Introduction to Carbonyls

Properties

A carbonyl is a carbon-oxygen double bond (C=O).
Both atoms are sp^2 and share both a σ and a π bond.

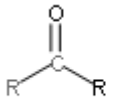
The C will have triangular planar geometry (120^o).
So, it will have two additional σ bonds.
Because C is less electronegative than O, the C will be δ+.
The δ+ C is an electrophile (E^+) and a Lewis acid (e^{-1} pair acceptor).

The O, on the other hand, has a higher e/n than C, and is δ−.
The δ− O is a nucleophile (Nu^-) and a Lewis base (e^{-1} pair donor).
The O will have two lone pairs, unless it has a + charge.

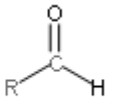
Types

There are two general types of carbonyls, either with or without leaving groups (LG's).

A bond between the carbonyl C and an H or other C will not break easily.
So, there are two types of carbonyls without LG's: ketones and aldehydes.

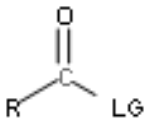


ketone

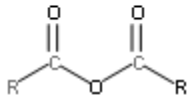


aldehyde

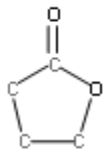
A bond between the carbonyl C and a higher e/n atom (O, N, or a halogen)
can be broken much more easily.
So, substituents bonded to the carbonyl C with an O, N, or halogen can act as LG's.



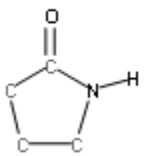
Carboxylic Acid	LG = OH
Acid Halide	LG = Cl or Br
Acid Anhydride	LG = O_2CR (see below)
Ester	LG = OR (see also below)
Amide	LG = NH_2, NHR, or NR_2 (see also below)



acid anhydride



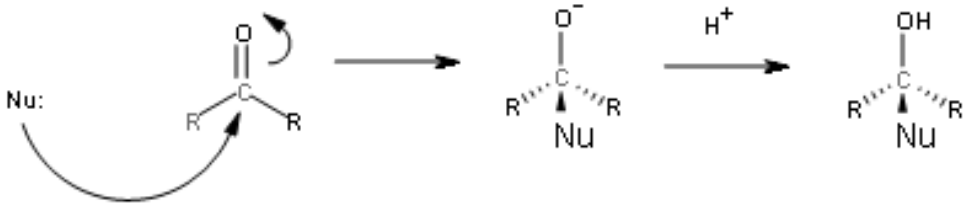
lactone
(cyclic ester)



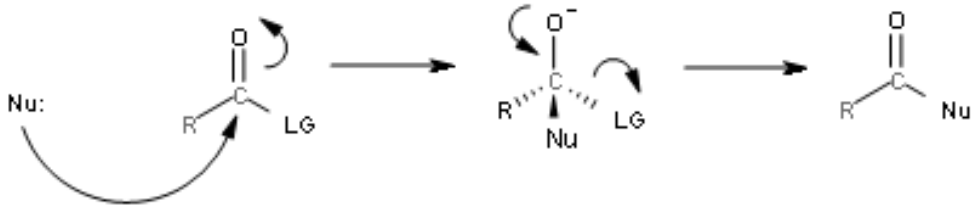
lactam
(cyclic amide)

Reactions

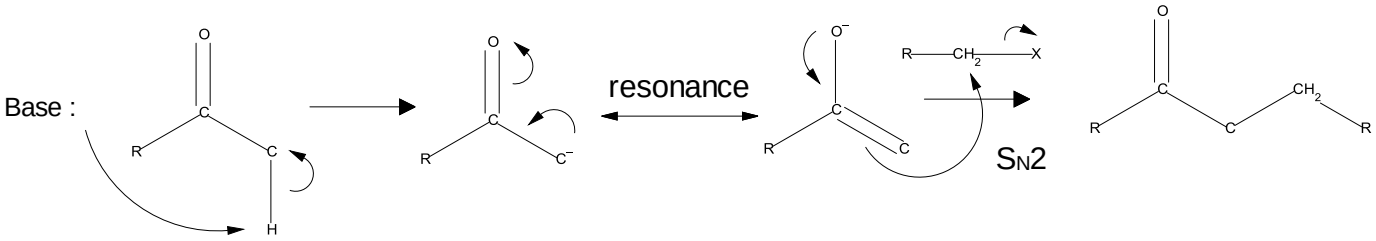
Nu Addition The Nu forms bond with the carbonyl C, and no LG is involved.



Nu Acyl Substitution The Nu replaces the LG, and there is a tetrahedral sp^3 intermediate.



Alpha Substitution The carbon next to carbonyl loses an H^{+1},
and becomes a Nu in an S_N2 reaction.
The Nu is called an enolate, and is stabilized by resonance.



Carbonyl Condensation Carbon next to carbonyl loses H^{+1} and becomes a Nu.
The Nu bonds to a second carbonyl C in either
a Nu addition (no LG) or Nu acyl substitution (with LG)