

Do Not Use Pencil

Do Not Staple, Please!

Course Chem 345

Lecturer Gellman

Day At Wednesday

Date 3-2-16

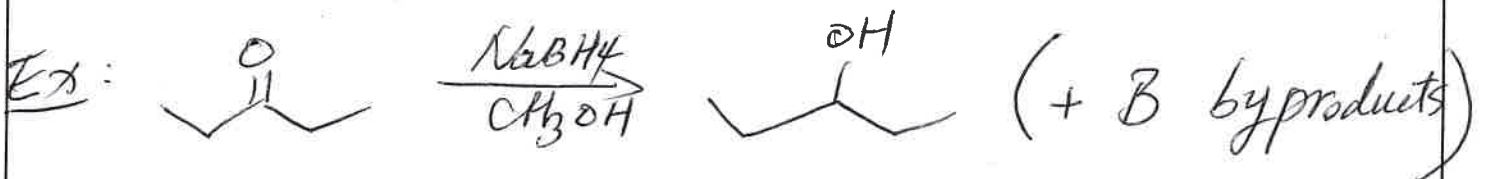
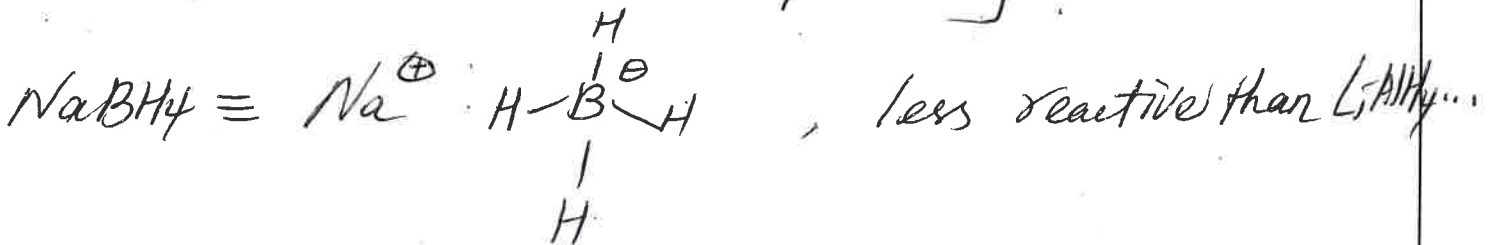
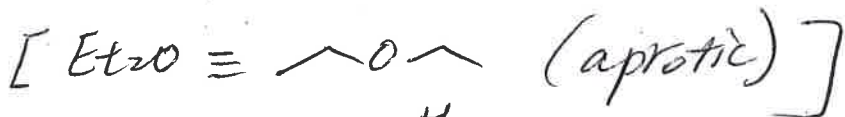
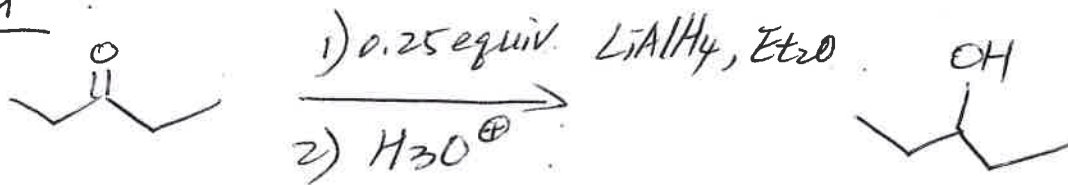
Notes Taken by LA

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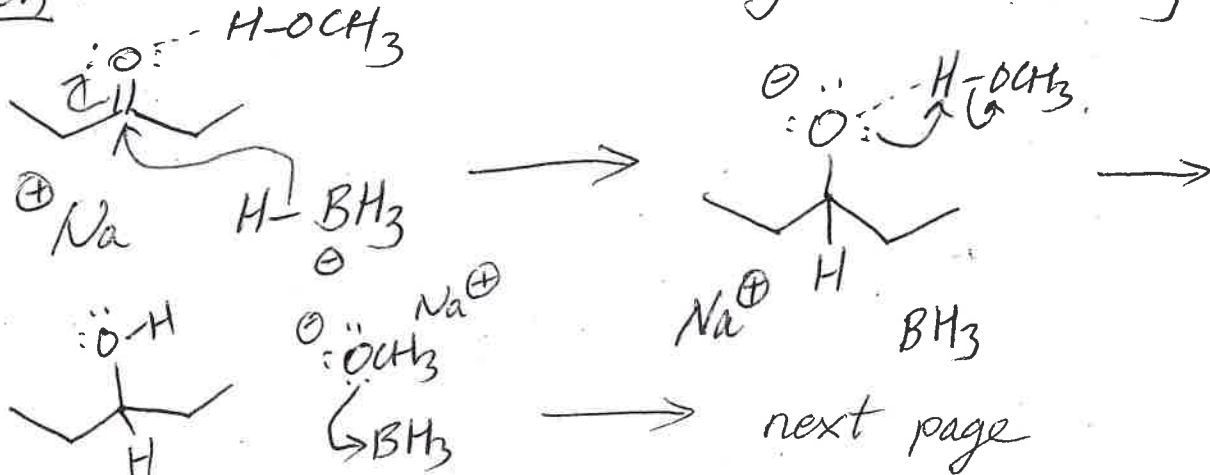
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Recall: "Hydride" agents for reducing aldehydes / Ketones to alcohols: LiAlH_4 (Nucleophilic) NaBH_4 ("H:⁻")

Ex



Mech: [Note: Solvent H-bonding "activates" $\text{C}=\text{O}$]



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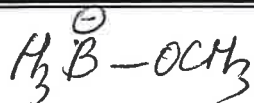
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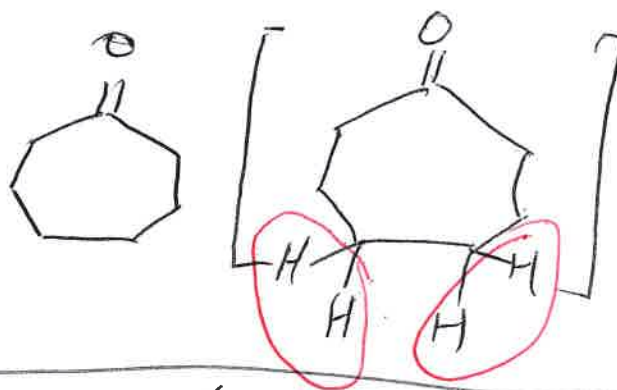
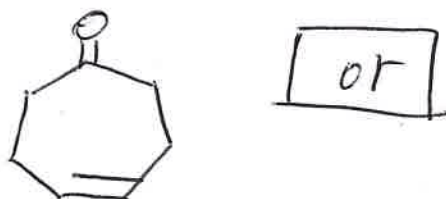
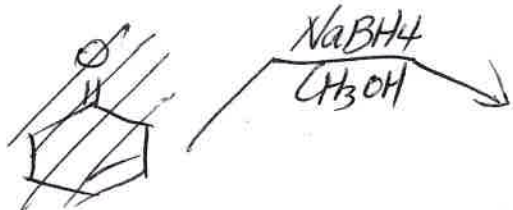


These H's remain reactive

Recall: $\text{H}_2 + \text{Pd/C}$ for reduction of alkenes to alkanes
→ Doesn't work for $\text{C}=\text{O}$.

Thus, we can accomplish "chemoselective" reductions of
 $\text{C}=\text{C}$ vs. $\text{C}=\text{O}$ bonds.

Ex:



Rxns of aldehydes & ketones w/ carbanion-like reagents

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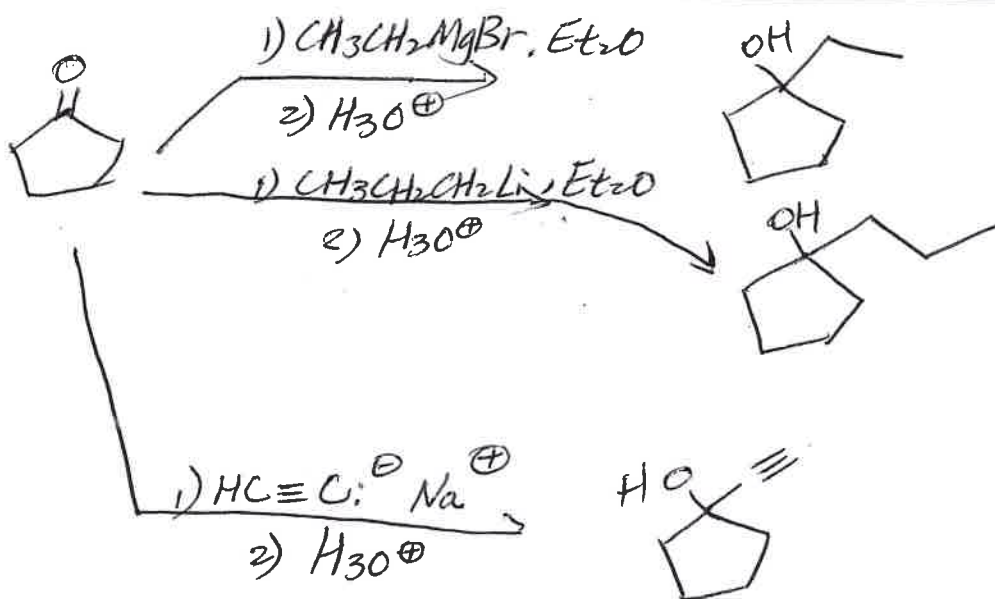
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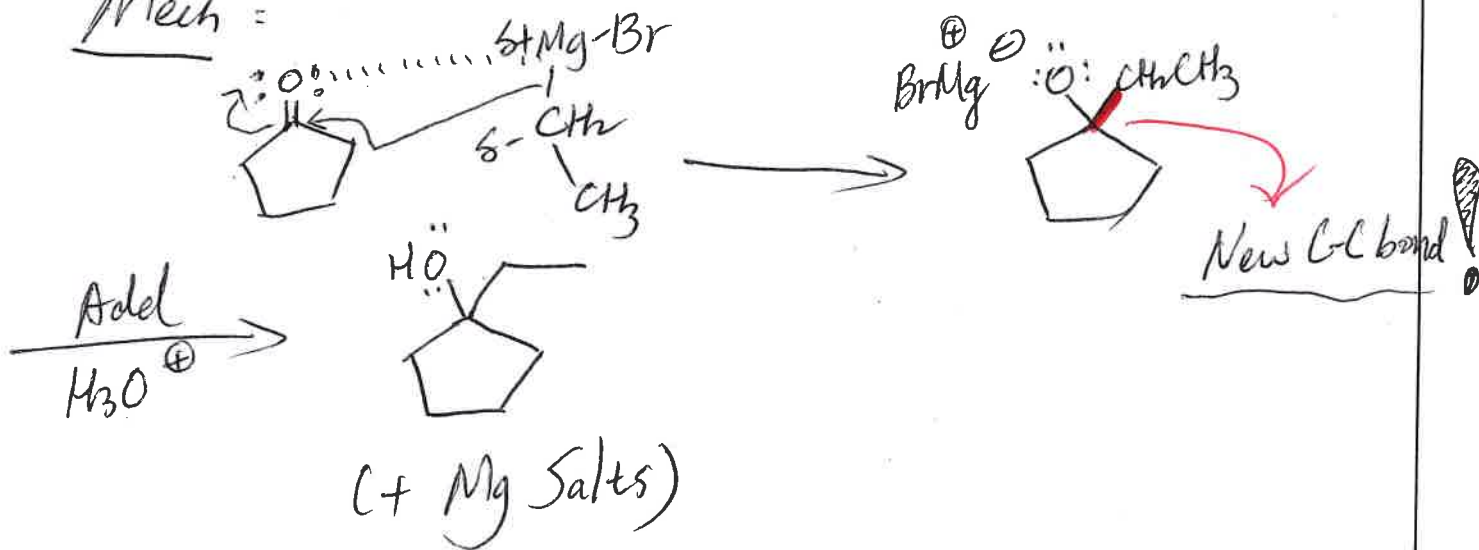
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Ex:



Mech =



Recall:

RMgX , RLi , $\text{RC}\equiv\text{CNa}$, very basic!
Very powerful set of rxns for constructing complex carbon skeletons from simpler building blocks.

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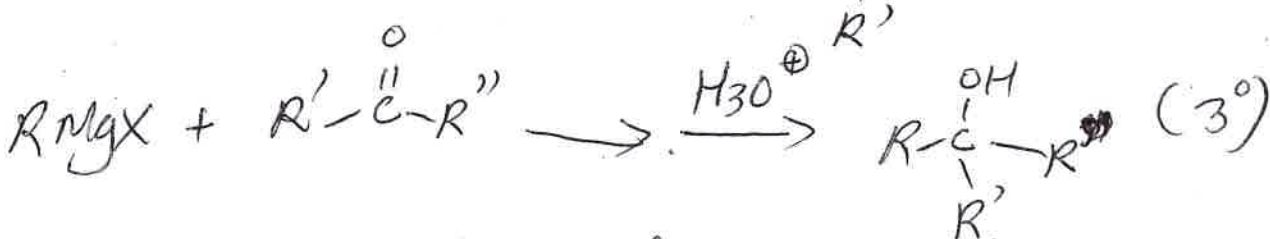
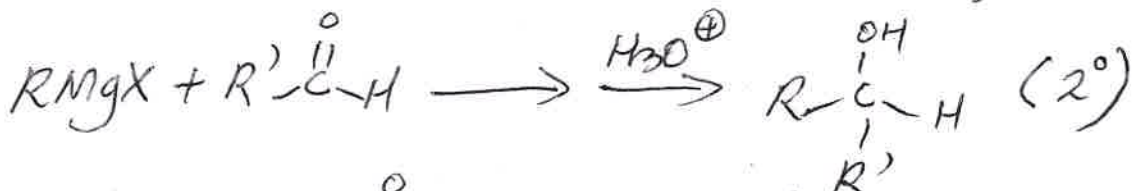
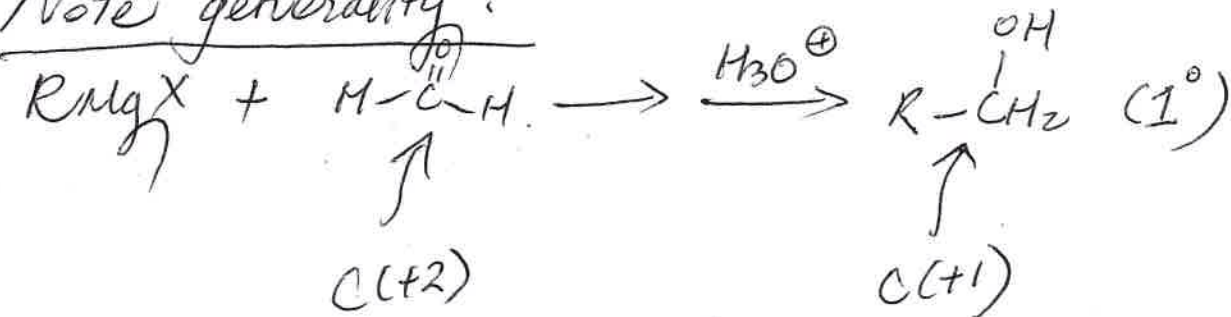
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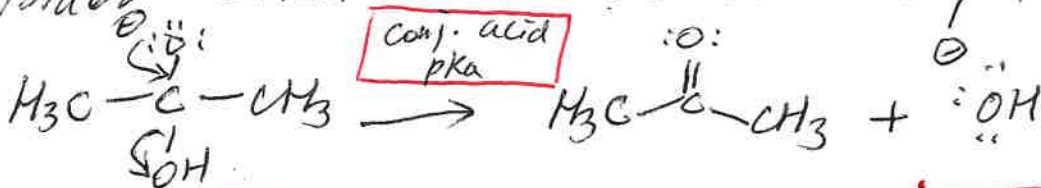
Note generality:



Analogous possibilities for RLi or $\text{RC}\equiv\text{C}^\ominus\text{Na}^\oplus$

Note: Hydride & carbanion-like reagent additions to carbonyls are irreversible

Consider selected "reverse" mech steps.



~12

~16

B/c conj. acid pKa values on either side of arrow are similar, mech. step is reasonable

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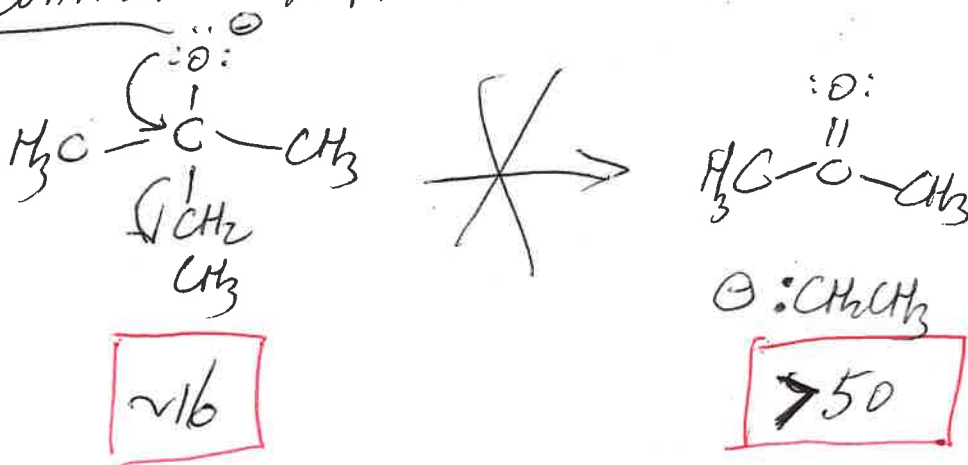
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Contrast - HYPOTHETICAL



Acetals, and their use as "protecting groups".

Generic structure:

