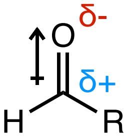
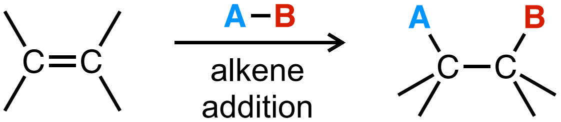
Carbonyl Additions - Aldehydes and Ketones

This Core Concept Sheet describes the general reactivity observed when aldehydes and ketones undergo ***nucleophilic addition***. Keep in mind that the C=O bond is polarized, therefore nucleophiles are attracted to the electrophilic carbon.

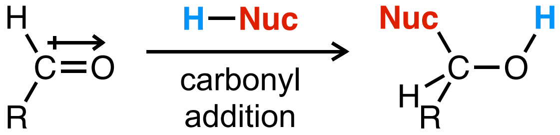


As mentioned above, aldehydes and ketones typically undergo ***addition*** reactions. You first encountered these reactions with alkenes in Organic 1. Overall, an addition reaction yields a product in which new groups have been added ***across*** the original π bond.

Addition to C=C π bond



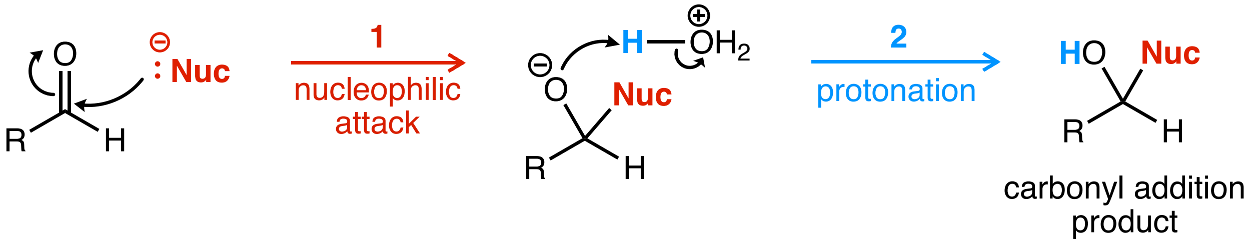
Addition to C=O π bond



Mechanism for C=O addition with strong nucleophiles (Nucleophilic Pathway)

In the presence of a **strong nucleophile**, **nucleophilic attack** occurs first, then **protonation** of the cabonyl oxygen occurs, as shown below.

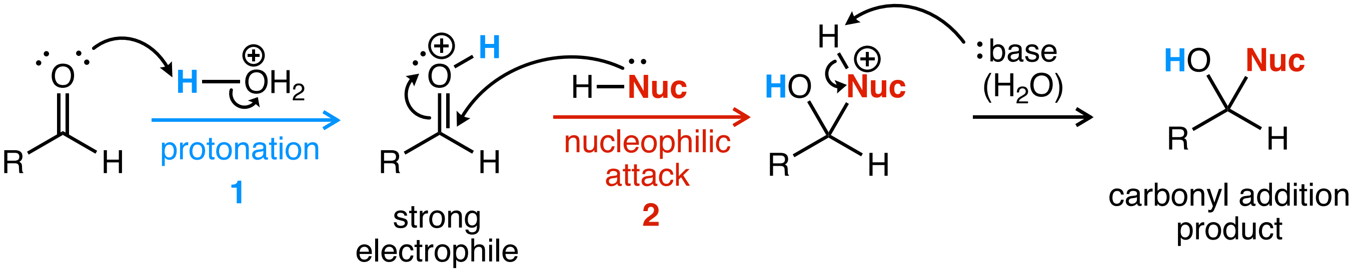
Note: this is a typical pathway when using an anionic nucleophile, like hydride (H^{1-}).



Mechanism for C=O addition with weak nucleophiles (Acid-mediated Pathway)

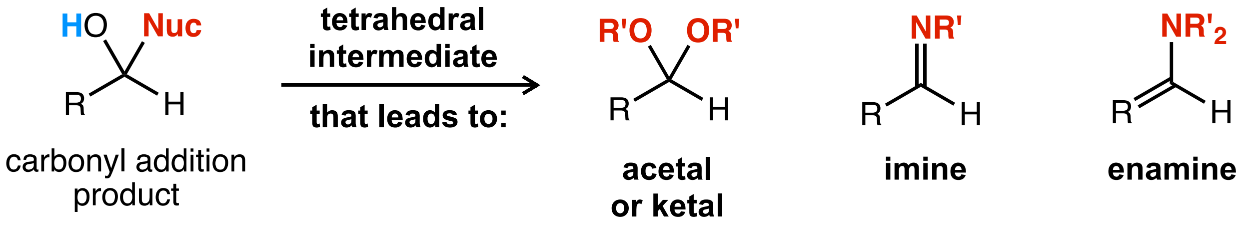
In the presence of a weak nucleophile, the reaction is mediated by a strong Brønsted acid (e.g. HCl, H_2SO_3, or H_3O^+). Under acidic conditions like this, **protonation** occurs first to create a stronger carbonyl electrophile, then **nucleophilic attack** on the carbonyl carbon.

Note: this is a typical pathway when using a neutral nucleophile, such as $HOCH_3$ or H_2NR.

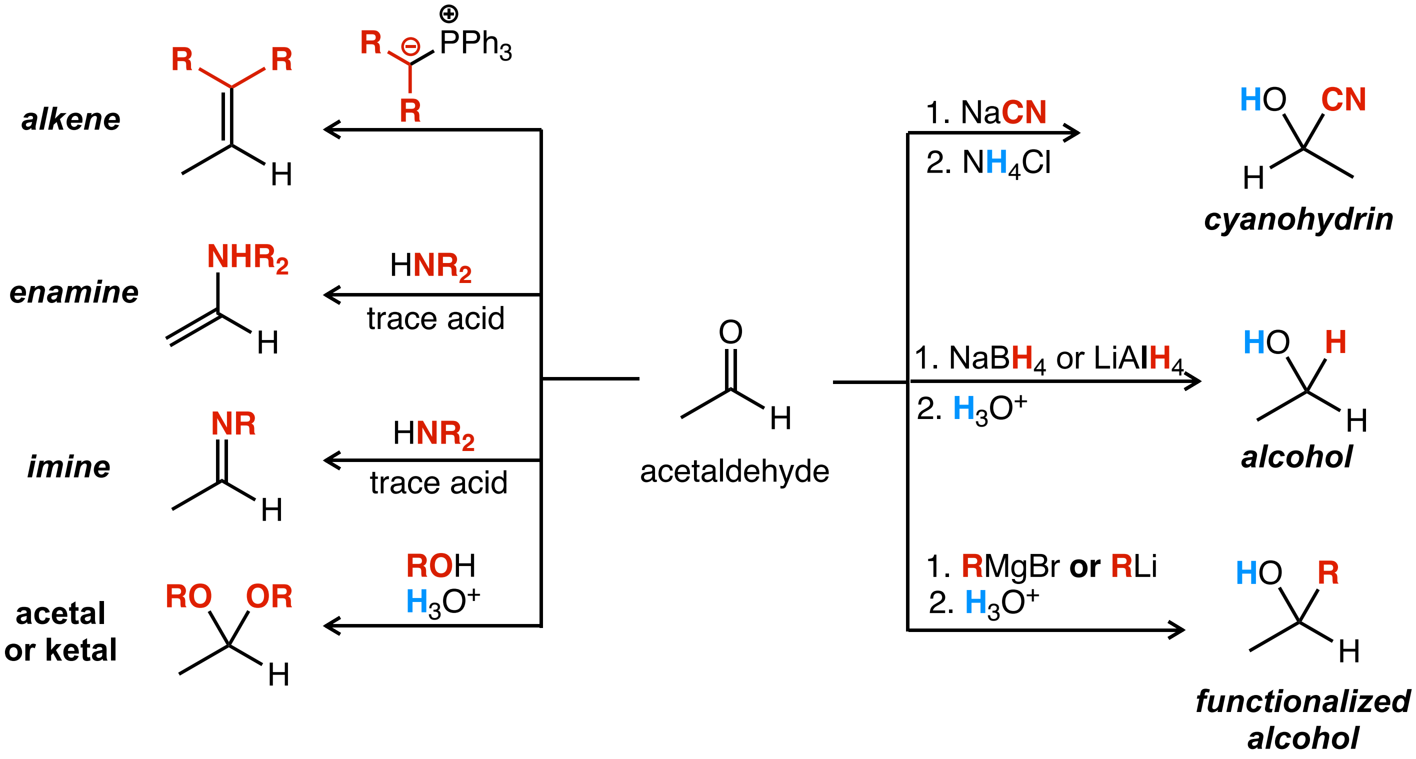


You have likely noticed that **heteroatom nucleophiles** (e.g. ROH, RNH_2, R_2NH) **proceed beyond the structure** shown above **to form acetals**, **imines**, and **enamines**, respectively.

In these reactions, the “carbonyl addition product” is not the final product, but rather an intermediate formed along the mechanistic pathway to the acetal, imine, or enamine.



Aldehydes and ketones generate a wide range of functional groups as shown below:
**acetaldehyde is shown as the substrate*



It is also important to note that many of these reactions are reversible. The mechanisms of the "reverse" reaction leverage the same intermediates as the forward reaction. For example, deprotection of an acetal, follows the same mechanistic pathway used to *create the acetal*, just in reverse.