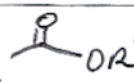
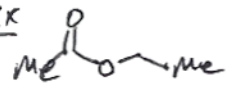
Chapter 18 Carboxylic Acid Derivatives Weeks 10-11

(1) Esters



Naming (A) small esters (#C < 5)

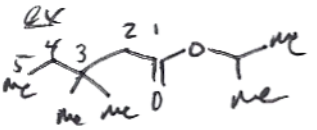
1. use parent name of carboxylic acid
2. replace "ic" with "ate"
3. R'-name goes first

ex 

acetic acid ⇒ acetate ⇒ Ethyl acetate

(2) (B) Larger Esters (#C > 5)

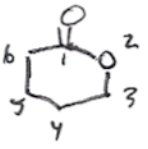
1. name of parent alkane
2. drop "e" ; add "oate"
3. Carboxyl carbon = highest priority
4. R'-name goes first

ex 

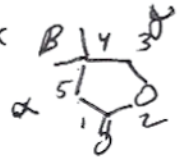
pentane ⇒ pentanoate ⇒ 3,3-dimethyl-pentanoate ⇒ isopropyl-3,3-dimethyl-pentanoate

(3) Lactones = cyclic esters

1. Name as "oxacycloalkanones"

ex  2-oxacyclohexanone

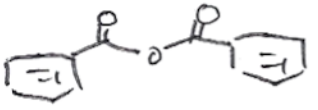
2. Ring size via Greek letters
non-ester carbons = α, β, γ

ex  a "γ-lactone" ← "gamma"

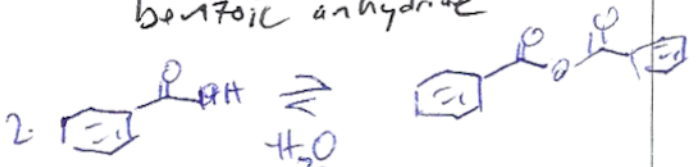
name 4,4-dimethyl-2-oxacyclopentanone

(4) Anhydrides

Name based on carboxylic acid + anhydride

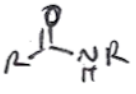


benzoic anhydride



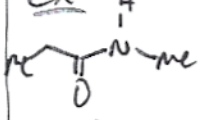
formally

(5) Amides

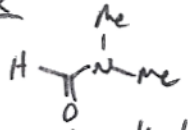


Naming

1. drop "e" from parent alkane
2. add amide
3. substitution at Nitrogen designated w/ N- prefix

ex 

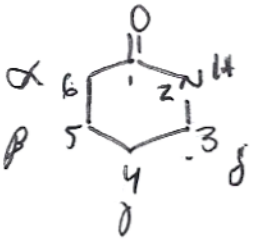
N-methyl propanamide

ex 

N,N-dimethyl formamide

(6) Lactams = cyclic amides

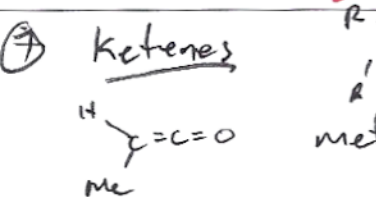
Named as "azacycloalkanones"



2-Azacyclohexanone is a δ-lactam ("delta")

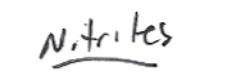
skip ketenes

④ Ketenes



Nitriles (Behaves like Acyl compound)

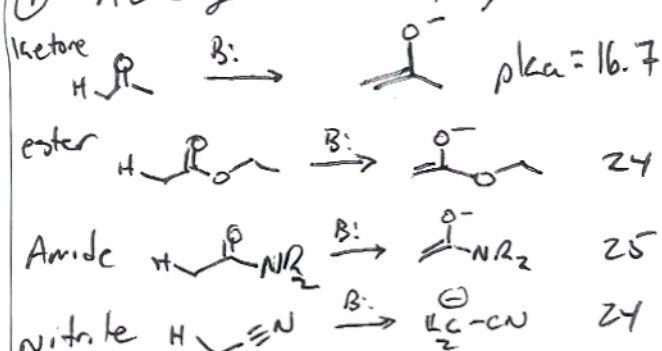
R – C≡N



do not worry about naming ketene & Nitriles

⑤ Reactivity of Acyl compounds

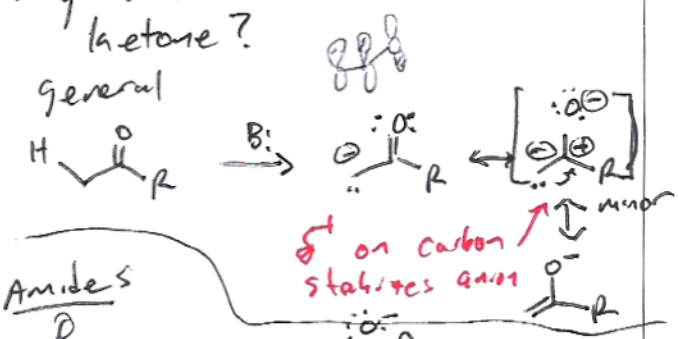
① Acidity of α-hydrogens



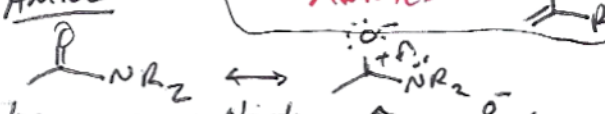
⑨ Trends in pka

Why is Amide less acid than ketone?

general



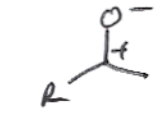
Amides



lone pair on N-atom donates to carbonyl! less δ+

⑩ Trends con't

How about ketones?



much less stabilized

Esters?

less efficetive than amides

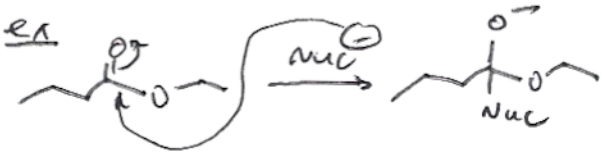
oxygen more e-neg!

specific

⑪ ⑫ Electrophilic of Carbonyl carbons & Nitrile carbons

Implications for Rxns

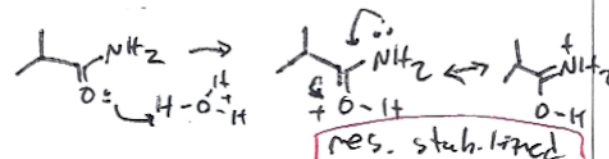
ex



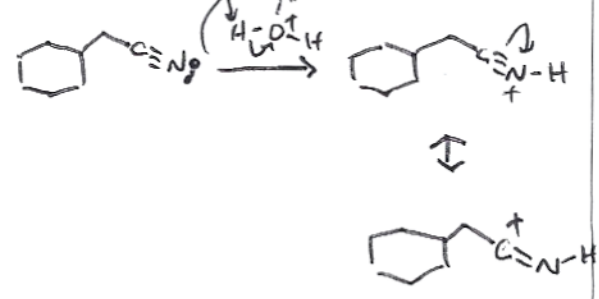
ex

⑫ ⑬ Acyl Compound can be Basic

ex

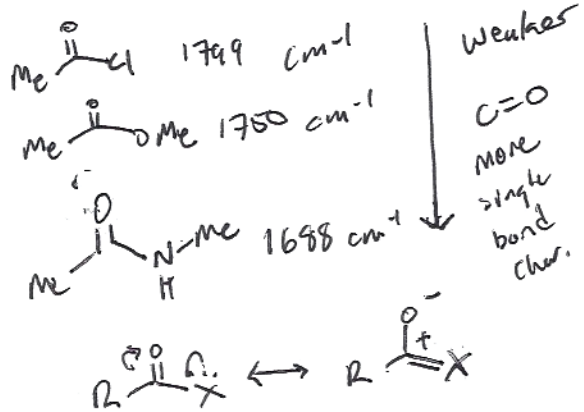


ex

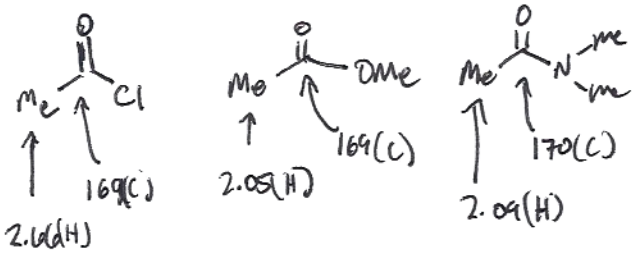


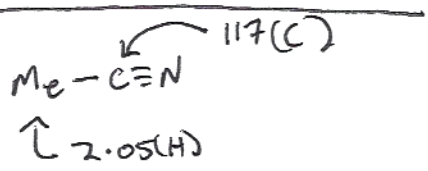
12A Spec

IR



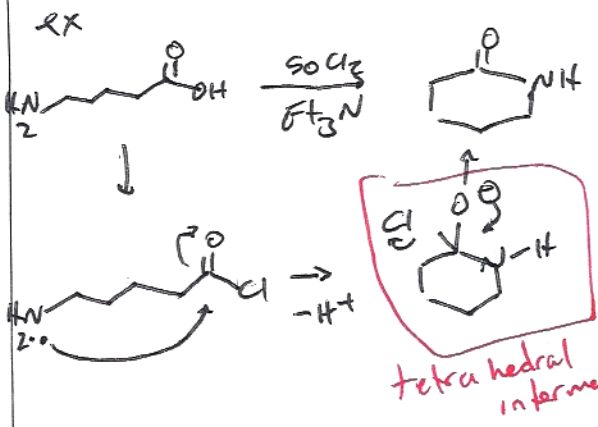
12B NMR ^1H & ^{13}C (ppm)



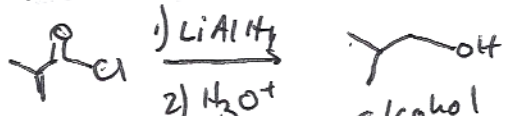


(13) Rxns of Acid chlorides (see chapter 17)

ex

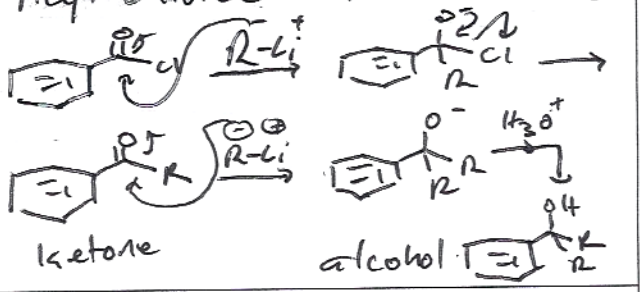


(14) $R^{R}Cl$ + metal hydrides.

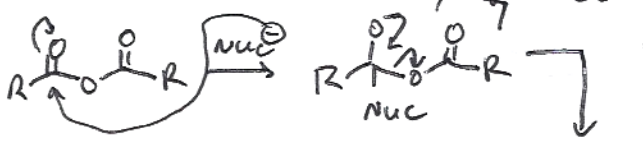


(See Ch 17)

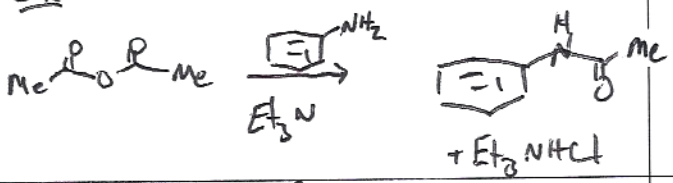
Acyl chloride + R-Li or R MgBr



(15) Reaction of Anhydrides

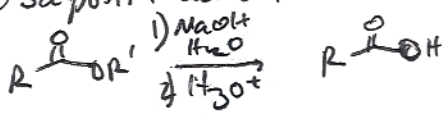


ex

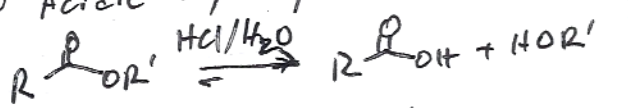


(16) Rxns of Esters (see Ch 17 Notes)

(A) Saponification

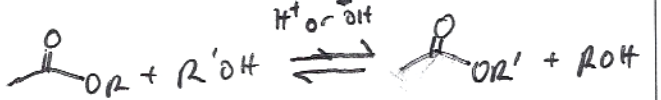


(B) Acidic hydrolysis

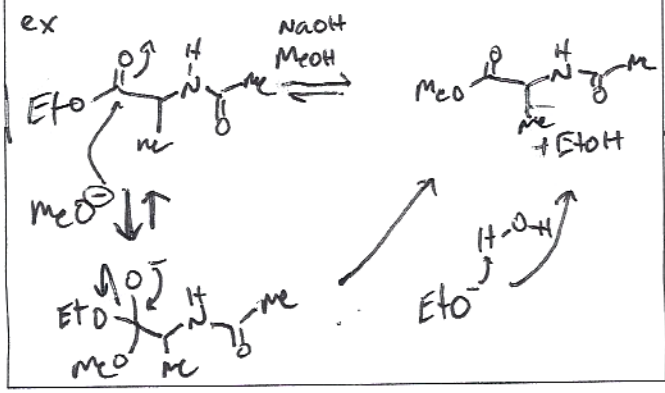


(Mech same as Ester esterification)

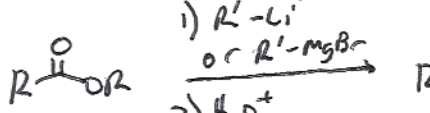
(17) Transesterification



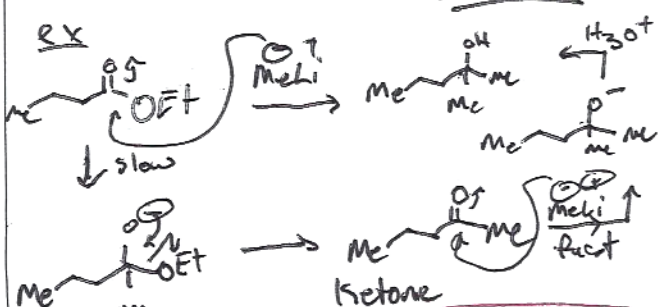
ex



(18) Ester and organometallic Reagents

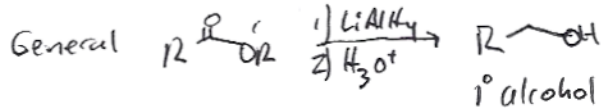


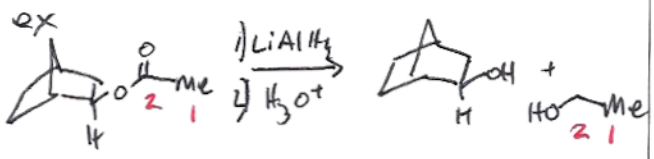
ex



more reactive than ester

(19) Esters & metal Hydrides

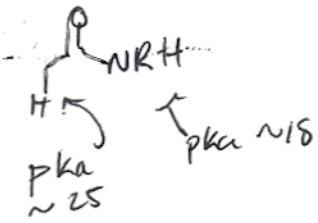
General 

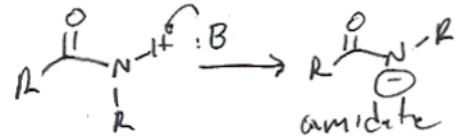
ex 

Mech ? work out on own

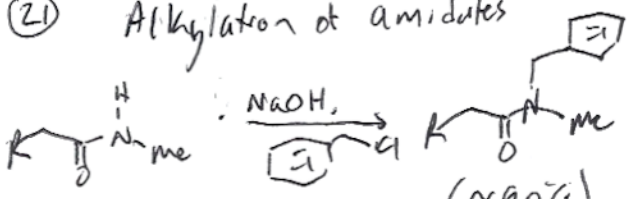
(20) Rxns of Amides

Amidates

Recall 



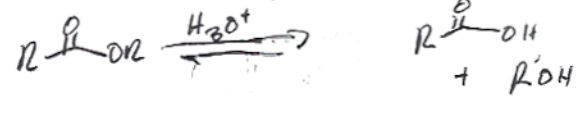
(21) Alkylation of amidates

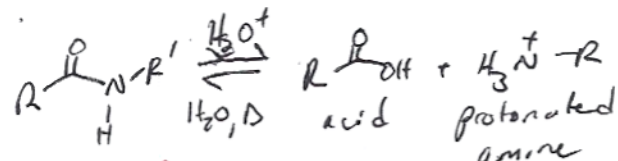


(~90%)

(22) Hydrolysis of Amides

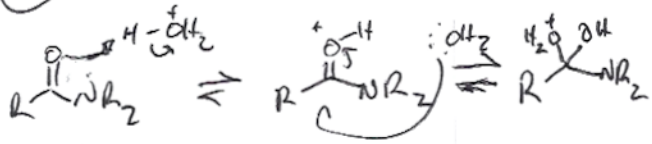
Recall ester hydrolysis



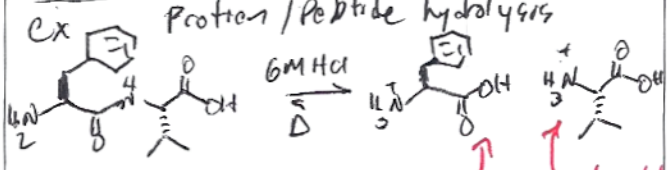


requires strong acid w/ heat & pressure!

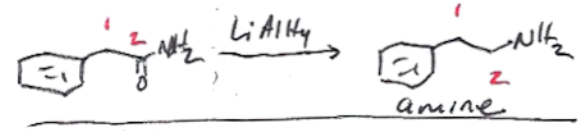
(23) Mech same as for esters



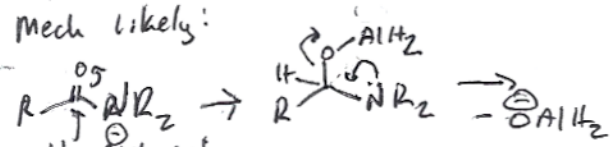
Protein / Peptide hydrolysis

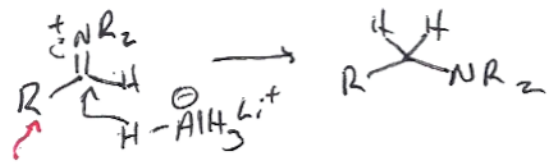
ex 

(24) Reduction of Amides

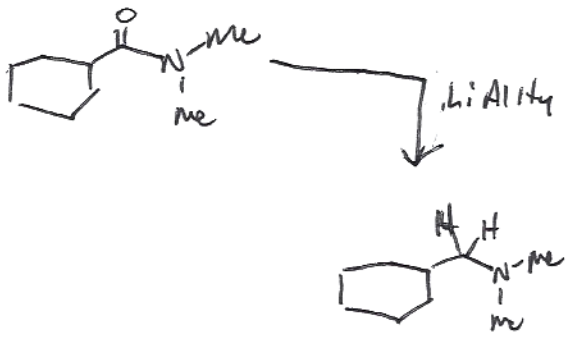


Mech likely:



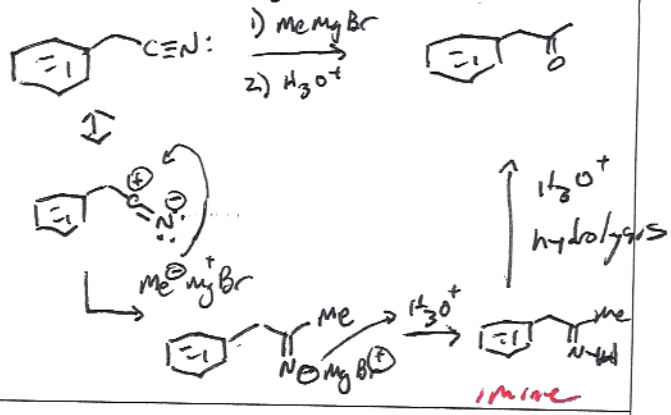


(25) example



(26) Rxns of Nitriles

Addition of organometallic Reagents



(27) Metal hydrides