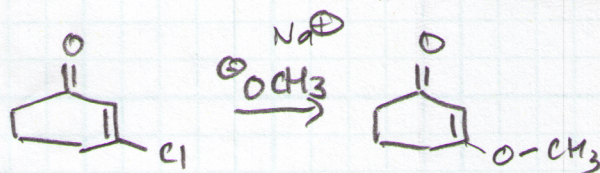
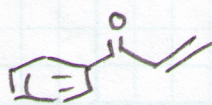


show the mechanism of the following



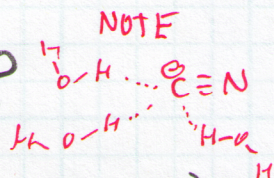
Hint: start with a conjugate (1,4)-addition

show the mechanism

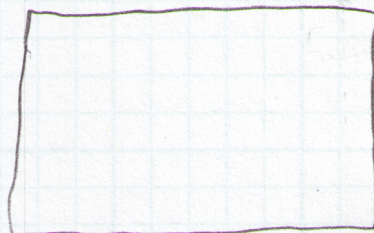


KCN, H^+
(acid catalyzed)
in H_2O .

MECHANISM?



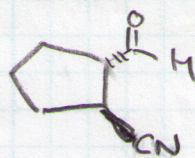
H -bonding tunes C^+ and directs towards 1,4-Addⁿ.



conjugate addⁿ product

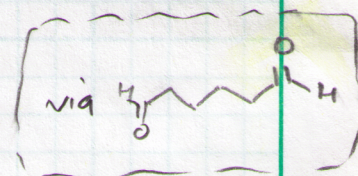
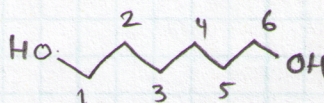
Let's work backwards

Product



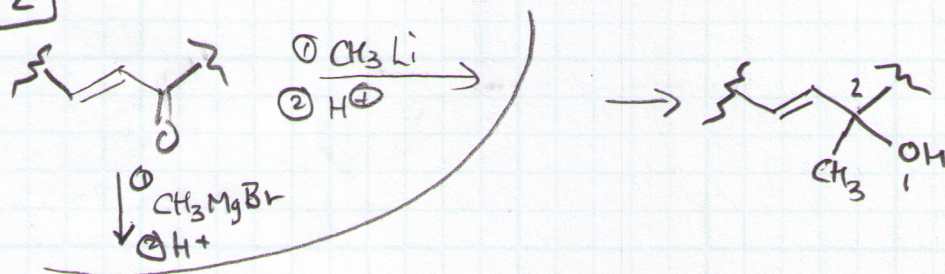
back to

Reactant



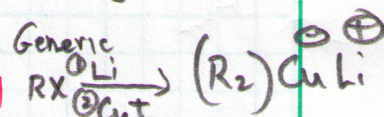
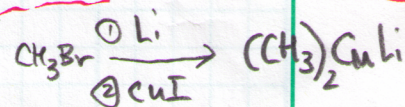
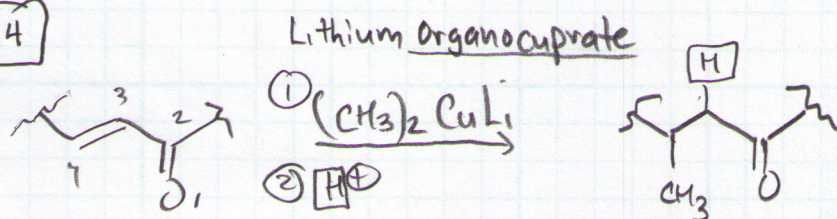
1,2 vs 1,4-addⁿ with Organometallic Reagents

1,2

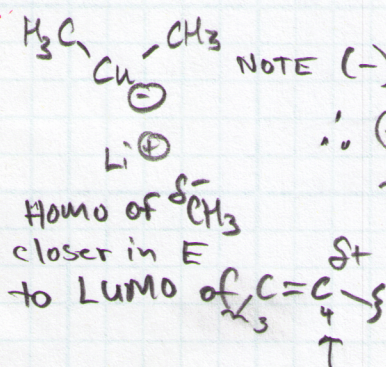


strongly electroneg
C⁻ rxn at
higher δ^+
C-O center
 δ^+ δ^-

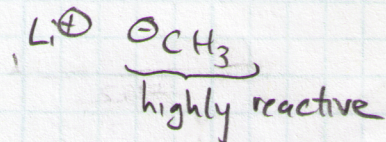
1,4



see
rationale
here

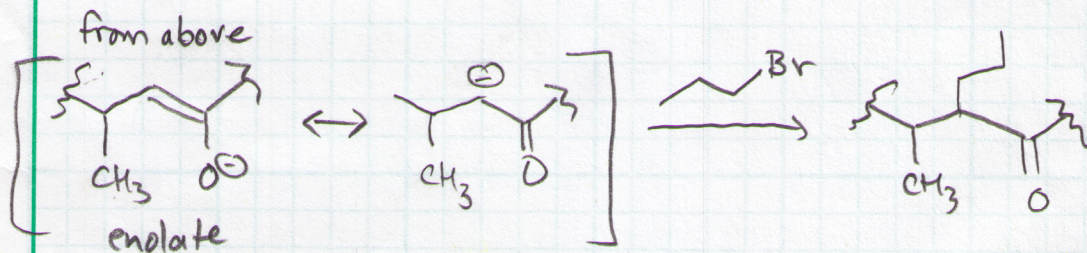


NOTE (-) charge is borne by $\text{Cu}^{\ominus}$ and $\delta^- \text{CH}_3$
 $\therefore$ (-) charge on CH_3 is reduced compared
 to that in Grignard and CH_3Li



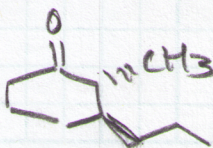
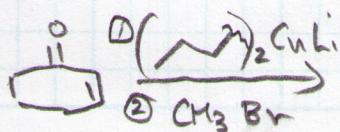
HOMO closer in E
 to LUMO of $\text{C}=\text{O}$

NOTE: Before $\text{H}^{\oplus}$ 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 compd^s

why trans?

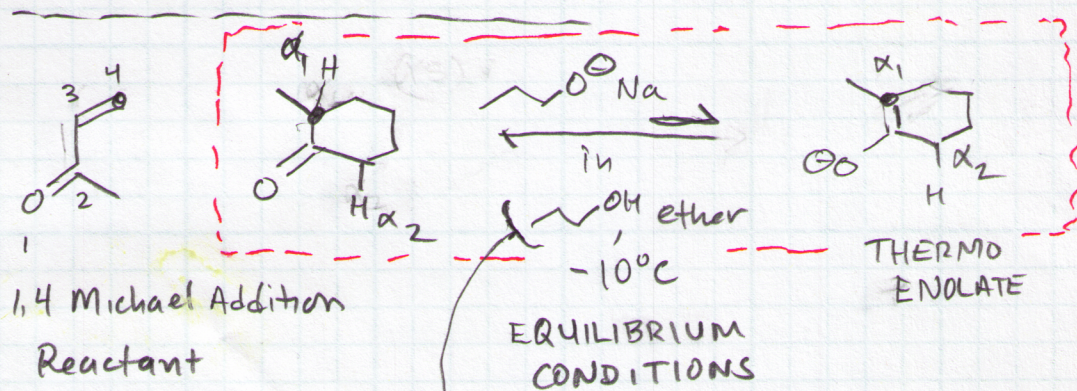
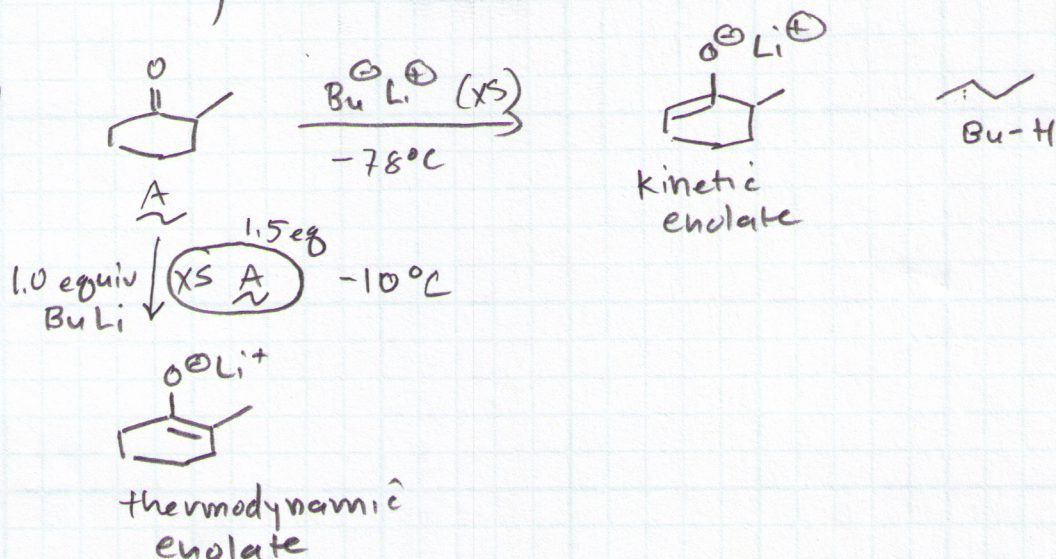


+ Enantiomer

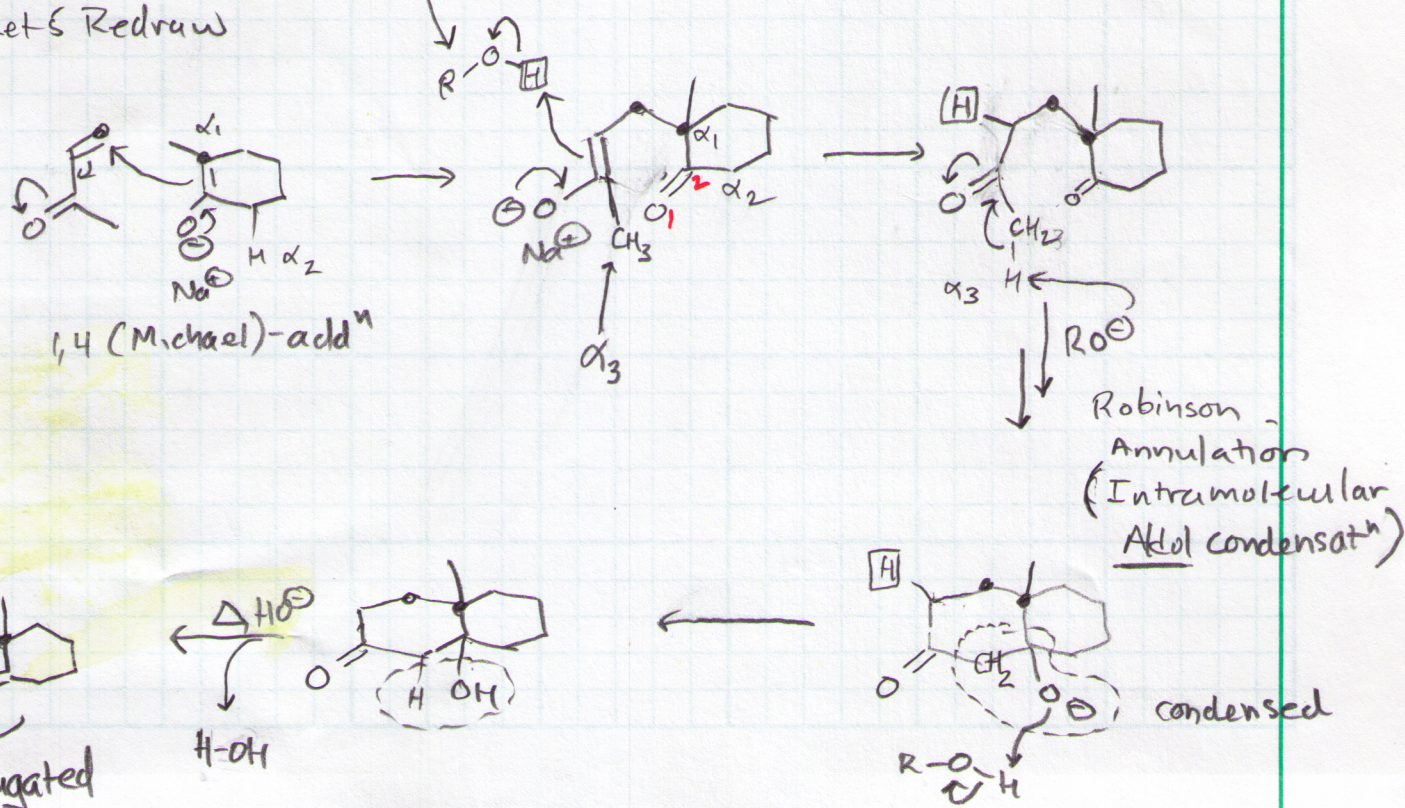
Explain trans
 stereoisomerism

1,4-addⁿ followed by intramolecular aldol condensation.

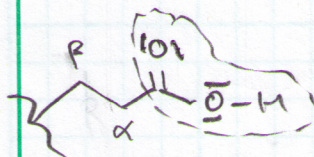
Recall



Let's Redraw

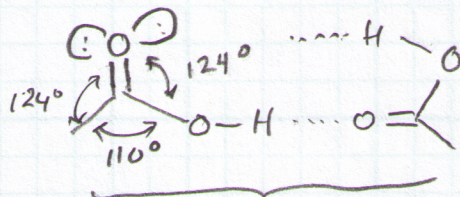
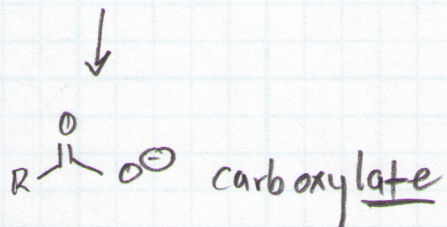
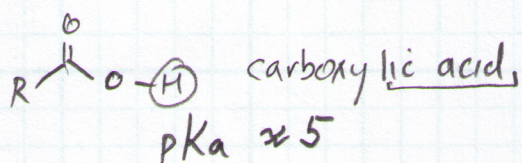


Carboxylic Acids (Functional Group)



sp^2 , trigonal planar.

1-C removed from functional group; β -2 C removed ...



H-bonding dimer
↑ m.p. ↑ b.p
over alkanes + alcohols

^{13}C , ^1H -NMR and IR Spectroscopy

overhead

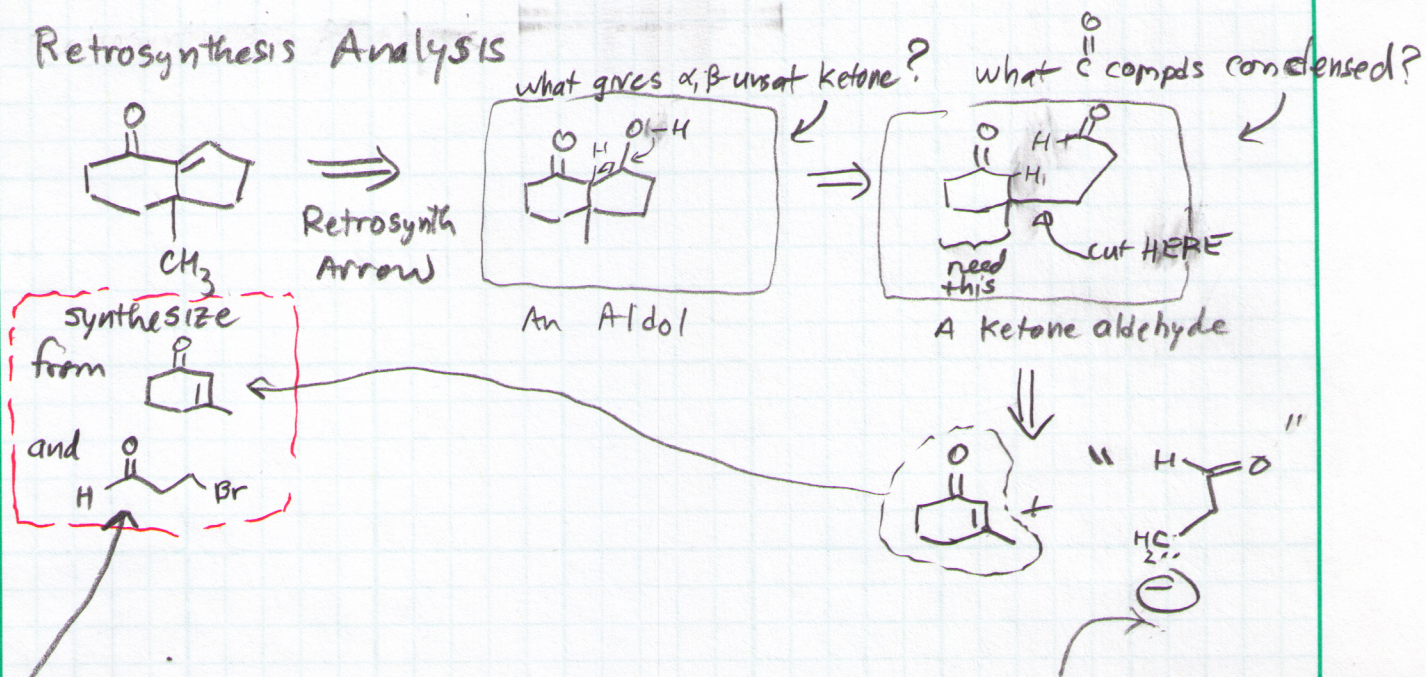
pentanoic acid

common name: valeric acid

Isolated from plant species

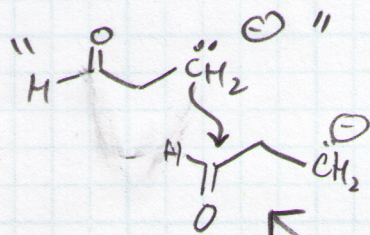
Valeriana (minor amount)

Retrosynthesis Analysis

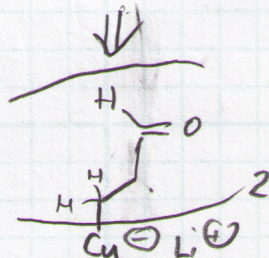


Need (-) charged carbon that will do a 1,4-addition

Please NOTE



would react with itself
DONT WANT THIS TO HAPPEN



This organocuprate will do a 1,4-addn

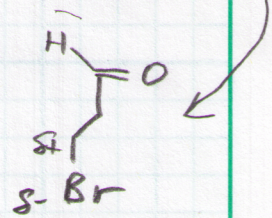
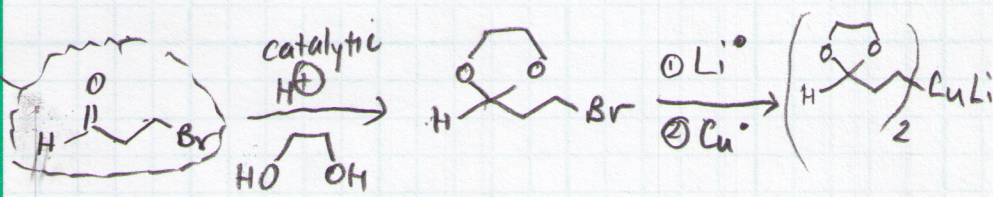
BUT

what did the cuprate come from?

LOOK

SEE THIS!

Need to protect before reacting w/ Li⁺ or Cu⁺



FORWARD RxN

