

Course 345

Instructor Gellman

Day Wed

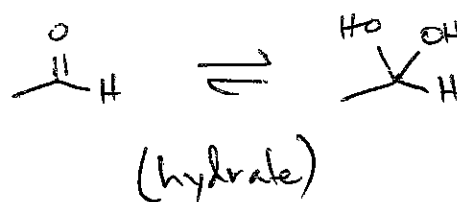
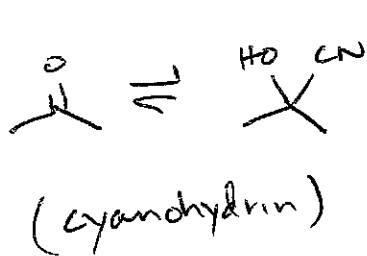
Date 3/05/2014

Notes Taken By Adams

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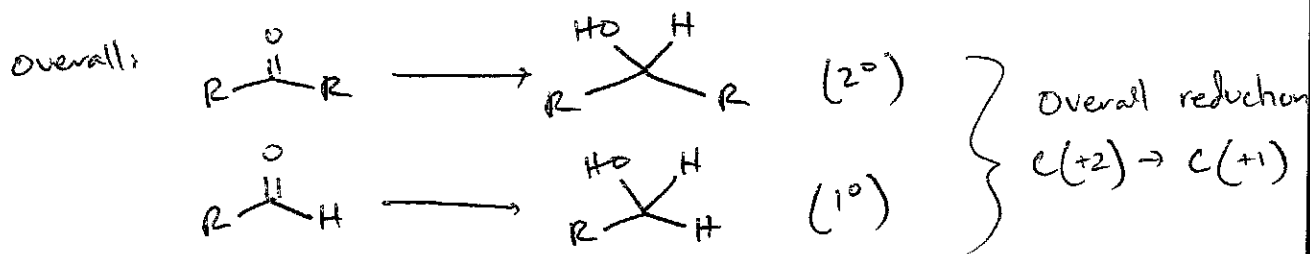
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**PLEASE COMPLETE NOTES IN INK AND DO NOT STAPLE.**

Recall: Reversible addition rxns of aldehydes + ketones



Now on to irreversible reactions:

• Reduction of aldehydes/ketones ~~to~~ <sup>to</sup> alcohols

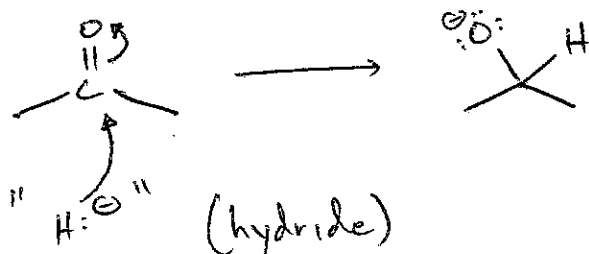


• 2 common reagents:

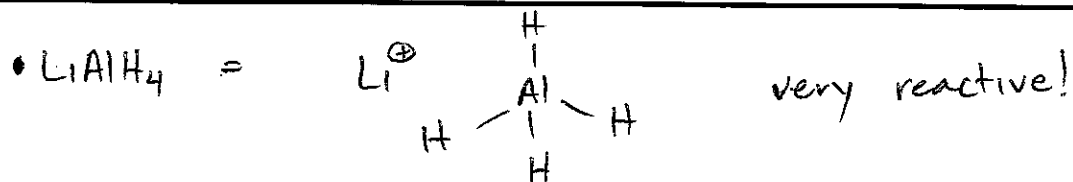
-  $\text{LiAlH}_4$ : very reactive

-  $\text{NaBH}_4$ : less reactive, more selective

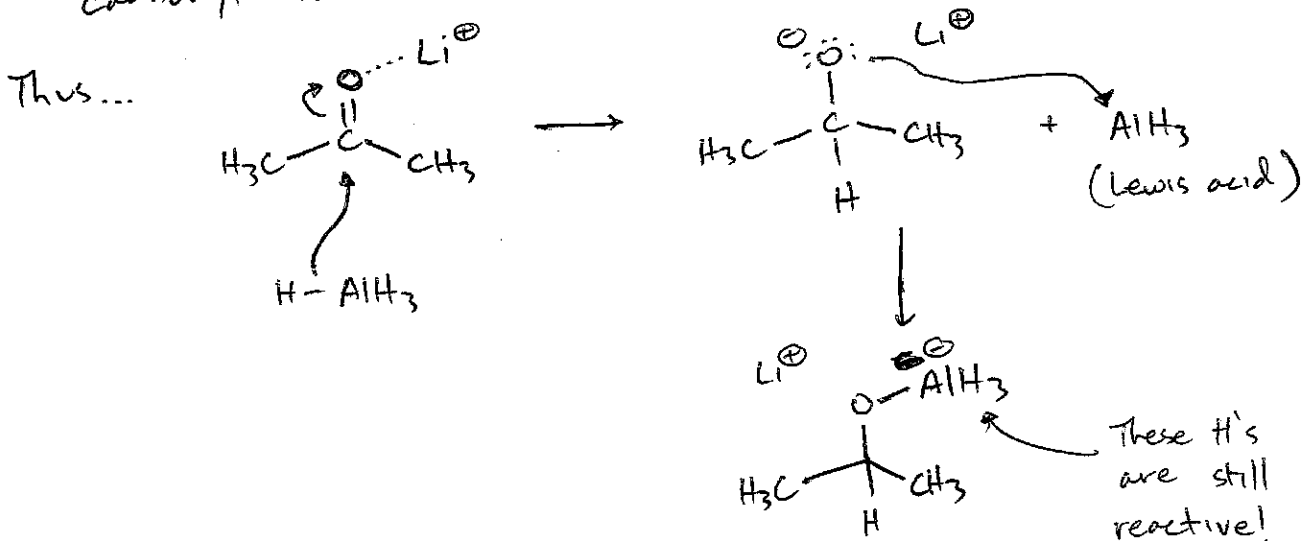
• Common mechanistic theme: (not actual, real mech)



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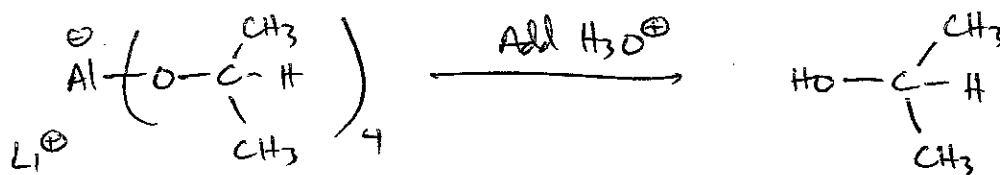


• Reduction mechanism is complex (see text)  
 -  $\text{Li}^\oplus$  acts as a Lewis acid to "activate" the carbonyl toward reaction with hydride



Note: One equiv. of  $\text{LiAlH}_4$  reduces 4 equivs of aldehyde/ketone

• When reaction is complete:



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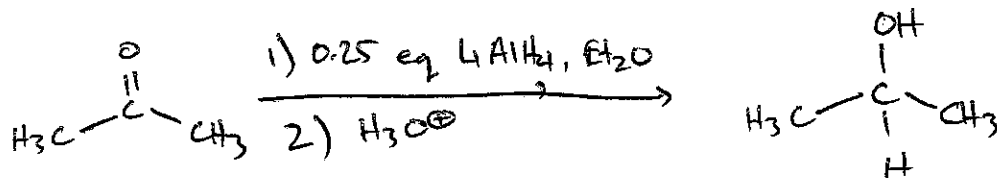
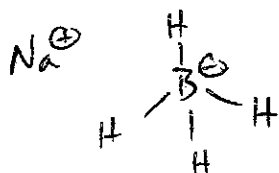
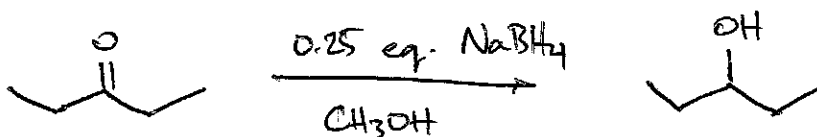
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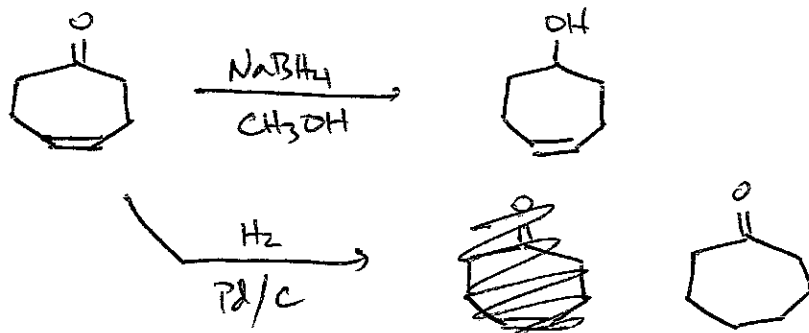
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Overall:- NaBH<sub>4</sub>:(Less reactive than LiAlH<sub>4</sub>)Overall:

(single step)

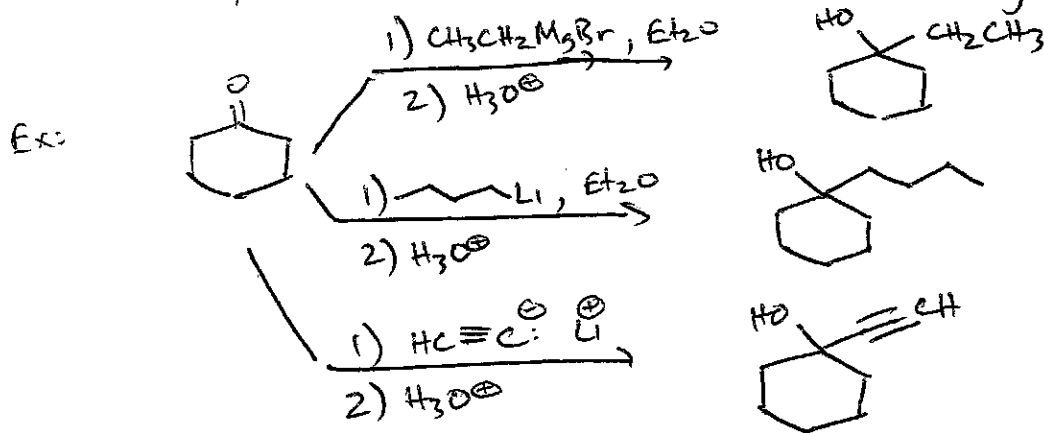
"Chemoselectivity" - reactions that are specific to one functional group relative to others

Chemoselective reductions: aldehyde/ketone vs alkene



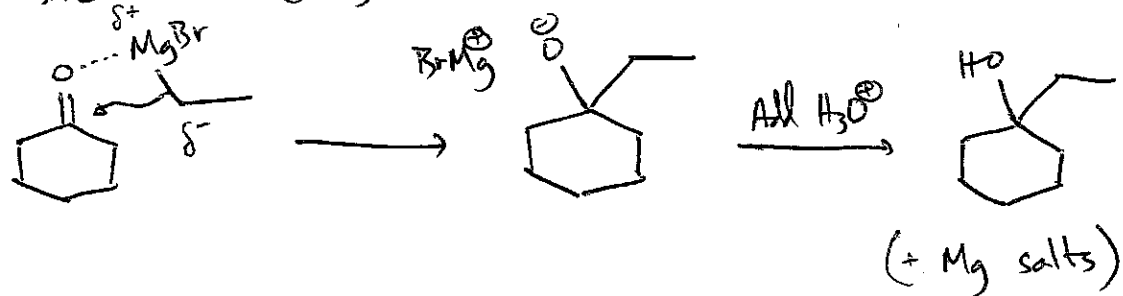
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• Reactions of aldehydes/ketones with carbanion-like reagents:

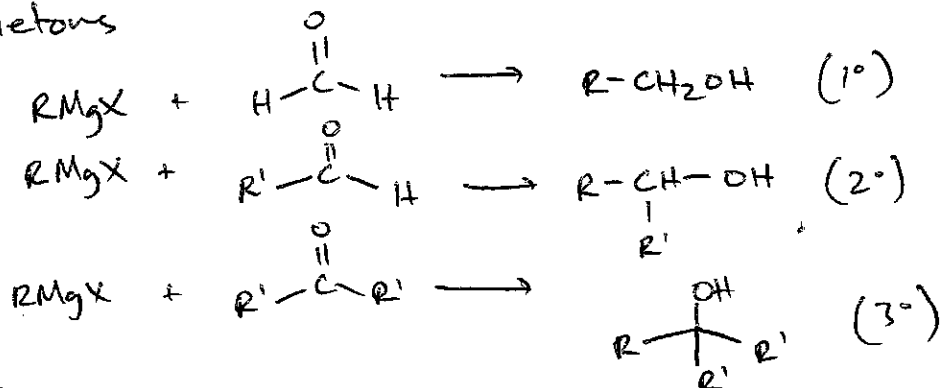


• New C-C bond formed!!!

• Mechanistic theme (Grignard)



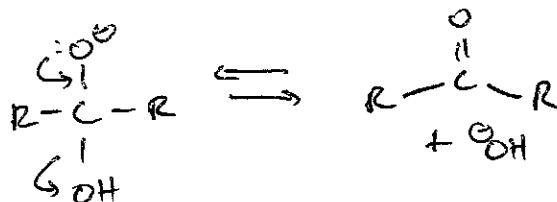
• Very versatile, from synthetic perspective - construct carbon skeletons



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• Why are these reactions "irreversible"?

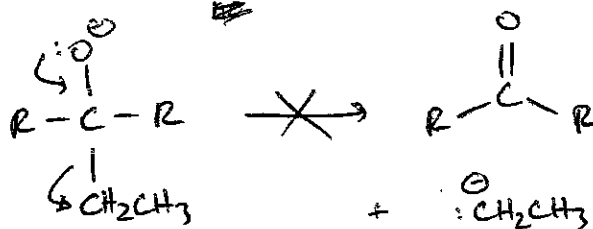
Example of reversible rxn:



this is reasonable when you consider  
 pKa's of conj. acids  $\approx$   $\text{H}_2\text{O} = \sim 15$

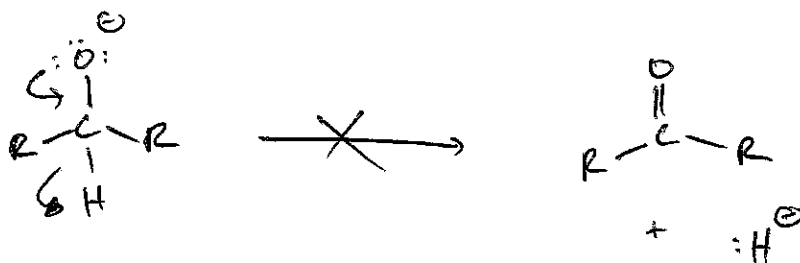
• Reversible Grignard rxn?

No!



not a good "leaving group"  
 pKa of  $\text{CH}_3\text{CH}_3 = \sim 50$

• Similarly....



• pKa of  $\text{H}_2 = 35$   
 • not good "leaving group"

• Carbanion-like and hydride ~~the~~ reagents add irreversibly  
 to carbonyls