
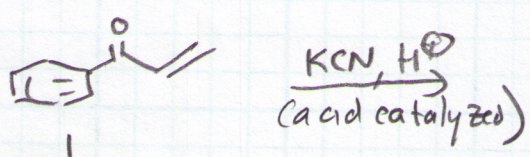
Show the mechanism of the following



Hint: start with a conjugate (1,4)-addition

SEEK TA's for ASSISTANCE

Show the mechanism

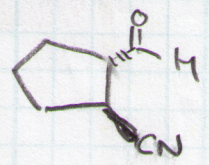


conjugate add<sup>n</sup> product

MECHANISM?

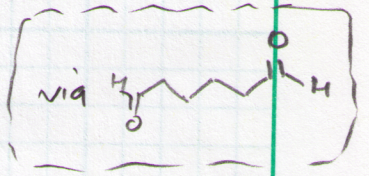
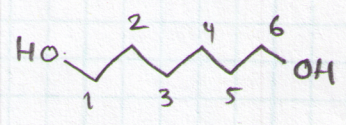
Let's work backwards

Product



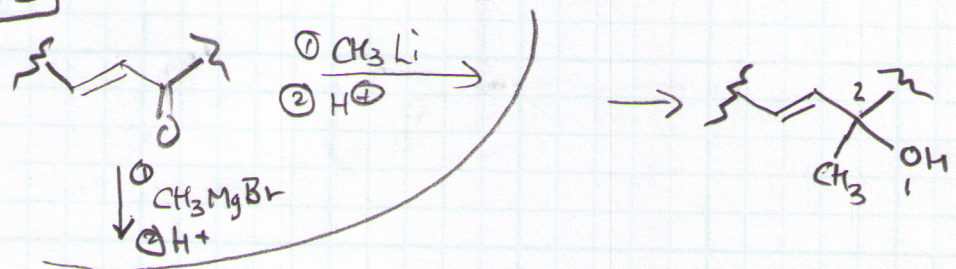
back to

Reactant



1,2 vs 1,4-add<sup>n</sup> with Organometallic Reagents

1,2

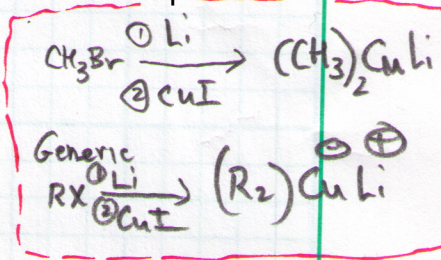
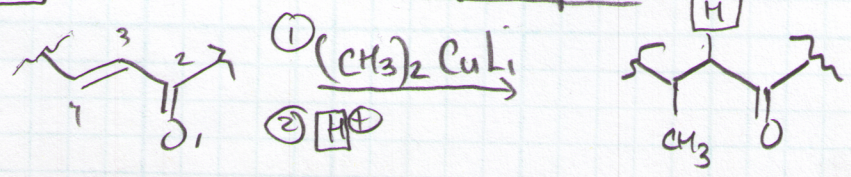


strongly electroneg  
 $\ominus$  rxn at  
 higher  $\delta^+$   
 C-O center  
 $\delta^+$   $\delta^-$

2 equiv Li

1,4

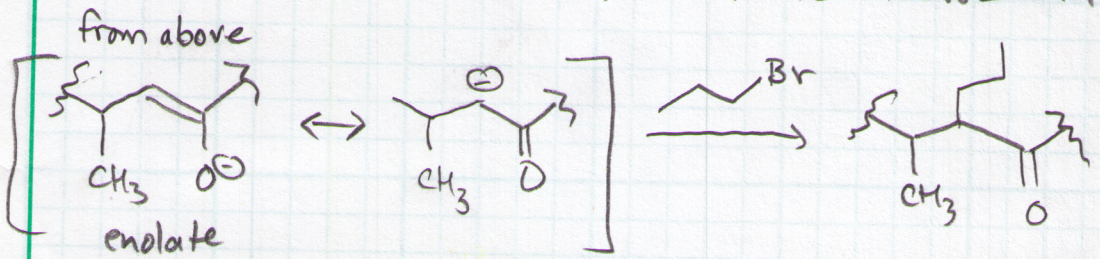
Gilman Reagent  
 Lithium Organocuprate



$\text{H}_3\text{C}-\text{Cu}^{\ominus}-\text{CH}_3$   
 $\text{Li}^{\oplus}$   
 HOMO of  $\delta^- \text{CH}_3$   
 closer in E  
 to LUMO of  $\text{C}=\text{C}$   
 NOTE (-) charge is borne by  $\text{Cu}^{\oplus}$  and  $\delta^-$   
 $\therefore$  (-) charge on  $\text{CH}_3$  is reduced compared  
 to that in Grignard and  $\text{CH}_3\text{Li}$

$\text{Li}^{\oplus} \text{CH}_3^{\ominus}$   
 highly reactive  
 HOMO closer in E  
 to LUMO of  $\text{C}=\text{O}$

NOTE: Before  $\text{H}^+$  is added in 2nd step,  
 enolate can react w/ haloalkane in  $\text{S}_{\text{N}}2$  rxn



Interesting processes to add C-C bonds to carbonyl compds

why trans?

