

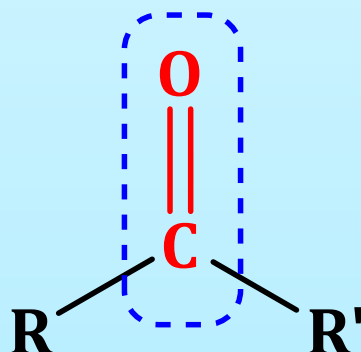
Aldehydes and Ketones

Aldehydes and ketones

- Aldehydes and ketones are organic compounds that belong to another very important family of compounds – the family containing the **carbonyl group, C=O**
- This functional group is found in three main families of compounds: **aldehydes, ketones and carboxylic acids and its derivatives like esters, acid chlorides, acid anhydrides and amides**

Carbonyl compounds

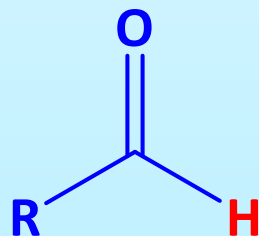
- These are compounds that contain the carbonyl functional group



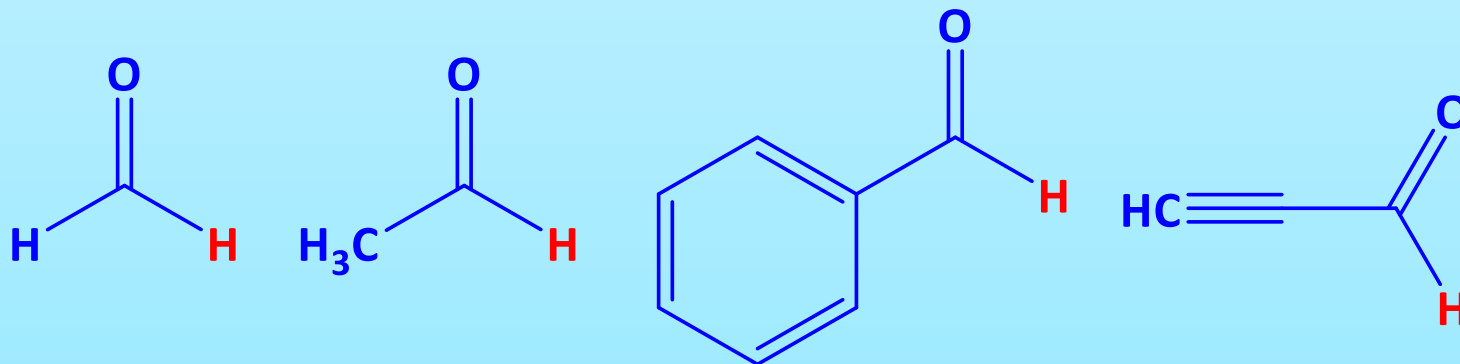
Examples: Aldehydes, ketones, carboxylic acids, esters, amides, acyl halides, etc.

Aldehydes and ketones

- The functional group of an aldehyde is a carbonyl group bonded to a hydrogen atom

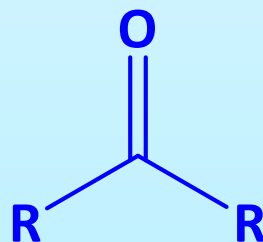


- The R group can be a hydrogen atom or an sp^1 , sp^2 , or sp^3 hybridized carbon atom

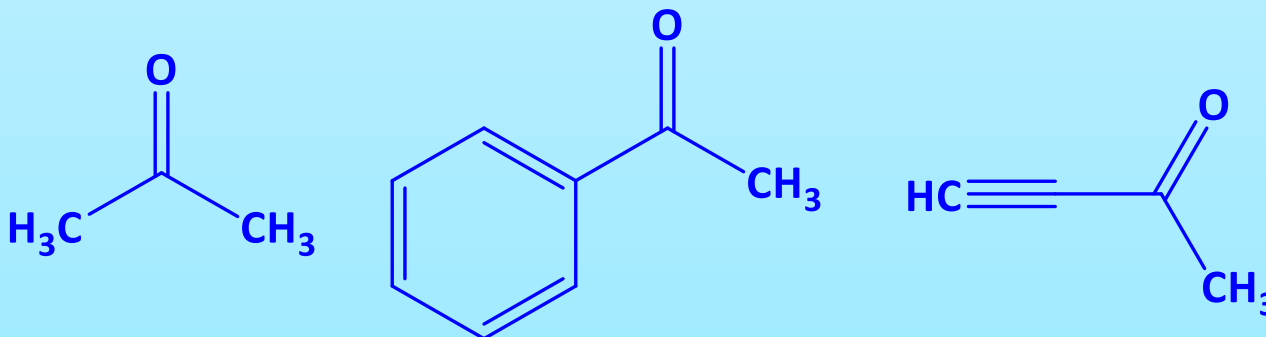


Aldehydes and ketones

- Ketones on the other hand are compounds in which the carbonyl group is attached to two carbon atoms



- Similar to the aldehydes, the R group can be an sp^1 , sp^2 , or sp^3 hybridized carbon atom

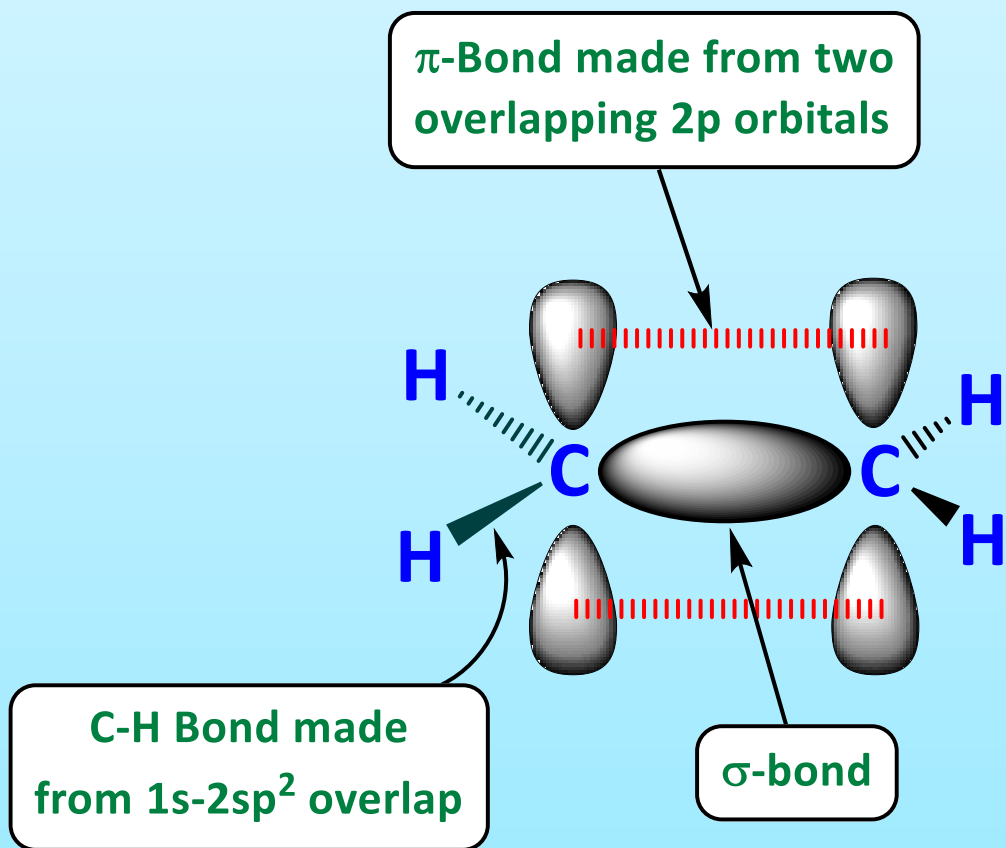


Aldehydes and ketones

- As we have already seen, the carbon-oxygen double bond consists of a sigma bond formed by the overlapping of the sp^2 hybridized orbitals of carbon and oxygen and one pi bond formed by the overlapping of the parallel $2p$ orbitals
- This is very similar to the bond we find in alkenes

Importance of carbonyl compounds

- Earlier we saw structures and the chemistry of alkenes with their double bonds;

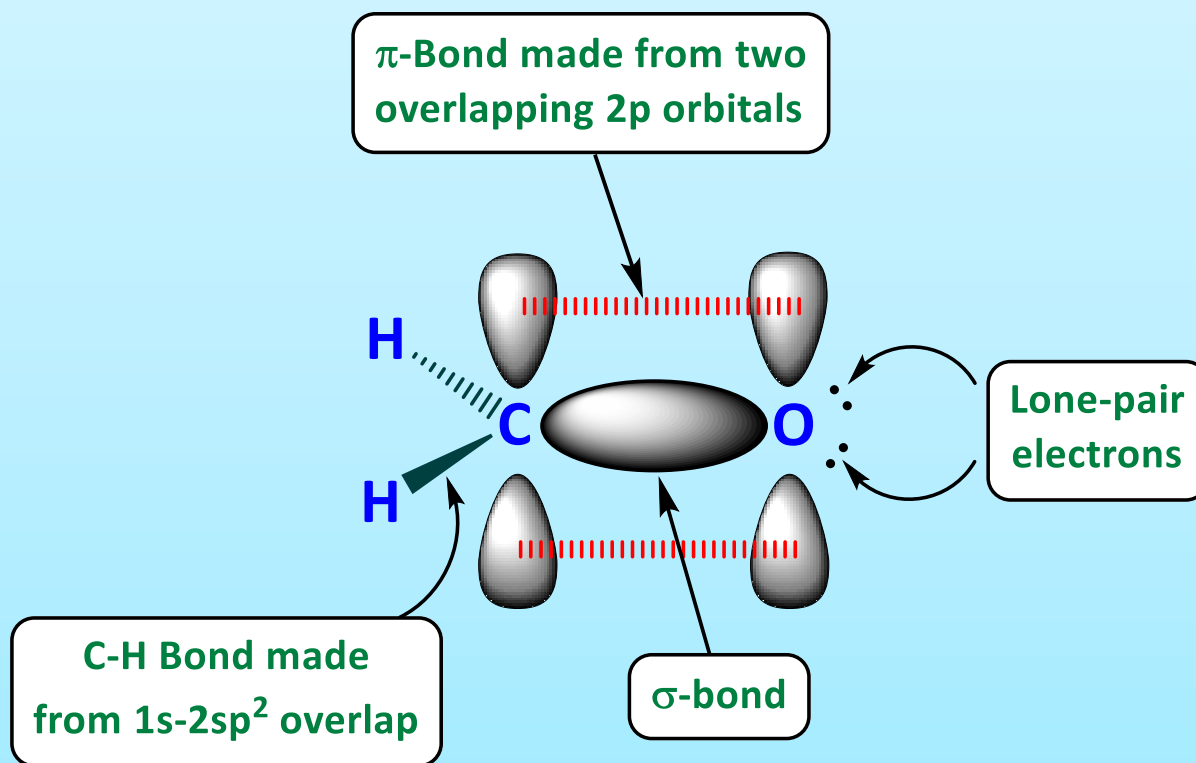


Importance of carbonyl compounds

- We can extend our study of double bonds to exploring the chemistry of the carbon-oxygen double bond
- Although it bears many similarities to the carbon-carbon double bonds, the carbon-oxygen double is not “just another double bond”
- The chemistry of this functional group is quite unique, versatile and different

Bonding in a carbonyl group

- Let us examine the bonding in a carbonyl group:

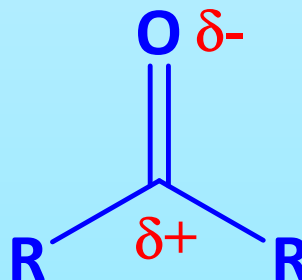
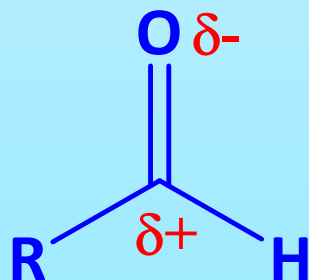


Many important differences...

- While they appear to be similar, there are many important differences;
- These differences make the chemistry of the carbonyl group the cornerstone of synthetic (organic) chemistry
- Much of our ability to make new molecules depends on the manipulation of carbonyl groups because they allow us to make carbon-carbon bonds

Aldehydes and ketones

- This bond is a very polar bond due to the differences in electronegative values of the carbon and the oxygen
- It is due to the unsymmetrical distribution of electrons in this bond that carbonyl compounds are quite reactive to electron-rich species, i.e. nucleophiles



Nomenclature

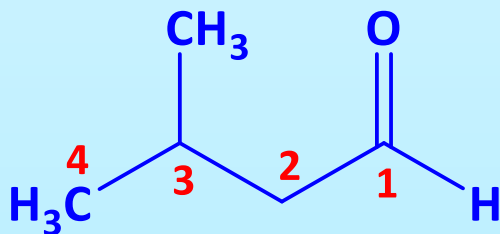
- The IUPAC system for naming aldehydes and ketones follows a similar pattern of selecting the longest continuous chain containing the carbonyl group as its parent compound
- In aldehydes, the carbonyl carbon will assume position number 1 on the carbon chain and the substituents are numbered relative to the position of the carbonyl group on the chain

Nomenclature

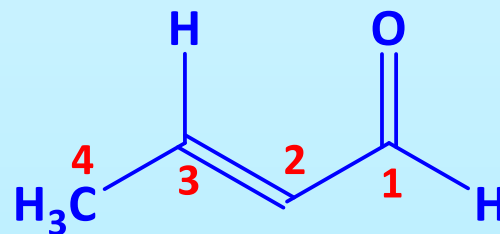
- Because the carbonyl carbon is at the beginning of the chain, there is no need to use a number to locate it
- The name of the aldehyde is obtained by changing the suffix “-e” of the parent alkane to “-al”, such as methan**al**, ethan**al**, propan**al**
- For unsaturated aldehydes, the presence of a carbon-carbon double bond is indicated by the infix “-en-”

Nomenclature

- As with other molecules with both an infix and suffix, the location of the suffix determines the numbering pattern



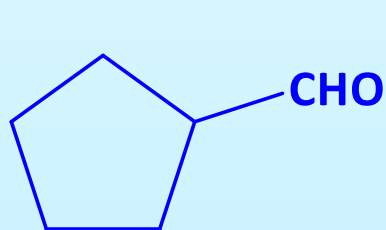
3-methylbutanal



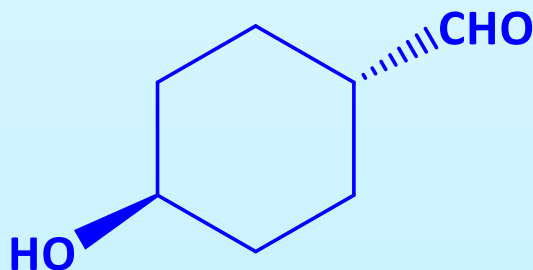
2-butenal (or but-2-enal)

- For monocyclic molecules in which the -CHO is attached directly to the ring, the molecule is named by adding the suffix ***-carbaldehyde*** to the name of the ring

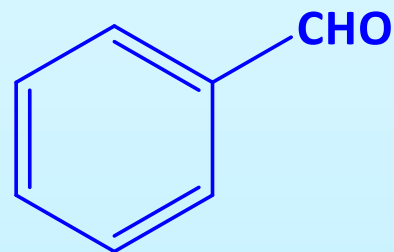
Nomenclature



cyclopentane-
carbaldehyde



trans-4-hydroxycyclo
hexanecarbaldehyde

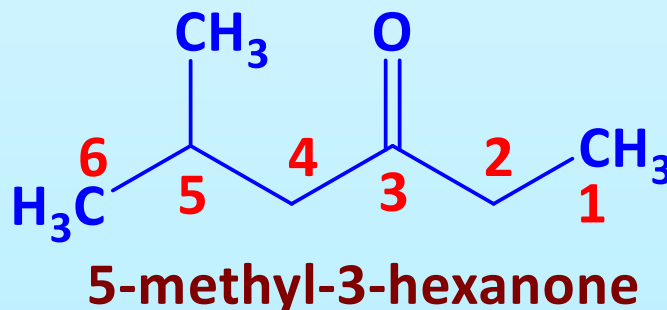


benzaldehyde

- Ketones are named by selecting the longest continuous chain containing the carbonyl group as the parent compounds and then indicating its presence by changing the suffix from “-e” to “-one”

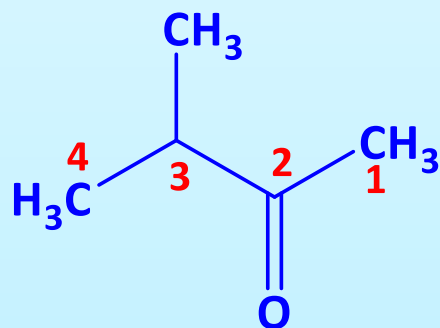
Nomenclature

- The parent chain is numbered from the direction that gives the carbonyl group the smaller number

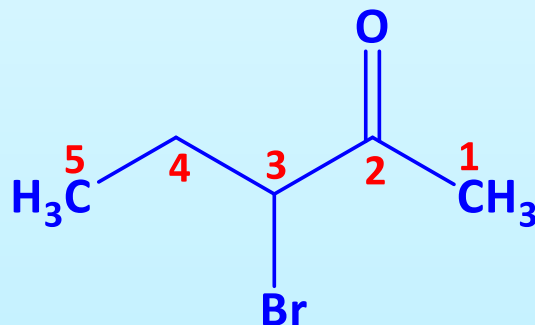


- All other substituents on the chain or ring are numbered with respect to the position of the carbonyl group and as this group is not at the end of the chain, a number is used to indicate its location on the chain or the ring system

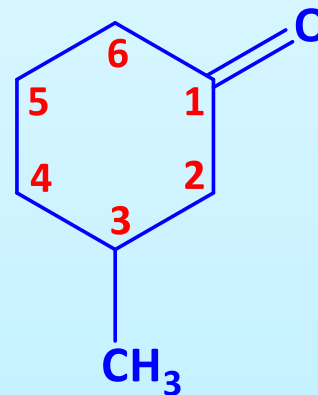
Nomenclature



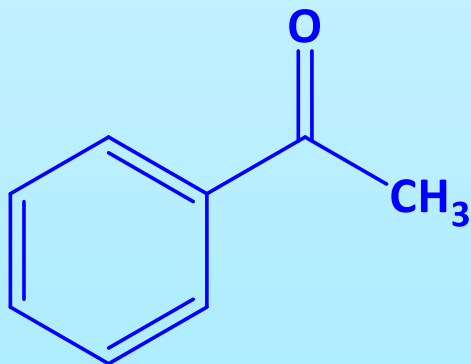
3-methylbutanone



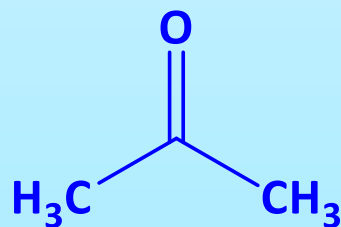
3-bromo-2-pentanone



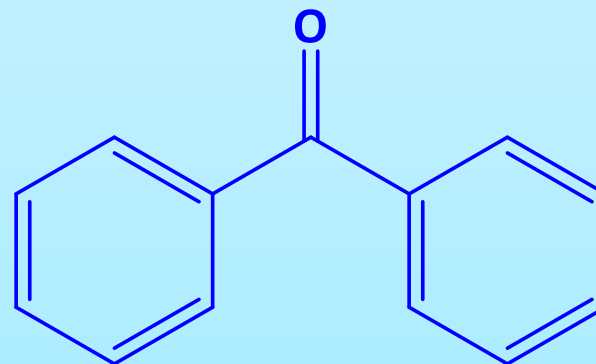
3-methylcyclohexanone



acetophenone



**acetone
(propanone)**




benzophenone

Nomenclature

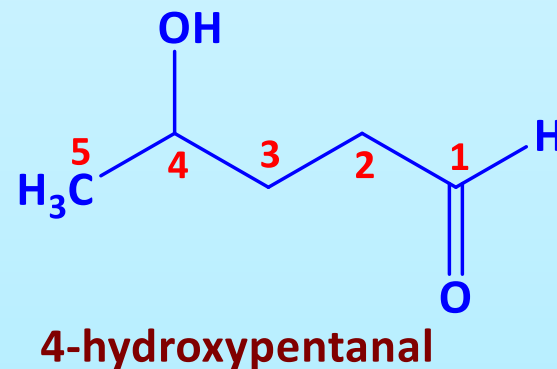
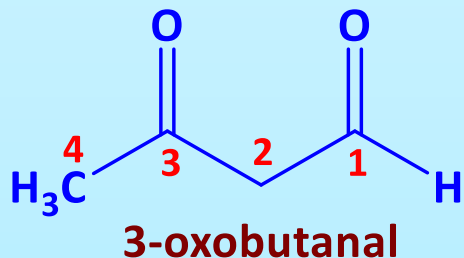
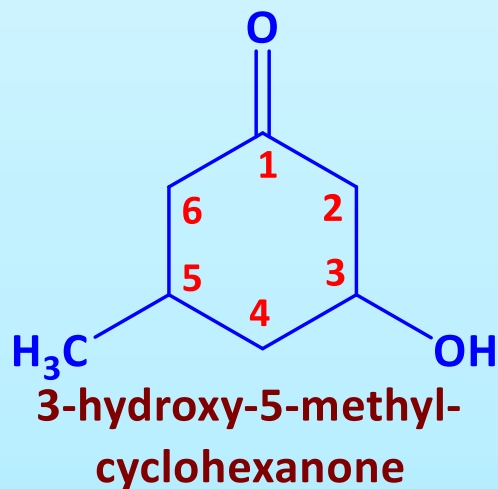
- There are many compounds that have several functional groups on them and naming them can be a very confusing and problematic exercise
- When naming these compounds, use the table below to help with identifying the parent compound
- The table contains the order of precedence of functional groups to deduce the name

Nomenclature

Functional group	Suffix if higher in precedence	Prefix if lower in precedence
-COOH	-oic acid	-
-CHO	-al	oxo-
	-one	oxo-
-OH	-ol	hydroxy-
-NH₂	-amine	amino-
-SH	-thiol	mercapto-

Nomenclature

➤ Take the following examples:

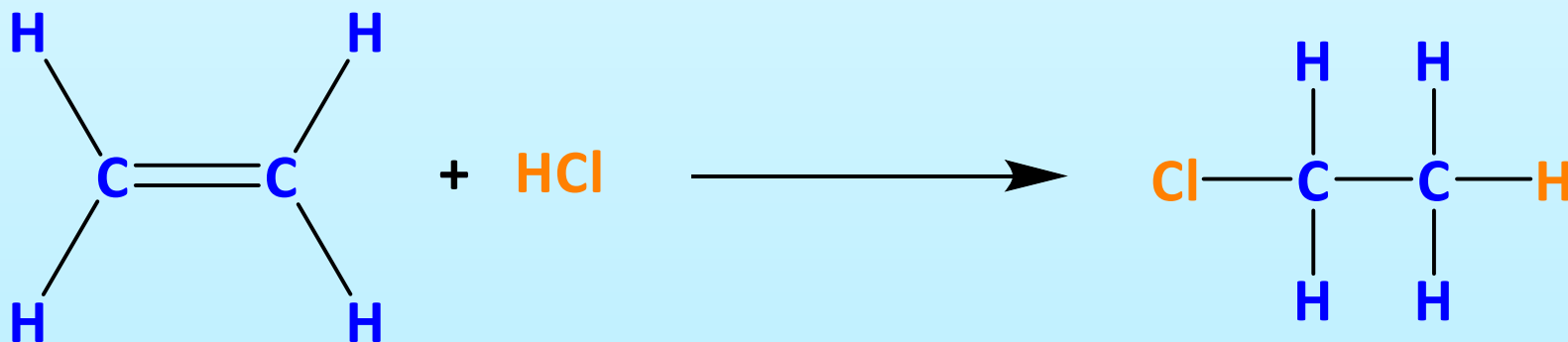


Reactions of aldehydes and ketones

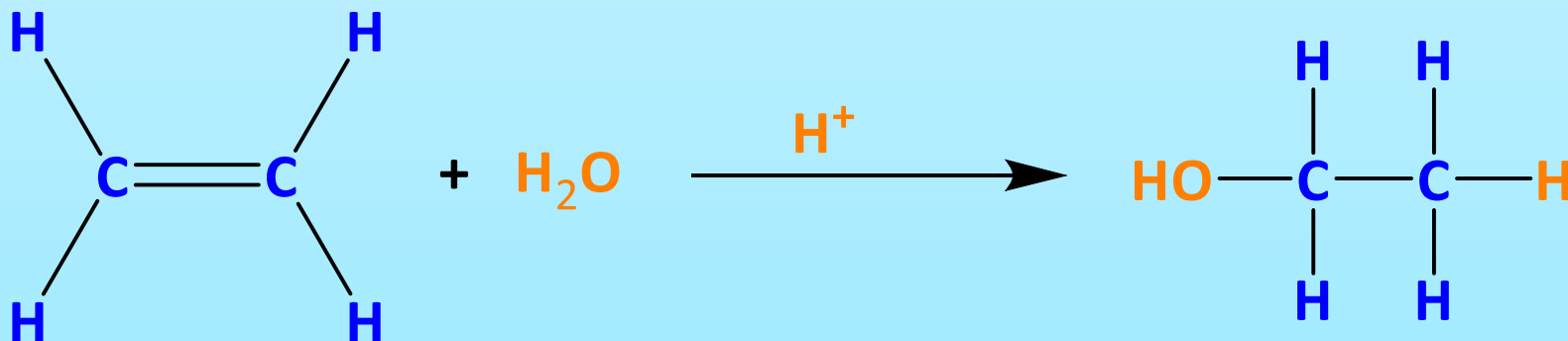
- Aldehydes and ketones undergo a number of reactions that are based around the very polar bond – the *carbonyl group*
- The basis of all these reactions is governed by the unsymmetrical distribution of electrons in this bond that carbonyl compounds are quite reactive to electron-rich species, i.e. nucleophiles
- This is because of the difference in electronegativities of the oxygen and carbon

Recall – Example of alkene reaction...

Addition of HCl to ethene



Addition of H₂O to ethene



Resonance of the carbonyl group...

- In resonance terms, the carbonyl group can be described as a combination of the two major contributing forms...



Reactivity of the carbonyl group...

- There are several centres of reactivity in a molecule containing a carbon-oxygen double bond
- This versatility contributes to the widespread use of carbonyl compounds in synthesis
- There is the π -bond itself (don't forget the anti-bonding π^* orbital) and the lone pair of electrons on the oxygen

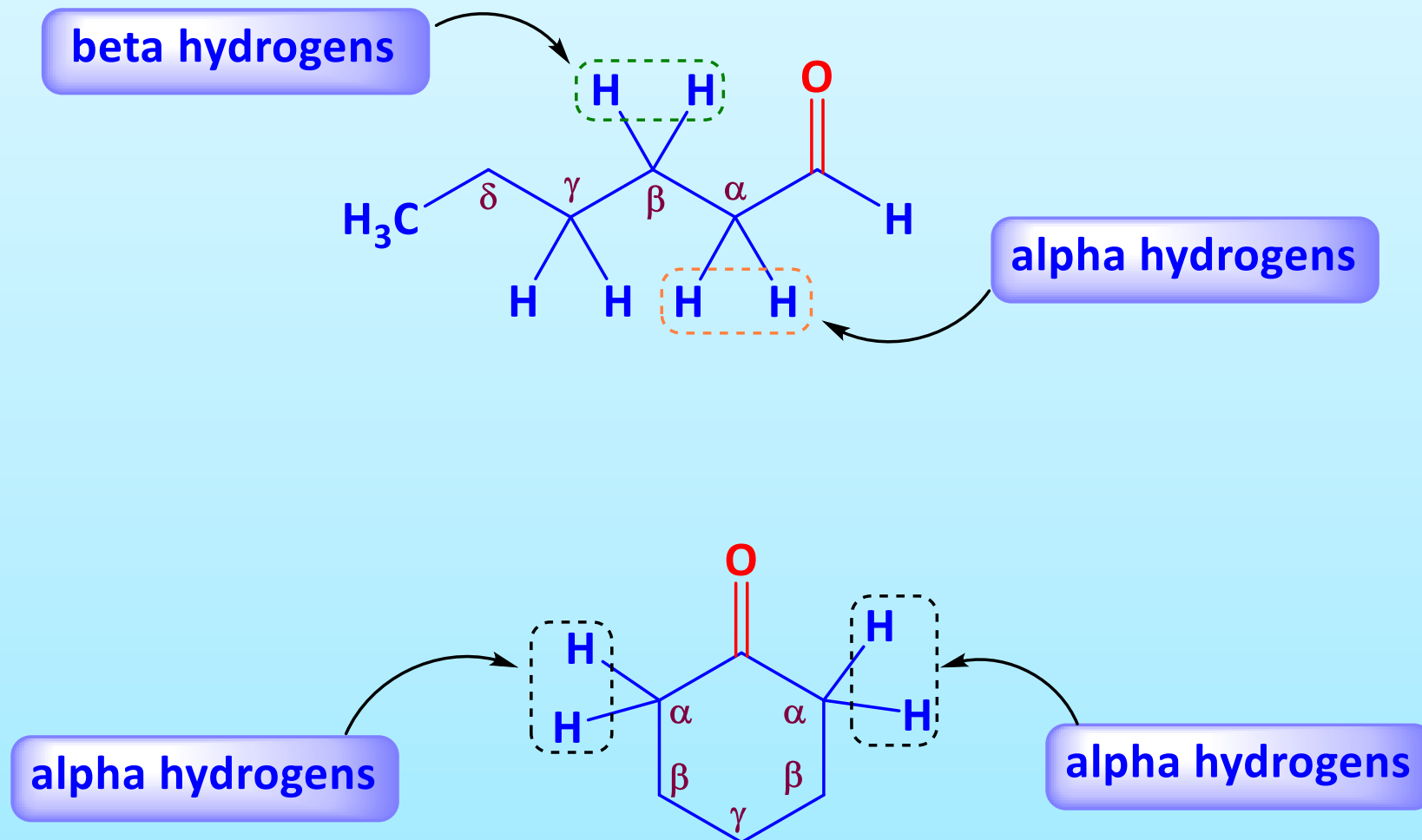
Polarisable π -bond...

- As shown, the carbonyl group has an easily polarisable π -bond with an electrophilic carbon atom at one end that is easily attacked by nucleophiles
- In addition to the electrophilic carbon centre of the carbonyl group, there is a special reactivity associated with the carbon-hydrogen bonds in the position adjacent (α) to the carbon-oxygen double bond

Positions on a carbon chain...

- Other positions in a molecule in relation to the carbonyl group may be referred to by Greek letters
- The carbon adjacent to the C=O group is called the **alpha** (α) carbon. The next carbon is **beta** (β), then **gamma** (γ), **delta** (δ) and so forth.
- The groups (or atoms) attached to an α carbon are called α groups, those on β carbon are β groups etc.

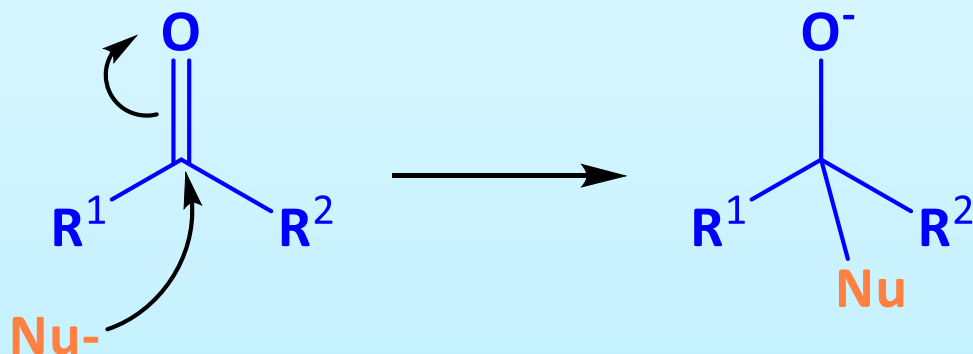
Positions on a carbon chain...



Reactions of aldehydes and ketones

- For this course we will concentrate on the reaction that takes place at the electrophilic carbonyl carbon atom
- The most common reaction these compounds undergo is addition reactions of nucleophiles to form a tetrahedral carbonyl addition intermediate
- The following represents a general reaction showing the addition of the nucleophile to the electrophilic carbonyl carbon

Reactions of aldehydes and ketones

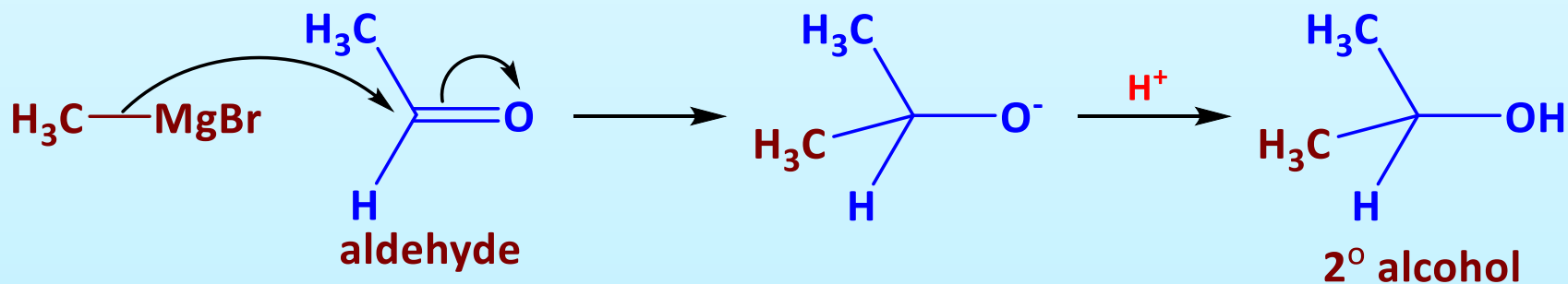


- The following represents a general reaction showing the addition of the nucleophile to the electrophilic carbonyl carbon
- From a synthetic viewpoint, the addition of carbon nucleophiles is the most important type of nucleophile addition to the C=O

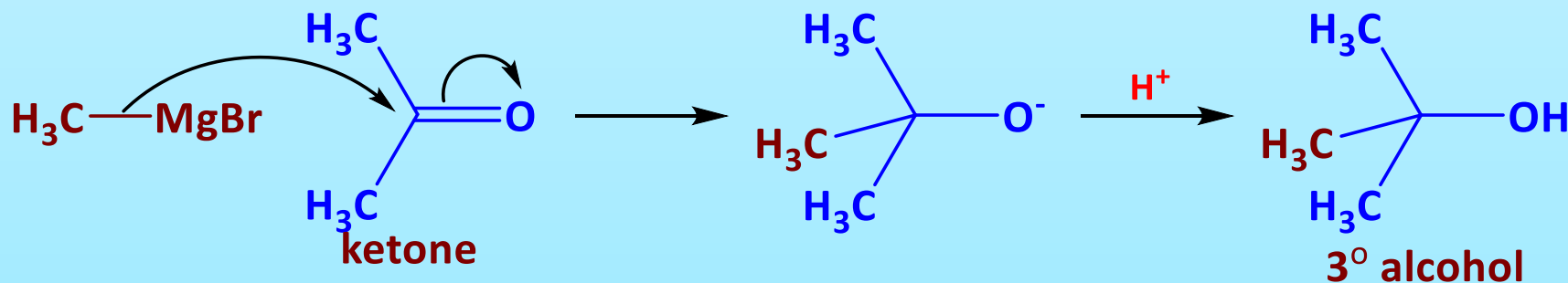
Reactions of aldehydes and ketones

- This is because these reactions form new carbon-carbon bonds which mean that the molecule can be made larger
- The main carbon nucleophile discussed here is the Grignard reagent (R-MgX)
- When Grignard reagents are added to aldehydes, secondary alcohols are formed upon acidification of the tetrahedral intermediate

Reactions of aldehydes and ketones

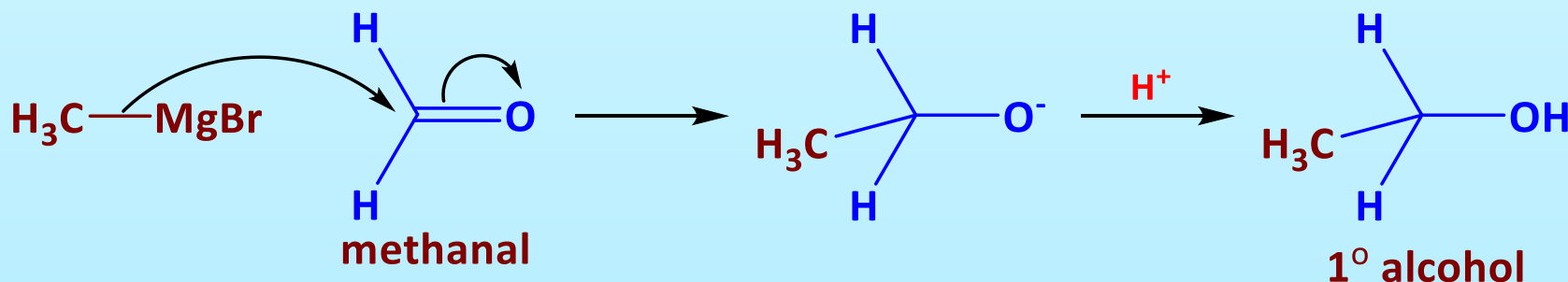


➤ When ketones are reacted with Grignard reagents, tertiary alcohols are formed upon acidification of the tetrahedral intermediate



Reactions of aldehydes and ketones

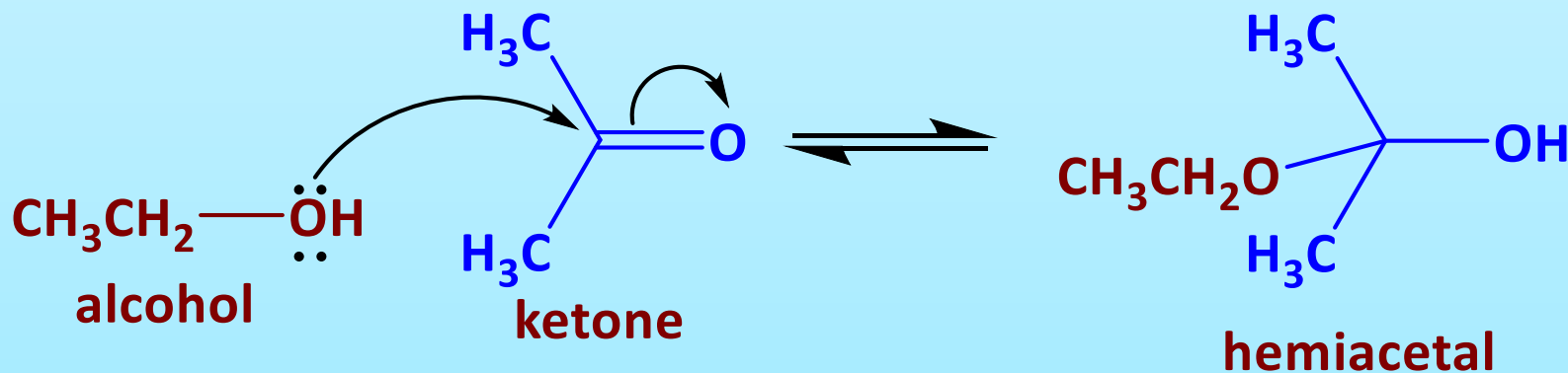
- When methanal is reacted with Grignard reagents, primary alcohols are formed upon acidification of the tetrahedral intermediate



- Another useful reaction is the addition of oxygen nucleophiles to the electrophilic carbonyl carbon to form several products

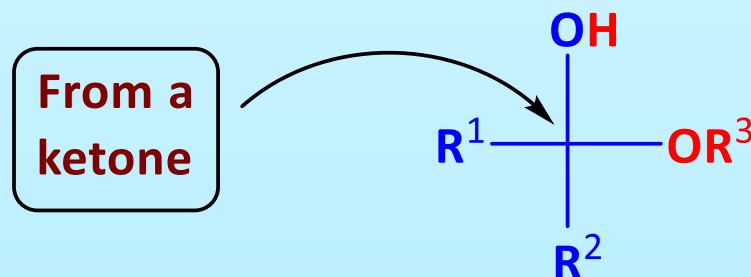
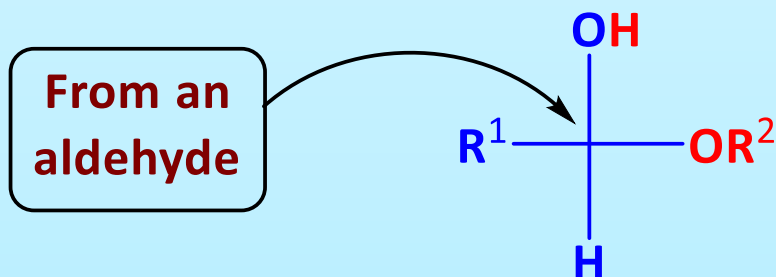
Reactions of aldehydes and ketones

- The main source of oxygen nucleophiles is the alcohol
- When a molecule of alcohol is added to the carbonyl group of an aldehyde or ketone, a **hemiacetal** is formed



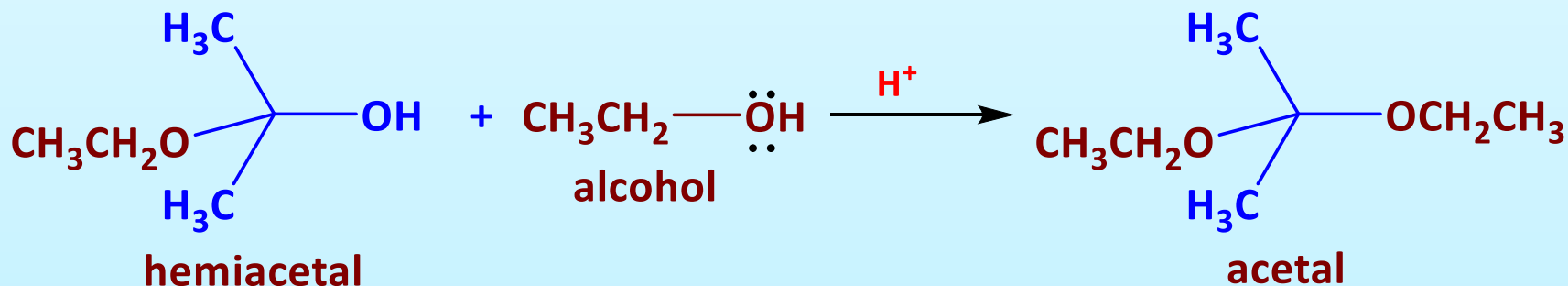
Reactions of aldehydes and ketones

- The functional group of a hemiacetal is a carbon atom vicinally bonded to a -OH and an -OR or -OAr group

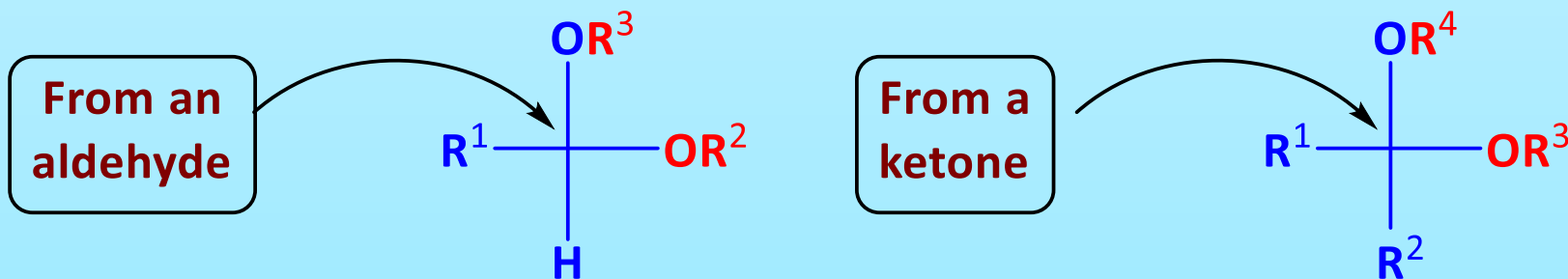


- These hemiacetals are relatively unstable and can react further to produce acetals plus a molecule of water. These reactions are generally acid-catalyzed

Reactions of aldehydes and ketones



- As with hemiacetals, the functional group of an acetal is a carbon atom bonded vicinally to two -OR or -OAr groups

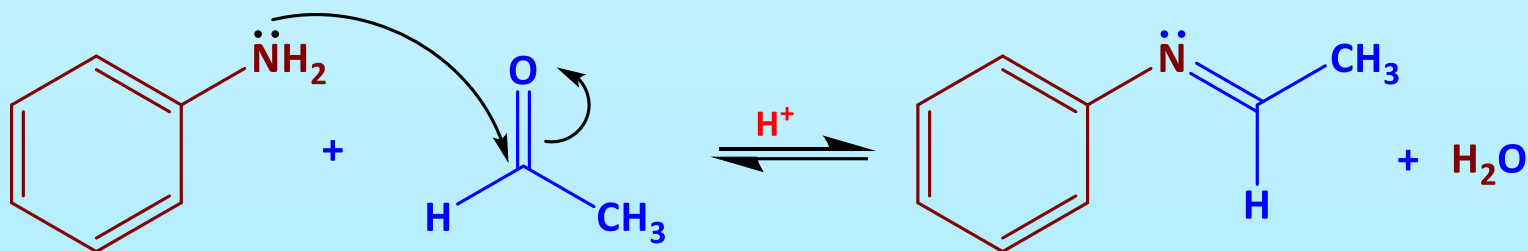
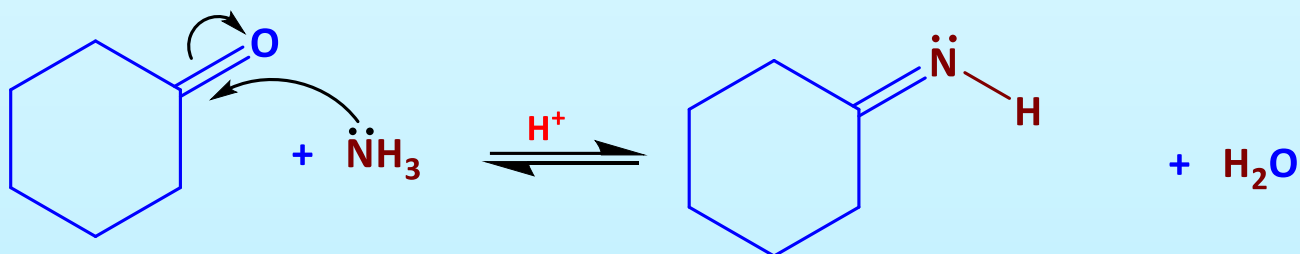


Reactions of aldehydes and ketones

Addition of nitrogen nucleophiles

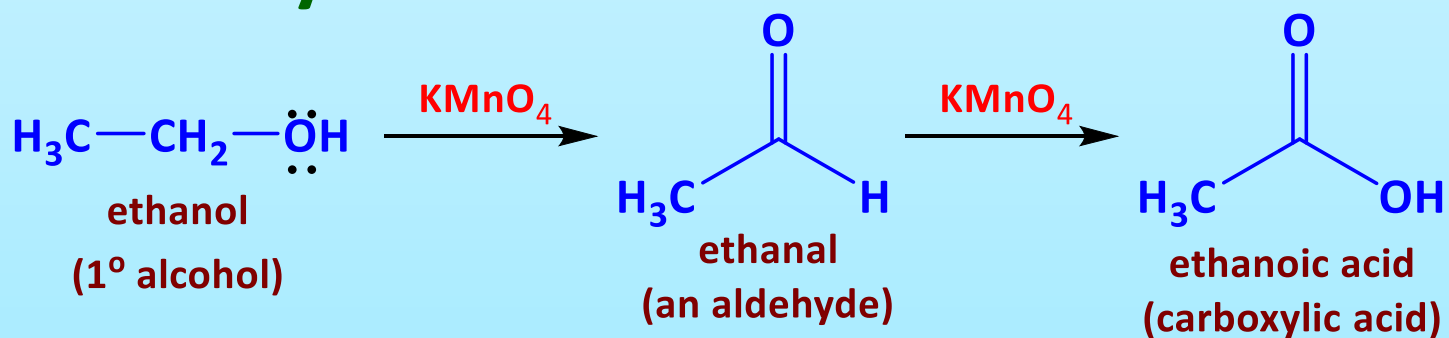
- Ammonia (NH_3), primary aliphatic amine (R-NH_2) and primary aromatic amines (Ar-NH_2) react with the carbonyl group of aldehydes and ketones in the presence of an acid catalyst to give a product containing a carbon-nitrogen (C=N) double bond
- These compounds are called **imines**

Reactions of aldehydes and ketones



Synthesis of aldehydes and ketones

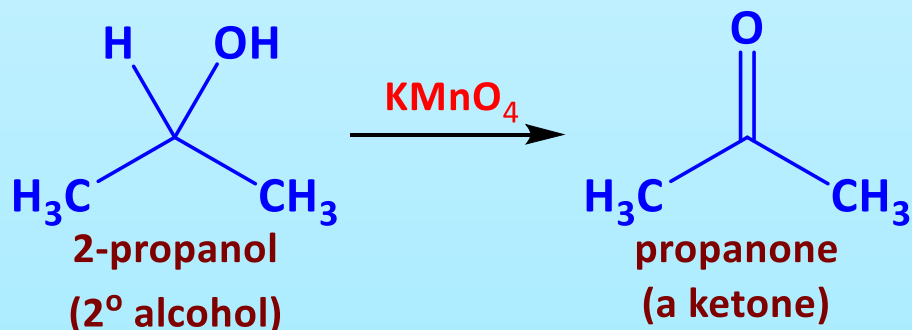
- The most common way of preparing aldehydes and ketones is through the oxidation of alcohols
- When primary alcohols are oxidized, they are initially converted to aldehydes and then on to carboxylic acids



Other oxidants such as H_2CrO_4 , CrO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, oxone can do the same thing as well

Synthesis of aldehydes and ketones

- But when secondary alcohols are oxidized, they are converted to ketones only
- Further oxidation of the ketone involves the cleavage of the carbon-carbon bond to yield a carboxylic acid



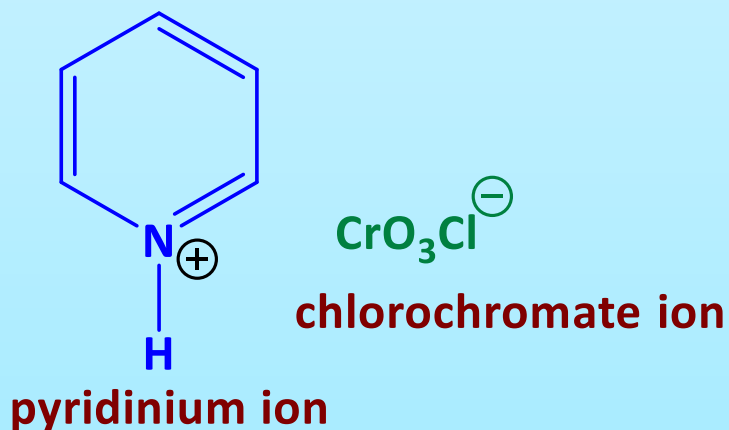
Again other oxidants such as H_2CrO_4 , CrO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, oxone can do the same thing as well

Synthesis of aldehydes and ketones

- When attempting to prepare an aldehyde from a primary alcohol by oxidation, it is not a very good strategy to use chromic acid (H_2CrO_4), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), and potassium permanganate (KMnO_4)
- This is because the oxidation conditions do not allow for the reaction to stop at the aldehyde stage
- It always over-oxidizes it to the carboxylic acid stage

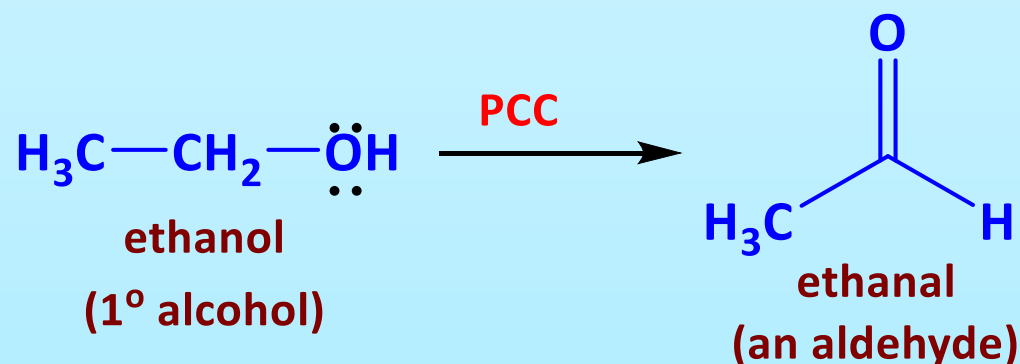
Synthesis of aldehydes and ketones

- A milder variant of the chromium-based oxidant, which selectively oxidizes primary alcohols to aldehydes is called pyridinium chlorochromate (PCC)



Synthesis of aldehydes and ketones

- When used in the oxidation of primary alcohols like ethanol, it will stop only at the aldehyde stage and not over-oxidize to the carboxylic acid stage



- PCC can also be used to oxidize secondary alcohols to the ketone stage