

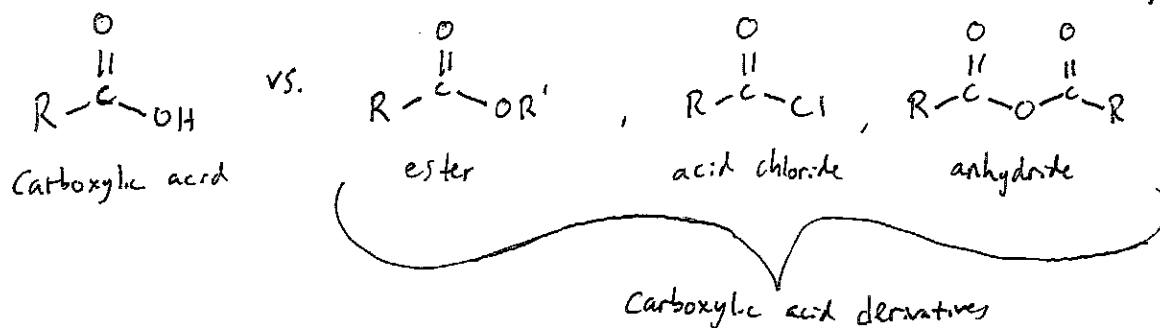
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PLEASE COMPLETE NOTES IN INK AND DO NOT STAPLE.

Exam #2: Wednesday
 (Chapters 17, 18, and 19)

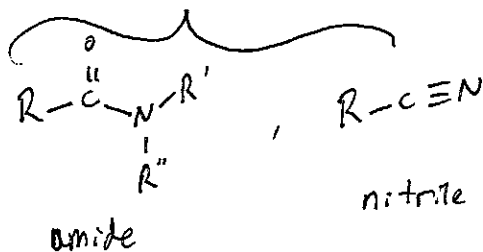
Exam locations will be clarified by email later today, but
 in general, same as last time.

Chapter 21 - Carboxylic Acid Derivatives

Rec. Problems - 3, 4, 7-34, 36-44, 46-53, 54a,b,c,f,g, 55-58, 60, 61.

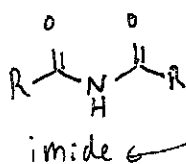
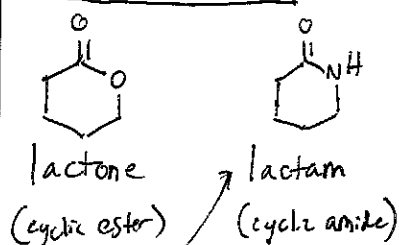


Additional carboxylic acid derivatives:

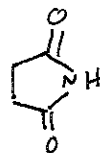


Notice that all of these have a C (+3) oxidation state carbon.

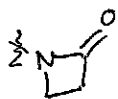
Terms/Nomenclature



Recall succinimide from NBS



Note: β -lactam antibiotics (e.g. penicillin)
 all include this motif

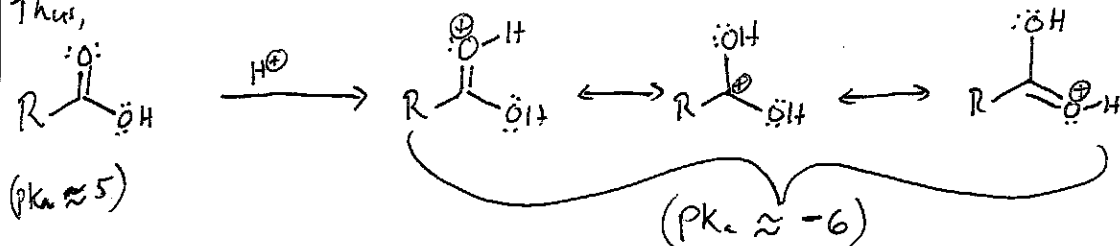


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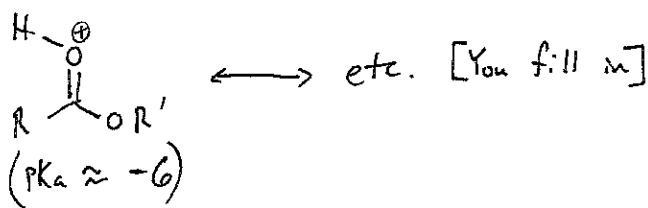
Spectroscopy - Read ch. 21.4

Acid-base chemistry - All carboxylic acids and their derivatives are Brønsted bases

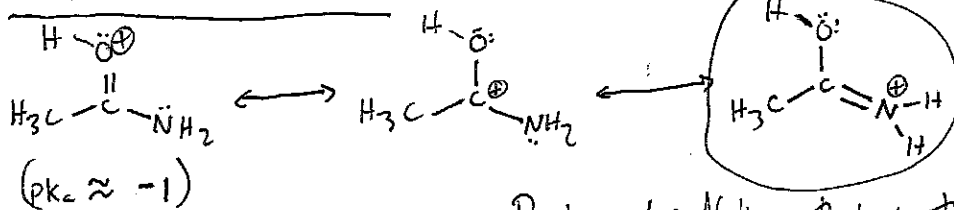
Thus,



Very similar basicity for esters:



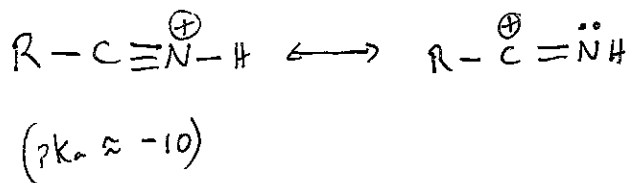
Amide is more basic:



Rationale: Notice that in this resonance contributor, we have \oplus on N, which is less electronegative than O. So N^{\oplus} is more favorable than O^{\oplus} .

weaker ~~more~~ conj. acid = stronger conj. base

Nitriles are very weak bases

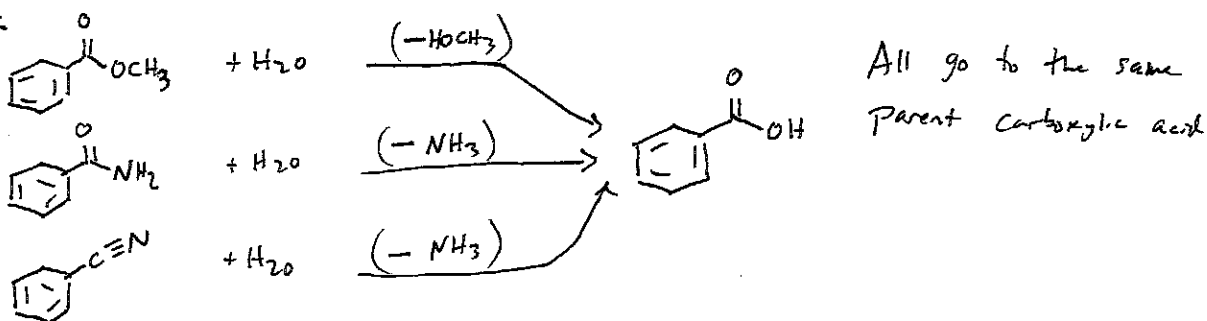


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Reaction of carboxylic acid derivatives. Start with hydrolysis

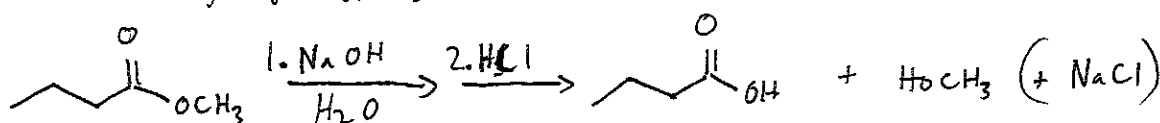
Carboxylic acid derivatives are hydrolyzed to the "parent" carboxylic acid.

Ex:

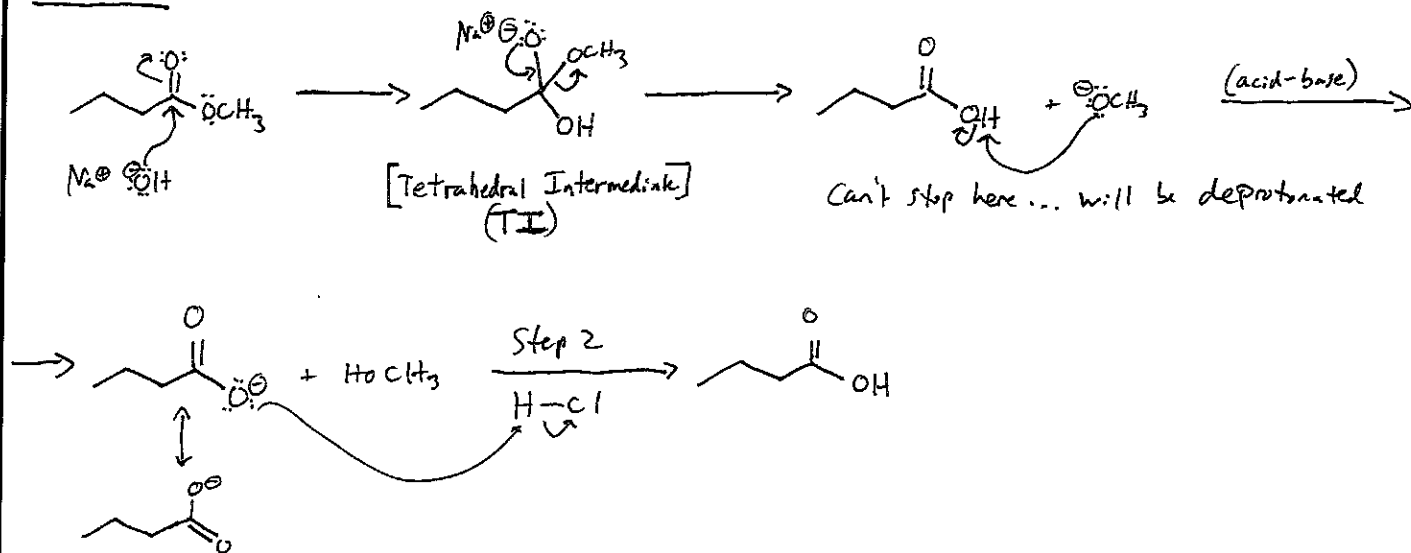


These hydrolysis reactions typically require strong acid or strong base conditions.

Ex: alkaline hydrolysis of esters



Mechanism:



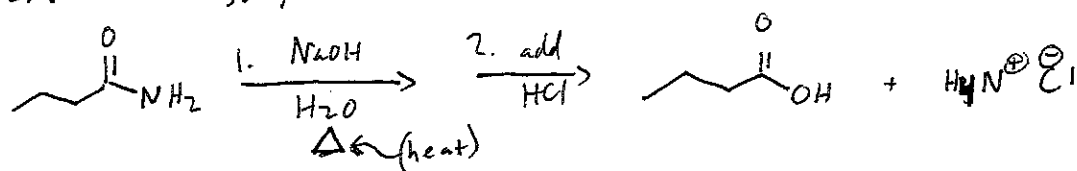
Note: This is not a base-catalyzed process. A full 1 equivalent of NaOH is ~~consumed~~ ^{consumed} (1 equiv. relative to ester), because of irreversible proton transfer from the Carboxylic acid to the alkoxide.

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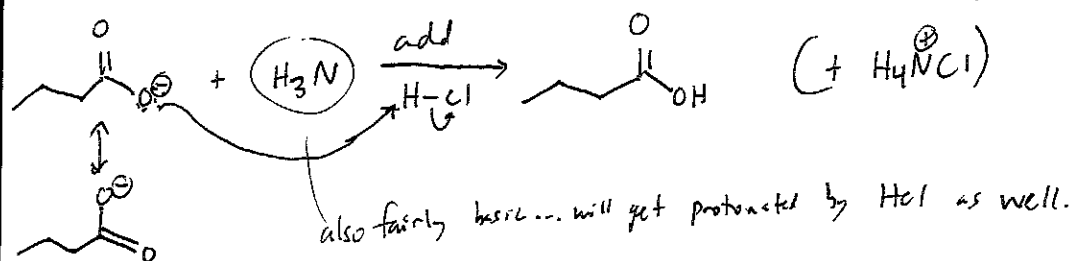
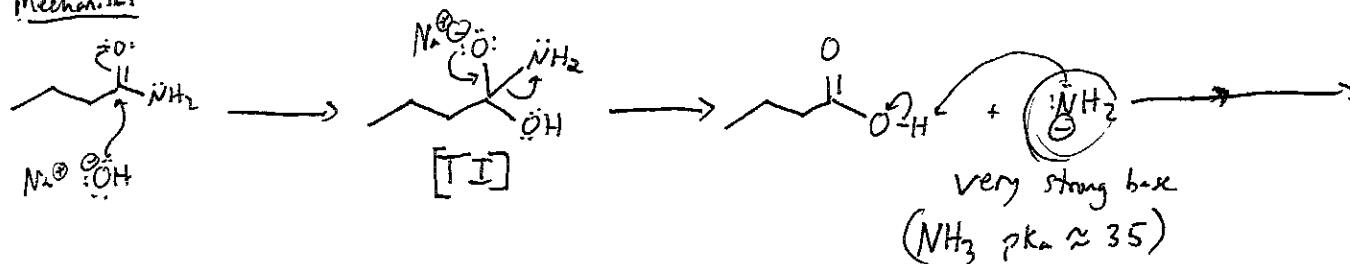
Also note: ② Acid-catalyzed ester hydrolysis can occur as well - [You fill in mechanism]
 (Reverse reaction of acid-catalyzed esterification (Fisher esterification))

Amide hydrolysis - also possible under alkaline or acidic conditions. This is "harder" than for analogous esters.

Ex: Alkaline hydrolysis



Mechanism:



Analogous mechanism to ester hydrolysis... So why is the amide hydrolysis so much harder? What is the reason for this large difference in reactivity?

① Resonance delocalization in the starting material (both ester & amide) is lost upon forming the TI. \rightarrow Greater resonance in amide, so greater loss upon OH^- attack.

