Course Chem 345 Lecturer Gellman

Day Friday Date 3/13/2015

Notes Taken By Leslie Total # of Pages 4

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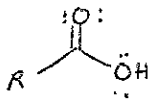
Exam 2 = Wednesday. Chps. 17-19.

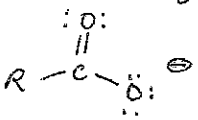
- previously assigned locations
- office hour Monday 5-6 PM
- Review Tuesday 4:00 PM, 8371

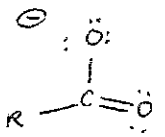
Recall: Carboxylic acids....



pka ~5

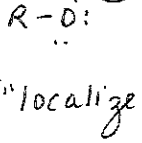
Stabilizing features in conjugate base ("carboxylate"):





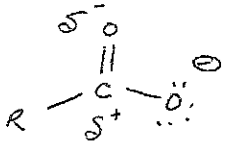
"charge delocalization"

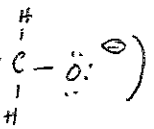
R-OH (pka ~16)



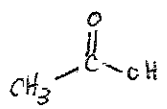
("localized")

another factor:



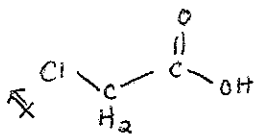


Substituent effects on pka, qualitative predictions



pka ~4.8

vs



pka ~ 2.8

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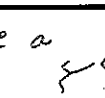
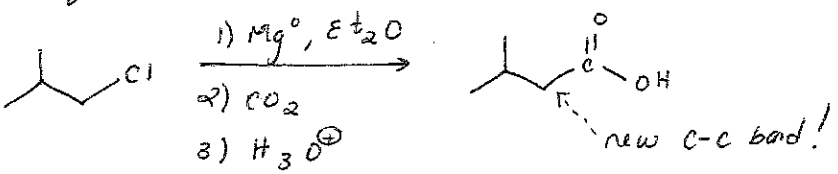
Synthesis of Carboxylic acid ("generate a  group")

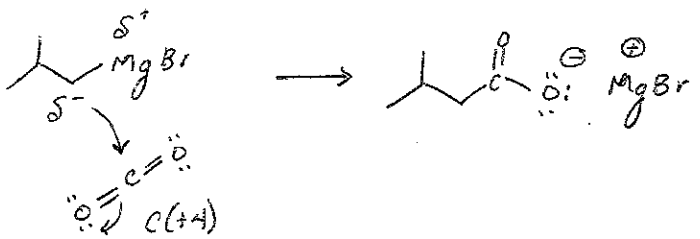
1) oxidation of 1° alcohols or aldehydes (Ag_2O)

2) alkyl benzene oxidations ($KMnO_4$)

3) Grignard reagent + CO_2

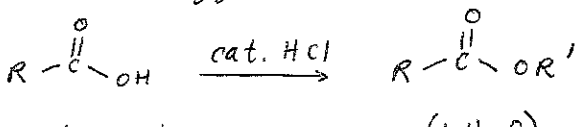
Ex: 

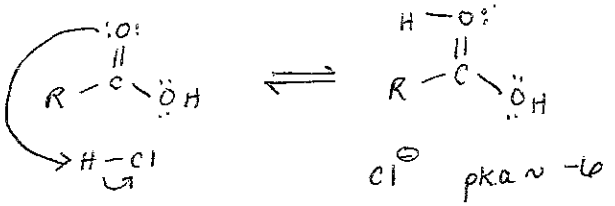
Key mechanistic step:



Rxns of carboxylic acids . . .

1.) Acid-catalyzed ester formation



Prelude: 

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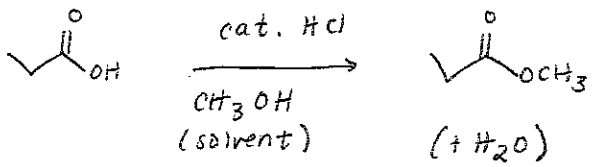
Rxns of carboxylic acids ....

1) acid-catalyzed ester formation

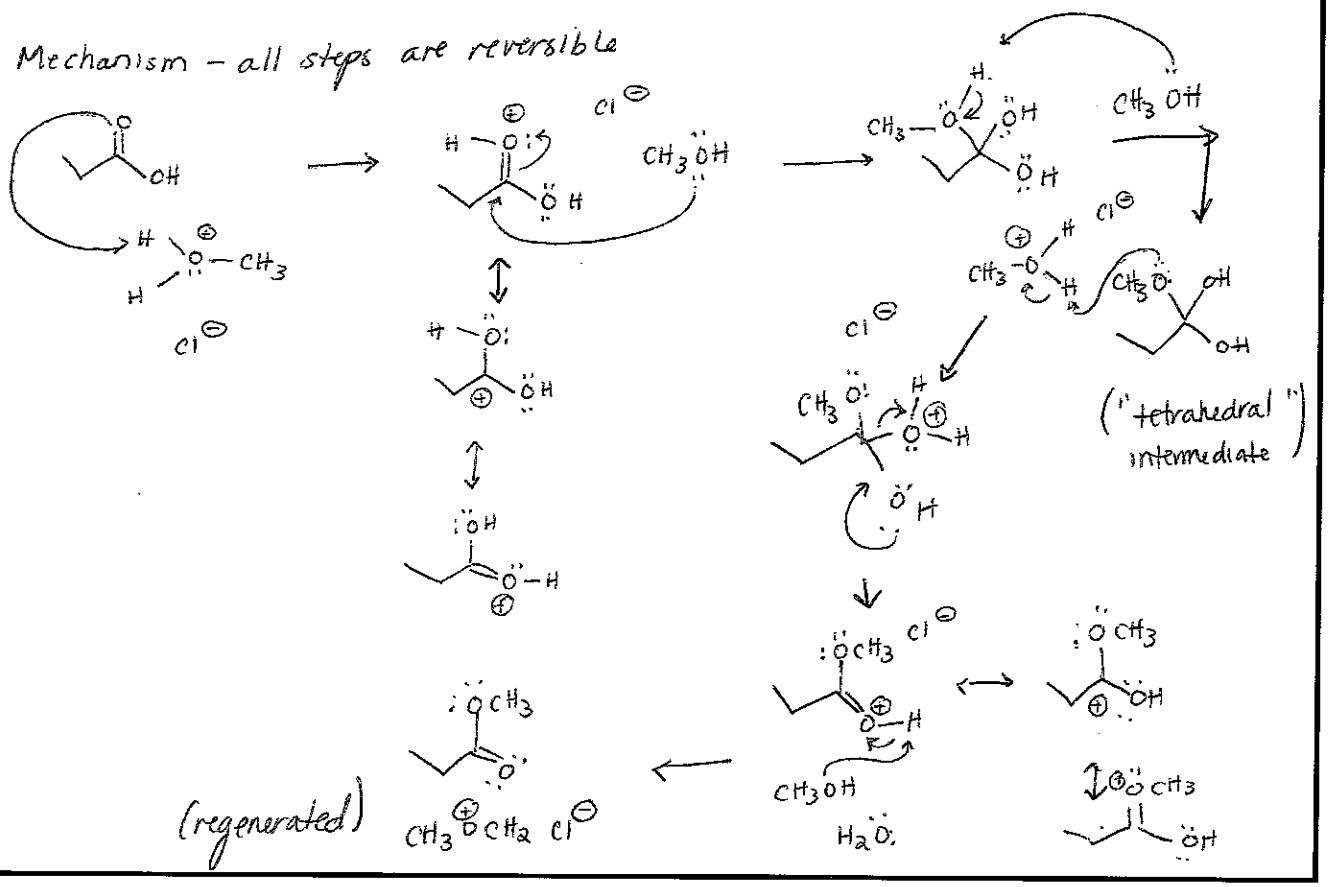
Note: limitations (synthesis perspective)

→ use alcohol as solvent (in excess): simple, cheap alcohols (CH_3OH, CH_3CH_2OH)

→ Impossible for 3° alcohols or phenols.



* Mechanism - all steps are reversible



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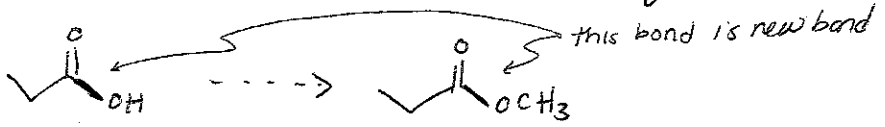
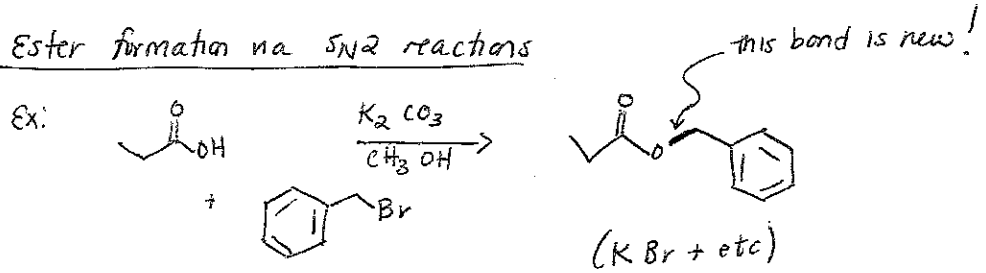
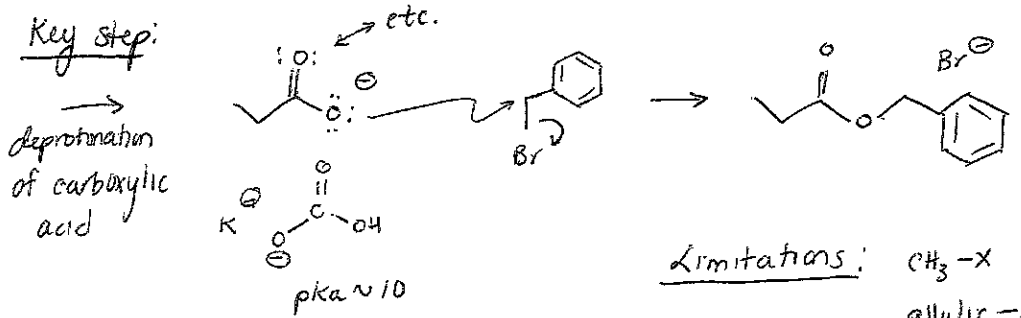
Note: substitution @ sp^2 carbon of carboxylic acid



2). Ester formation via S_N2 reactions



Key step:



Limitations: CH_3-X, allylic $-X$, benzylic $-X$ } most S_N2 reactive alkyl halides

Special case (methyl esters)