Course CHEM 345 Lecturer Gellman

Day Friday Date April 1, 2016

Notes Taken By Lu/Eileen Total # of Pages 4

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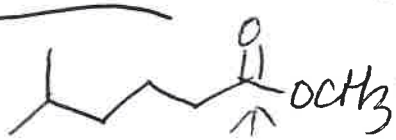
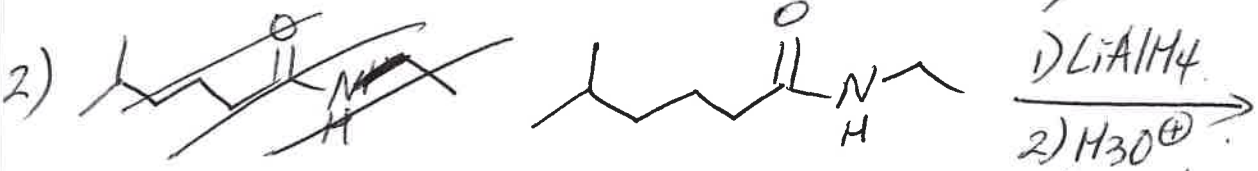
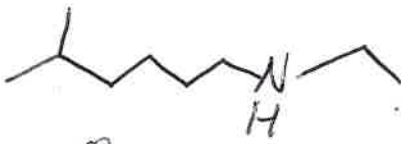
Recall: Reduction of Carboxylic Acid Derivatives ...

1) 

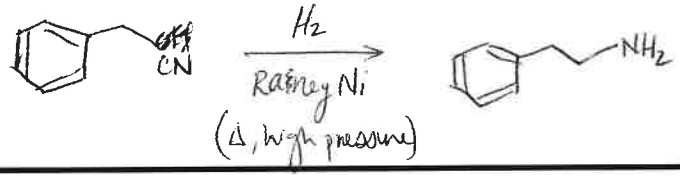
2) 



$R-\overset{O}{\overset{\|}{C}}-OR'$ vs. $R-\overset{O}{\overset{\|}{C}}-NHR'$

3) Nitrile redn, to 1° amine.

(a) 

(b) 

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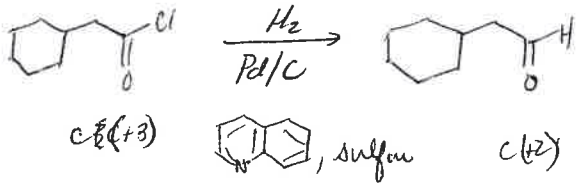
How stop such reductions at C(+2) ox state?

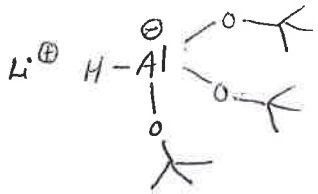
- start w/ ~~more~~ a more reactive carb. acid derivative, an acid chloride
- also, use a highly specialized reducing agent

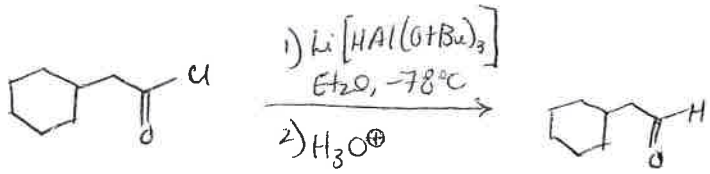
1) Rosenmund Reduction – poisoned catalyst

ex:



2) Bulky derivative of $LiAlH_4$ → $Li[HAl(OtBu)_3]$





Reactions of carboxylic acid derivatives w/ organometallic reagents

- "carbanion-like"
- form C–C bonds

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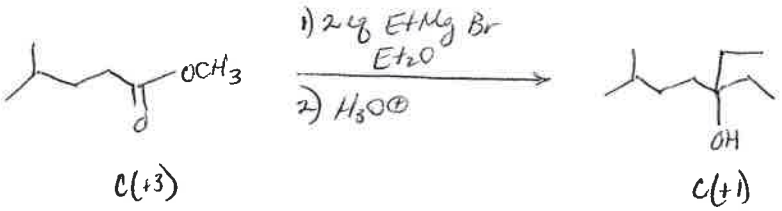
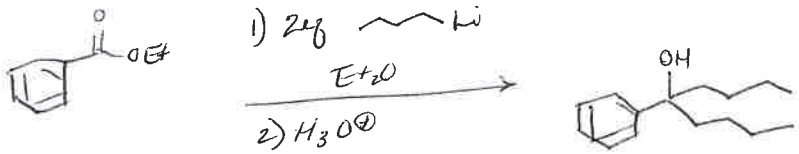
1) Ester ! Gringard Reagents or organolithium reagents

ex:

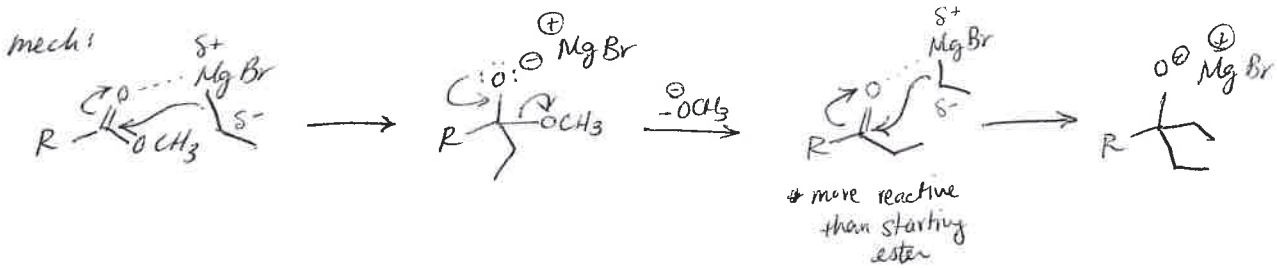


C(+3) C(+1)



- cannot stop rxns @ C(+2) stage b/c ketones more reactive than starting ester

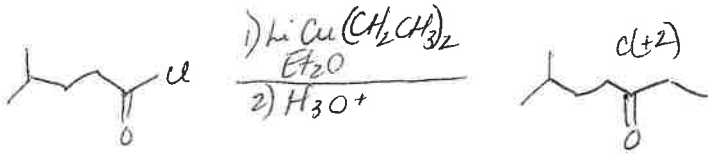
mech:



- how stop at ketone stage C(+2) ?

- acid chloride ! lithium diorganocuperate

ex:



Course CHEM 343 Lecturer Gellman

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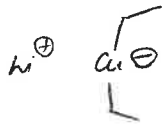
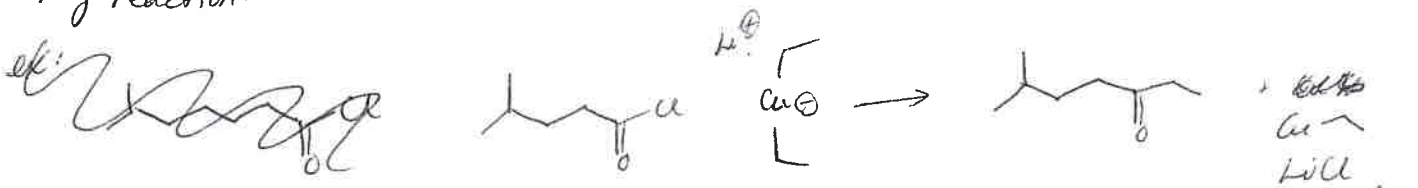
Recall (chem 343):

CH_3CH_2Li + CuBr ⟶ $LiCu(CH_2CH_3)_2$ + LiBr

(CH_3CH_2Li: 2 equiv)



Key reaction:

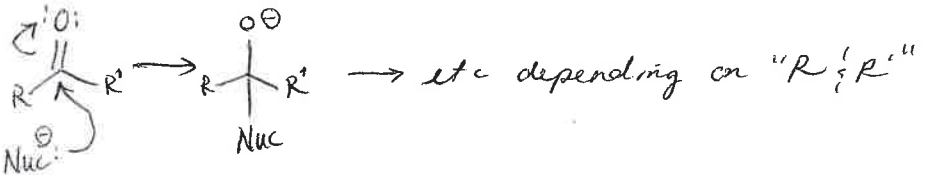


Read 21.11 - Synthesis of Carboxylic Acid Derivatives

Ch 22 - Enols ; Enolates

Rec Probs - 1-9, 11-23, 26-31, 35, 36, 37a, 38, 40-44, 46-49, 51-95

Past Theme:



New Theme: "α-acidity"