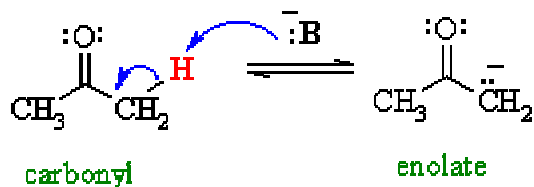


Carbonyl α -Substitution Reactions

Treatment of aldehydes and ketones with a suitable base can lead to the formation of a **nucleophilic species called an enolate** that reacts with **electrophiles**.

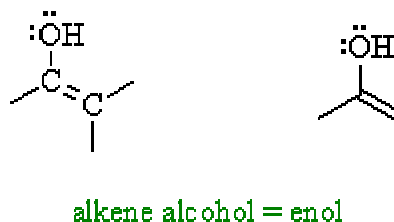
These **C nucleophiles** are useful for making new carbon-carbon bonds.



ENOLS

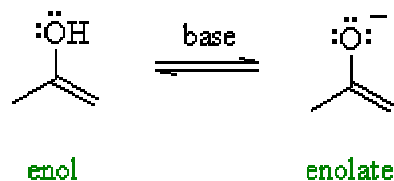
Trying to put it as simply as possible, **enols** are compounds that have alcohol groups, **-OH**, substituted directly onto alkenes, **C=C**, hence "alkene-ols" or *enols*.

Enols can be viewed as alkenes with a strong electron donating substituent. Since alkenes themselves ([review](#)) typically react as nucleophiles, the **-OH** group makes them even more reactive than a simple alkene.



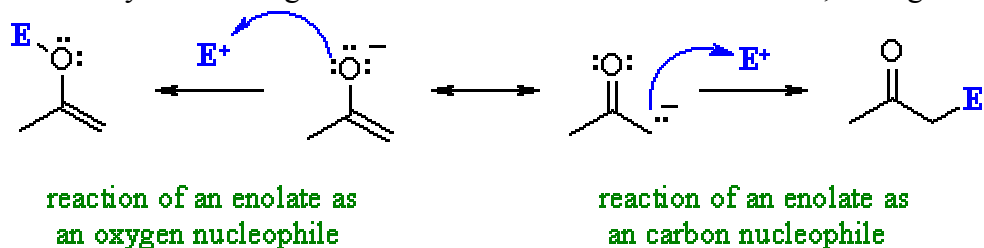
ENOLATES

Enolates are the conjugate bases or anions of enols (like alkoxides are the anions of alcohols) and can be prepared using a base.



Enolates are in principle, capable of reacting as nucleophiles at either the C atom or at the O atom (see below).

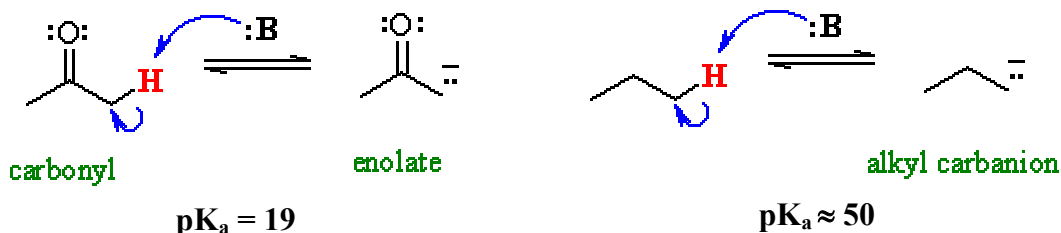
This is shown by the drawing out the main two resonance contributors, see right.



Acidity of α -Hydrogens

Compared to simple hydrocarbons, the α -protons adjacent to carbonyl groups are much more acidic and can be removed by common bases (*e.g.* HO^- , RO^- etc.).

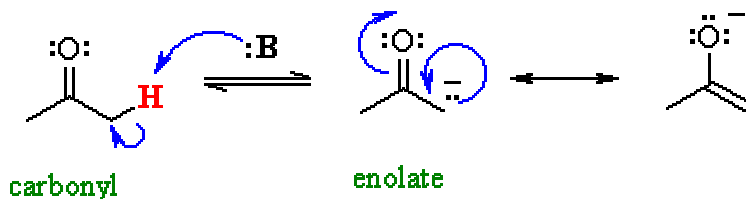
For example, compare the acidity of propanone and propane :



Why are the protons adjacent to carbonyl groups acidic?

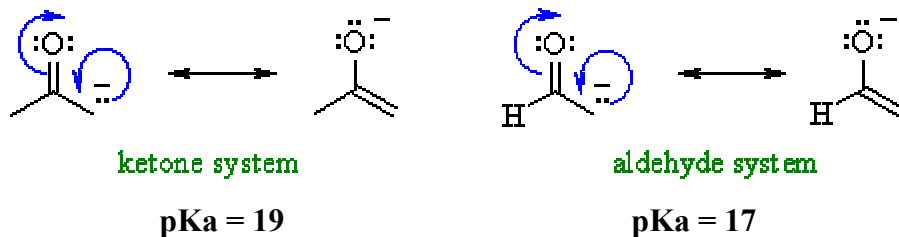
As we have advocated [before](#), look at the stabilisation of the conjugate base.

Notice the proximity of the adjacent π system, and hence the possibility for **RESONANCE** stabilisation by delocalisation of the negative charge to the more electronegative oxygen atom.



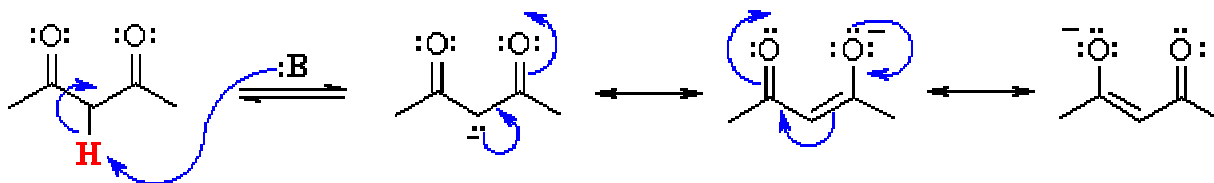
The more effective the resonance stabilisation of the negative charge, the more stable the conjugate base is and therefore the more acidic the parent system.

Typical pKa values for a ketone and an aldehyde are shown:



We can rationalise the trend by comparing the two structures, the difference simply being the alkyl- group versus the hydrogen. Since alkyl groups are weakly electron donating, they tend to *destabilise* anions.

In some cases there could be H atoms that are adjacent to 2 carbonyl groups. This means that there is more resonance stabilisation of the anion since the charge can be delocalised to 2 electronegative oxygen atoms. As a result, we have an even more acidic pKa. These type of compounds are sometimes called "active methylenes".



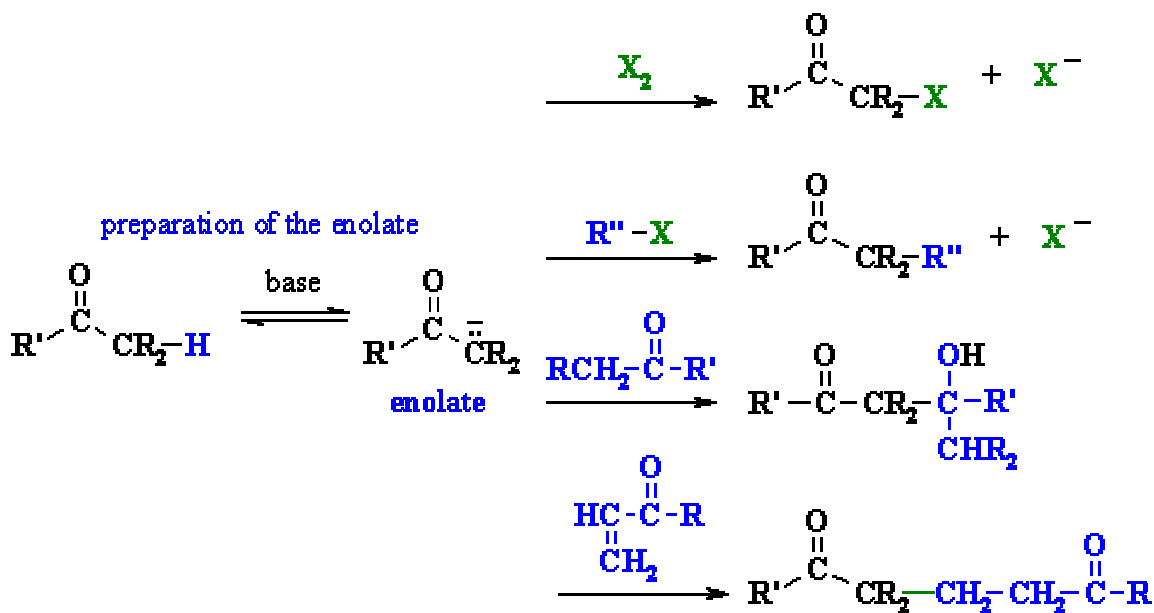
1,3-diketone

pK_a = 9

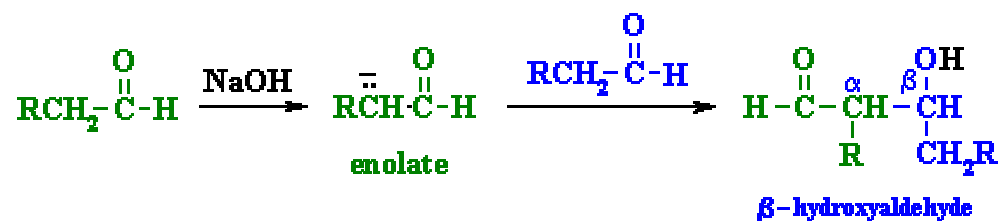
Overview of Enolate reactions

The more important reactions of enolates are summarised below.

Remember that enolates are sources of nucleophilic C and react with electrophiles:



The Aldol Condensation of Aldehydes



Reaction type : Nucleophilic addition

Summary

- Reagents : commonly a base such as NaOH or KOH is added to the aldehyde.
- The reaction involves an enolate reacting with another molecule of the aldehyde.
- Remember enolates are good nucleophiles and carbonyl C are electrophiles.
- The products of these reactions are β -hydroxyaldehydes or aldehyde-alcohols = aldols.
- The simplest aldol reaction is the condensation of acetaldehyde. This is shown below in 2 different representations (the line diagrams are less cluttered).

