1 Structure and Nomenclature

- C=O Bond has Larger dipole moment than C–O bond because the pi-electrons are more polarizable

**IUPAC nomenclature** uses numbering system

Aldehydes - Suffix -al, Ketones - Suffix -one

*priority: aldehyde > ketone > alcohol > alkene > alkyne > halide* (higher priority with higher oxidation)

- Example above, no number for simple aldehyde, C=O must always be 1

- Example above, number to give carbonyl smallest number

- Example above, ketone takes priority over alcohol, when -OH is a substituent it is a "hydroxy" substituent

- Example above, multiple suffixes for multiple functional groups

2 Synthesis of Aldehydes and Ketones: Review of "Old" Methods
3 New Syntheses of Aldehydes and Ketones: Acid Catalyzed Mechanisms

3.1 Using 1,3-Dithiane

New reagent: 1,3-dithiane, can be deprotonated, but only using a very strong base

Recall: Alkyl lithium reagents (seen before), are VERY strong Bronsted bases, example, butyl lithium (n-BuLi)

\[ n\text{-BuLi} = \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Li} \]

Increasing base strength:

- \( \text{H}^- \)
- \( \text{N}^- \)
- \( \text{Bu}^-\text{Li} \)

\( \delta^- \rightarrow \delta^+ \)

- Here the "n-" means straight chain butyl lithium, to distinguish from, for example, t-Bu-Li (tertiary butyl lithium)
- Alkyl lithium reagents in general (R-Li, e.g. MeLi, BuLi, PhLi) are very strong nucleophiles AND very strong Bronsted bases, they can deprotonate suitable carbon atoms, as shown below for dithiane

Recall: How does this last step with the \( \text{H}_3\text{O}^+ \) work??

- The reaction is hydrolysis, breaking bonds (lys), two C-S bonds in this case, with water (hydro)

Recall

Aldehydes and Ketones: Page 2
But

- protonation of oxygen allows bond breaking, makes a good leaving group
- think about what bond break and what bonds are made in the following reaction.....

• need to break two C-S bonds (protonate S to make good leaving group) make two C-O bonds (1 sigma 1 pi)
• O comes from water, AND, we are in acid, so protonate first!!

Examples

\[
\begin{align*}
\text{S-S} & \xrightarrow{1. \text{BuLi}} \text{CO} \xrightarrow{2. \text{PhCH}_2\text{Br}} \text{Me-C}=\text{CH}_2 \xrightarrow{3. \text{H}_3\text{O}^+} \text{Me} \text{C}-\text{CH}_2\text{Ph} \\
\text{S-S} & \xrightarrow{1. \text{BuLi}} \text{Me-S} \xrightarrow{2. \text{MeBr}} \text{Me-S} \xrightarrow{1. \text{BuLi}} \text{Me-S} \xrightarrow{2. \text{PhCH}_2\text{Br}} \text{Me} \text{C}-\text{CH}_2\text{Ph} \xrightarrow{3. \text{H}_3\text{O}^+} \text{Me} \text{C}-\text{CH}_2\text{Ph}
\end{align*}
\]
3.2 Grignard Addition to a Nitrile

The reaction: an example

Recall: addition of a Grignard to a C=O bond

Mechanism: part 1, formation of an imine (basically same as Grignard addition to a C=O bond)

Mechanism: part 2, hydrolysis of the imine (basically the same as hydrolysis of dithiane etc.)

*NOTE: protonation of the ammonia (NH₃) in the acidic medium, the ammonium cation will be formed*
3.3 Hydrolysis Reactions

- Not technically a synthesis for C=O bonds, but a common phenomenon that we need to be able to recognize
- **Hydrolysis**: bond breaking (-lysis) using water, i.e.

\[
\text{break these two C-Z bonds} \quad \xrightarrow{H_3O^+} \quad \text{make these two C-O bonds}
\]

- where the Z atoms can be nitrogen, oxygen, sulfur etc.
- we have now seen TWO of these reactions
- in the imine, the two bonds are both to the same Z atom in this case (N), and the ammonia that is initially produced will actually protonate to form the ammonium cation
- we can extrapolate to other examples, some of which we will discuss in more detail later in this section

3.4 Oxidative Cleavage of Alkenes: Ozonolysis

**New Reagent**

\[
\text{ozone} = O_3 = \left[ \begin{array}{c}
\text{O} \\
\text{O} \\
\text{O}
\end{array} \right]
\]

- has separated charges and more non-bonding electrons, much more reactive than molecular oxygen

**Mechanism**

- don't need to know!!
• the ozonide is the primary product, but it is never isolated
• in the presence of Me$_2$S it is reduced to (in this case) an aldehyde and ketone
• if Me$_2$S is replaced by the oxidizing hydrogen peroxide, different products result.......

Examples

4 Reactions of Aldehydes and Ketones

4.1 Strong and Weak Nucleophiles
• In MOST reactions, aldehydes/ketones act as the Lewis Acid/Electrophile
• We can UNDERSTAND the reaction principles for aldehydes/ketones based on what we already know about the chemistry of EPOXIDES, which ALSO act as Lewis Acids/Electrophiles
• STRONG Lewis Bases/Nucleophiles react DIRECTLY with epoxides
• WEAK Lewis Bases/Nucleophiles require PROTONATION OF THE EPOXIDE

• The SAME APPLIES for reactions of aldehyde/ketones
• STRONG Lewis Bases/Nucleophiles react DIRECTLY with aldehydes/ketones

• We have ALREADY SEEN many of these reactions, Grignards, acetylides, lithium aluminum hydride, etc.
• Strong Nucleophiles react IRREVERSIBLY!
**Weak Lewis Bases/Nucleophiles** require protonation of the aldehyde/ketone

- PROTONATION of aldehydes/ketones makes them STRONGER Lewis Acids/Electrophiles that can then react with weak nucleophiles such as water, alcohols etc, just like EPOXIDES
- WEAK Nucleophiles ALSO tend to react REVERSIBLY (see further below…)

**4.3 Relative Reactivities of Aldehydes and Ketones**

- chemistry dominated by nucleophilic/LB attack at the carbon of the C=O bond
- relative reactivity thus determined by the ability of substituents to stabilize the C towards nucleophilic attack
- weak electron donating groups, such as alkyl, stabilize the C=O carbon on a ketone compared to an aldehyde, the C=O is a simple π-system

- Aldehydes have intrinsically higher energy (more reactive) electrons, as can be seen in the heats of formation of an isomeric aldehyde and ketone

$$3 \text{ C} + 3 \text{ H}_2 + \frac{1}{2} \text{ O}_2 \rightarrow \overset{\Delta H_f}{\text{CH}_3-\text{CH}_2=\text{O}^- \text{H}^+}$$

**ΔHₚ, kcal mol⁻¹**

- higher energy, less stable  
  -45.5

$$3 \text{ C} + 3 \text{ H}_2 + \frac{1}{2} \text{ O}_2 \rightarrow \overset{-51.9}{\text{H}_3\text{C}^-\text{C}_3\text{H}_3}$$

- lower energy, more stable

- the total energy of the electrons is lower when the atoms assemble themselves in the form of a ketone rather than the aldehyde isomer
- that ketones are more stabilized can be seen in the ketones are stabilized by resonance more than aldehydes and have slightly stronger bonding overall.
Comparing Donating Groups on Different Pi-Systems

- Donating groups on a benzene ring **activate** the ring, make it more reactive, because the benzene ring is the Lewis Base in most of its reactions.
- Weak donating groups on a C=O group (which is a simple pi-system) **DEACTIVATE** it, make it less reactive, because the C=O group is the Lewis Acid in most of its reactions.

4.4 Reactions with Grignard and Acetylide Reagents as Strong Nucleophiles (Review)

- We have seen this previously, deprotonation of a terminal alkyne with sodium amide (NaNH2) forms an acetylide anion that can do nucleophilic addition to the C=O bond of an aldehyde or ketone.

\[ \text{Ph}-\text{C}≡\text{CH} \xrightarrow{\text{NaNH}_2} \text{Ph}-\text{C}≡\text{C}^- \xrightarrow{\text{Nu}^-} \text{Ph}-\text{C}≡\text{C}^-\text{C}^−\text{O}^- \xrightarrow{\text{H}_3\text{O}^+} \text{Ph}-\text{C}≡\text{C}^-\text{C}^−\text{O}^-\text{H} \]

An INTRAMOLECULAR example...

\[ \begin{array}{c}
\text{Ph}-\text{C}≡\text{C}^- \xrightarrow{\text{Mg, THF}} \text{Ph}-\text{C}≡\text{C}^-\text{Na}^- \xrightarrow{\text{H}_3\text{O}^+} \text{Ph}-\text{C}≡\text{C}^-\text{C}^−\text{O}^-\text{Na}^- \xrightarrow{\text{H}_3\text{O}^+} \text{Ph}-\text{C}≡\text{C}^-\text{C}^−\text{O}^-\text{H} \\
\text{INTRA}molecular \\
\end{array} \]

- The competition between bimolecular INTERmolecular reaction and unimolecular INTRAmolecular reaction can be controlled by concentration, at higher concentrations the intermolecular reaction often dominates.
- But what concentration do you need to make intermolecular reaction compete with intramolecular reaction? It often turns out to be quite high, often around 1 - 5M.
- Therefore INTRamolecular reactions usually "win" over a competing INTERmolecular reaction, and you can assume that if an intramolecular reaction is possible in this course you should do it and not the corresponding intermolecular reaction.
- NOTE: when forming (or opening rings) it is often a good idea to NUMBER the carbon atoms so that you don't lose track of any of the carbon atoms.

4.5 Reactions with Hydride Reagents as Strong Nucleophiles (Review)

Example

\[ \begin{array}{c}
\text{OH} \xrightarrow{\text{1. LiAlH}_4} \xrightarrow{\text{2. H}_3\text{O}^+} \text{CO}_2\text{Me} \\
\text{CH}_2\text{OH} \xrightarrow{\text{NaBH}_4} \text{CH}_3\text{CH}_2\text{OH} \\
\end{array} \]

- LiAlH₄ "stronger" reducing agent, Al-H bond is weaker, the energy of the electrons in the bond are higher, more reactive.
4.6 Hydrate Formation: Water as a Weak Nucleophile

- Addition of water to a C=C bond is exothermic and is generally not reversible, the enthalpy decrease due to forming stronger bonds overcomes the entropy decrease due to two molecules becoming one.

\[
\begin{align*}
R\text{-}C\equiv C\text{-}H & \quad + \quad H_2O & \quad \rightleftharpoons & \quad R\text{-}C\text{-}C\text{-}H & \quad H_3O^+ \\
\end{align*}
\]

- Acid or base catalyzed addition of water to a C=O bond, however, is NOT as exothermic, and is often REVERSIBLE at room temperature.

- The reasons for this is that the C=O bond is stronger than the C=C bond (oxygen is more electronegative).
- Addition to C=O still converts a pi bond and a sigma bond into two sigma bonds, but the enthalpy decrease due to forming stronger bonds in this case may not be enough to overcome the entropy decrease due to two molecules becoming one.
- We have already seen that keto-enol tautomerization favors the keto form due to the more stable C=O compared to C=C.

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4.7 Factors Controlling Addition of Water and Other Weak Nucleophiles

- As above, reactions of weak nucleophiles/weak bases with C=O bonds are often reversible

\[
\text{R}^\cdot \text{C} = \text{O} (\text{R'}, \text{H}) + \text{H}_2\text{O} \xrightleftharpoons[k_2]{k_1} \text{R}^\cdot \text{C} = \text{O} (\text{R'}, \text{H})
\]

\[
K_{eq} = \frac{k_1}{k_2} = \frac{[\text{Hydrate}]}{[\text{Carbonyl}]} = \text{Equilibrium Constant}
\]

- larger \(K_{eq} (>1)\) means the hydrate is favored
- smaller \(K_{eq} (<1)\) means the carbonyl is favored

\[
\begin{array}{c|c}
\text{Increasing} & \text{Reactivity} \\
\hline
\text{Hydrate} & \text{Carbonyl} \\
\hline
\text{H}_3\text{C} - \text{CH}_3 & \text{H}_3\text{C} - \text{CH}_3 \\
\hline
\text{H} - \text{C} - \text{CH}_3 & \text{H} - \text{C} - \text{CH}_3 \\
\hline
\text{H} - \text{C} - \text{CF}_3 & \text{H} - \text{C} - \text{CF}_3 \\
\end{array}
\]

\[
K_{eq} \sim 10^{-3} - 10^{-4}
\]

\[
K_{eq} \sim 1
\]

\[
K_{eq} \sim 2000
\]

\[
K_{eq} \sim 5000
\]

- Decreasing stability of the carbonyl increases the equilibrium constant and the propensity to form the hydrate

4.8 Acetal and Hemiacetal Formation: Alcohol as Weak Nucleophile, Alkoxide as Strong Nucleophile

1. acid catalyzed: alcohol as weak nucleophile, for the example of methanol (CH\textsubscript{3}OH)

\[
\begin{align*}
\text{R}^\cdot \text{C} = \text{O} (\text{R'}, \text{H}) + \text{CH}_3\text{OH}, \text{H}^\oplus & \xrightleftharpoons[k_2]{k_1} \text{R}^\cdot \text{C} = \text{O} (\text{R'}, \text{H}) \quad \text{hemiacetal} \\
\text{O}^- & \xrightarrow{\text{CH}_3\text{OH}, \text{H}^\oplus} \text{OCH}_3 & \quad \text{acetal}
\end{align*}
\]

- requires acid catalysis, \textit{the acid may be HCl or TsOH, or CF\textsubscript{3}CO\textsubscript{2}H etc, BUT NOT H3O+} since H2O is in the products and a high water concentration pushes the reaction BACK to aldehyde/ketone and alcohol

2. base catalyzed: alkoxide as strong nucleophile, for the example of methanol (CH\textsubscript{3}OH)

\[
\begin{align*}
\text{R}^\cdot \text{C} = \text{O} (\text{R'}, \text{H}) + \text{CH}_3\text{O}^- & \xrightleftharpoons[k_2]{k_1} \text{R}^\cdot \text{C} = \text{O} (\text{R'}, \text{H}) \quad \text{hemiacetal} \\
\text{O}^- & \xrightarrow{\text{CH}_3\text{OH}} \text{OCH}_3 & \quad \text{acetal}
\end{align*}
\]

- the base catalyst is the alkoxide corresponding to the alcohol that is added, methoxide in this case, with the alcohol as the solvent, in base the reaction tends to stop at the hemiacetal
- the explanation for the above observations lies in the mechanisms

Aldehydes and Ketones : Page 10
Mechanism of Acid catalyzed Formation of an Acetal: the reverse of dithiane hydrolysis

The Corresponding Base catalyzed mechanism

- 'RO\(^-\) cannot attack 2nd time, no good leaving group!
- hemiacetals (acetals) do not react with bases!
- compare the acid catalyze mechanism, where protonation makes a good leaving group

4.9 Controlling Reversibility in Acetal Formation : Introduction to Protecting Groups

- Favors acetal for aldehydes (generally more reactive)
- Favors carbonyl for ketones (generally less reactive)

Like hydrates

- equilibrium can be controlled by....

1. Solvent

- high concentration of ALCOHOL, e.g. it is the solvent, equilibrium pushed TOWARDS THE ACETAL
- high concentration of WATER, e.g. it is the solvent, equilibrium pushed TOWARDS THE CARBONYL + alcohol
- This is why H3O\(^+\) can NOT be used as the acid catalyst to form an acetal from an aldehyde/ketone, an organic acid such as TsOH or TFA must be used instead
2. Entropy

- There is an entropy cost associated with formation of acetal + water because 3 molecules become 2 molecules (the products have fewer degrees of freedom).
- Enthalpy usually dominates chemical reactivity; enthalpy is equivalent to electron energy, so we can usually get away with describing organic chemistry in terms of the energy of the electrons because enthalpy dominates.
- However, in this case formation of the acetal is not very favored by enthalpy, the enthalpy change is very small, so we have one of those few cases where entropy can actually influence the reaction, because the change in enthalpy is small.

Fixing the Entropy "Problem"

- This reaction now is entropically neutral (there is no entropy cost to make the acetal in this case) because 2 molecules become 2 molecules.
- Ethylene glycol can thus be used to favor acetal formation.

Making use of equilibrium: protecting groups (New Concept!)

- Use of acetals as protecting groups relies on the following...
  - Acetals can be hydrolyzed.
  - Acetals do not react with bases.
  - No good leaving group.

Example problem

- Desired product not formed.
- Dimer, wrong product.

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Solution: "Protect" the carbonyl group!

Example

- aldehydes make acetals more readily than ketones (more reactive)

Example
- the ketone can react with the Grignard ketone reduced in presence of aldehyde by use of protecting group
- note that the H3O+ BOTH hydrolyzes the O-Mg bond AND hydrolyzes the acetal back to the aldehyde

Example

H3O+ hydrolyzes both the acetal (deprotects the aldehyde) and also the O-MgBr bond.
4.10 Amines as Intermediate Nucleophiles: Mechanisms start to get a bit ambiguous!

- Reactions with 1° amines (and related structures that react like primary amines) make imines

- Reactions with 2° amines makes enamines

- Both reactions are acid catalyzed - but tricky, because……

- It is harder to protonate a ketone than amine, and so we need just enough acid to catalyze the reaction, but not too much otherwise the amine becomes protonated and thus non-nucleophilic (not reactive)

- In fact, amines are better nucleophiles than water/alcohols, and protonation is not even required in the FIRST step of the mechanism (although an acid catalyst is still needed overall, see below)

Mechanism of formation of imines: Reaction with 1° amines (acid catalyzed)
Amine mechanisms are tricky, it is hard to say exactly where the protons come from and go to in these mechanisms, for example, a proton could come from the acid catalyst as shown, or from a protonated nitrogen, they could go to the conjugate base of the acid catalyst or to an unreacted amine.

This is our first slightly ambiguous mechanism, at this point we need to introduce some NEW mechanism NOTATION (and that we will use later to make very long mechanisms more compact).

This is something very NEW and at first sight, a rather strange looking way of writing mechanism!

There are TWO valid mechanisms (protonation of C=O first or protonation of C=O after amine addition)

The source of the protons is ambiguous, hence the abbreviated +H+ (protonation) and -H+ (deprotonation)

Even the ORDER of the protonation/deprotonation steps can be ambiguous.

Although a bit strange to us right now, this is actually a more realistic mechanism since it doesn't pretend that the deprotonation and protonation steps are well defined and that we always know their actual order.

We all ALSO use this abbreviated mechanism notation when mechanisms get very long.

**Example Reactions**

The usual order of reactivity of carbonyl compounds applies to amine reactions, i.e. aldehydes are more reactive.

![Aldehyde](image)

**Mechanism of Formation of Enamines**

- Reaction with 2° amines (acid catalyzed)

![Mechanism](image)

- NOTE the use the new abbreviated +H+/-H+ notation, more realistic.
- again, there is more than one possible first step
- at the IMINIUM salt intermediate and enamine MUST be formed because there are no protons on the nitrogen to deprotonate.
Enamines are used in synthesis

\[
\begin{align*}
\text{O} & \quad \text{H}^\ominus (\text{cat.}) \quad \text{enamine} \\
\text{(cat.)} & \quad \text{1. PhCH}_2\text{Br} \\
& \quad \text{2. } \text{H}_3\text{O}^+ \\
\text{O} & \quad \text{Ph} \quad (-) 
\end{align*}
\]

• we will return to this important reaction later!

### 4.11 Complete Reduction of Carbonyl Groups: Clemmensen (Revisit) and Wolff-Kishner (New)

#### 1. Clemmensen Reduction

**The mechanism** of the Clemmensen reduction - actually it is complex and not well known!
• we can write some useful principles that may help you understand/remember
• need to do 2 things:
  1. We need to break the 2 C=O bonds, the usual way, using H3O+
  2. We need to add 2 hydrogen atoms, H•. The hydrogen atoms are "supplied" in the form of electrons from the metal and protons from the acid

\[
\begin{align*}
\text{O} & \quad \text{H}^\ominus (\text{cat.}) \quad \text{enamine} \\
\text{(cat.)} & \quad \text{1. PhCH}_2\text{Br} \\
& \quad \text{2. } \text{H}_3\text{O}^+ \\
\text{O} & \quad \text{Ph} \quad (-) 
\end{align*}
\]

• the zinc metal gets oxidized (loses electrons) and the ketone gets reduced
• the reaction actually takes place on the surface of the metal, the Hg makes a more active zinc surface

**This mechanism is schematic, alcohols tend not to be formed as side products and the actual mechanism may not proceed exactly this way and it is not really properly understood, you obviously don't have to know it**

• The Clemmensen reaction represents an example of a "dissolving metal" reduction, since as the metal is oxidized (by giving the electron to the substrate), it dissolves in the form of an ionic metal salt
• Other examples of a dissolving metal reducing agents are sodium in ethanol (Na/EtOH) that can reduce a C=O to an alcohol, and also sodium in liquid ammonia, Na/NH3(l), which reduces an alkyne to a trans-alkene

\[
\begin{align*}
\text{O} & \quad \text{Na (supplies electrons)} \quad \text{EtOH (supplies protons)} \quad \text{OH} \\
& \quad \text{you don't have to know!!!} \\
& \quad \text{you do have to know!!!} \\
\text{(cat.)} & \quad \text{Na (supplies electrons)} \\
& \quad \text{NH}_3 (\text{supplies protons}) \\
\end{align*}
\]
2. Wolff-Kishner Reduction

The reaction

- does the same thing as the Clemmensen reduction, complete reduction of the C=O bond using BASIC REAGENTS/CONDITIONS
- the oxygen of the C=O bond is removed when the hydrazone (imine) is formed, and the hydrogen atoms from the imine are then transferred to the carbon with overall loss of molecular nitrogen

Mechanism of the Wolff-Kishner reduction
- starts off with formation of a hydrazone (a special kind of imine), we know THIS part
- the rest involves deprotonations and reprotonations that facilitate loss of molecular nitrogen and overall transfer of hydrogen atoms to carbon, you don't have to know this mechanism...

- need to choose reduction conditions carefully......

reacts with acid


doesn't react with base

1° bromide attacked by nucleophile/base

• There are many examples in organic chemistry in which there are more ways of performing a specific reaction, this is only one of them.
• There are different reasons for having more than one reaction that does the same thing, in this case it is so that you can do chemistry on one functional group in the presence of another one.
4.12 Wittig Reaction: Direct Synthesis of a C=C Double Bond

The basic idea is best illustrated with a real example:

![Diagram of Wittig Reaction]

- The ylide is a carbon nucleophile that adds to the C=O bond, the Ph₃P⁺ group "removes" the oxygen from the C=O, the end product is formation of a C=C bond, i.e. an alkene.
- One "half" of the alkene comes from the ylide, the other "half" comes from the aldehyde/ketone.

The Phosphonium Ylide
- An ylide is defined as a structure that has adjacent atoms that each satisfy the "octet rule" and have positive and negative charges.
- Prepared by an SN2 reaction on a halide followed by deprotonation, for example:

\[
\text{Ph}_3\text{P}^- + \text{H}_2\text{C}X \xrightarrow{\text{S}_\text{N}2} \text{Ph}_3\text{P}^+\text{HMe} \xrightarrow{\text{deprotonation}} \text{Ph}_3\text{P}^+\text{HMe} \xrightarrow{\text{ylide}} \text{Ph}_3\text{P}^-\text{C}^+\text{H} 
\]

- Needs a usual good SN2 halide, e.g. primary, allylic etc.
- Deprotonate using the strongest base that we come across in general organic chemistry, butyl lithium, Bu-Li.
- An ylide is a carbon nucleophile, reacts like a carbon anion/nucleophile/Lewis base that can be used to make a new carbon-carbon bond.
- We can only "have" a useful carbon anion if the electrons are stabilized somehow, we have seen this before...

- Can't have a simple carbon anion, too reactive.
- Stabilized by sp hybridization.
- Stabilized by weak carbon-metal bond.
- Stabilized by Ph₃P⁺ group and by resonance.

These are all useful carbon nucleophiles that can be used to make new C-C bonds.

Reaction of the ylide with the aldehyde/ketone

- The aldehyde/ketone reacts with the ylide to form a new C=C bond, i.e. an alkene.
Example showing how the Wittig reaction gives more "control" over alkene synthesis

Example Wittig Problem: Which is the best Wittig Route to this alkene?

Route 2 is preferred because it starts with a benzylic halide (best for SN2 reaction with Ph3P)

Example Wittig Problem: What Alkene is formed in this reaction?

* will often get both cis- and trans- isomers, this IS a problem with the Wittig reaction....
Summary of Aldehyde and Ketone Reactions

Do NOT start studying by trying to memorize the reactions here!

Work as many problems as you can, with this list of reactions in front of you if necessary, so that you can get through as many problems as you can without getting stuck on the reagents/conditions, and so that you can learn and practice solving reaction problems. Use this list AFTER you have worked all of the problems, and just before an exam. By then you will have learned a lot of the reagents/conditions just by using them and you will only have to memorize what you haven't learned yet. Then do the following:

• Cover the entire page of reagents/conditions with a long vertical strip of paper, see if you can write down the reagents/conditions for each reaction, check to see which you get correct, if COMPLETELY correct, circle Y, if incorrect or even slightly incorrect, circle N. In this way you keep track of what you know and what you don't know.
• Keep coming back to this list and so the same thing only for those reactions you circled N, until all are circled Y.

Knowing the reagents/conditions on this page is INSUFFICIENT to do well on an exam since you will ALSO need to recognize how to use and solve reaction problems in different contexts, this page ONLY helps you to learn the reagents/conditions that you have not YET learned by working problems.

You have seen several of these reactions in earlier sections!

Reactions that make aldehydes/ketones
Reactions of aldehydes/ketones seen previously

1. MeMgBr
   \[ \text{Ph} - 
   \text{Ph} \rightarrow \text{Me} \]

2. H$_3$O$^+$

1. Me-C≡C$^+$Na
   \[ \text{Ph} - 
   \text{Ph} \rightarrow \text{Me-C≡CPh} \]

2. H$_3$O$^+$

1. LiAlH$_4$
   \[ \text{Ph} - 
   \text{H} \rightarrow \text{Ph} \]

2. H$_3$O$^+$

NaBH$_4$
   \[ \text{EtOH} \rightarrow \text{Y / N} \]

Na$_2$Cr$_2$O$_7$
   \[ \text{H}_2\text{SO}_4/\text{H}_2\text{O} \rightarrow \text{Y / N} \]

H$_2$
   \[ \text{Pd/C} \rightarrow \text{Y / N} \]

H$_2$O
   \[ \text{Y / N} \]

H$^+$ or -OH
   \[ \text{Y / N} \]

Na$^+$-OCH$_3$
   \[ \text{CH}_3\text{OH} \rightarrow \text{Y / N} \]

NaH
   \[ \text{HCl (cat.)} \rightarrow \text{Y / N} \]

and other hydrolysis reactions

H$_3$O$^+$
   \[ \text{Y / N} \]

H$_2$N-Ph
   \[ \text{H}^+ \text{ (cat.)} \rightarrow \text{Y / N} \]

NH$_2$NH$_2$
   \[ \text{KOH, heat} \rightarrow \text{Y / N} \]

Zn(Hg)
   \[ \text{HCl, H}_2\text{O} \rightarrow \text{Y / N} \]

1. PPh$_3$
   \[ \text{Y / N} \]

2. BuLi

\[ \text{Y / N} \]

Ph$_3$C$^+$P(Ph$_3$)
   \[ \text{Y / N} \]

Wittig reaction

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