Course Chem 345 Lecturer Gellman
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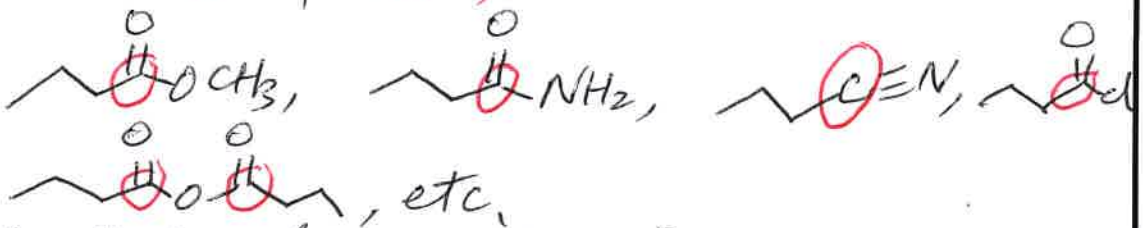
Recall: Carboxylic Acid Derivatives

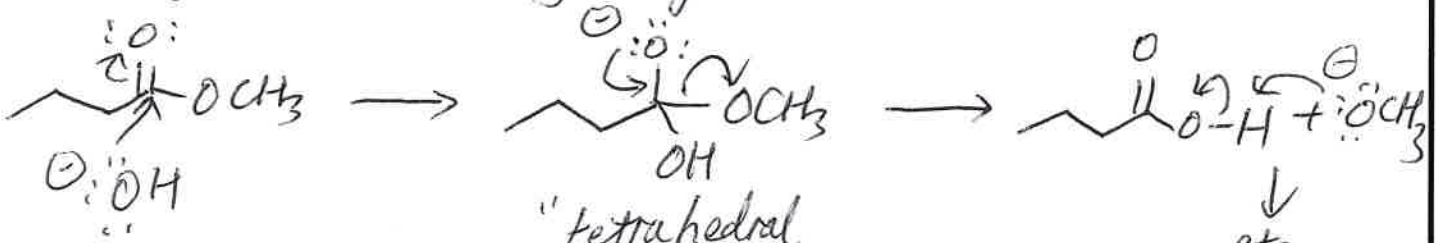
E.g., CA =  C(+3)

Derivatives =  , etc.

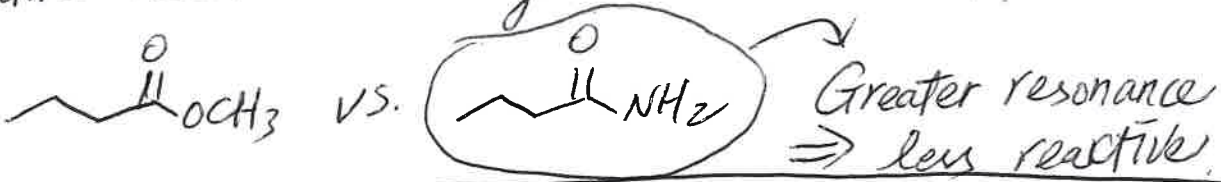
Rxns ~~for~~ of Carboxylic acid derivatives

1) hydrolysis – Ester hydrolysis ...

Mech for alkaline hydrolysis



Relative reactivities among C.A. derivatives



Nitrile hydrolysis

Acidic or basic conditions → very "hard" rxn – nitriles less reactive than even amides.

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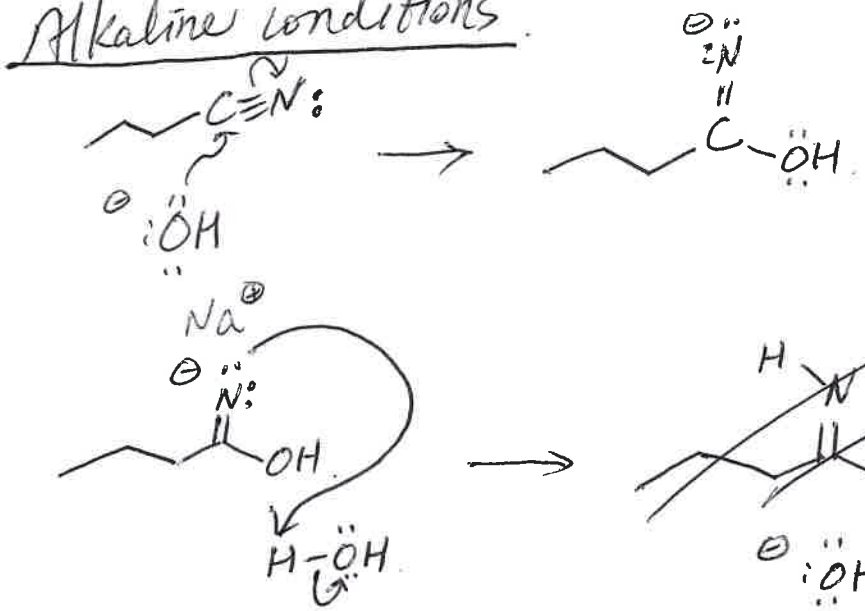
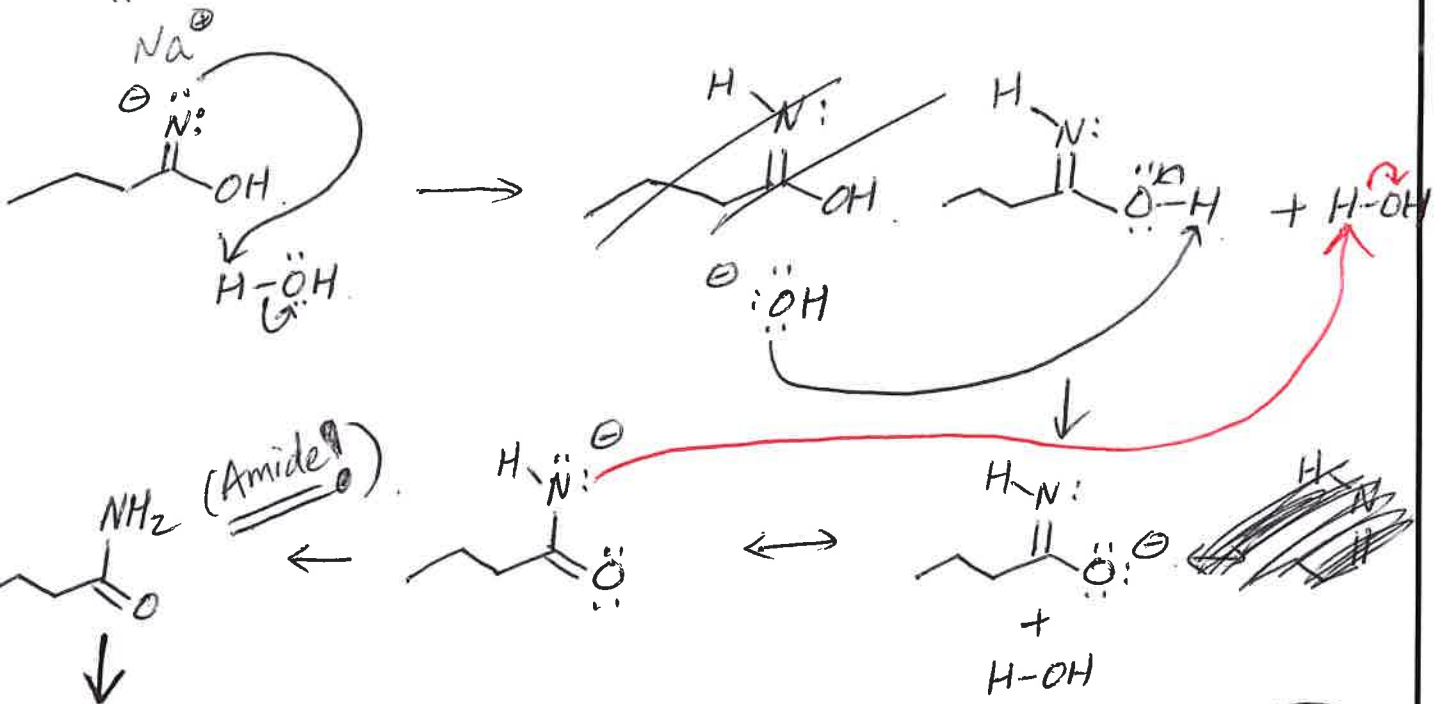
(via amide intermediate)

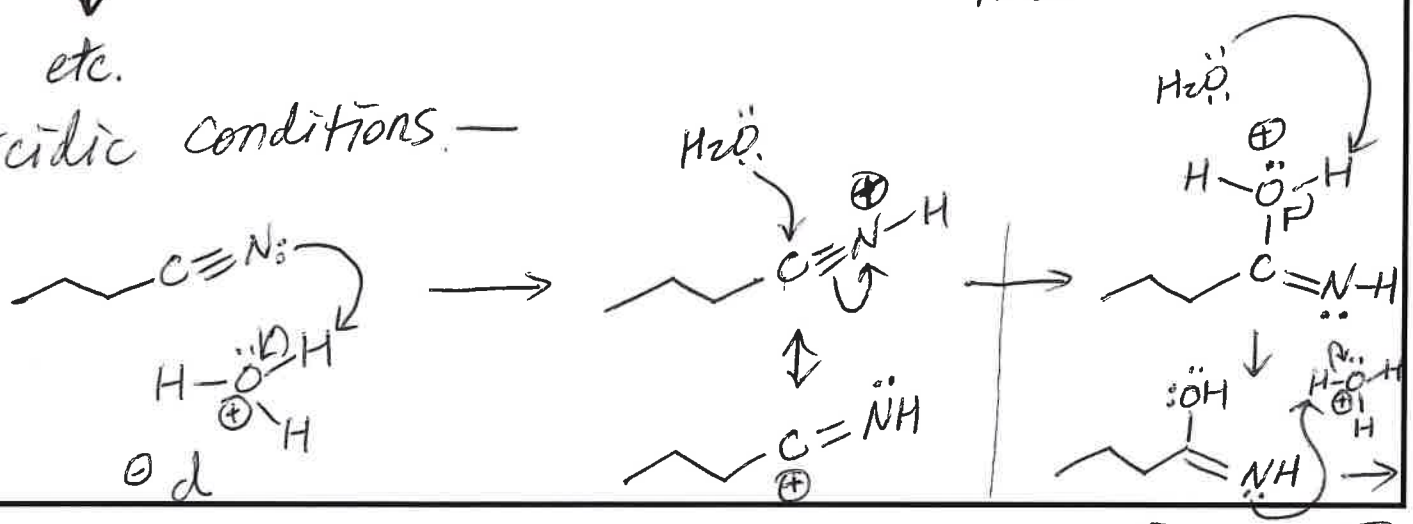
Alkaline conditions



Nitrile C is electrophilic but less so than carbon C.



Acidic conditions —



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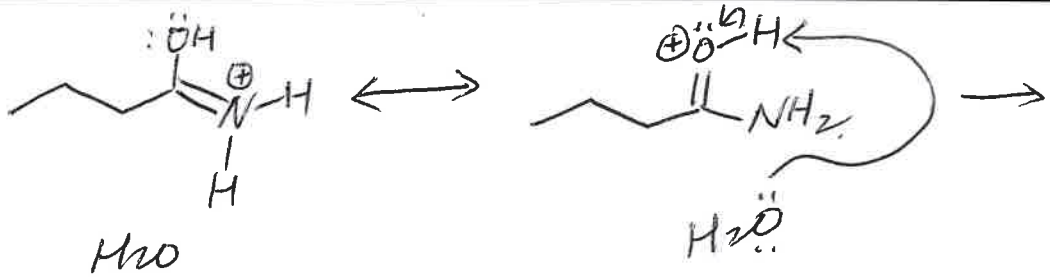
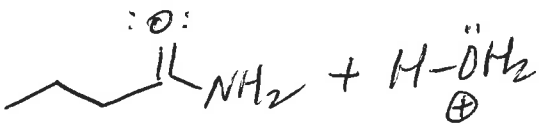


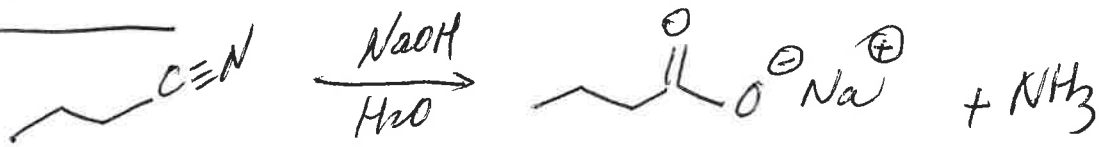
H_2O H_2O



↓

you fill in acid-catalyzed amide hydrolysis mech.

Overall:



Read carefully § 21.7, esp. section E – relative reactivities among carb. acid, derivs.
Reactivity of acid chlorides & anhydries w/ O or N nucleophiles – synthesis of esters & amides.

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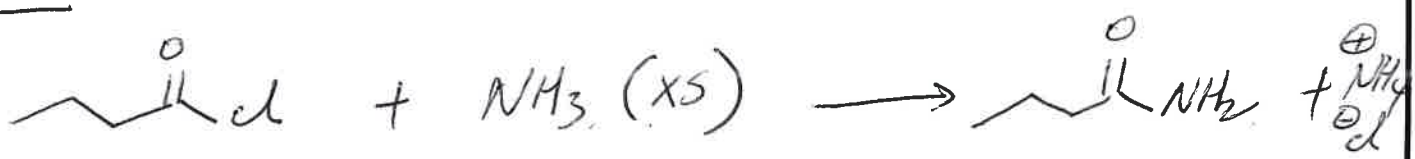
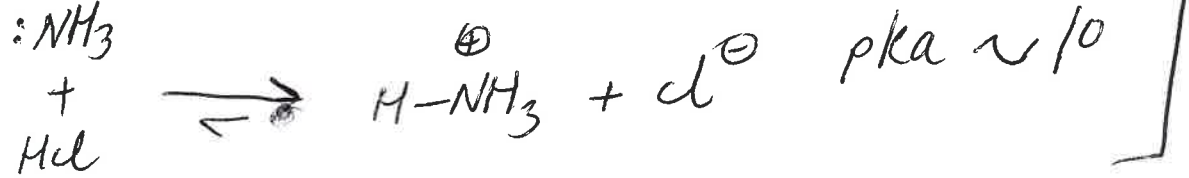
Acid chlorides & anhydrides are very reactive as electrophiles, & are generally used as building blocks to prepare esters or amides.

Ex: Acid chlorides + amines → amides.

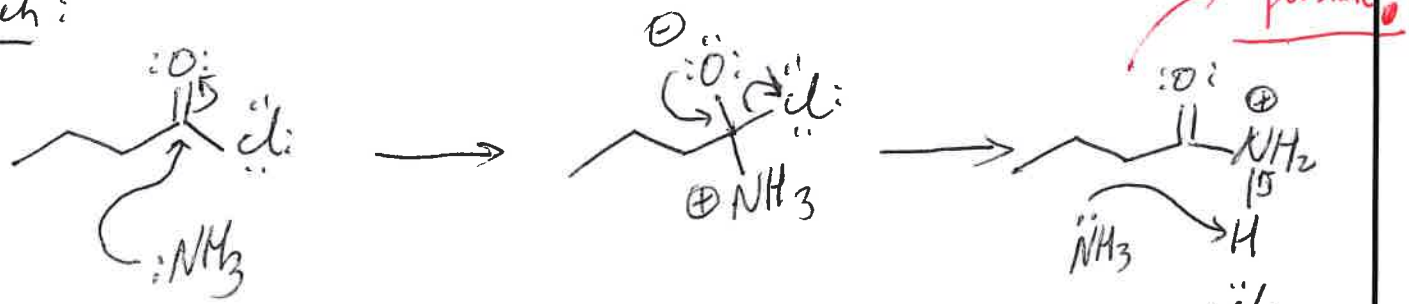


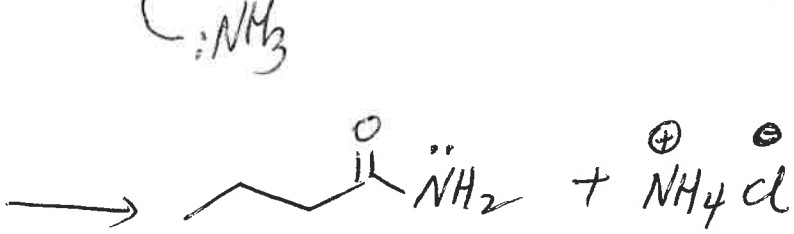
[Note: Amines are basic



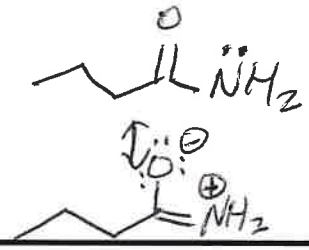
pka ~ 10]

Mech:





Why is $:NH_3$ a much stronger base than



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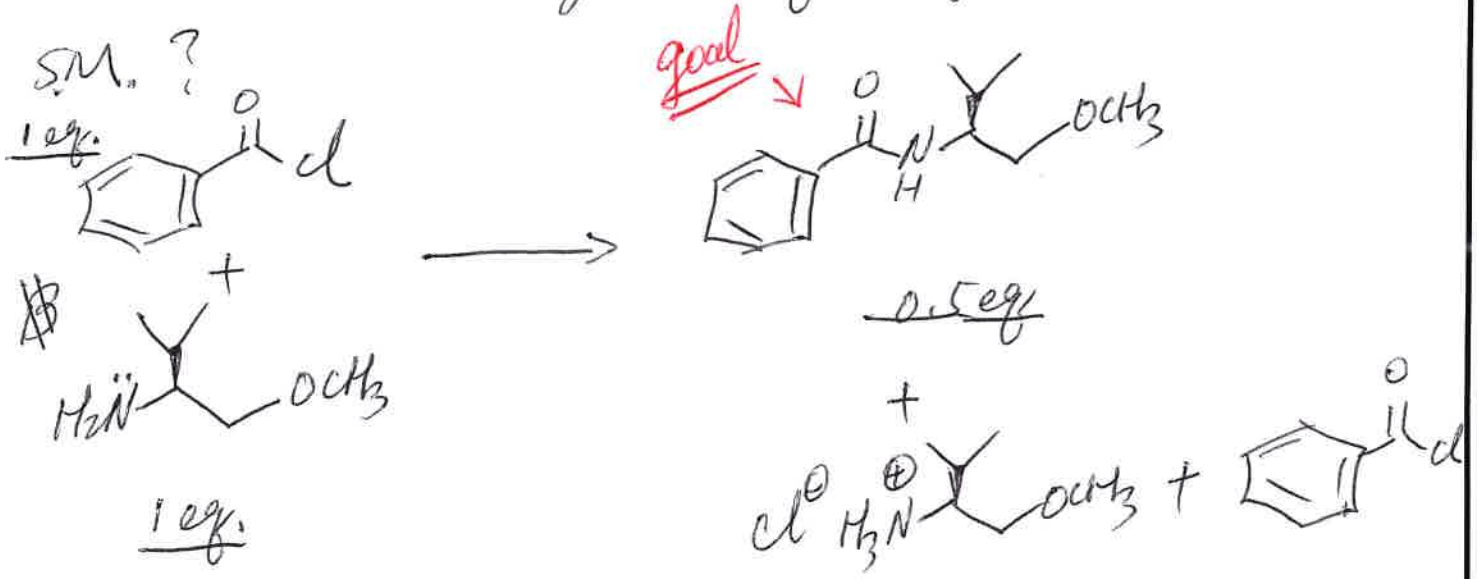
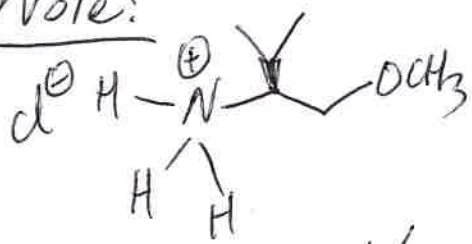
Need excess amine to neutralize HCl produced.
How avoid "wasting" 1 equiv. of a complex amine

S.M.?



Note:



No lone pair on N ⇒ not a nucleophile

Solution to problem – employ an amine base that is cheap & cannot form a stable amide

Most common examples:  or 

(pyridine)

} Neither has N–H; cannot form stable amide

Can function only as base