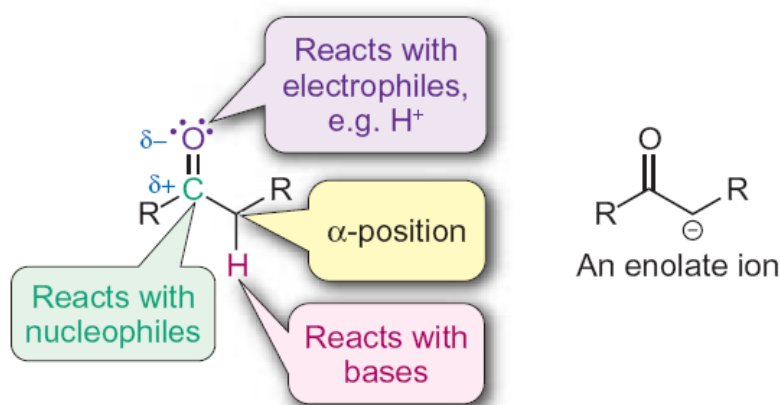


Aldehydes and ketones: nucleophilic addition and α - substitution reactions

23.1 The structure and reactions of aldehydes and ketones

- All aldehydes (RCHO) and ketones (RCOR) contain a C=O bond.
- The C=O bond is polar and the electrons are attracted to the oxygen atom—the oxygen atom reacts with electrophiles and the carbon atom reacts with nucleophiles.

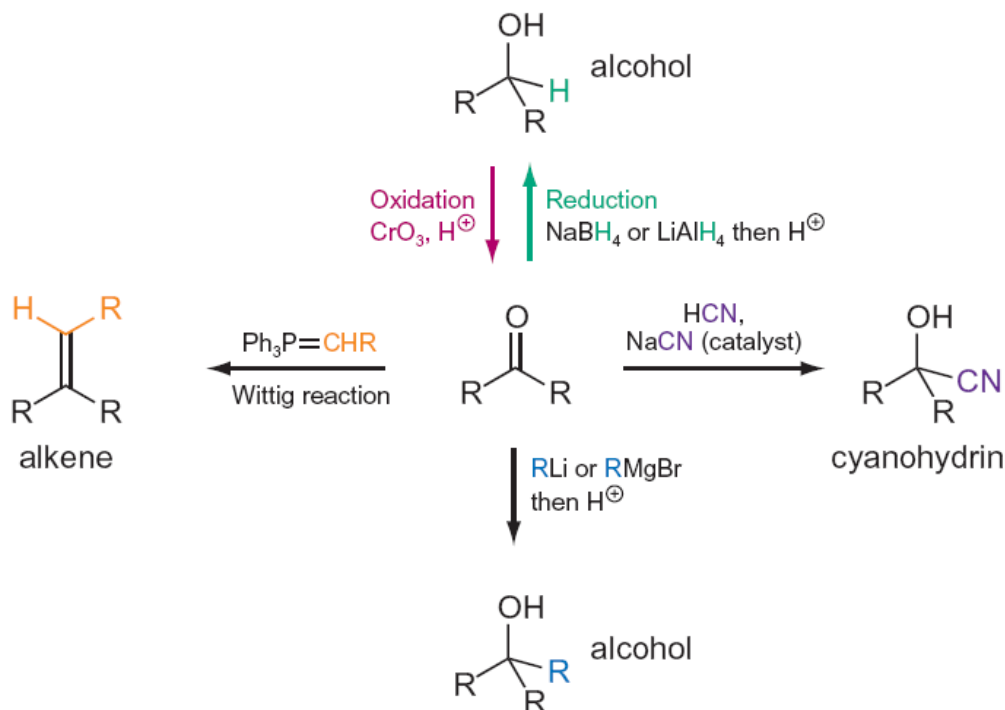


- The position of a carbon atom next to C=O is called the α -position.
- Deprotonation of an aldehyde or ketone at the α -position forms an enolate ion.
- Aldehydes and ketones undergo nucleophilic addition reactions, α -substitution reactions, and carbonyl–carbonyl condensation reactions.

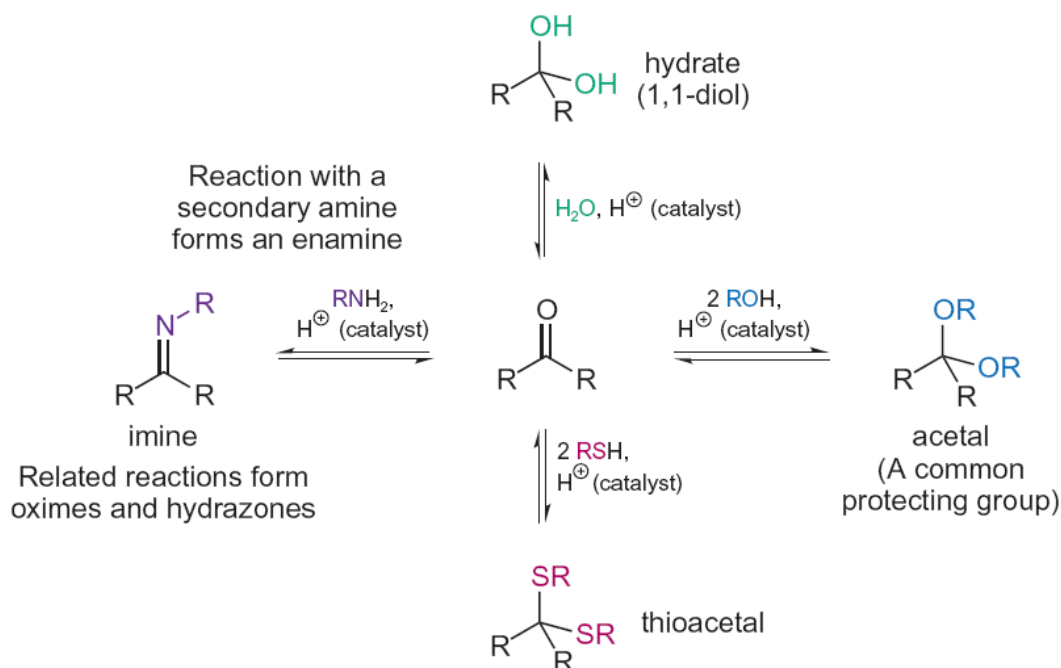
23.2 Nucleophilic addition reactions of aldehydes and ketones

- The C=O bond of aldehydes and ketones reacts with nucleophiles (such as H^- , an organometallic reagent, or ^-CN) in nucleophilic addition reactions.

- Nucleophiles add more rapidly to aldehydes than ketones because of steric and electronic effects.
- Reaction of a phosphonium ylide (ylid) with an aldehyde or ketone forms an alkene in the Wittig reaction.

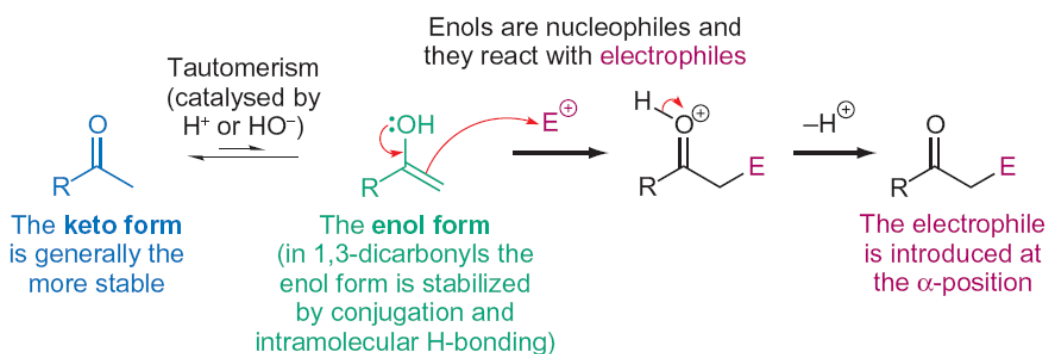


- The reactions of nucleophilic groups containing oxygen, sulfur or nitrogen with the C=O bond are reversible and are catalysed by an acid.

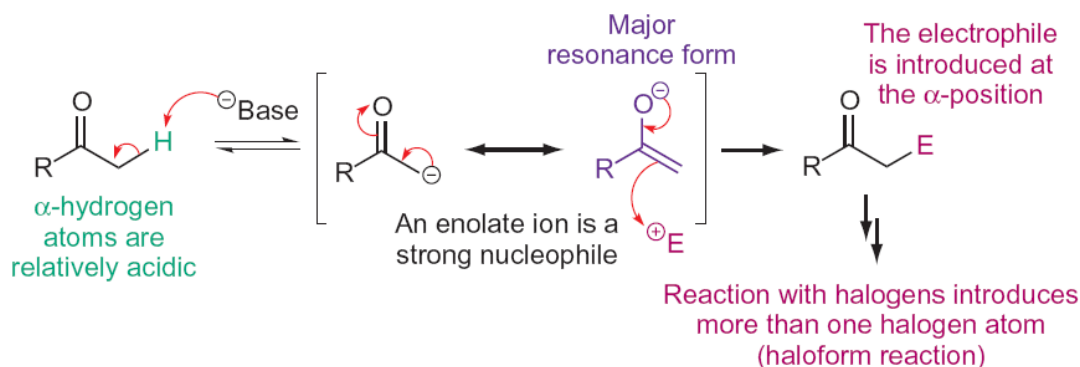


23.3 α -Substitution reactions of aldehydes and ketones

- α -Substitution reactions involve substitution of a hydrogen atom by another group, at the carbon atom next to the C=O bond
- α -Substitution reactions involve intermediate enols or enolate ions
- The interconversion of the keto and enol forms of an aldehyde or ketone is called tautomerism
- Formation of an enol and reaction with an electrophile:

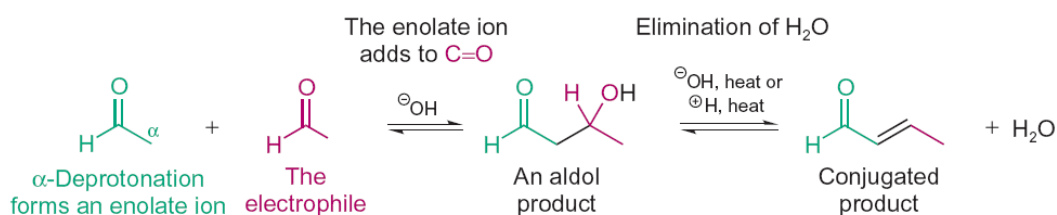


- Formation of an enolate ion and reaction with an electrophile:

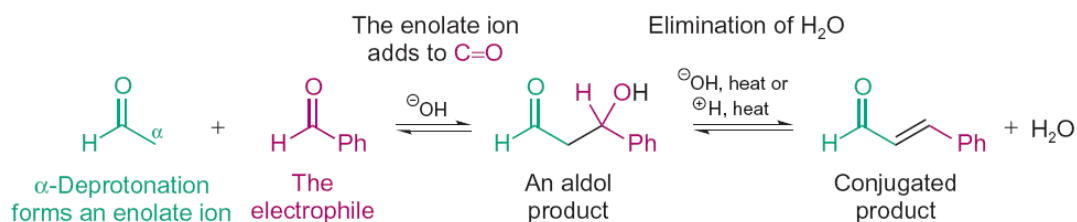


23.4 Carbonyl–carbonyl condensation reactions

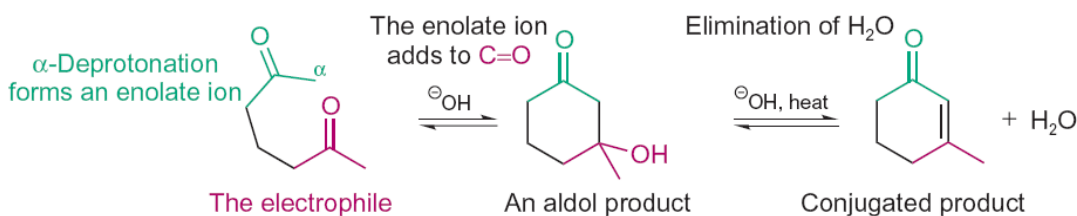
- In carbonyl–carbonyl condensation reactions, two carbonyl molecules react to form a single organic product together with a molecule of water.
- Reactions of two molecules of the *same* aldehyde or ketone are called aldol condensations.



- Reactions of two molecules of different aldehydes or ketones are called crossed (mixed) aldol condensations—a mixture of products is formed, except under certain conditions.



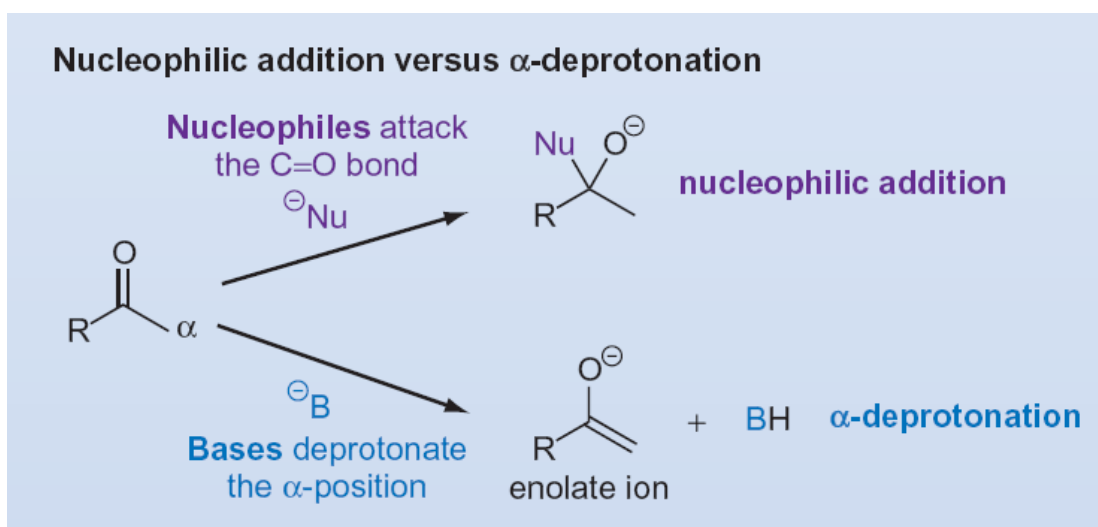
- When one molecule containing two C=O groups reacts with itself, this is called an intramolecular aldol condensation. This is a good method for making 5- and 6-membered rings



Learning outcomes

By the end of this chapter you should be able to do the following.

- For an aldehyde or ketone, describe how the C=O bond reacts with H^+ .
- For an aldehyde or ketone, describe how the C=O bond reacts with a nucleophile (in a nucleophilic addition) and how enolate ions are formed by deprotonation of α-hydrogen atoms.



- Draw general mechanisms for a nucleophilic addition reaction, an α -substitution reaction, and a carbonyl–carbonyl condensation reaction.
- Understand why aldehydes are more reactive to nucleophiles than ketones.
- Draw mechanisms for nucleophilic addition reactions of aldehydes and ketones using the following reagents:

NaBH_4 or LiAlH_4 then H^+	HCN , NaCN (catalyst)
RLi or RMgBr then H^+	$\text{Ph}_3\text{P}=\text{CHR}$
H_2O , H^+ (catalyst)	ROH , H^+ (catalyst)
RSH , H^+ (catalyst)	RNH_2 , H^+ (catalyst)
- Understand how aldehydes and ketones are prepared by oxidation of alcohols.
- Recognize that addition of oxygen, sulfur, or nitrogen nucleophiles to the $\text{C}=\text{O}$ bond is reversible and is catalysed by an acid.
- Discuss keto–enol tautomerism and understand the factors that influence the stability of keto and enol forms.
- Recognize that α -substitution reactions involve intermediate enols or enolate ions.
- Draw mechanisms for α -substitution reactions of aldehydes and ketones using the following reagents: H^+ , Br_2 ; base, RX ; HO^- , I_2 (both in excess).
- Draw mechanisms for aldol condensations, crossed (mixed) aldol condensations, and intramolecular aldol condensations.
- Predict the structure of a product derived from a nucleophilic addition, an α -substitution, or a carbonyl–carbonyl condensation reaction of an aldehyde or ketone.
- Propose reagents for converting an aldehyde or ketone into a product derived from a nucleophilic addition, an α -substitution, or a carbonyl–carbonyl condensation reaction.