Course Chem 345 Lecturer Eichman

Day Friday Date 3/27/2015

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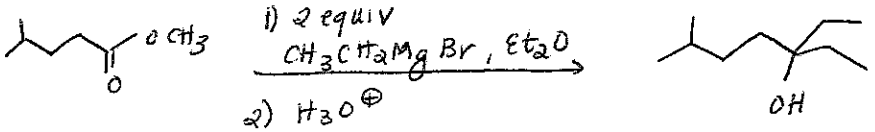
Recall: Rxns of carboxylic acid derivatives . . .

Rxns w/ organometallic agents ("carbanion like")

Ex:

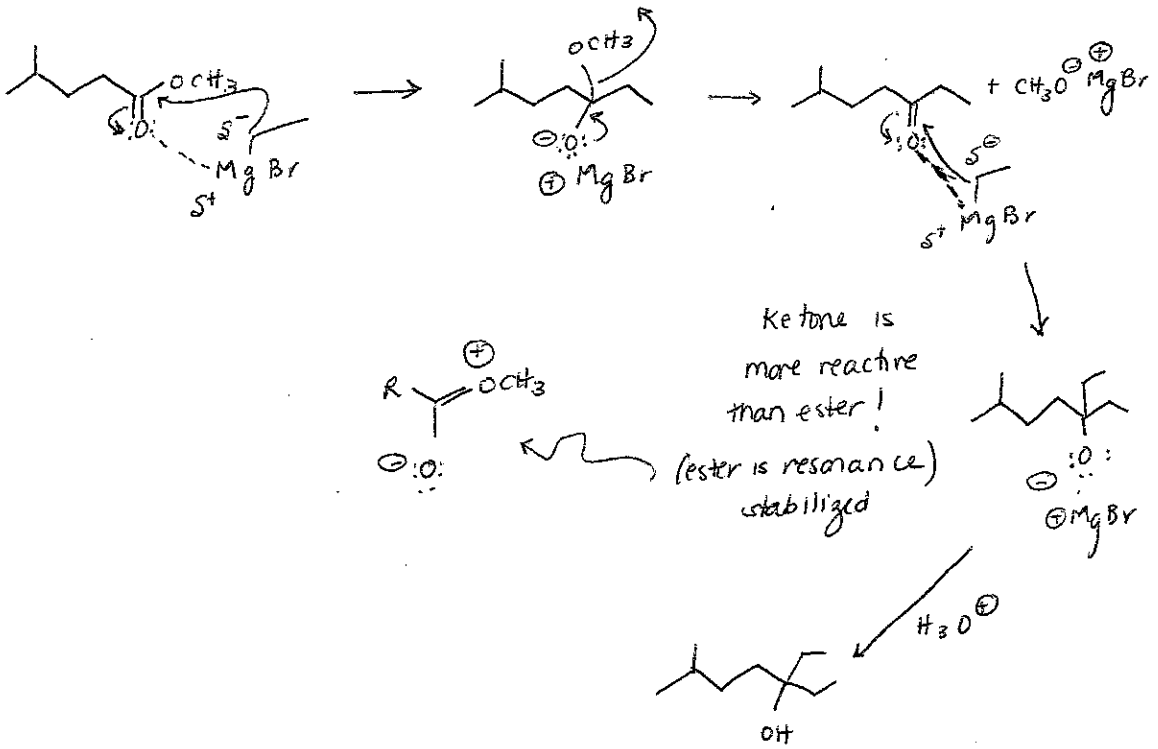


overall: C(+3) ⟶ C(+1)

[ester] [alcohol]

Proceeds via C(+2)[ketone] but cannot stop there

Mechanism:



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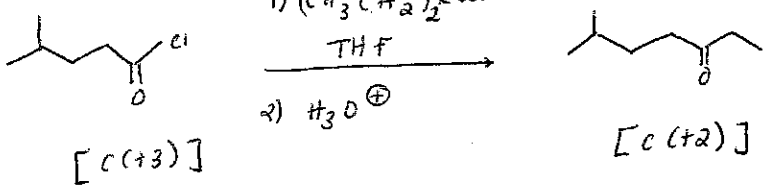
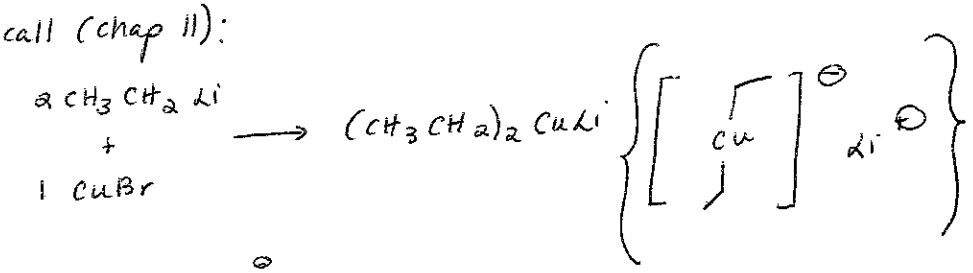
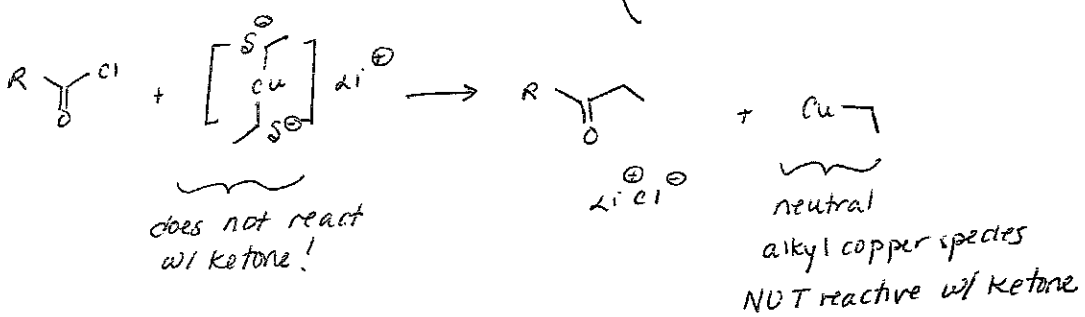
To prepare ketone from "C(+3)", use a less reactive organometallic agent:

- "cuprate"

Ex: 

Recall (chap 11):





stop at C(+2)

Read § 21.11: "Synthesis of carboxylic acid derivatives"

⟹ make flashcards

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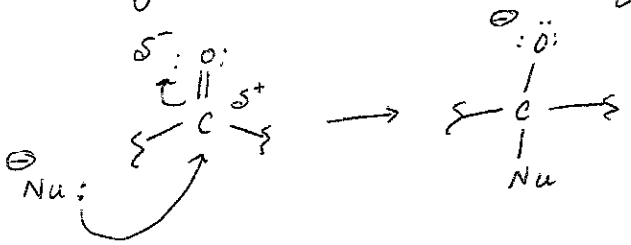
Chp 22 – Enols, enolates, etc.

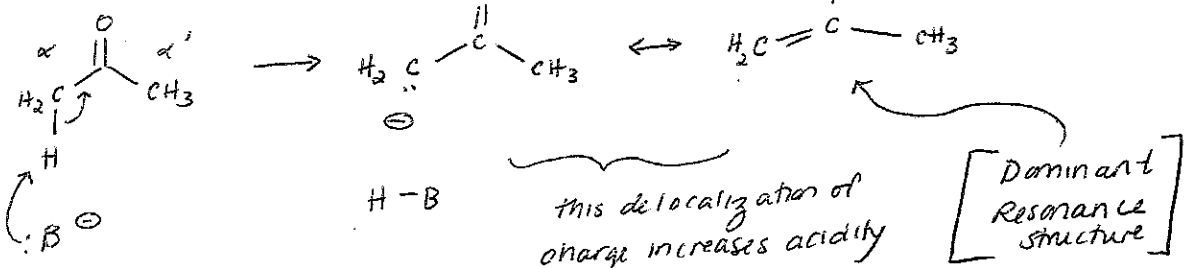
Rec. Problems = 1–9, 11–30, 33, 34, 36, 37, 39–89

So far, major mechanistic theme in carbonyl chemistry:



New mechanistic theme, acidity of H on C adjacent to C=O (α to C=O)

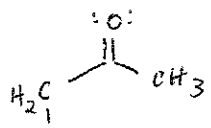
Thus,



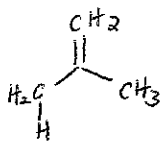
this delocalization of charge increases acidity of α hydrogen

[Dominant Resonance structure]

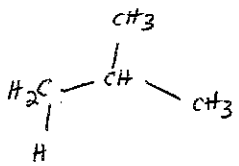
This species is called an "enolate"



pka ~ 19



pka ~ 42



pka ≥ 50

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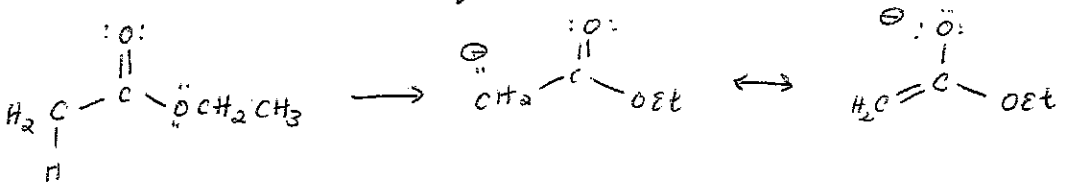
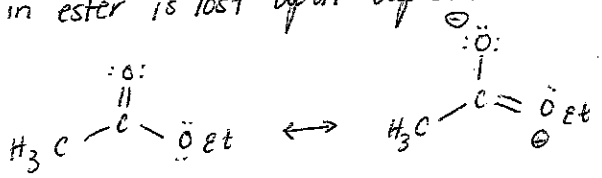
Esters are less acidic than aldehydes/ketones @ α-position

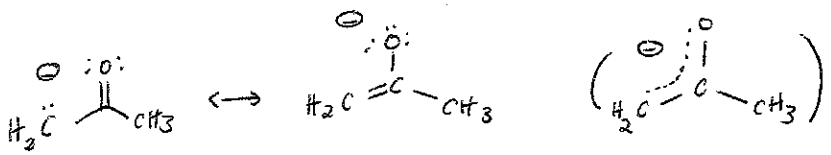


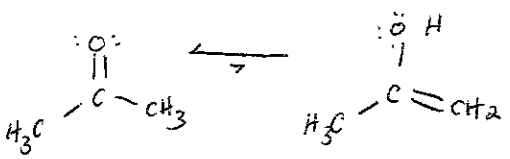
pKa ~ 25

resonance delocalization

α-H of esters a little less acidic than α H of aldehyde/ketone because resonance in ester is lost upon deprotonation.







("enol")

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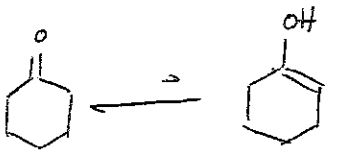
Eq. constants



K_{eq} 10^{-6} ketone

10^{-20} ester

5 or aldehyde

∴ ketone rxns can proceed via enol, but not ester rxns.

But ketones / aldehydes and esters can react via enolates.

Special cases - enol form are preferred.