Course Chem 345 Lecturer Hellman

Day Wednesday Date 3/4/2015

Notes Taken By Leslie Total # of Pages 4

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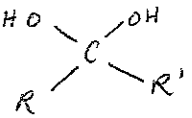
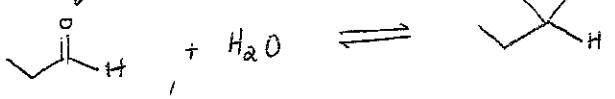
Recall: Reversible addition to ~~thermodo~~ aldehyde / ketone C=O ....

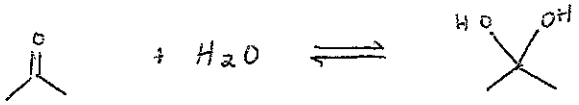
Hydrate formation:



Thermodynamic variation:



$K_{eq} \sim 1$

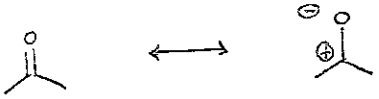


~ 0.001

Rationale:

(2° $C^{\oplus}$ secondary carbocation)

vs



(3° $C^{\oplus}$ tertiary carbocation)

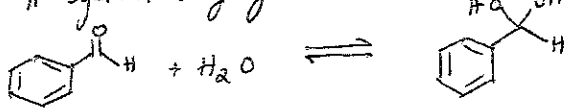
∴ Rationalize or predict substituent effects:

1) Impact of electronegative substituents near C=O

$K_{eq} \sim 10$ (vs  ; 0.001)

} electronegative groups destabilize partial $C^{\oplus}$ in C=O

2) π system conjugated to C=O



$K_{eq} \sim 0.01$

(Recall  ~ 1)

} Rationale - partial $C^{\oplus}$ in C=O form stabilized by delocalization

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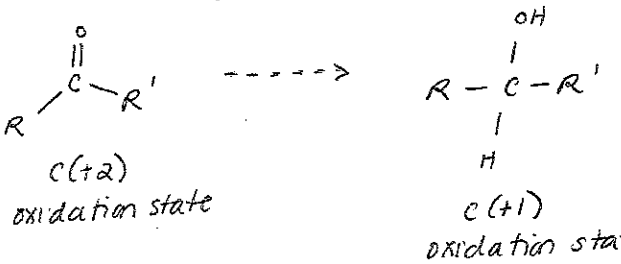
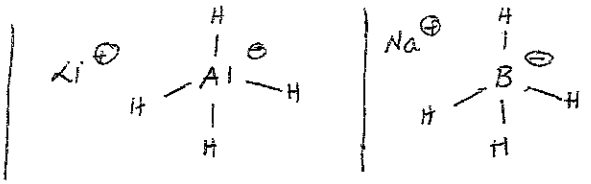
Transition: from reversible to irreversible additions to C=O

• Reduction rxns involving "hydride" reagents.

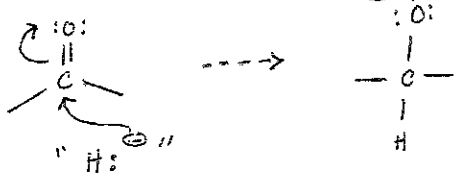
Overall:



Reagents: $LiAlH_4$, $NaBH_4$ } sources of "$H:^{\ominus}$"



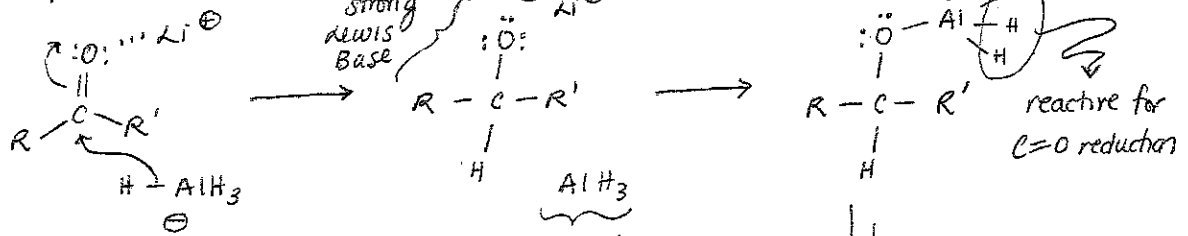
Overall Process – Key idea, mechanistically:



} Not exactly correct, but a good idea to keep this in mind

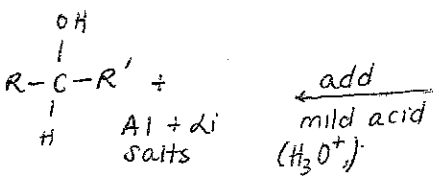
Note: $LiAlH_4$: $Li^{\oplus}$ serves as a Lewis acid to enhance C=O reactivity

Thus,



* coordination of Li to oxygen enhances electrophilicity of carbonyl carbon!

AlH_3 strong Lewis acid



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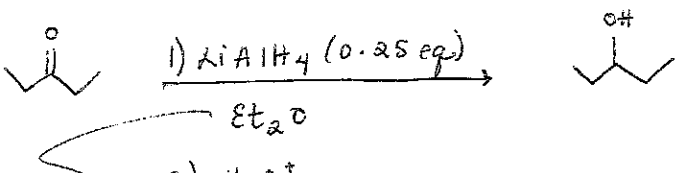
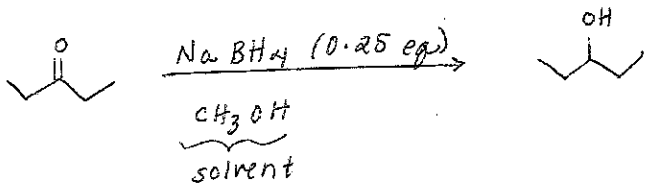
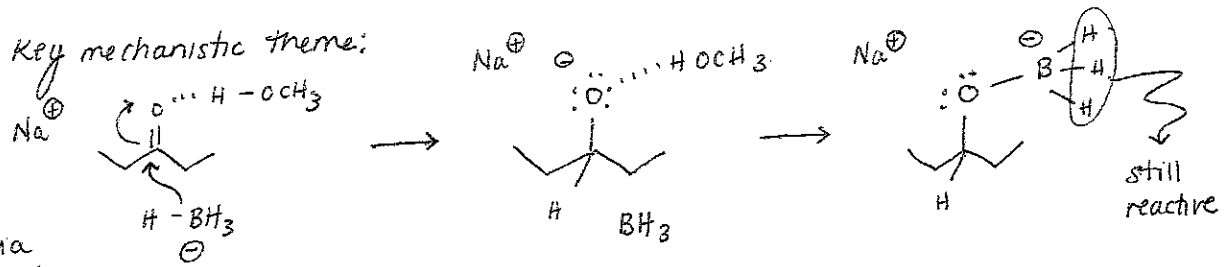
Summary (overall synthetic perspective):



- $NaBH_4$ less reactive than $LiAlH_4$, but both reduce aldehydes / ketones to alcohols
  - Because $NaBH_4$ is 'mild', can use protic solvents
  - Thus



  - Key mechanistic theme:



* solvent via hydrogen bond activates the carbonyl

- $NaBH_4$ or $LiAlH_4$ add "H_2" across a C=O bond ()

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Note: Chemo selectivity

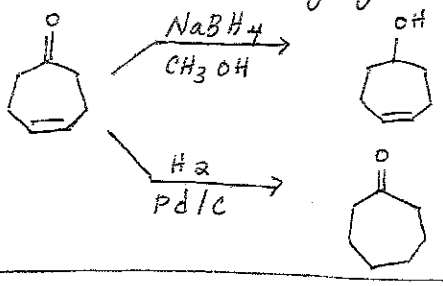
$LiAlH_4$ or $NaBH_4$ reduce C=O, not C=C

vs

H_2, Pd/C reduce C=C, Not C=O

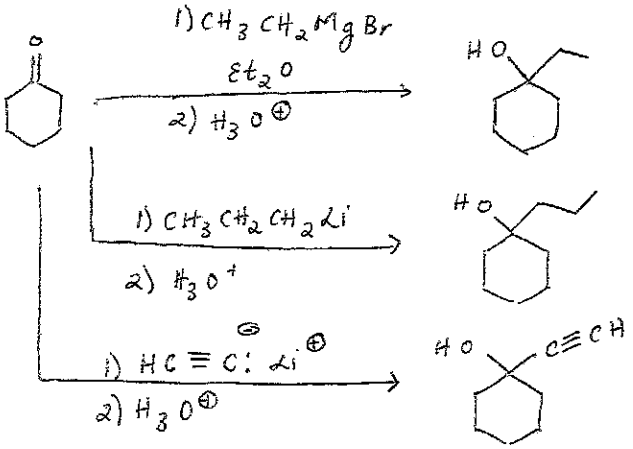
* Thus we can choose reactivity by choosing reagents

Ex:



Rxns of aldehydes/ketones with carbanion-like reagents

Ex:



Note

1). New C-C bonds!