الكلية	**العلوم**
القسم	**علوم الكيمياء**
المادة باللغة الانجليزية	Organic chemistry
المادة باللغة العربية	**الكيمياء العضوية**
المرحلة الدراسية	**الثانية**
اسم التدريسي	**وهج رائد عباس**
عنوان المحاضرة باللغة الانجليزية	Carbonyl compounds
عنوان المحاضرة باللغة العربية	**مركبات الكاربونيل**
رقم المحاضرة	**3**
المصادر والمراجع	Fundamental of organic chemistry, T. W. Craham Solomon
	Organic chemistry, 10th Ed, T. W. Craham Solomon & Craig B. fryhle
	Organic chemistry, 8th Ed, L. G. WADE JR

Aldehyde and ketone

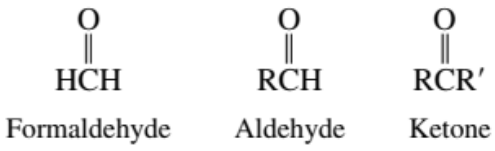
(by Wahaj Raed)

Introduction

Carbonyl compounds are everywhere. In addition to their uses as reagents and solvents, they are constituents of fabrics, flavorings, plastics, and drugs. Naturally occurring carbonyl compounds include proteins, carbohydrates, and nucleic acids that make up all plants and animals. All carbonyl compound contain a carbonyl group (C=O) (acyl group). The acyl group (R-C=O) bonded to another substituent. The R part of the acyl group can be practically any organic part-structure, and the other substituent to which the acyl group is bonded might be a carbon, hydrogen, oxygen, halogen, nitrogen, or sulfur. It's useful to classify carbonyl compounds into two categories based on the kinds of chemistry they undergo. In one category are aldehydes and ketones; in the other are carboxylic acids and their derivatives. The acyl group in an aldehyde or ketone is bonded to an atom (H or C, respectively) that can't stabilize a negative charge and therefore can't act as a leaving group in a nucleophilic substitution reaction. The acyl group in a carboxylic acid or its derivative, however, is bonded to an atom oxygen, halogen, sulfur, nitrogen) that can stabilize a negative charge and therefore can act as a leaving group in a nucleophilic substitution reaction.

Aldehydes and ketones

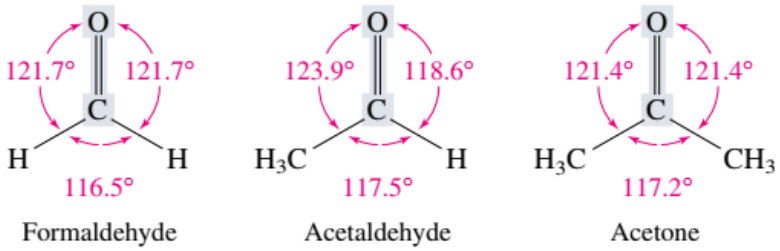
Aldehydes and ketones contain an acyl group bonded either to hydrogen or to another carbon. Aldehydes and ketones are responsible for many flavors and odors (e.g. vanilla), Many important biological compounds also exhibit the carbonyl moiety, including progesterone and testosterone, the female and male sex hormones. Acetone is used as a solvent and is commonly found in nail polish remover, while formaldehyde is used as a preservative in some vaccine formulations. Aldehydes and ketones are also used as building blocks in the syntheses of commercially important compounds, including pharmaceuticals and polymers. Compounds containing a carbonyl group react with a large variety of nucleophiles, affording a wide range of possible products. Due to the versatile reactivity of the carbonyl group, aldehydes and ketones occupy a central role in organic chemistry.



Aldehyde or ketone is bonded to an atom (-H or -R, respectively) that can't stabilize a negative charge and therefore can't act as a leaving group in a nucleophilic substitution reaction. Thus, its fundamental reaction type, nucleophilic addition to carbonyl groups.

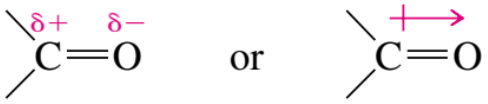
Structure and bonding:

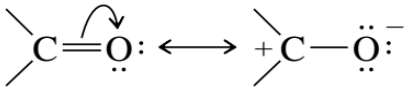
Two notable aspects of the carbonyl group are its geometry and its polarity. The carbonyl group and the atoms directly attached to it lie in the same plane. Formaldehyde, for example, is planar. The bond angles involving the carbonyl group of aldehydes and ketones are close to 120° and its shape trigonal planar.



Formaldehyde Acetaldehyde Acetone

The carbonyl group makes aldehydes and ketones rather polar, with molecular dipole moments that are substantially larger than those of comparable compounds that contain carbon–carbon double bonds. Bonding in formaldehyde can be described according to an sp^2 hybridization model analogous to that of ethylene. The oxygen affects the electron distribution in formaldehyde. The electron density in both the s and p components of the carbon–oxygen double bond is displaced toward oxygen. The carbonyl group is polarized so that carbon is partially positive and oxygen is partially negative. In resonance terms, electron delocalization in the carbonyl group is represented by contributions from two principal resonance structures, A, having one more covalent bond and avoiding the separation of positive and negative charges that characterizes B, better approximates the bonding in a carbonyl group.





A B

Alkyl substituents stabilize a carbonyl group in much the same way that they stabilize carbon–carbon double bonds and carbocations—by releasing electrons to sp^2-hybridized carbon. Thus, as their heats of combustion reveal, the ketone 2-butanone is more stable than its aldehyde isomer butanal.

Physical properties

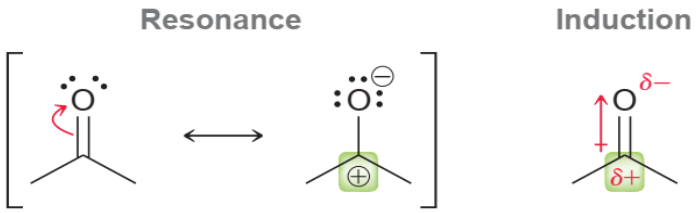
aldehydes and ketones have higher boiling points than alkenes because they

are more polar and the dipole–dipole attractive forces between molecules are stronger. But they have lower boiling points than alcohols because, unlike alcohols, two carbonyl groups can't form hydrogen bonds to each other. Aldehydes and ketones can form hydrogen bonds with the protons of OH groups. This makes them more soluble in water than alkenes, but less soluble than alcohols.

	$CH_3CH_2CH{=}CH_2$	$CH_3CH_2CH{=}O$	$CH_3CH_2CH_2OH$
	1-Butene	Propanal	1-Propanol
bp (1 atm)	−6°C	49°C	97°C
Solubility in water (g/100 mL)	Negligible	20	Miscible in all proportions

Chemical reaction

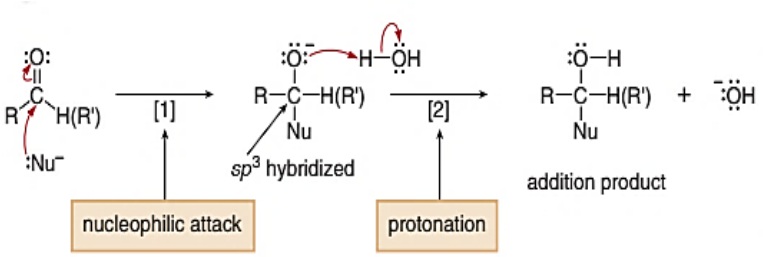
The electrophilicity of a carbonyl group derives from resonance effects as well as inductive effects. One of the resonance structures exhibits a positive charge on the carbon atom, indicating that the carbon atom is deficient in electron density (δ+). Inductive effects also render the carbon atom deficient in electron density. As a result, this carbon atom is particularly electrophilic and is susceptible to attack by a nucleophile.



The carbon atom is originally sp^2 hybridized with a trigonal planar geometry (a carbonyl carbon is uncrowded). After the attack, the carbon atom is sp^3 hybridized with a tetrahedral geometry. In recognition of this geometric change, the resulting alkoxide ion is often called a tetrahedral intermediate. The two R groups bonded to the ketone carbonyl group make it more crowded, so nucleophilic attack is more difficult. The two electron-donor R groups stabilize the partial charge on the carbonyl carbon of a ketone, making it more stable and less reactive.

Nucleophilic Addition to Aldehydes and Ketones

Aldehydes and ketones react with nucleophiles to form addition products by the two-step process shown in the following general mechanism, nucleophilic attack followed by protonation. The net result is that the π bond is broken, two new σ bonds are formed, and the elements of H and Nu- are added across the π bond.



- In Step [1], **the nucleophile (:Nu⁻) attacks the electrophilic carbonyl.** As the new bond to the nucleophile forms, the π bond is broken, moving an electron pair out on the oxygen atom. This forms an sp^3 hybridized intermediate.
- In Step [2], **protonation of the negatively charged oxygen atom by H_2O** (or another proton source) forms the addition product.

Aldehydes and ketones cannot undergo substitution because they have no leaving group bonded to the newly formed sp^3 hybridized carbon. Nucleophilic substitution with an aldehyde, for example, would form $H:^-$ (or R^- in ketones), an extremely strong base and therefore a very poor (and highly unlikely) leaving group. Thus, its deference from carbonyl compounds that have the leaving group which undergo Nu- addition.

The nucleophile can be either negatively charged ($:N\bar{u}$) or neutral (:Nu). If it's neutral, however, it usually carries a hydrogen atom that can subsequently be eliminated, :Nu-H. For example:

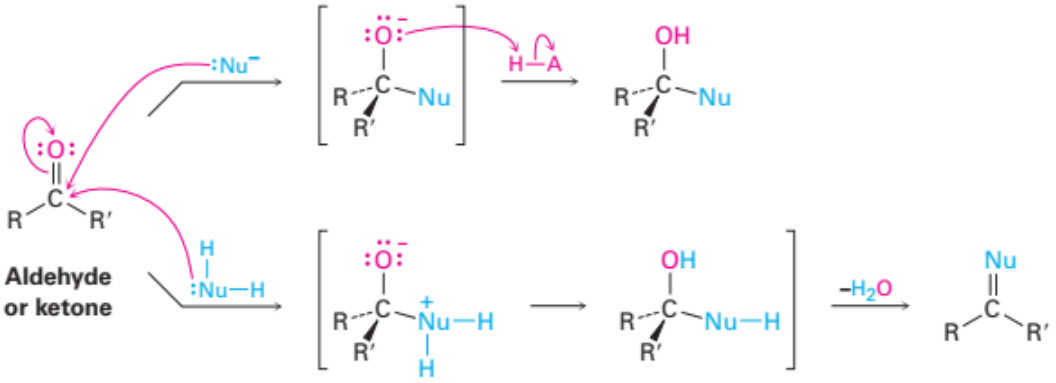
Some negatively charged nucleophiles

- $HO:^-$ (hydroxide ion)
- $H:^-$ (hydride ion)
- $R_3C:^-$ (a carbanion)
- $RO:^-$ (an alkoxide ion)
- $N{\equiv}C:^-$ (cyanide ion)

Some neutral nucleophiles

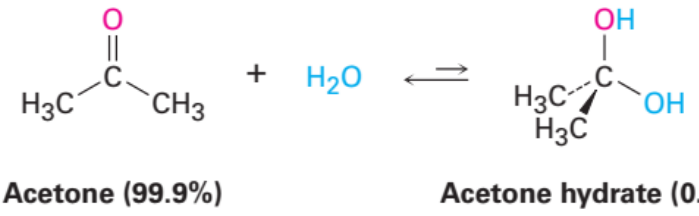
- HOH (water)
- ROH (an alcohol)
- $H_3N:$ (ammonia)
- RNH_2 (an amine)

Nucleophilic additions to aldehydes and ketones have two general variations. In one variation, the tetrahedral intermediate is protonated by water or acid to give an alcohol as the final product. In the second variation, the carbonyl oxygen atom is protonated and then eliminated as HO^- or H_2O to give a product with a C=Nu double bond.

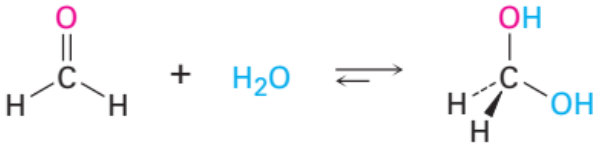


Addition of H_2O: Hydration

Aldehydes and ketones react with water to yield 1,1-diols, or geminal (gem) diols. The hydration reaction is reversible, and a gem diol can eliminate water to regenerate an aldehyde or ketone. The position of the equilibrium between a gem diol and an aldehyde or ketone depends on the structure of the carbonyl compound (what groups are attached to C=O and how they affect its steric and electronic environ-ment). Consider first the electronic effect of alkyl groups versus hydrogen atoms attached to C=O. The alkyl substituents stabilize C=O, making a ketone carbonyl more stable than an aldehyde carbonyl. As with all equilibria, factors that stabilize the reactants decrease the equilibrium constant. Thus, the extent of hydration decreases as the number of alkyl groups on the carbonyl increase. Thus, the equilibrium generally favors the carbonyl compound for steric reasons, but the gem diol is favored for a few simple aldehydes. So, the presence of ERG stabilizing the carbonyl group, while the EWG (or electronegative atoms) destabilize it by withdrawing electrons. A less stabilized carbonyl group is associated with a greater equilibrium constant for addition



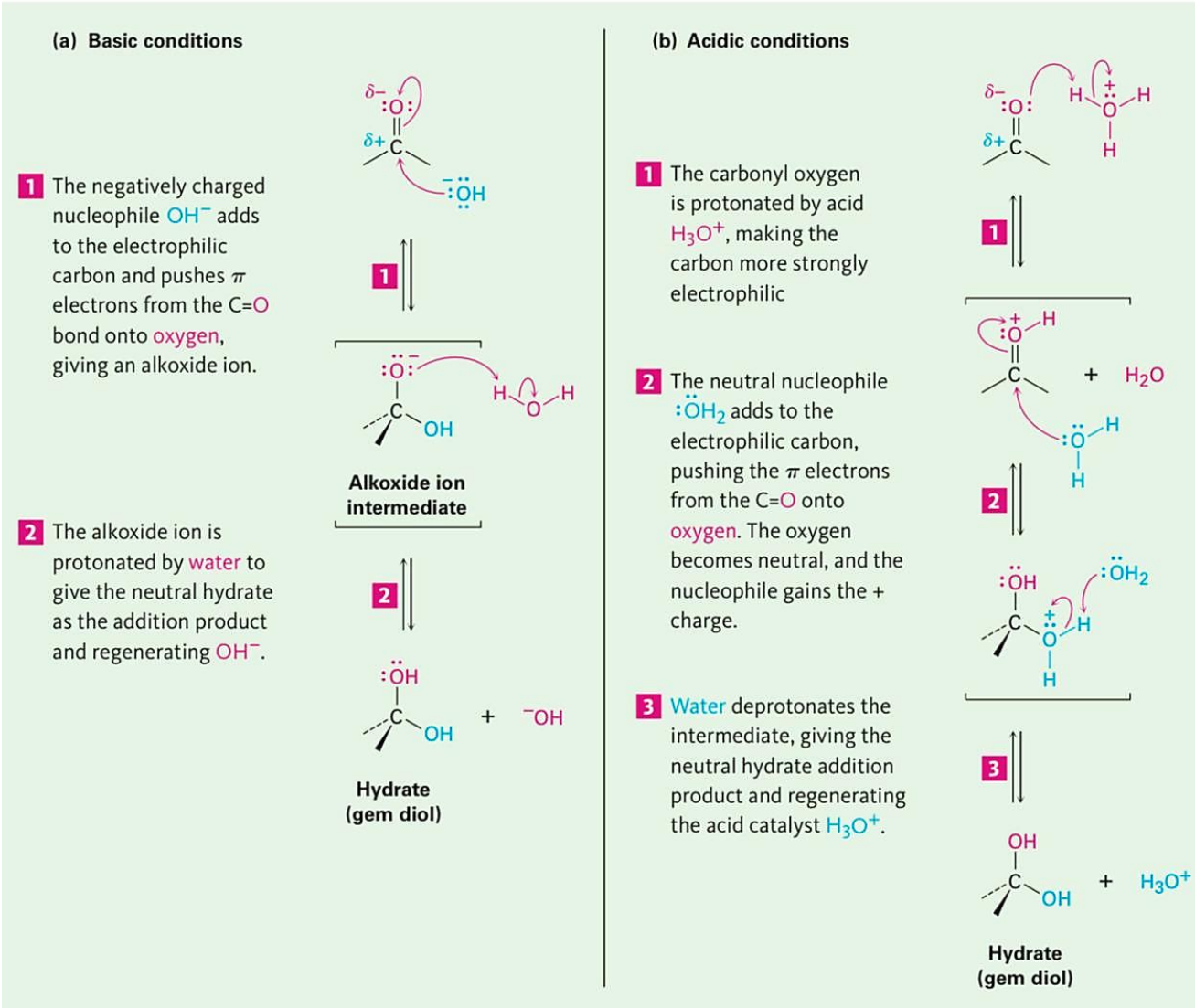
Acetone (99.9%) **Acetone hydrate (0.1%)**



Formaldehyde (0.1%) **Formaldehyde hydrate (99.9%)**

The nucleophilic addition of water to an aldehyde or ketone is slow under neutral conditions but is catalyzed by both base and acid. **Under basic conditions**, the nucleophile is negatively charged ($O\bar{H}$) and uses a pair of its electrons to form a bond to

the electrophilic carbon atom of the C=O group. **Under acidic conditions,** the carbonyl oxygen atom is first protonated by H_3O^+ to make the carbonyl group more strongly electrophilic. A neutral nucleophile, H_2O, then uses a pair of electrons to bond to the carbon atom of the C=O group.



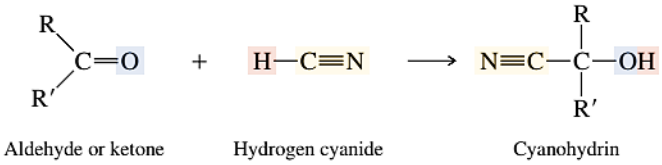
Note the key difference between the base-catalyzed and acid-catalyzed reactions. The base-catalyzed reaction takes place rapidly because water is converted into hydroxide ion, a much better nucleophile. The acid-catalyzed reaction takes place rapidly because the carbonyl compound is converted by protonation into a much better electrophile.

Addition of HCN: Cyanohydrin Formation

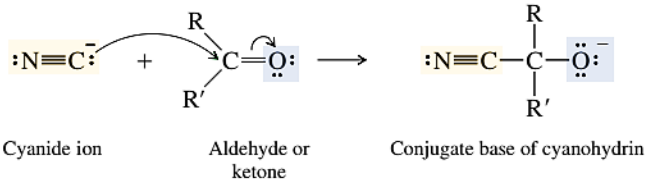
The product of nucleophilic addition of hydrogen cyanide (HCN) to an aldehyde or a unhindered ketone contains both a hydroxyl group and a cyano- group bonded to the

same carbon. Compounds of this type are called cyanohydrins RCH(OH)CN. This reaction adds one carbon to the aldehyde or ketone, forming a new (C-C)bond.

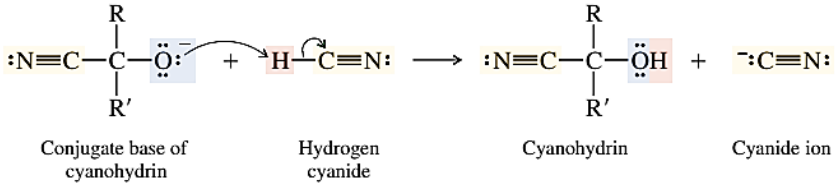
Cyanohydrin formation is reversible and base-catalyzed reaction . Reaction occurs slowly when pure HCN is used but rapidly when a small amount of base is added to generate the nucleophilic cyanide ion, $C\bar{N}$. Addition of $C\bar{N}$ takes place by a typical nucleophilic addition pathway, yielding a tetrahedral intermediate that is protonated by HCN to give cyanohydrin product plus regenerated $C\bar{N}$. The mechanism of reaction :



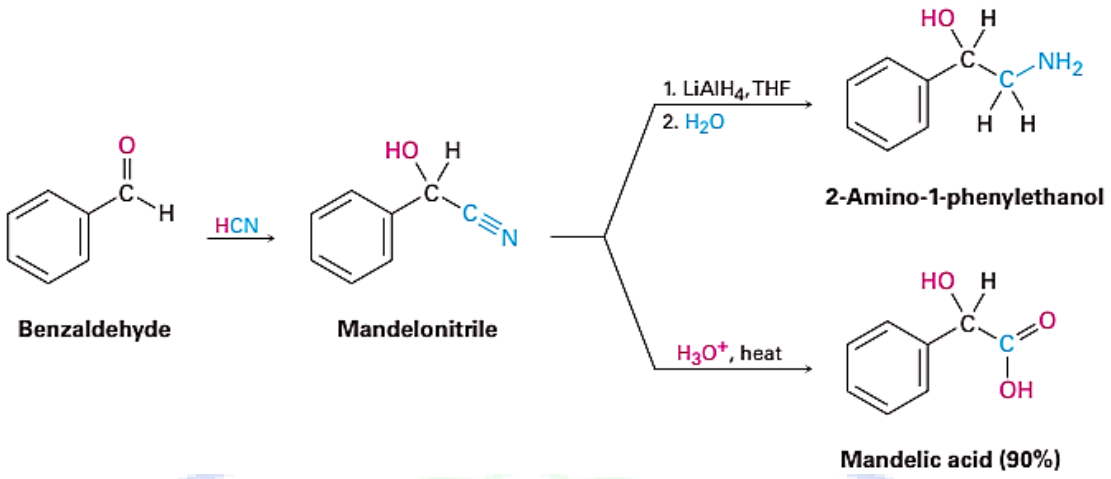
Step 1: Nucleophilic attack by the negatively charged carbon of cyanide ion at the carbonyl carbon of the aldehyde or ketone. Hydrogen cyanide itself is not very nucleophilic and does not ionize to form cyanide ion to a significant extent. Thus, a source of cyanide ion such as NaCN or KCN is used.



Step 2: The alkoxide ion formed in the first step abstracts a proton from hydrogen cyanide. This step yields the cyanohydrin product and regenerates cyanide ion.

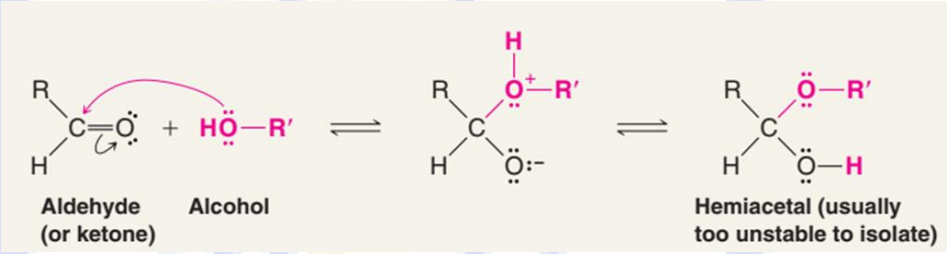


Cyanohydrin formation is somewhat unusual because it is one of the few examples of the addition of a protic acid (H-Y) to a carbonyl group. The protic acids such as H_2O, HBr, HCl, and H_2SO_4 don't normally yield carbonyl addition products because the equilibrium constants are unfavorable. With HCN, however, the equilibrium favors the cyano-hydrin adduct. The reaction is useful because of the further chemistry that can be carried out on the product. For example, a nitrile (R-CN) can be reduced with $LiAlH_4$ to yield a primary amine (RCH_2NH_2) and can be hydrolyzed by hot aqueous acid to yield a carboxylic acid. Thus, cyanohydrin formation provides a method for trans-forming an aldehyde or ketone into a different functional group.

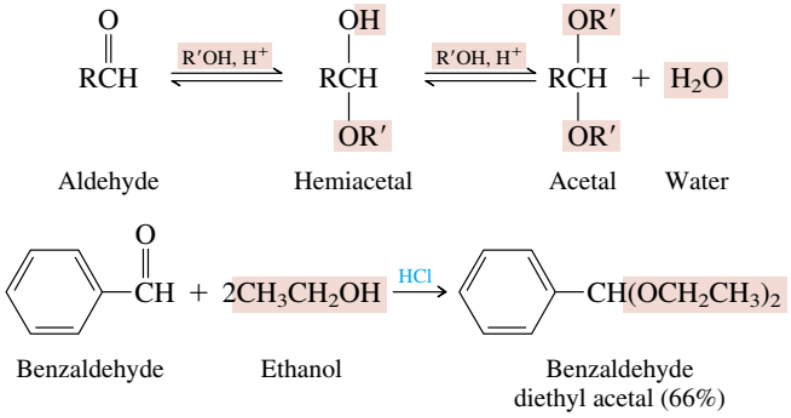


Addition of R-OH : Formation of Hemiacetals and Acetals

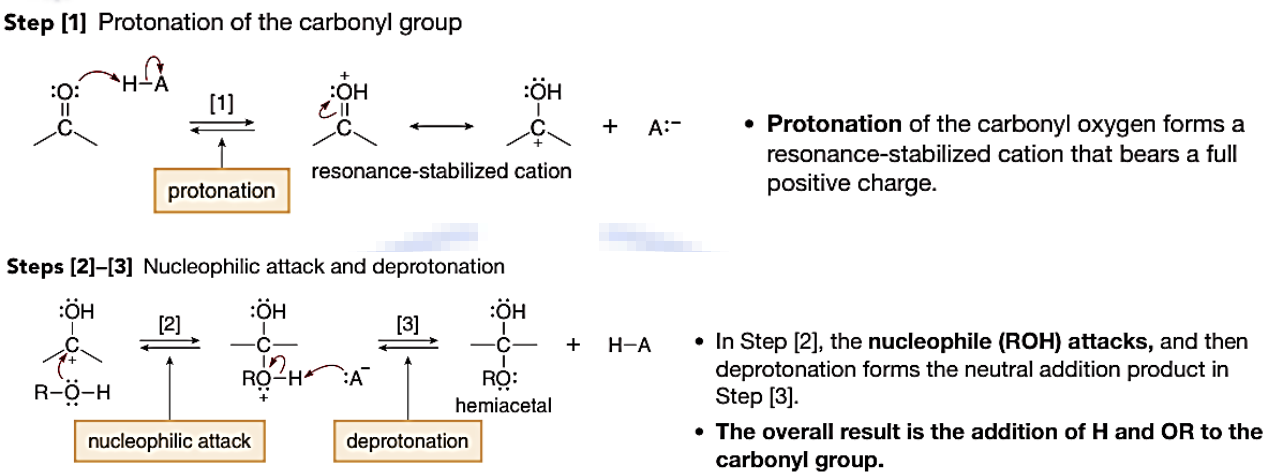
Aldehydes and ketones react with alcohols to form hemiacetals and acetals by an equilibrium reaction. The essential structural features of a hemiacetal are an OH and an OR group attached to the same carbon atom. The hemiacetal results by ($Nu:^-$) addition of an alcohol oxygen to the carbonyl carbon of an aldehyde or ketone. Is one of the most useful reactions of aldehydes and ketones involve transformation of the initial product of $Nu:^-$ addition to some other substance under the reaction conditions (e.g., acidic catalysis condition).



The product of reaction of one mole of the aldehyde with one mole alcohol give the hemiacetals. While, the corresponds reaction of one mole aldehyde with two moles of alcohol to give geminal diethers known as acetals.

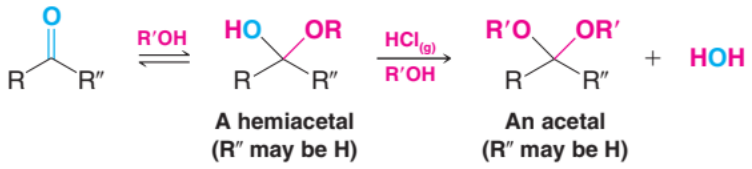


Mechanism of reaction

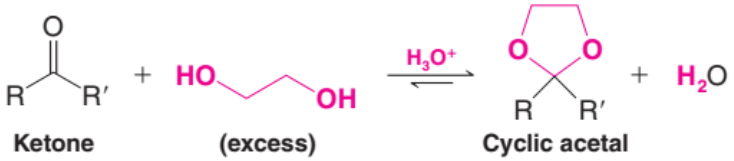


Aldehyde Hydrates, gem-Diols. Dissolving an aldehyde such as acetaldehyde in water causes the establishment of an equilibrium between the aldehyde and its hydrate. This hydrate is in actuality a 1,1-diol, called a geminal diol (or simply a gem-diol). The gem-diol results from a nucleophilic addition of water to the carbonyl group of the aldehyde.

An acetal has two OR groups attached to the same carbon atom. If we take an alcohol solution of an aldehyde (or ketone) and pass into it a small amount of gaseous HCl, a hemiacetal forms, and then the hemiacetal reacts with a second molar equivalent of the alcohol to produce an acetal.



Cyclic acetal formation is favored when a ketone or an aldehyde is treated with an excess of a 1,2-diol and a trace of acid

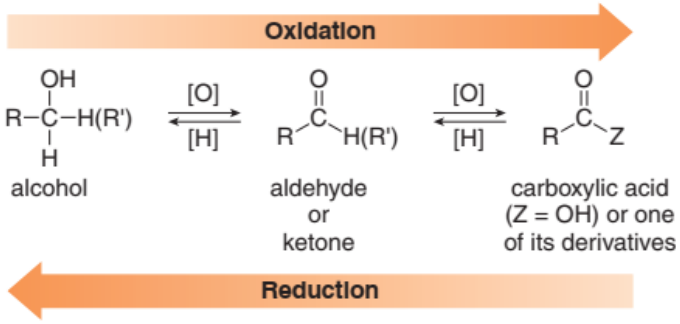


Oxidation And Reduction

Oxidation results in an increase in the number of C–Z bonds (usually C–O bonds) or a decrease in the number of C–H bonds. Reduction results in a decrease in the number of C–Z bonds (usually C–O bonds) or an increase in the number of C–H bonds.

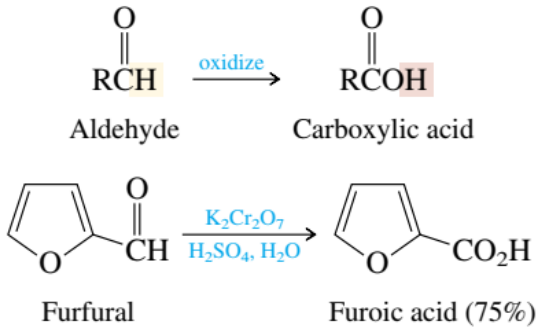
Oxidation Of Aldehydes and ketones:

Carbonyl compounds are either reactants or products in many of these reactions, as illustrated in the accompanying diagram. For example, because aldehydes fall in the middle of this scheme, they can be both oxidized and reduced. Carboxylic acids and their derivatives (RCOZ, where Z=O), on the other hand, are already highly oxidized, so their only useful reaction is reduction.



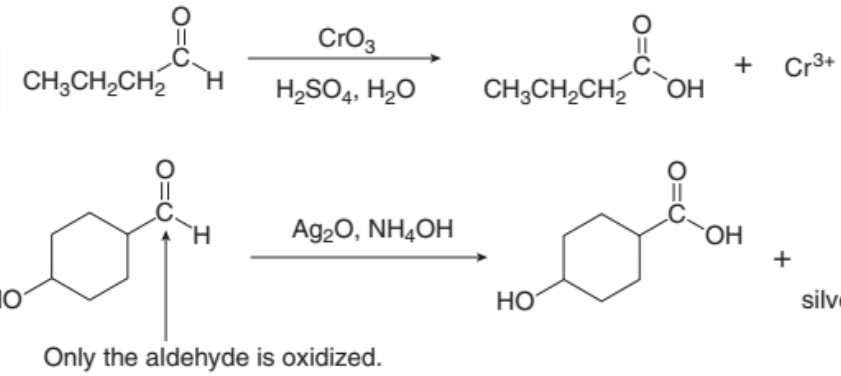
Oxidation

Aldehydes are readily oxidized to carboxylic acids by a number of reagents, including those based on Cr(VI) in aqueous media.



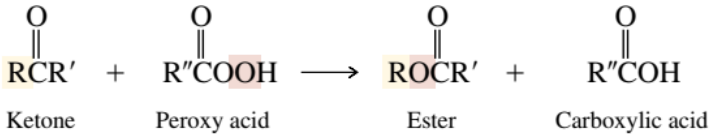
A variety of oxidizing agents can be used, including CrO_3, $Na_2Cr_2O_7$, $K_2Cr_2O_7$, and $KMnO_4$. Cr^{6+} reagents are also used to oxidize 1° and 2° alcohols. Aldehydes are oxidized selectively in the presence of other functional groups using silver(I) oxide in aqueous ammonium hydroxide (Ag_2O in NH_4OH). This is called Tollens reagent. Oxidation with Tollens reagent provides a distinct color change, because the Ag+ reagent is reduced to silver metal (Ag), which precipitates out of solution.

Oxidation of RCHO

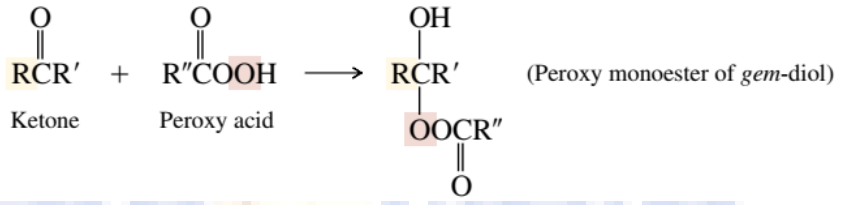


Baeyer–Villiger Oxidation Of Ketones

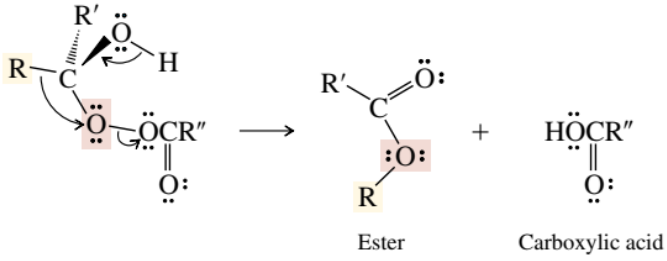
The reaction of ketones with peroxy acids is both novel and synthetically useful. An oxygen from the peroxy acid is inserted between the carbonyl group and one of the attached carbons of the ketone to give an ester. Reactions of this type were first described by Adolf von Baeyer and Victor Villiger in 1899 and are known as Baeyer–Villiger oxidations.



Step 1: The peroxy acid adds to the carbonyl group of the ketone. This step is a nucleophilic addition analogous to *gem*-diol and hemiacetal formation.

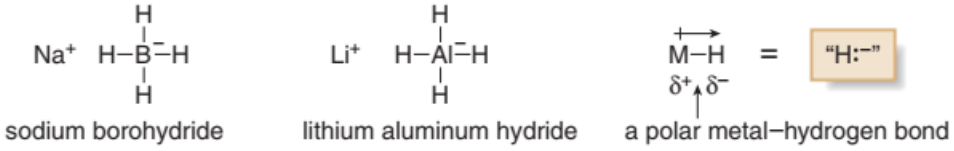


Step 2: The intermediate from step 1 undergoes rearrangement. Cleavage of the weak O—O bond of the peroxy ester is assisted by migration of one of the substituents from the carbonyl group to oxygen. The group R migrates with its pair of electrons in much the same way as alkyl groups migrate in carbocation rearrangements.



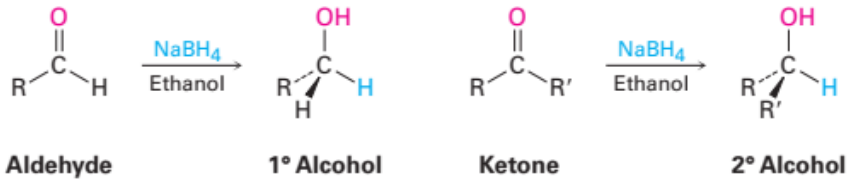
Reduction

The most useful reagents for reducing aldehydes and ketones are the metal hydride reagents. The two most common metal hydride reagents are sodium borohydride ($NaBH_4$) and lithium aluminum hydride ($LiAlH_4$). These reagents contain a polar metal–hydrogen bond that serves as a source of the nucleophile hydride, H:–. $LiAlH_4$ is a stronger reducing agent than $NaBH_4$, because the Al–H bond is more polar than the B–H bond.



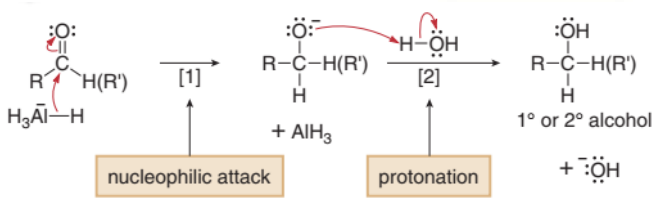
Reduction with Metal Hydride Reagents:

Treating an aldehyde or a ketone with $NaBH_4$ or $LiAlH_4$, followed by water or some other proton source, affords an alcohol. This is an addition reaction because the elements of H_2 are added across the π bond, but it is also a reduction because the product alcohol has fewer C–O bonds than the starting carbonyl compound.



$NaBH_4$ selectively reduces aldehydes and ketones in the presence of most other functional groups. Reductions with $NaBH_4$ are typically carried out in CH_3OH as solvent. $LiAlH_4$ reduces aldehydes and ketones and many other functional groups as well.

Carbonyl reduction occurs by a typical nucleophilic addition mechanism under basic conditions. $LiAlH_4$ and $NaBH_4$ act as if they were donors of hydride ion nucleophile, $:H^-$, and the initially formed alkoxide ion intermediate is then protonated by addition of aqueous acid. The reaction is effectively irreversible because the reverse process would require expulsion of a very poor leaving group.

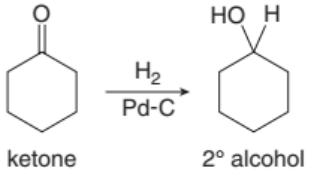


- In Step [1], **the nucleophile (AlH_4^-) donates $H:^-$ to the carbonyl group,** cleaving the π bond, and moving an electron pair onto oxygen. This forms a new C – H bond.
- In Step [2], **the alkoxide is protonated by H_2O (or CH_3OH)** to form the alcohol reduction product. This acid–base reaction forms a new O – H bond.

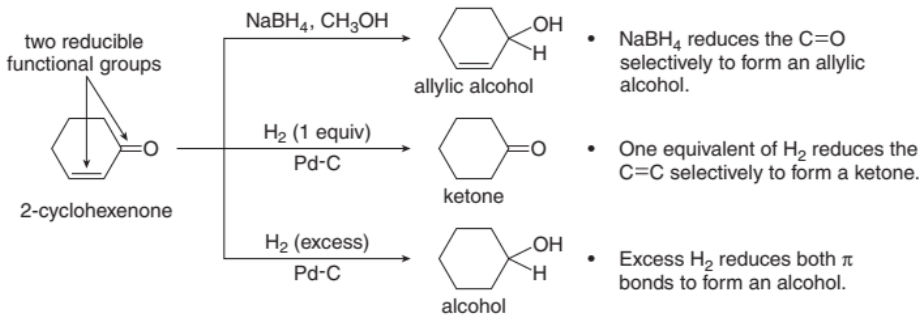
Catalytic Hydrogenation of Aldehydes and Ketones:

Catalytic hydrogenation also reduces aldehydes and ketones to 1° and 2° alcohols,

respectively, using H_2 and Pd-C (or another metal catalyst). H_2 adds to the C=O in much the same way that it adds to the C=C of an alkene. The metal catalyst (Pd-C) provides a surface that binds the carbonyl starting material and H_2, and two H atoms are sequentially transferred with cleavage of the π bond.



When a compound contains both a carbonyl group and a carbon–carbon double bond, selective reduction of one functional group can be achieved by proper choice of reagent. A C=C is reduced faster than a C=O with H2 (Pd-C). A C=O is readily reduced with $NaBH_4$ and $LiAlH_4$, but a C=C is inert. a compound that contains both a carbon–carbon double bond and a carbonyl group, can be reduced to three different compounds an allylic alcohol, a carbonyl compound, or an alcohol depending on the reagent.



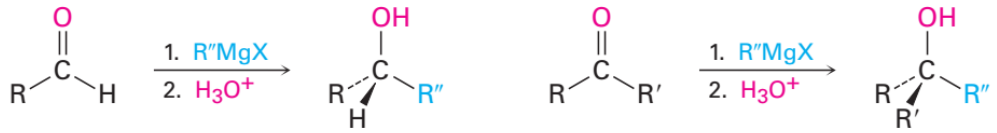
Reaction with organometallic:

Organometallic reagents are also strong nucleophiles that react with electrophilic carbon atoms to form new carbon–carbon bonds. These reactions are very valuable in forming the carbon skeletons of complex organic molecules.

Reaction of R – M with aldehydes and ketones to afford alcohols: Aldehydes and ketones are converted to 1°, 2°, or 3° alcohols with R"-Li or R"-Mg-X. Treatment of an aldehyde or ketone with either an organolithium or Grignard reagent followed by water forms an alcohol with a new carbon–carbon bond. This reaction is an addition reaction because the elements of R" and H are added across the π bond.

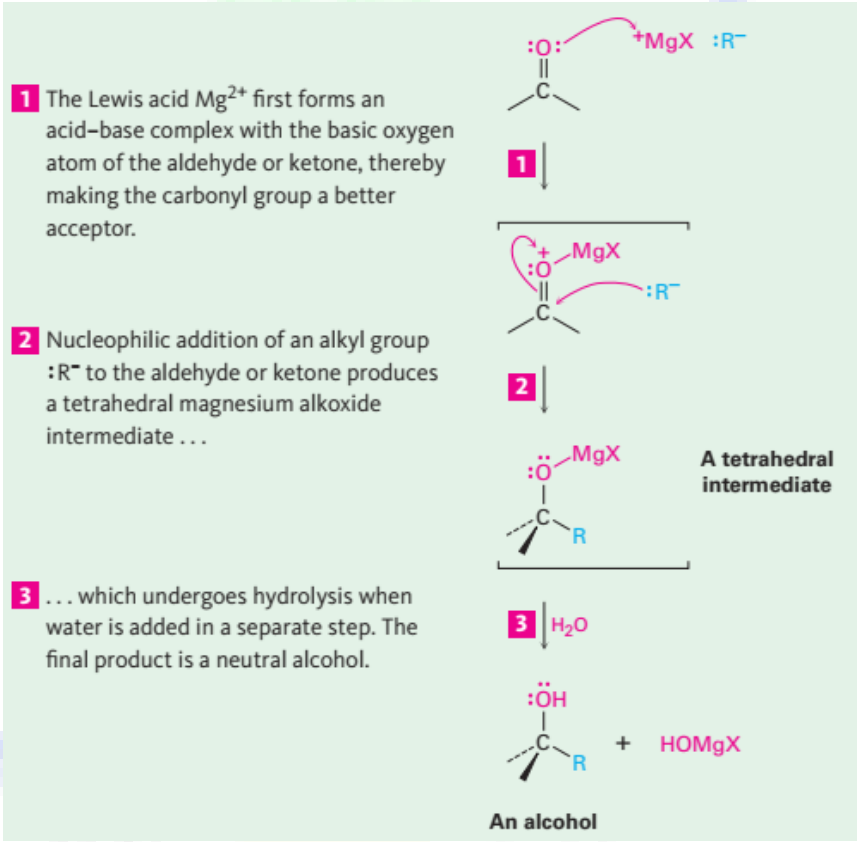
Addition of Grignard Reagents, R-Mg-X:

Just as aldehydes and ketones undergo nucleophilic addition with hydride ion to give alcohols, they undergo a similar addition with Grignard reagent nucleophiles, ($R:^{-}\ ^{+}Mg$-X). Addition of R"MgX to formaldehyde (CH_2=O) forms a 1° alcohol. Addition to all other aldehydes forms a 2° alcohol. Addition to ketones forms a 3° alcohol.



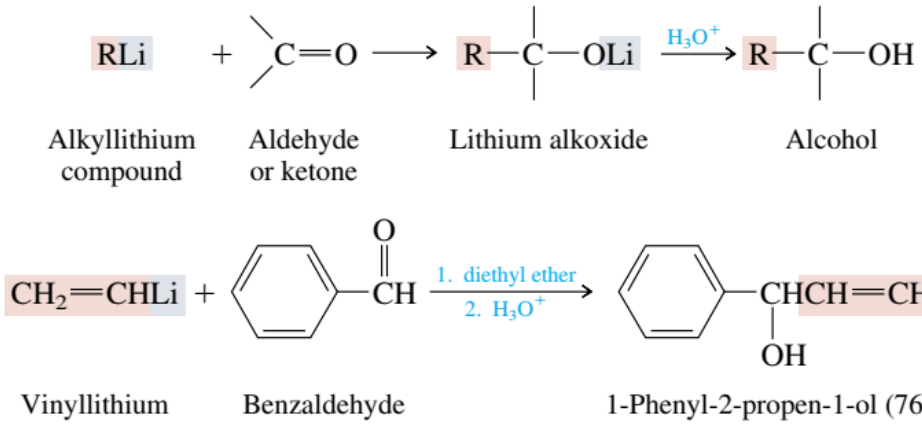
Aldehyde **2° Alcohol** **Ketone** **3° Alcohol**

Grignard reaction begins with an acid–base complexation of Mg^{2+} to the carbonyl oxygen atom of the aldehyde or ketone, thereby making the carbonyl group a better electrophile. Nucleophilic addition of $R:^-$ then produces a tetrahedral magnesium alkoxide intermediate, and protonation by addition of water or dilute aqueous acid in a separate step yields the neutral alcohol. Like reduction, Grignard additions are effectively irreversible because a carbanion is too poor a leaving group to be expelled in a reversal step.

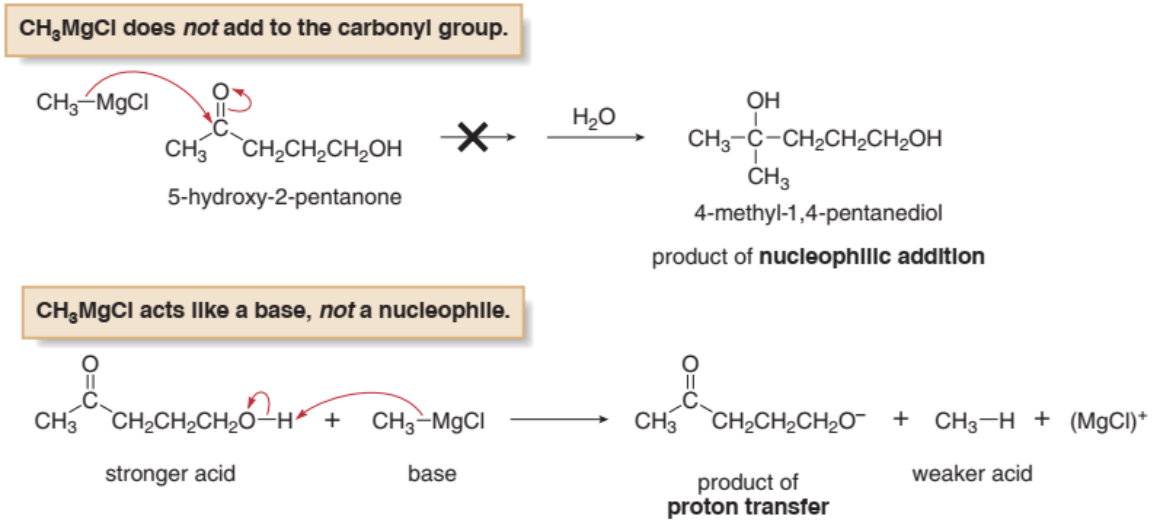


Addition Of Organolithium R"-Li:

Organolithium reagents R"-Li react with carbonyl groups in the same way that Grignard reagents do. In their reactions with aldehydes and ketones, organolithium reagents are somewhat more reactive than Grignard reagents.



Because organometallic reagents are strong bases that rapidly react with H_2O, the addition of the new alkyl group must be carried out under anhydrous conditions to prevent traces of water from reacting with the reagent, thus reducing the yield of the desired alcohol. Water is added after the addition to protonate the alkoxide. There are some limitation in R"-Li and R"-Mg-X, Carbonyl compounds that also contain N–H or O–H bonds undergo an acid–base reaction with organometallic reagents, not nucleophilic addition. because Grignard reagents are strong bases and proton transfer reactions are fast, CH_3MgCl removes the O–H proton before nucleophilic addition takes place.

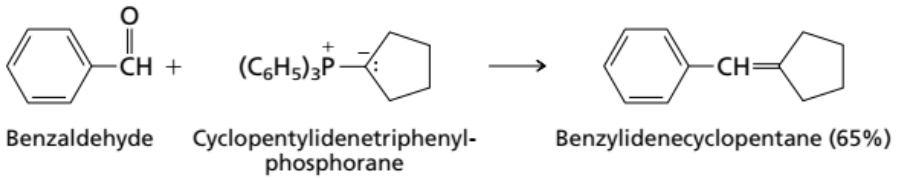


The Wittig Reaction

Aldehydes and ketones react with phosphorus ylides (Witting reagent) to yield alkenes and triphenyl-phosphine oxide (a by-product). This reaction is known as the Wittig reaction. The Wittig reaction uses a carbon nucleophile, the Wittig reagent, to form alkenes. When a carbonyl compound is treated with a Wittig reagent, the carbonyl oxygen atom is replaced by the negatively charged alkyl group bonded to the phosphorus—that is, the C = O is converted to a C = C. Ylides are neutral molecules that

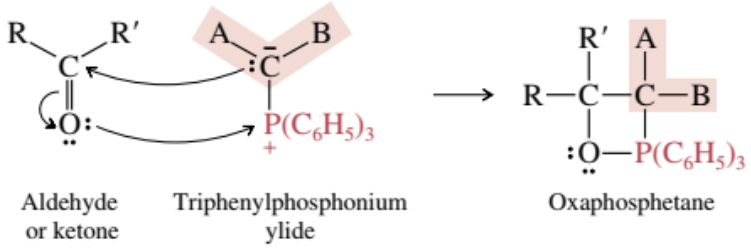
have two oppositely charged atoms, each with an octet of electrons, directly bonded to each other. In an ylide such as , phosphorus has eight electrons and is positively charged; its attached carbon has eight electrons and is negatively charged. The ylide required for the reaction is a molecule with no net charge but which has a negative carbon atom adjacent to a positive heteroatom, which in the Wittig reaction is a phosphorus atom. Phosphorus ylides are also called phosphoranes. Wittig reactions may be carried out in a number of different solvents; normally tetrahydrofuran (THF) or dimethyl sulfoxide (DMSO) is used.

The most attractive feature of the Wittig reaction is its regiospecificity. The location of the double bond is never in doubt. The double bond connects the carbon of the original C=O group of the aldehyde or ketone and the negatively charged carbon of the ylide.

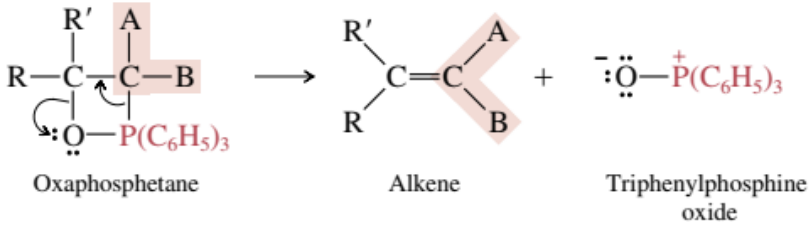


The mechanism of reaction

Step 1: The ylide and the aldehyde or ketone combine to form an oxaphosphetane.



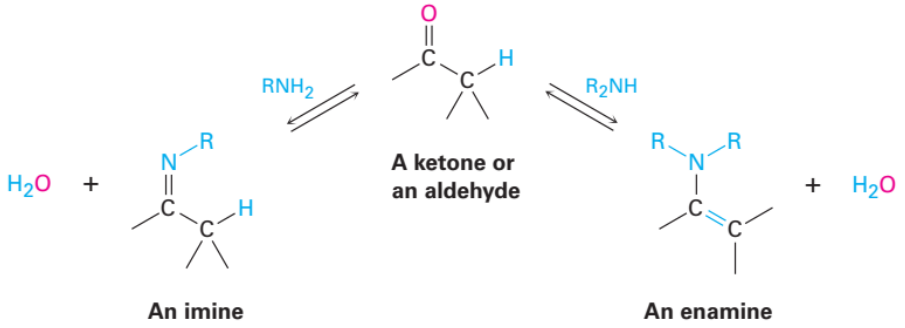
Step 2: The oxaphosphetane dissociates to an alkene and triphenylphosphine oxide.



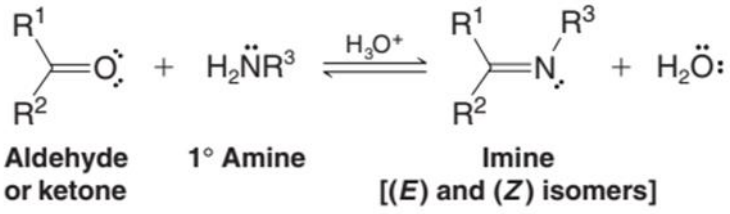
Addition of Amines : Imine and Enamine Formation:

Primary amines, RNH_2, add to aldehydes and ketones to yield imines, R2CPNR. Secondary amines, R_2NH, add similarly to yield enamines, $R_2N\text{-}CR{=}CR_2$ (ene + amine = unsaturated amine).

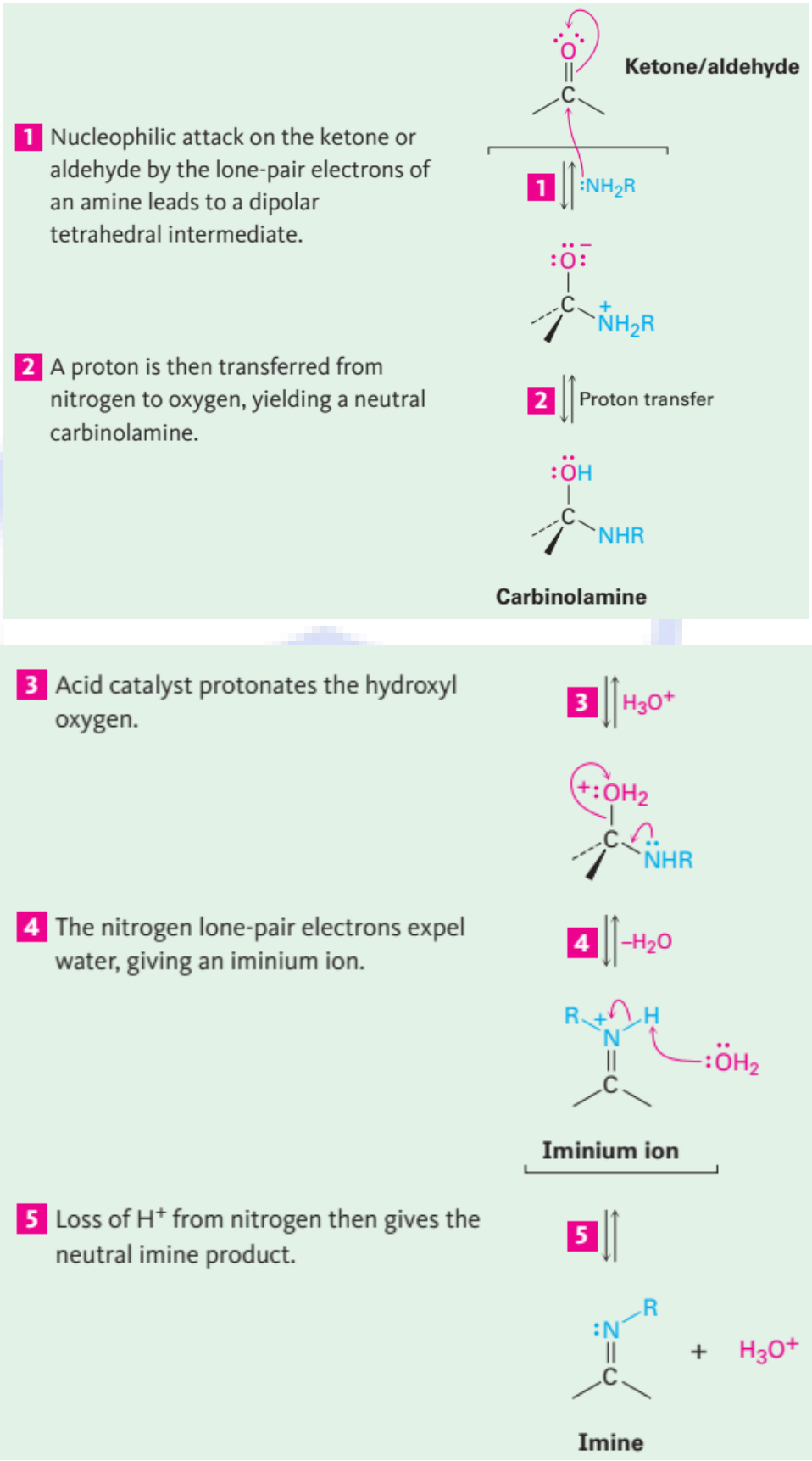
Two-stage reaction that begins with nucleophilic addition to aldehydes and ketones is their reaction with primary amines, compounds of the type RNH_2 or $ArNH_2$. In the first stage of the reaction the amine adds to the carbonyl group to give a species known as a carbinolamine. Once formed, the carbinolamine undergoes dehydration to yield the product of the reaction, an N-alkyl- or N-aryl-substituted imine.



A general equation for the formation of an imine from a primary amine and an aldehyde or ketone is shown here. Imine formation is acid catalyzed, and the product can form as a mixture of (E) and (Z) isomers. Imine formation generally takes place fastest between pH 4 and 5 and is slow at very low or very high pH.

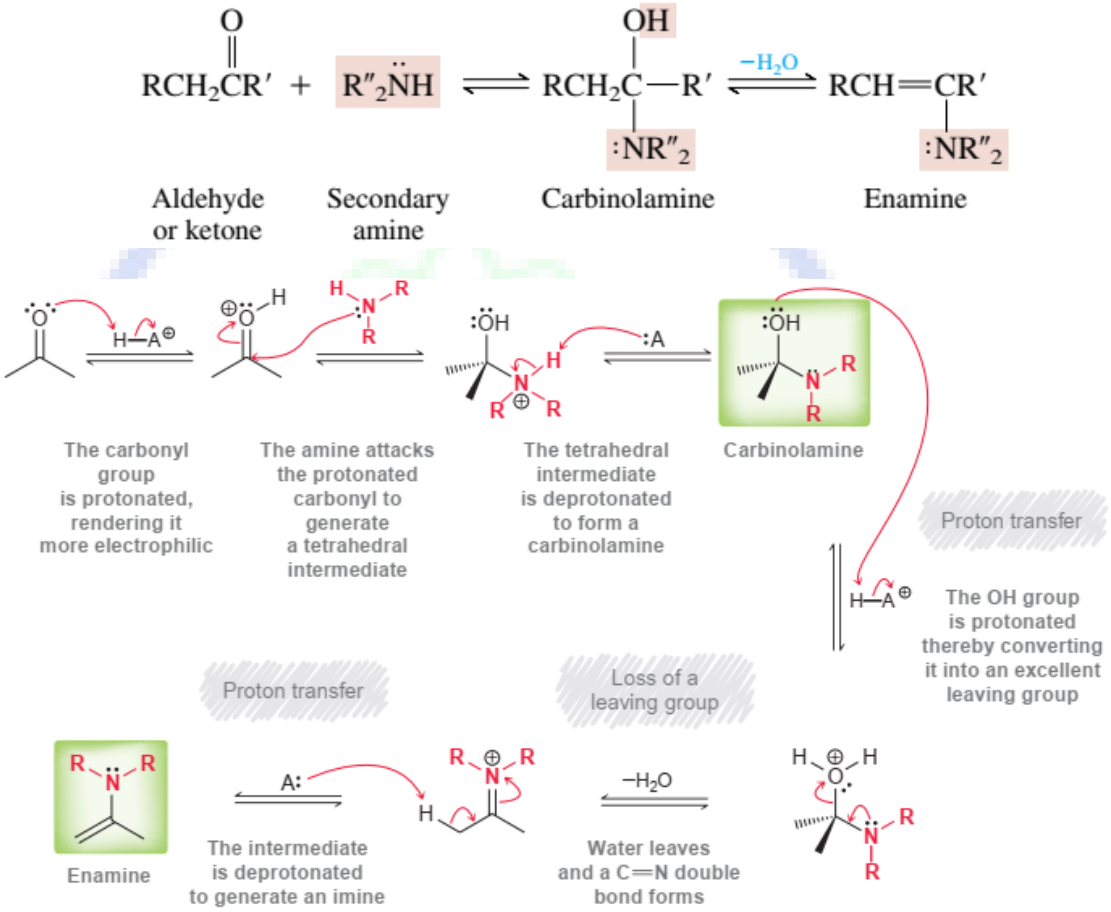


The mechanism of reaction with primary amine



Imines are particularly common as intermediates in many biological pathways, where they are often called Schiff bases.

Secondary amines are compounds of the type R_2NH. They add to aldehydes and ketones to form carbinolamines, but their carbinolamine intermediates can dehydrate to a stable product only in the direction that leads to a carbon–carbon double bond. The product of this dehydration is an alkenyl-substituted amine, or enamine



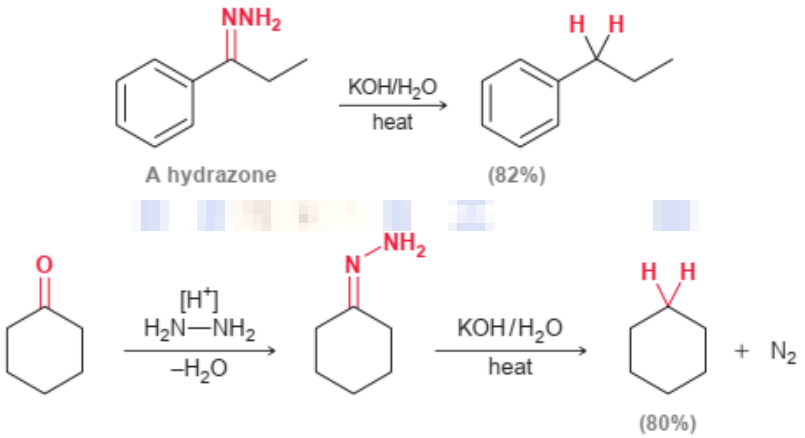
This mechanism of enamine formation is identical to the mechanism of imine formation except for the last step. The difference in the iminium ions explains the different outcomes for the two reactions. During imine formation, the nitrogen atom of the iminium ion possesses a proton that can be removed as the final step of the mechanism. In contrast, during enamine formation, the nitrogen atom of the iminium ion does not possess a proton. As a result, elimination from the adjacent carbon is necessary in order to yield a neutral species.

A number of compounds of the general type H_2NZ react with aldehydes and ketones in a manner analogous to that of primary amines. The carbonyl group (C=O) is converted to C=NZ, and a molecule of water is formed. The mechanism by which each proceeds is similar to the nucleophilic addition–elimination mechanism described for the reaction of primary amines with aldehydes and ketones.

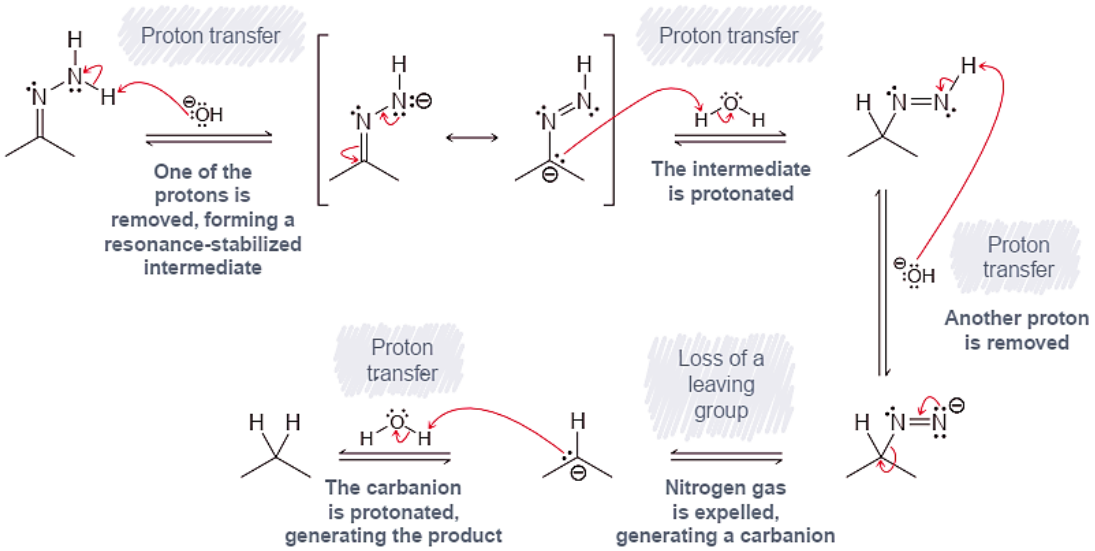
Reagent (H_2NZ)	Name of reagent	Type of product	Example
H_2NOH	Hydroxylamine	Oxime	$CH_3(CH_2)_5CH=O$ → $CH_3(CH_2)_5CH=NOH$ (Heptanal → Heptanal oxime (81–93%))
$H_2NNHC_6H_5$*	Phenylhydrazine	Phenylhydrazone	$CCH_3=O$ → $CCH_3=NNHC_6H_5$ (Acetophenone → Acetophenone phenylhydrazone (87–91%))
$H_2NNHCNH_2$	Semicarbazide	Semicarbazone	$CH_3C(CH_2)_9CH_3=O$ → $CH_3C(CH_2)_9CH_3=NNHCNH_2$ (2-Dodecanone → 2-Dodecanone semicarbazone (93%))

Nucleophilic Addition of Hydrazine: The Wolff–Kishner Reaction

ketones can be converted into hydrazones. The reaction involves the treatment of an aldehyde or ketone with hydrazine, H_2NNH_2, in the presence of KOH. This transformation has practical utility, because hydrazones are readily reduced under strongly basic conditions. This transformation is called the Wolff-Kishner reduction. Its provides a two-step procedure for reducing a ketone to an alkane



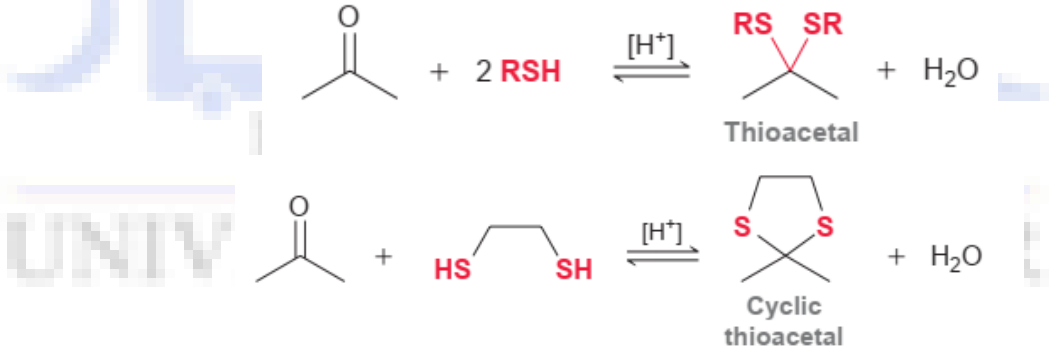
The mechanism of reaction



the Wolff–Kishner reaction involves formation of a hydrazone intermediate, $R_2C{=}NNH_2$, followed by base-catalyzed double-bond migration, loss of N_2 gas to give a carbanion, and protonation to give the alkane product. Note that the Wolff–Kishner reduction accomplishes the same overall transformation as the catalytic hydrogenation of an acylbenzene to yield an alkylbenzene. The Wolff–Kishner reduction is more general and more useful than catalytic hydrogenation, however, because it works well with both alkyl and aryl ketones.

Sulfur Addition Thioacetal Formation

In acidic conditions, an aldehyde or ketone will react with two equivalents of a thiol to form a thioacetal. The mechanism of this transformation is directly analogous to acetal formation, with sulfur atoms taking the place of oxygen atoms. If a compound with two SH groups is used, a cyclic thioacetal is formed:



Spectroscopic Analysis Of Aldehydes And Ketones

Infrared: Carbonyl groups are among the easiest functional groups to detect by infrared spectroscopy. The C=O stretching vibration of aldehydes and ketones gives rise to strong absorption in the region 1710–1750 cm^{-1} . In addition to a peak for C=O stretching, the CH=O group of an aldehyde exhibits two weak bands for C±H stretching

near 2720 and 2820 cm^{-1}.

^{1}H NMR: Aldehydes are readily identified by the presence of a signal for the hydrogen of CH=O at δ 9–10 ppm. This is a region where very few other protons ever appear.

^{13}C NMR: The signal for the carbon of C=O in aldehydes and ketones appears at very low field, some δ 190–220 ppm downfield from tetramethylsilane. For example 3-heptanone, in which separate signals appear for each of the seven carbons. The six sp3-hybridized carbons appear in the range δ 8–42 ppm, while the carbon of the C=O group is at δ 210 ppm. Note, too, that the intensity of the peak for the C=O carbon is much less than all the others, even though each peak corresponds to a single carbon.

Mass Spectrometry: Aldehydes and ketones typically give a prominent molecular ion peak in their mass spectra. Aldehydes also exhibit an M-1 peak. A major fragmentation pathway for both aldehydes and ketones leads to formation of acyl cations (acylium ions) by cleavage of an alkyl group from the carbonyl. The most intense peak in the mass spectrum of diethyl ketone, for example, is m/z 57, corresponding to loss of ethyl radical from the molecular ion.