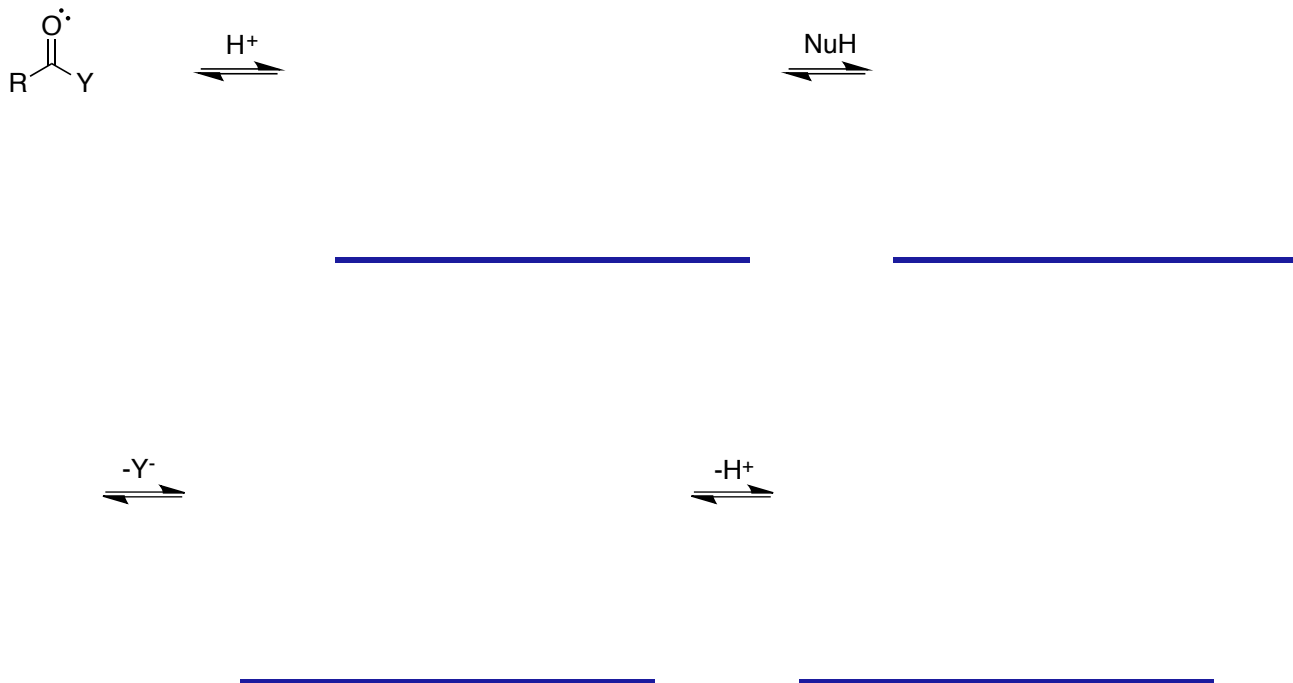


Acylation Under Acidic Conditions

Acidic conditions are used in nucleophilic acylations to increase the reactivity of the carbonyl group by protonation on the C=O, and/or to protonate a leaving group to enable it to depart more easily.

Protonation of the carbonyl group *increases / decreases* its reactivity towards nucleophiles. Show this for a generic, non-basic, anionic nucleophile, by completing the diagram below (show curly arrows).



D Reactivities Of Acylating Agents

Chemical Intuition

Acylating agents with relatively unstable leaving groups tend to be relatively *reactive / unreactive*.

Acyl fragments attached to good leaving groups tend to be *reactive / unreactive* acylating agents.

Highly electronegative leaving groups *activate / deactivate* carbonyl carbons atoms they are attached to and this tends to give *reactive / unreactive* acylating agents.

Basic nucleophiles *can / cannot* be used under acidic conditions.

Deprotonation of an acylating agent renders it *more / less* reactive to nucleophiles.

Acids (protons and other Lewis acids) can complex carbonyl oxygen atoms making the associated carbonyl carbon *more / less* electrophilic.

Bulky leaving groups can sometimes *retard / accelerate* additions of nucleophiles to acylating agents (*cf* base-mediated hydrolysis of *tert*-butyl esters is *favorable / unfavorable*).

Small nucleophiles are acylated *faster / slower* than large ones, if all other factors are equal.