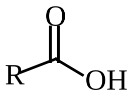
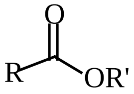
Chapter 20-- Nomenclature sec 20.1
Note bp data, p 1009 Table 20.1; Note pKa data, p 1010 Table 20.2; IR C=O stretch table 20.3
Note: NMR data Table 20.4

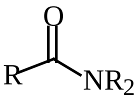
DERIVATIVES OF CARBOXYLIC ACIDS:



carboxylic acid

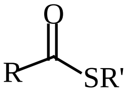
carboxylic acid ester
"ester"

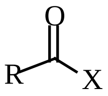




amide

thiol ester

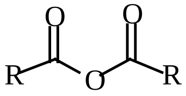


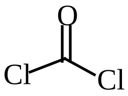


X = F,Cl, Br, I

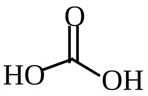
carboxylic acid
halide
"acid halide"

anhydride

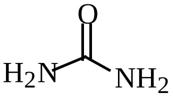




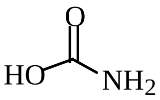
phosgene



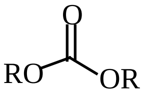
carbonic acid



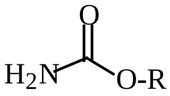
urea



carbamic acid



a carbonate ester



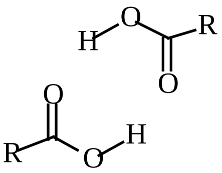
a carbamate

READ: Nomenclature, text 19.1

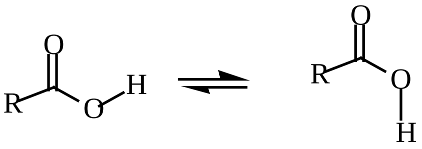
Caboxylic Acids:

Dominant feature: acidity and influence of structure on acidity. You know all of this stuff.

Structure:

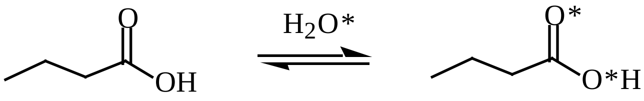


H-bonded dimer
General intermolecular H-bonding



Dominant reaction:

Accelerated by acid and base

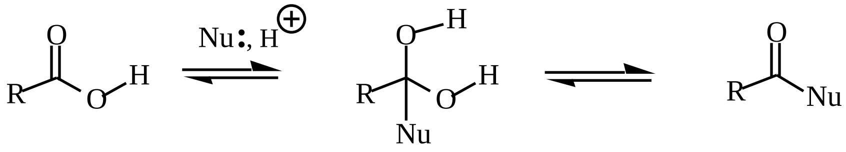


O* = ^{17}O

Mechanism:

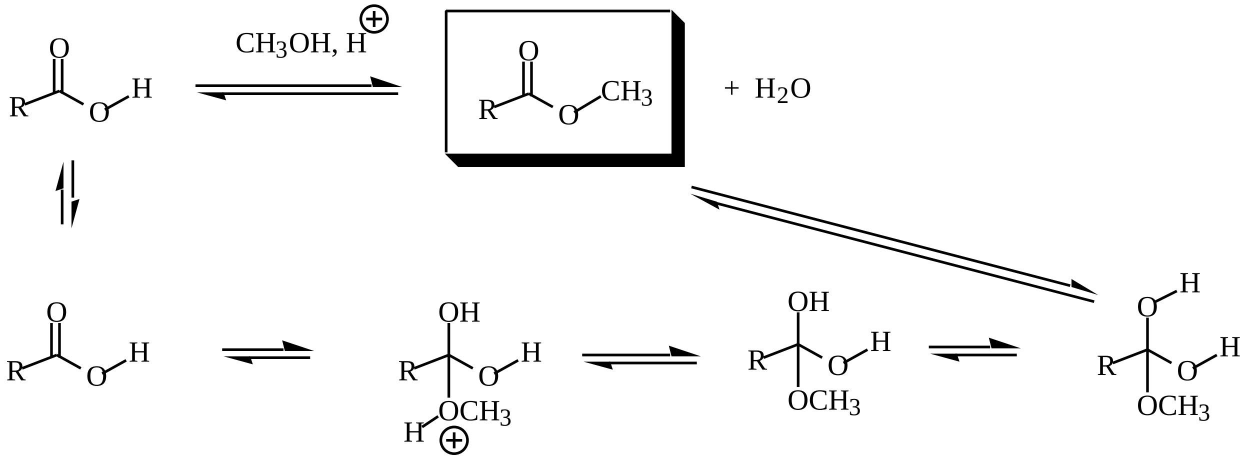
Not very interesting for carboxylic acids; not even noticeable unless the water is labeled.

BUT: a major reaction with other nucleophiles. Addition/elimination

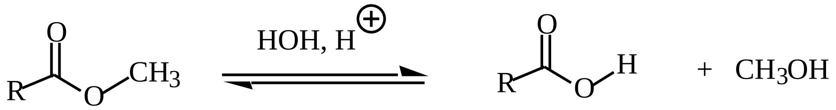


Nu: RO-, R_2N-, halide, RS-, etc

Formation of Esters:

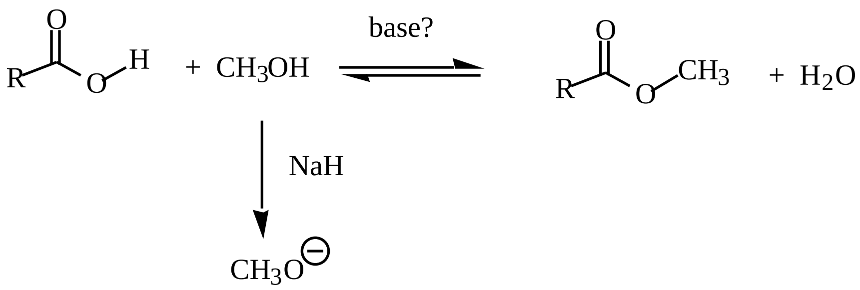


Completely reversible: also serves as a mechanism for hydrolysis of esters to carboxylic acids:

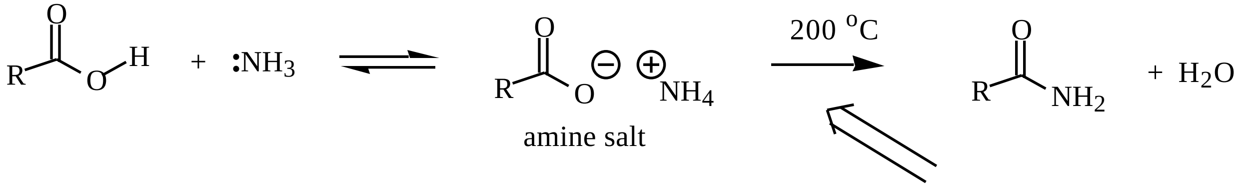


Drive the reaction by using excess of one or the other of the reactants: e.g., MeOH as solvent to make ester
water as solvent to hydrolyze ester

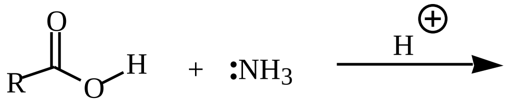
What about reaction under basic conditions?

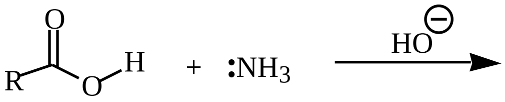


What about amines as the nucleophile? Amide bond formation.

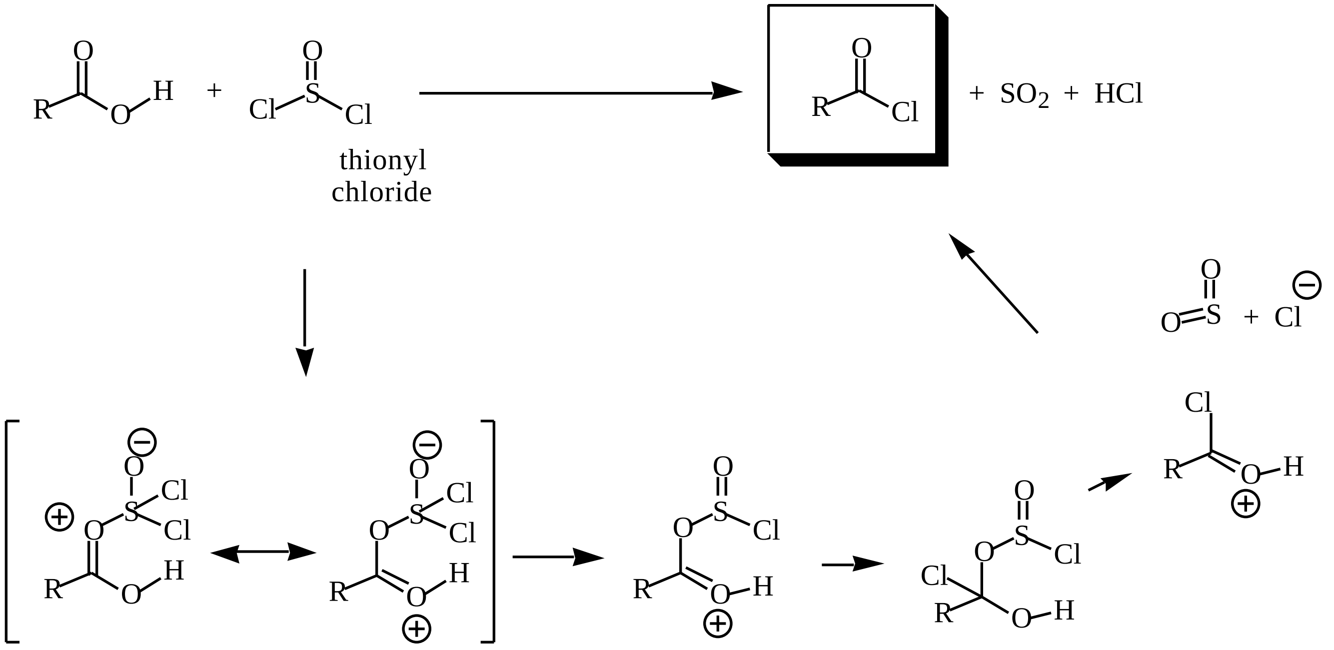


need better leaving group

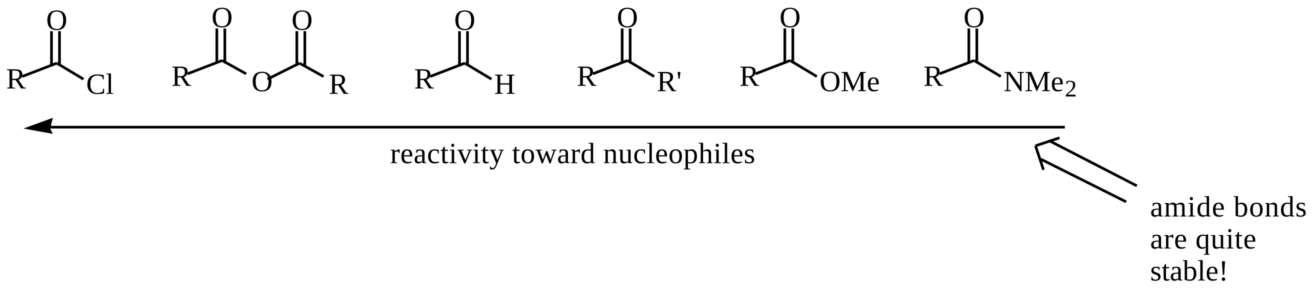




Better Leaving Group? Cl^- text p 978

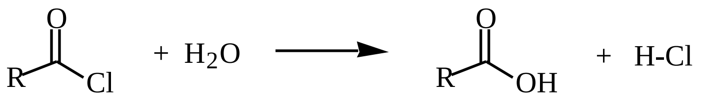


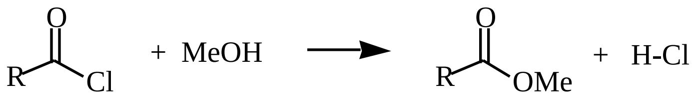
Chapter 20: Reactions of Acid Chlorides (fig 20.23)

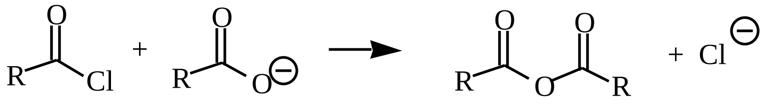


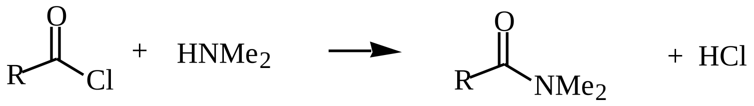
Recall correlation of IR stretching frequencies of C=O with substituent effect, via polar resonance structure (more resonance stabilization, less reactive toward nucleophiles)

A. Addition of stabilized nucleophiles (O, N)

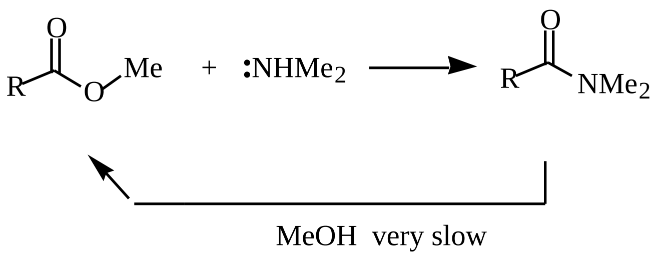




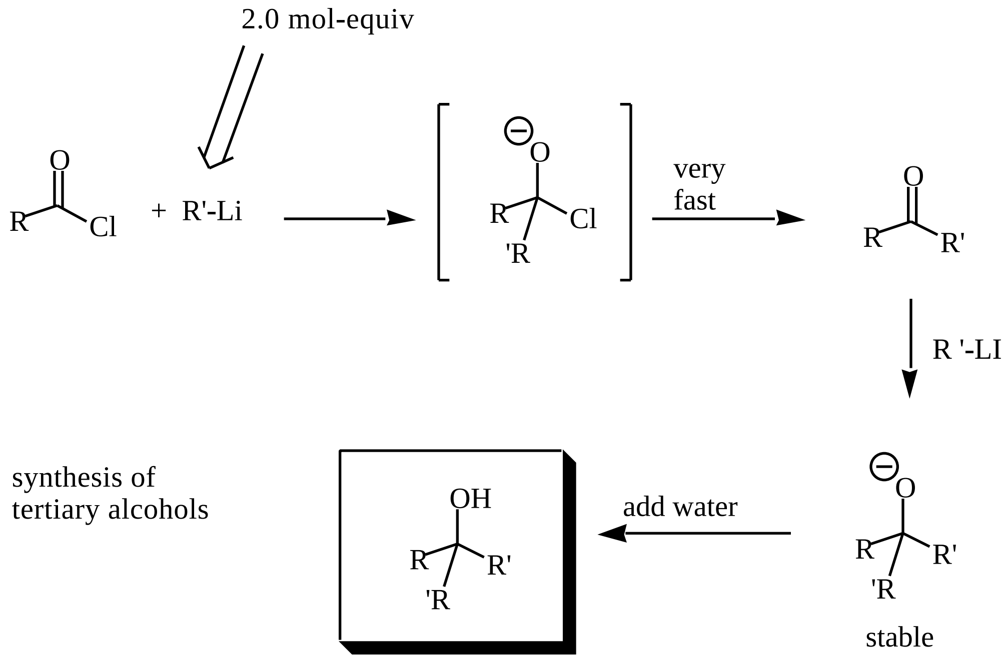




Aslo:



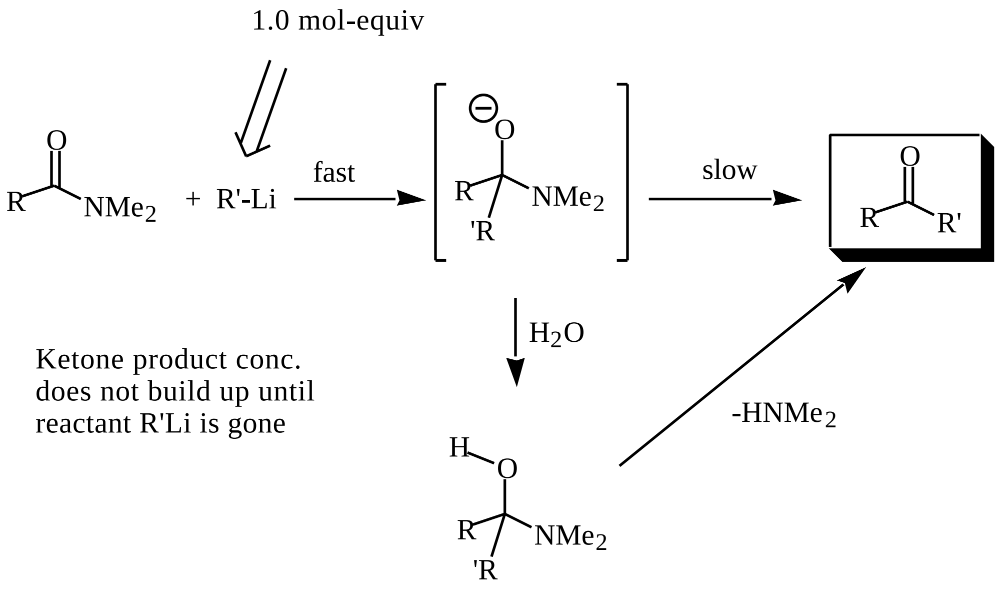
B. Addition of reactive carbon anions



synthesis of
tertiary alcohols

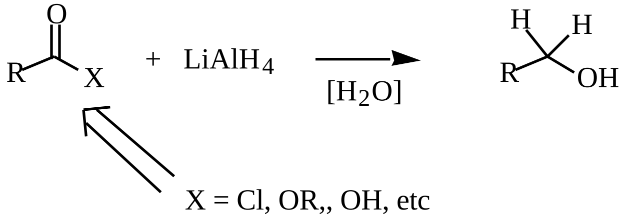
Same for esters, anhydrides.

But



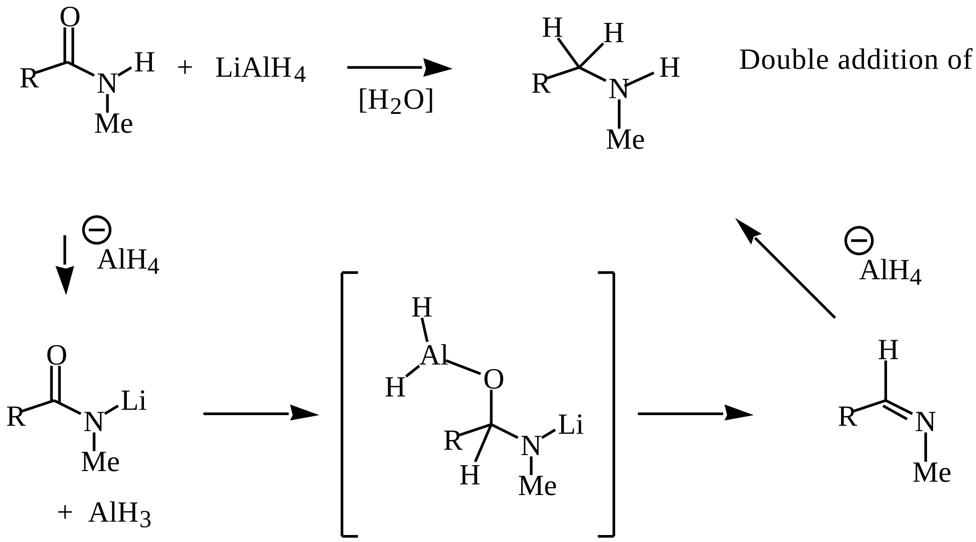
Ketone product conc.
does not build up until
reactant R'Li is gone

C. Addition of metal hydrides



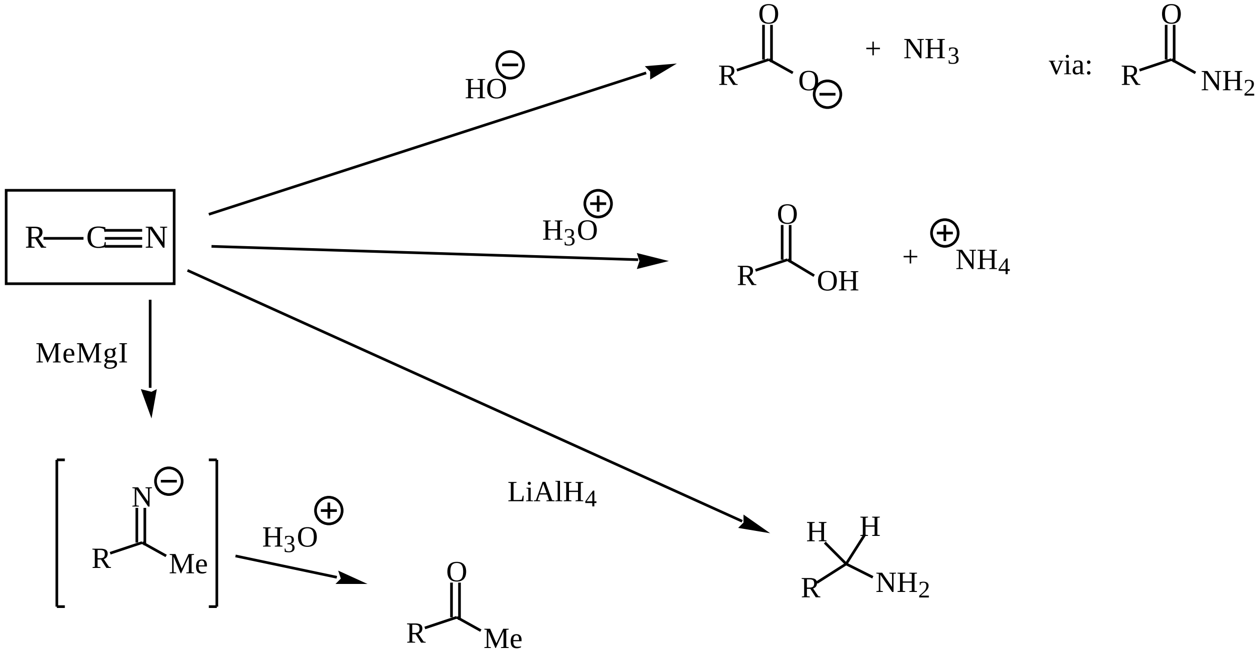
X = Cl, OR,, OH, etc

Double addition of $H^{\ominus}$
Mechanism?



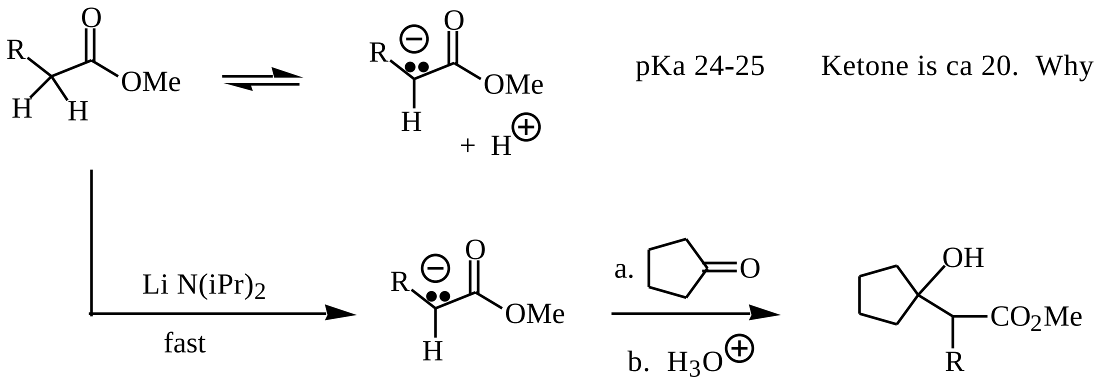
Double addition of $H^{\ominus}$

Analogy with Nitriles:



Write mechanisms: multistep

Enolate chemistry of esters:



pKa 24-25 Ketone is ca 20. Why the difference?

aldol-like reaction