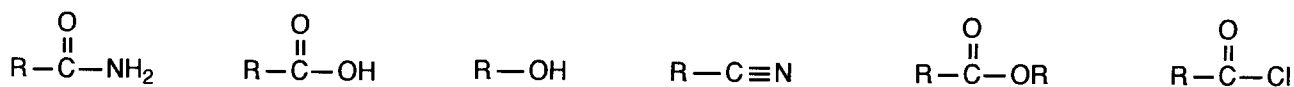


CHAPTER 21: CARBOXYLIC ACID DERIVATIVES (acyl derivatives and nitriles)

- most can be directly or indirectly prepared from RCO_2H
- all can be hydrolyzed to RCO_2H

Physical Properties - see section 21-3

Boiling Point: (in general):



Reactivity / Interconversion of Derivatives - Nucleophilic Acyl Substitution



Order of reactivity results from a combination of factors.

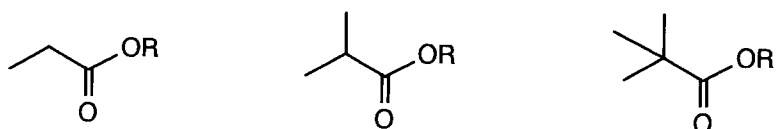
1. Basicity (stability) of the leaving group.



2. Resonance stabilization in derivative. (or: How + is the carbonyl carbon? the more +, the more reactive)

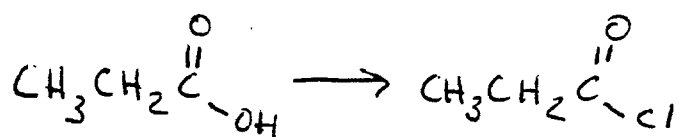


3. Steric factors. (consider when comparing different compounds of the same derivative)

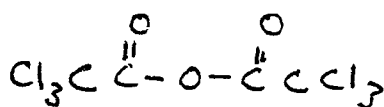
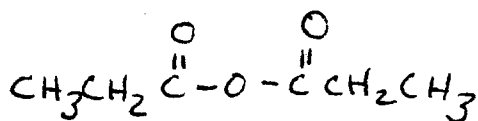


Naming Carboxylic Acid Derivatives: (From Carboxylic Acid Names)

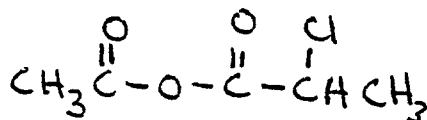
I. Acid Halides: drop "ic acid" add "yl halide" or
drop "carboxylic acid" add "carbonyl halide"



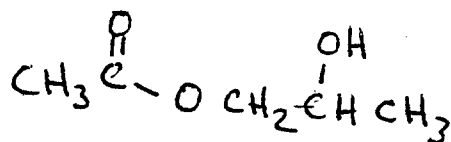
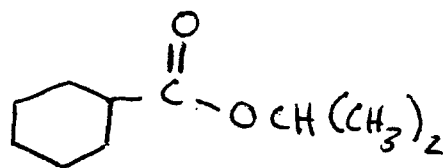
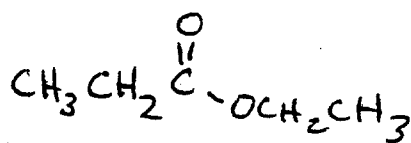
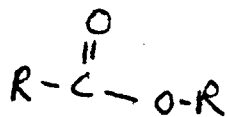
II. Anhydrides: Symmetrical - drop "acid" add "anhydride"



Unsymmetrical - name both acids composing the anhydride, omit each "acid" and add "anhydride"

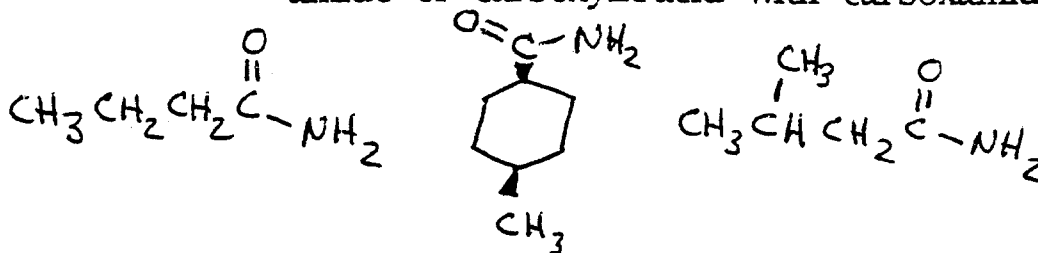


III. Esters: Written as - name of alkyl group attached to O plus acid name; drop "ic acid" add "ate"

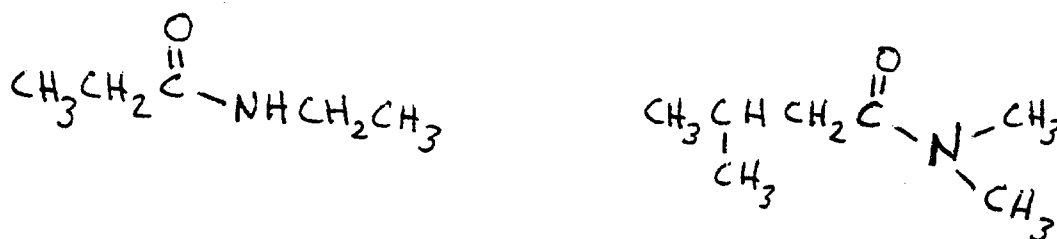


IV. Amides:

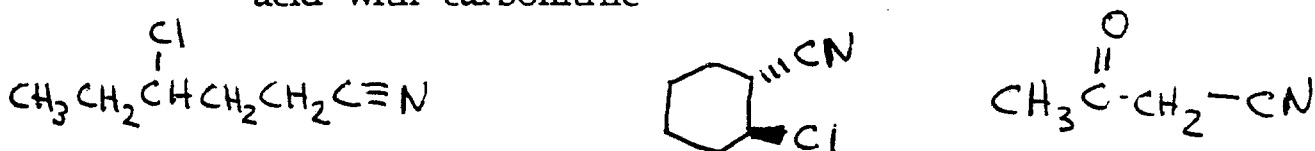
Unsubstituted (-NH₂) - replace "ic/oic acid" with "amide" or "carboxylic acid" with "carboxamide"



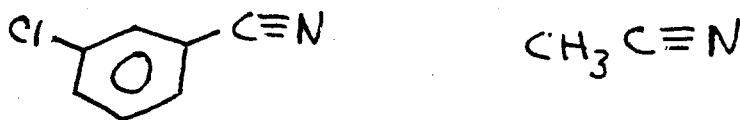
Substituted (-NHR or -NR₂) - written as: name of substituent bonded to nitrogen preceded by "N" followed by amide name formed as above

V. Nitriles:

Add "nitrile" to corresponding IUPAC alkane name or for alkanecarboxylic acids, replace "carboxylic acid" with "carbonitrile"



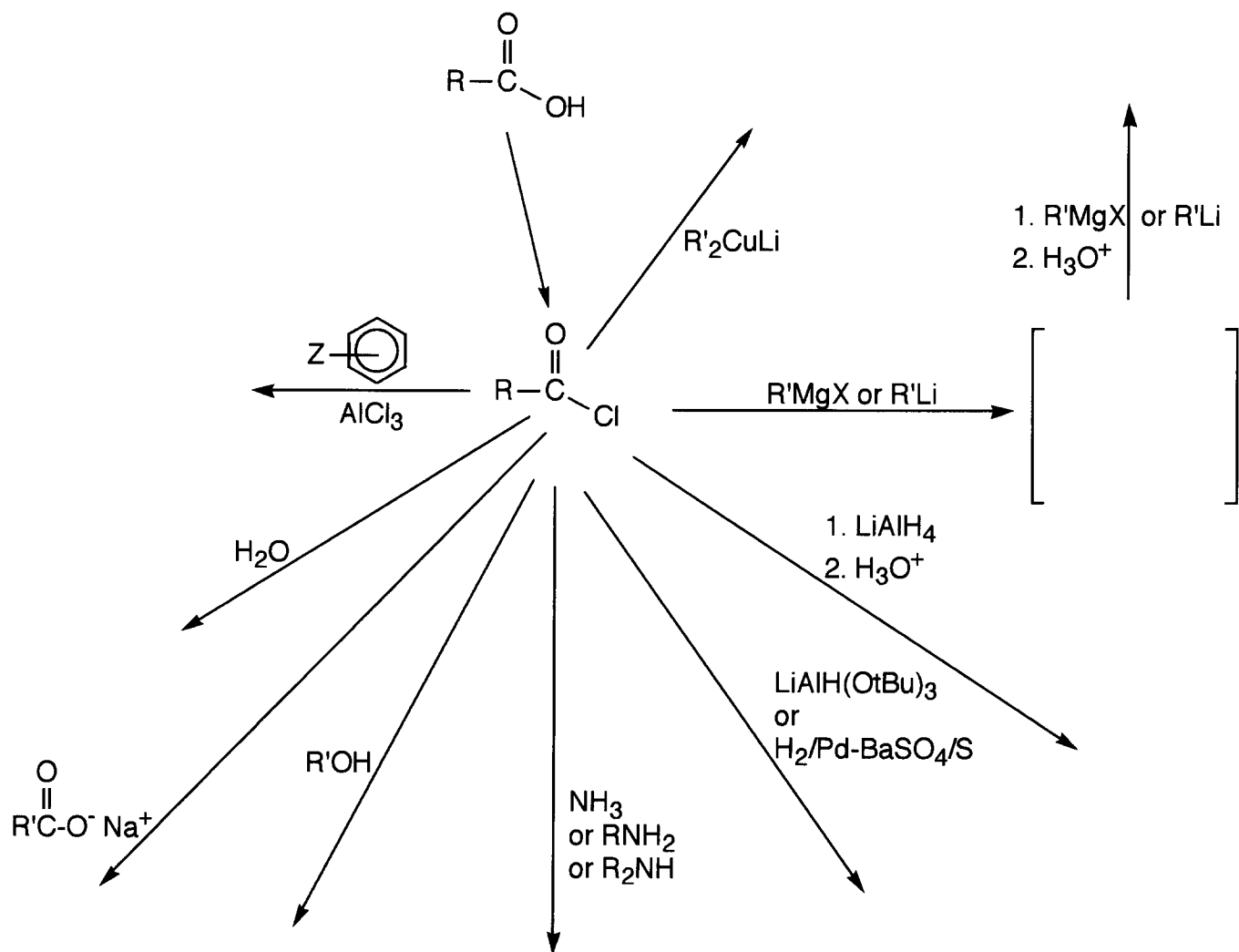
Nitrile name derived from an acid's common name - drop "ic (or oic) acid" and add "onitrile"



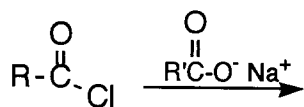
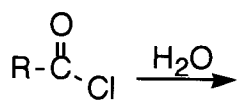
As a substituent: name as a cyano group



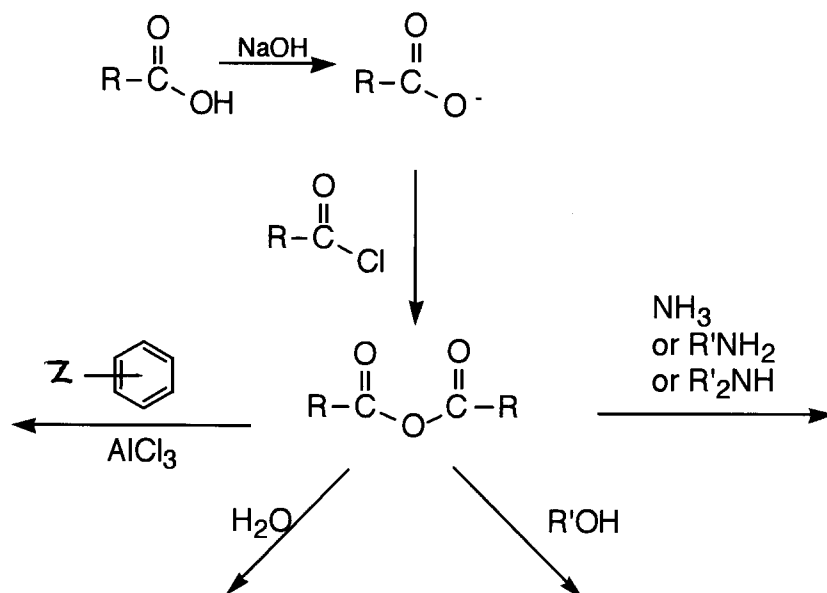
Synthesis and Reactions of Acid Chlorides (RCOCl)



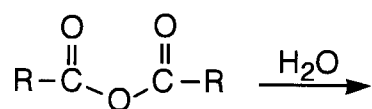
Example Mechanisms:



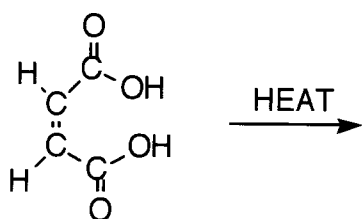
Synthesis and Reactions of Anhydrides:



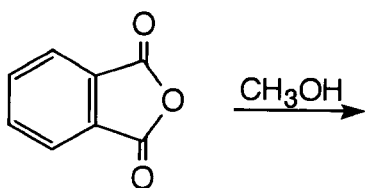
Example Mechanism:



Cyclic Anhydrides:

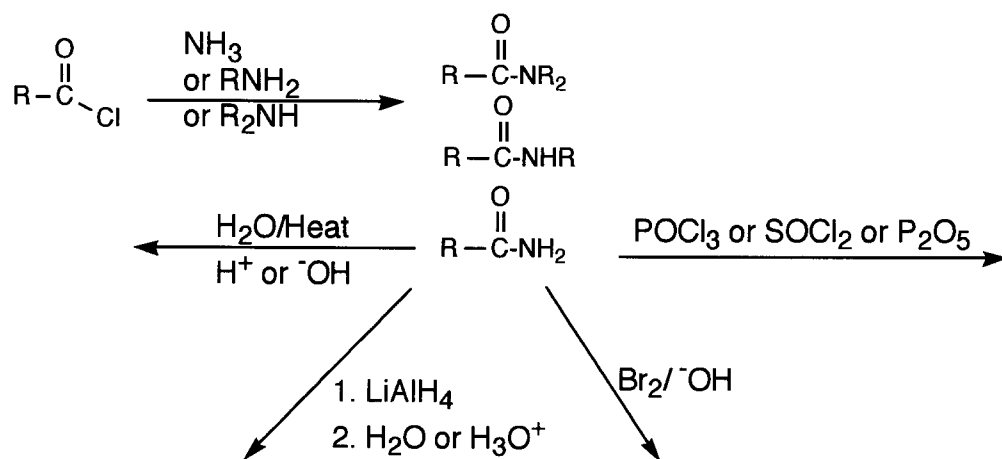
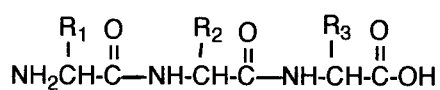


Example:

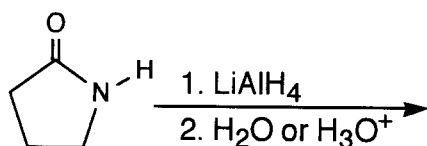
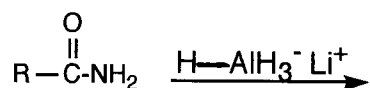


Synthesis and Reactions of Amides

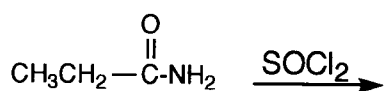
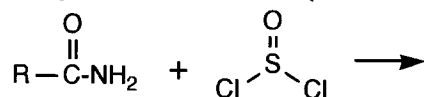
Few reactions - fortunately!



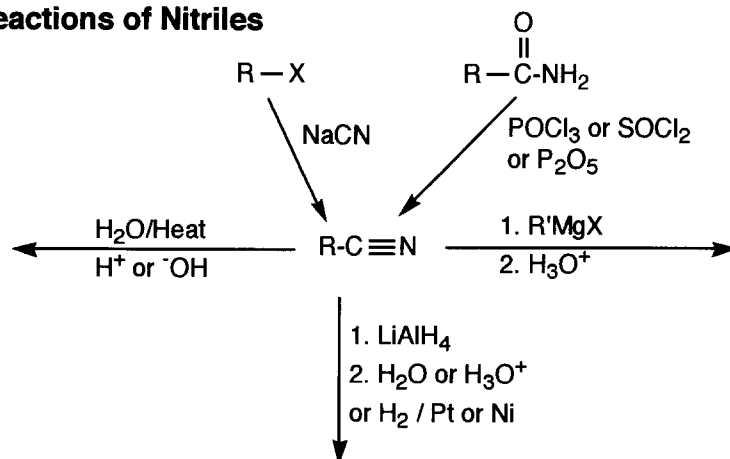
Reduction of Amide to Amine:



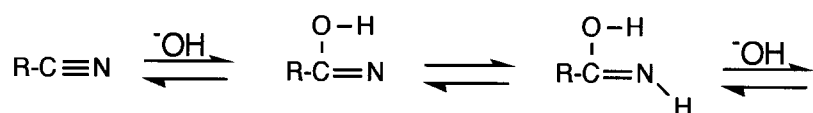
Dehydration to Nitrile: (1° amide only)



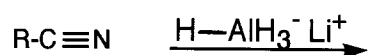
Synthesis and Reactions of Nitriles



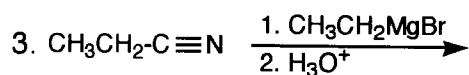
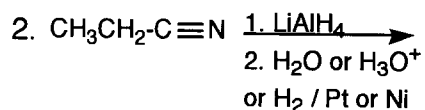
Hydrolysis: (basic conditions)



Reduction to Amine:



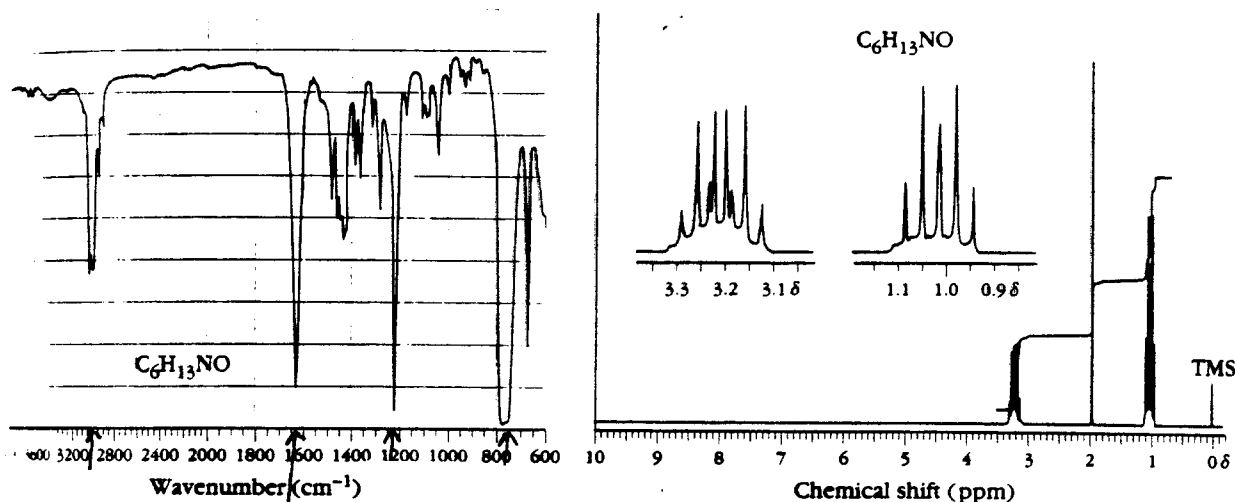
Examples:



Spectroscopy Summary of Carboxylic Acid Derivatives

	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}$ stretch (IR)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}$ carbon (^{13}C NMR)	other
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{Cl} \end{array}$	1800 - 1775 cm^{-1}	170 ppm	
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R} \end{array}$	1800 cm^{-1} 1750 cm^{-1}	170 ppm	
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OR} \end{array}$	1735 cm^{-1}	170 - 180 ppm	
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}_2 \end{array}$	1640 - 1680 cm^{-1}	180 ppm	IR: N-H stretch 3200-3500 cm^{-1} 1° - 2 peaks 2° - 1 peak 3° - no peak ^1H NMR: N-H 5-9 δ , often broad D_2O exchangeable
$\text{R}-\text{C}\equiv\text{N}$			IR: $\text{C}\equiv\text{N}$ stretch 2200 cm^{-1} , sharp, medium

Example:



-NO

