Carboxylic Acids & Derivatives

February 24, 2019

- The chemistry of esters and lactones.
  - Hydrolysis mechanisms (basic and acidic).
  - Synthesis of esters.
- The chemistry of amides and lactams.
  - Hydrolysis mechanisms (basic and acidic).
  - Synthesis of amides.

110b Teaching Fellows: Felipe Becerril, Christina Beck, Isabelle Cheng, Junha Gu, Nathalie Hong, Shy Lavasani, Allison Liu, Casey Morrison, Jerusalem Nerayo, Eric Tang, Baili Zhong, Martín Acosta Parra.

O'Leary office hours: T/Th 9:30-10:00 am, SN 208.

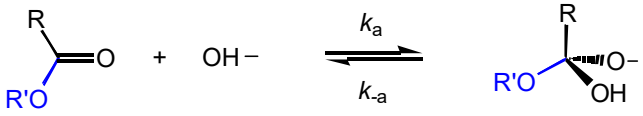
Robbins Lectures Next Week! Professor Geri Richmond, University of Oregon. Topic: "The Importance of Science in the Future of a Healthy Planet." Lectures: 8:00 PM Monday (public lecture), 11:00 AM Tuesday (Environmentally Important Processes at Water Surfaces), 4:30 PM Wednesday (Oil on Water: Calming the Seas but Not the Science), 4:30 PM Thursday (Nanoemulsions). All lectures in SN Auditorium.

O'Leary's evening review session: Wednesdays 7:00 PM, SN Aud. **Course website**: http://pages.pomona.edu/~djo04747/110/

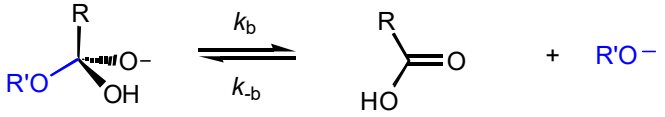
Suggested Problems for Exam 2. 10e: 16.20, 24, 30, 33, 35, 41, 44, 45, 47. 11e: 16.23, 27, 33, 36, 38, 44, 47, 48, 50. 10e/11e: 17.20, 17.28, 17.31, 17.33, 17.35, 17.38, 17.41, 17.42, 17.47.

Base-Promoted Hydrolysis of Esters

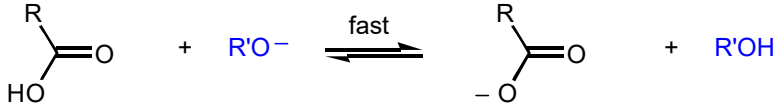
step a



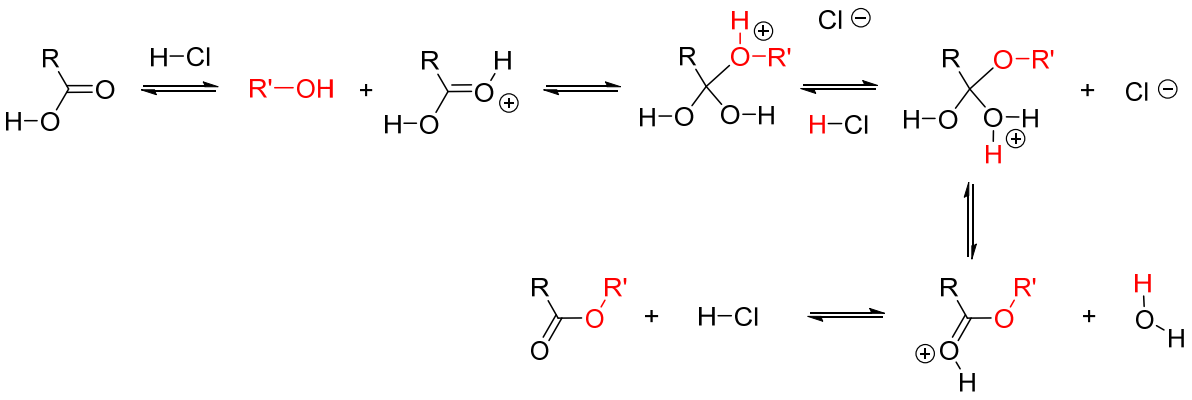
step b



step c



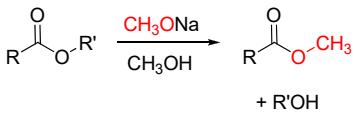
If RO- is a better leaving group than HO-, then the k_b step is fast, k_a is rate determining.



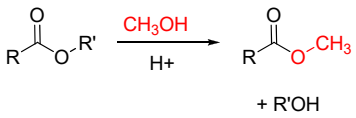
Forward Reaction: Acid-Catalyzed Ester Formation
Reverse Reaction: Acid-Catalyzed Ester Hydrolysis

Transesterification & Biodiesel Production

Base-promoted transesterification:

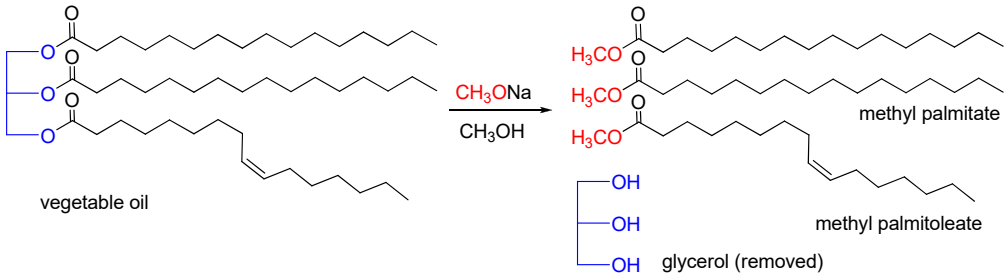


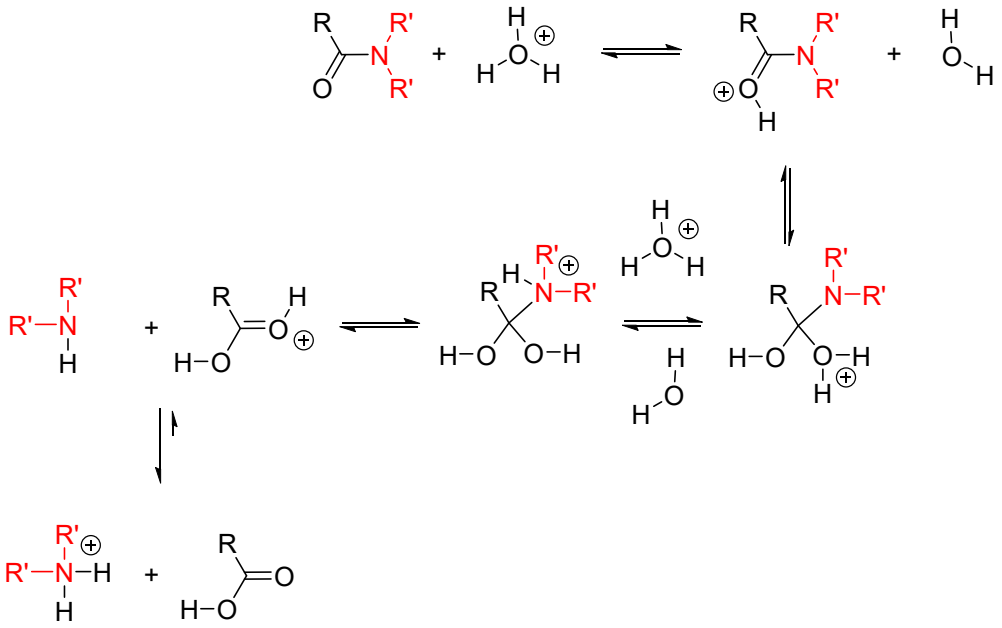
Acid-Catalyzed transesterification:



The mechanism for these processes is identical to the base-promoted and acid-catalyzed hydrolysis reactions!

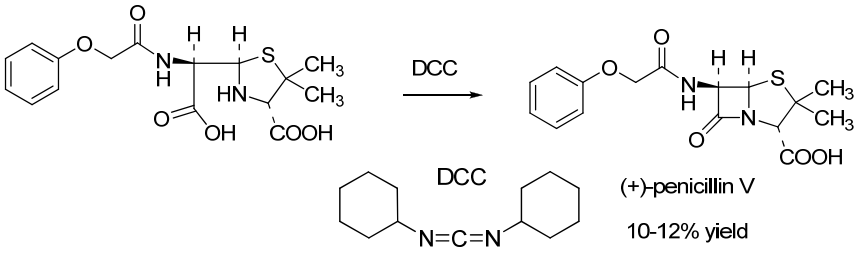
Application in biodiesel production:

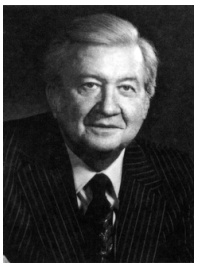




Forward Reaction: Acid-Catalyzed Amide Hydrolysis (requires heat and strong aq. acid)
Reverse Reaction: Acid-Catalyzed Amide Formation (not generally useful)

DCC was invented to make β-lactam syntheses possible

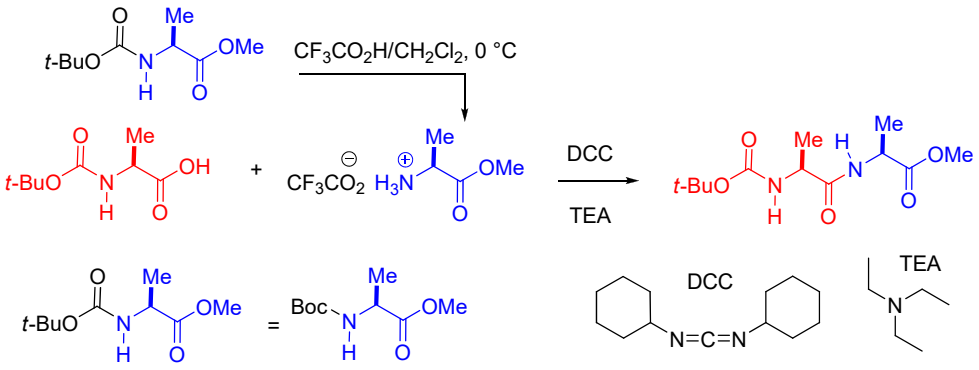




J.C. Sheehan
MIT
-synthesized penicillin for the first time
-invented DCC as a mild dehydrating reagent

Dorothy Crowfoot-Hodgkin
Oxford, 1964 Nobel Laureate
-established the structure of β-lactams
using X-ray crystallography

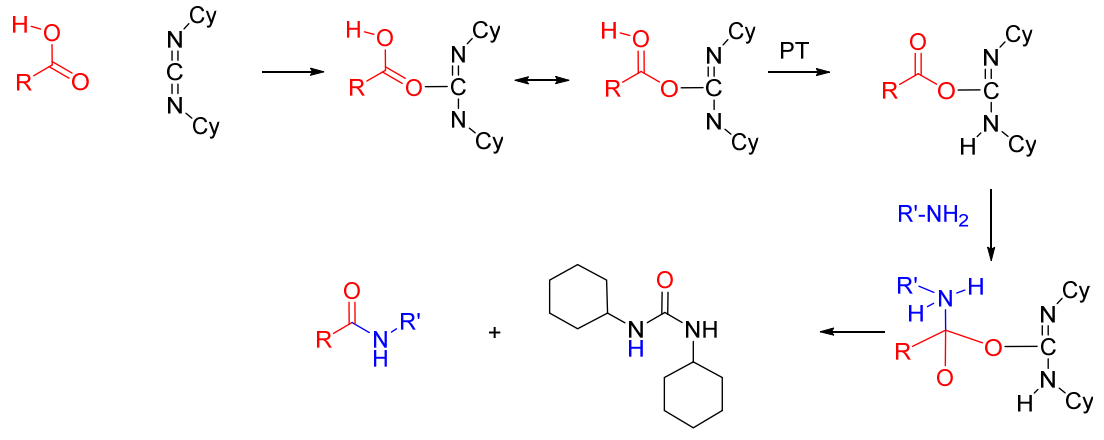
DCC-Promoted Amide Synthesis



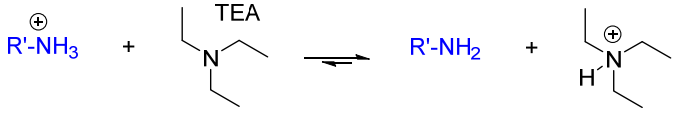
DCC = dicyclohexylcarbodiimide

DCC-Promoted Amide Synthesis

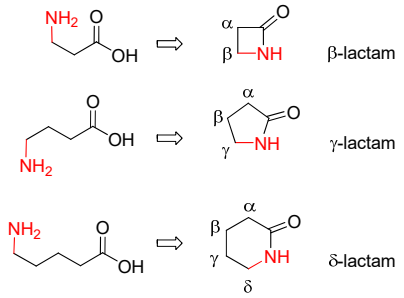
Mechanism:



Note:

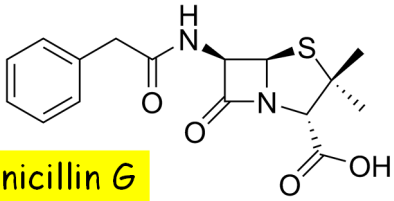


Cyclic Amides are Called Lactams



Sir Alexander Fleming
1881-1955
1945 Nobel Laureate (Medicine)

Fleming's accidental discovery and isolation of penicillin in September 1928 marks the start of modern antibiotics.



penicillin G

Famous Decarboxylation Reactions