

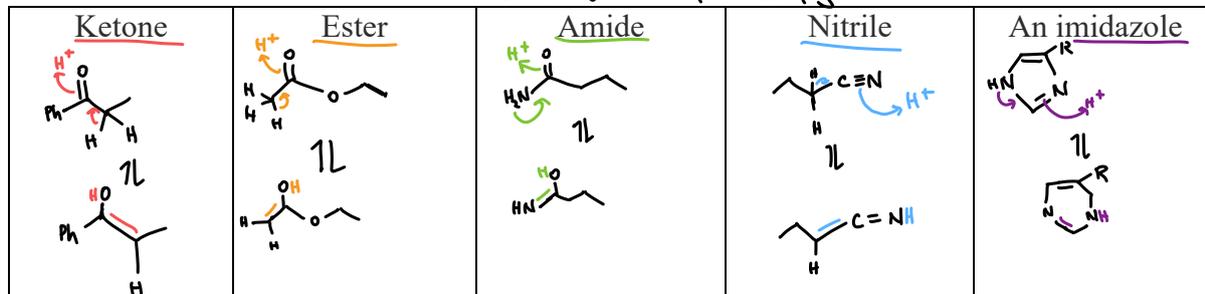
Week 1:

Tautomerism:

A reaction involving only the intramolecular transfer of a proton:

Tautomers can be detected with NMR or IR spectroscopy.

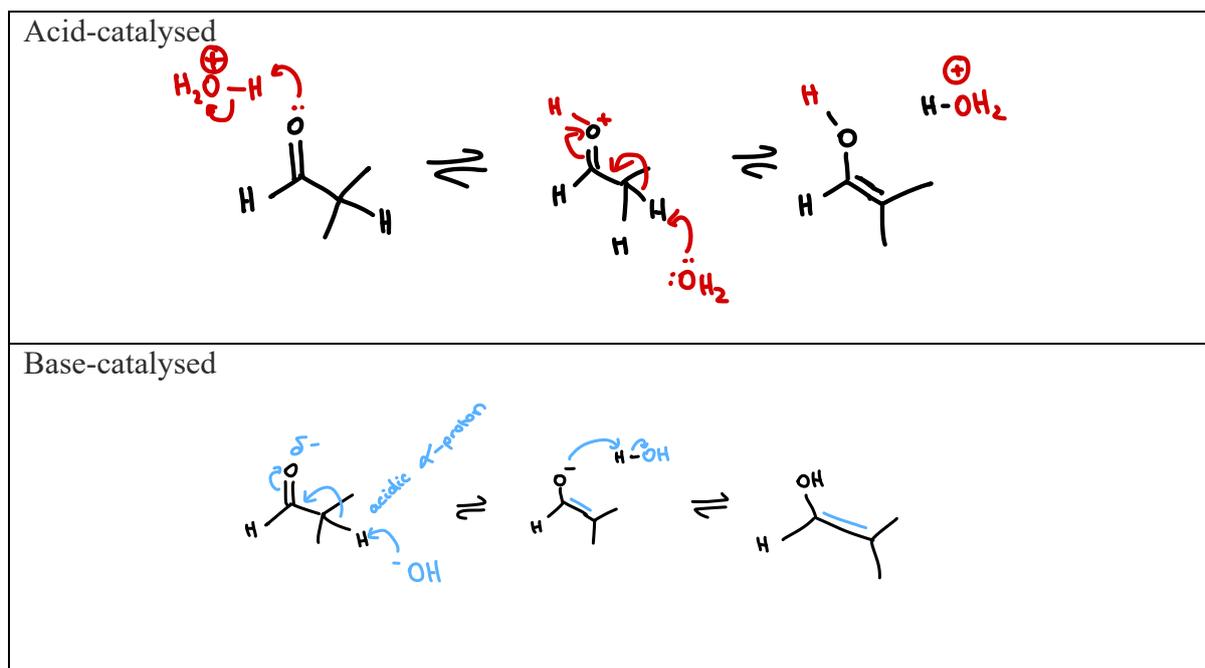
Note: an enol/enolate tautomer will display properties of BOTH tautomers



Note: carboxylic acids don't readily enolise as a base first removes the acidic hydroxyl proton.

Mechanisms for enolisation:

Enolisation can be a relatively slow process in a neutral solution, but we can speed it up with an acid/base catalyst.

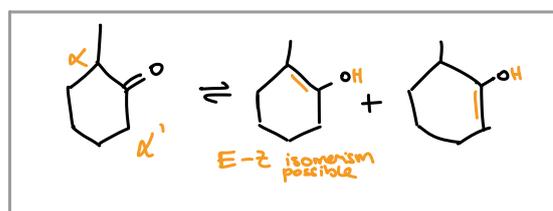
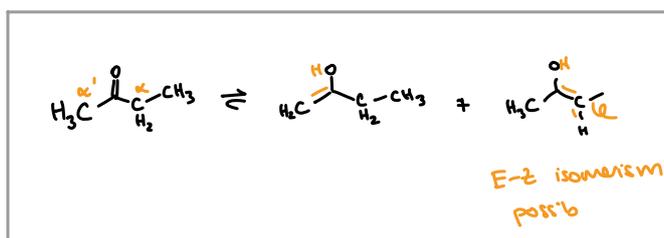


Symmetric ketones will only have geometric isomers (if any?)

Unsymmetrical Ketones:

With an unsymmetrical ketone, more than one enol/enolate product is possible. (we call the products regioisomeric enols/enolates).

two α carbons which have α -hydrogens and are different

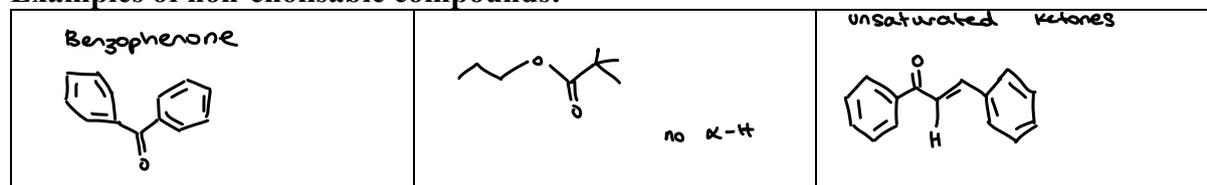


Enolisation requirements:

The organic compound must have an electron-withdrawing functional group, with at least one π bond joined to a saturated carbon atom having at least one hydrogen atom.

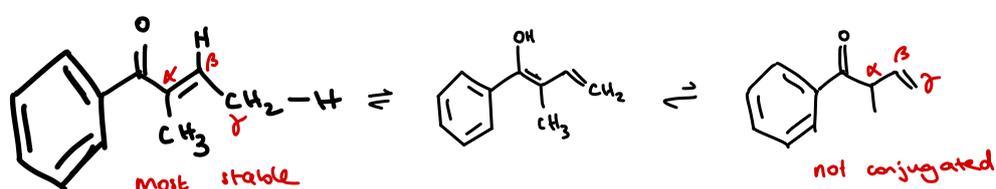
Note that in basic solutions, carboxylic acids and primary/secondary amides do not form enols.

Examples of non-enolisable compounds:



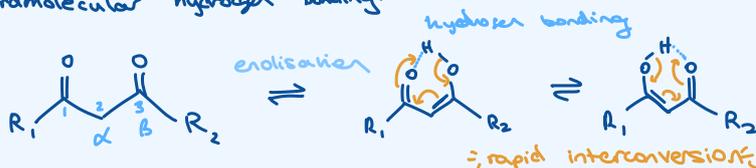
Conjugate systems:

$\beta - \gamma$ unsaturated carbonyls tend to interconvert to a conjugated regioisomer readily as γ -protonation leads to a conjugated carbonyl.



1,3-dicarbonyls (β -dicarbonyls) give more [thermodynamically] stable enol forms since they lead to conjugated enols, and in some cases, we see additional stabilisation in intramolecular hydrogen bonding.

Intramolecular hydrogen bonding:



Since they're so favourable, we can deprotonate them with hydroxide/alkoxide. A higher proportion of enol will be present for a 1,3-dicarbonyl than for a simple carbonyl.

β -dicarbonyl compounds are more acidic than simple carbonyls, since they're resonance stabilised in their enolate form, and thus equilibrium favours the loss of a proton (some [Ethyl acetoacetate and acetylacetone] can be deprotonated in water).

Enolization 'inverts' carbonyl reactivity from electrophile to nucleophile

