Aldehydes and Ketones — Nucleophilic Addition

1 Structure and Nomenclature

Nucleophilic end (*can protonate*)

Electrophilic end
(*reacts with nucleophiles*)   Dipole Moment ~3.0D

~1.8D
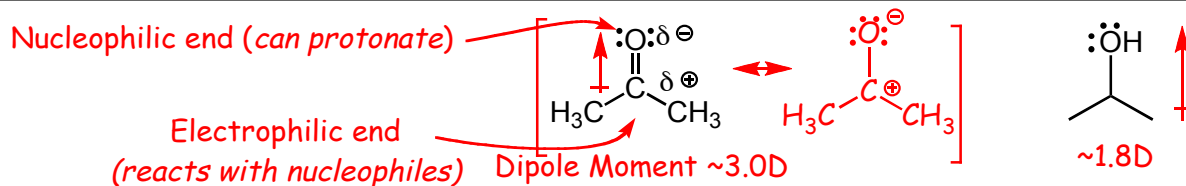
• The C=O Bond has Larger dipole moment than the C–O bond because the π-electrons are more polarizable.
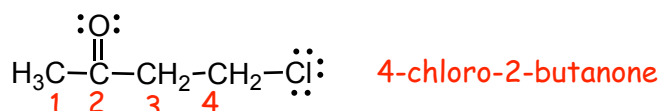
IUPAC nomenclature uses numbering system:
Aldehydes have the suffix "**-al**", ketones have the suffix "**-one**".
Never, ever, ever spell ketone as ke**y**tone ☺
priority: **aldehyde**> **ketone**> alcohol > alkene > alkyne > halide (higher priority with higher oxidation).

sterochemistry ignored   H₃C-CH–CH₂–CH₂–C–H

4-chloropentanal   (–CHO =)
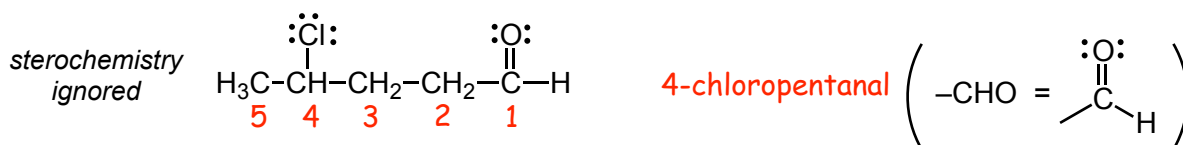
• Example above, no number for simple aldehyde, C=O must always be 1.

H₃C–C–CH₂–CH₂–Cl   4-chloro-2-butanone

• Example above, number to give carbonyl smallest number.

(6S)-chloro-hept-(3E)-en-2-one
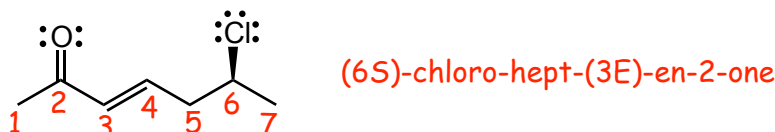
• Example above, multiple suffixes for multiple functional groups.

2 Synthesis of Aldehydes and Ketones : Review
• We have already seen several methods of synthesizing aldehydes and ketones.
• The most important ones are oxidations of alcohols. You will use these reactions again extensively.

1° alcohol $\xrightarrow[\text{CH}_2\text{Cl}_2]{\text{PCC}}$

2° alcohol   H₃C–C–CH₃ $\xrightarrow[\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4/\text{H}_2\text{O}]{\text{PCC} \; \text{— OR}}$ H₃C–C–CH₃
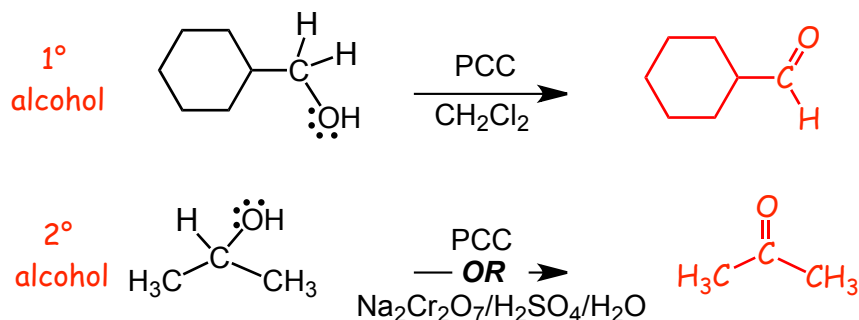
3 Reactions of Aldehydes and Ketones
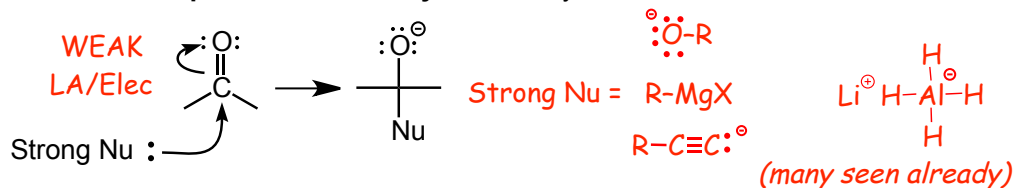
3.1 Strong and Weak Nucleophiles
• In **most** reactions, aldehydes/ketones act as the Lewis Acid/Electrophile.
• We can **understand** the reaction principles for aldehydes/ketones based on what we already know about the chemistry of **epoxides**, **also** act as Lewis Acids/Electrophiles.

Strong Lewis Bases/Nucleophiles react **directly** with epoxides.
Weak Lewis Bases/Nucleophiles require **protonation of the epoxide.**
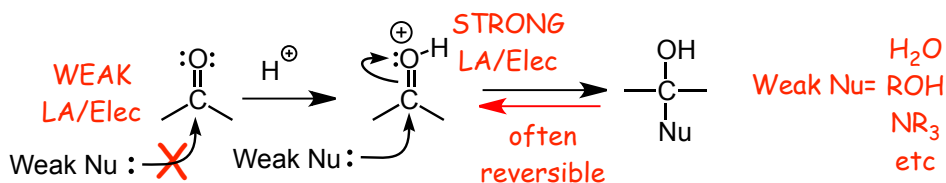
Weak LA/Elec

STRONG LA/Elec

Me–MgBr

STRONG LB/Nuc

WEAK LB/Nuc H_3C

The **same applies** for reactions of aldehyde/ketones.
Strong Lewis Bases/Nucleophiles react **directly** with aldehydes/ketones.

WEAK
LA/Elec

Strong Nu :—

Nu

Strong Nu =   R–MgX

R–C≡C:⁻

$\overset{\ominus}{:}\!\overset{..}{O}$–R

$Li^{\oplus}\ H\!-\!\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{Al}}\!-\!H$

(many seen already)

• We have **already seen** many of these reactions, Grignards, acetylides, lithium aluminum hydride, etc.
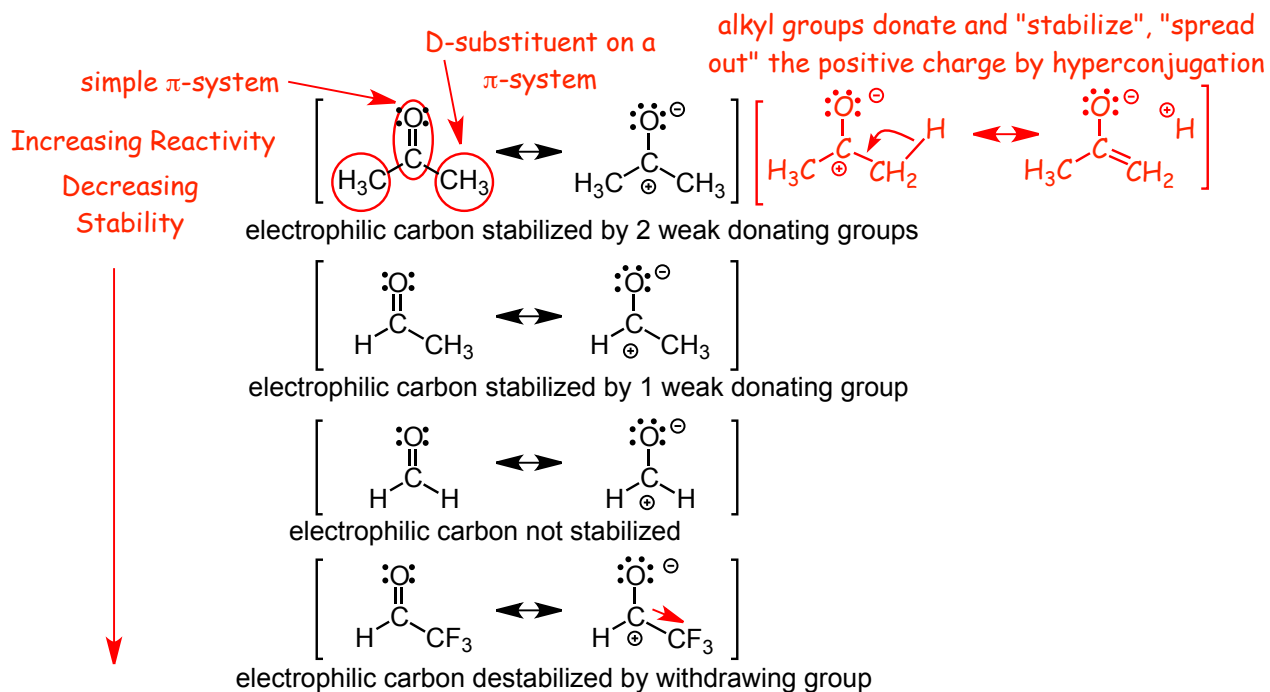• **Strong Nucleophiles** tend to react **irreversibly.**

Weak Lewis Bases/Nucleophiles require **protonation of the aldehyde/ketone**, just like an epoxide:

WEAK
LA/Elec

Weak Nu :—✗

$H^{\oplus}$

Weak Nu:—

STRONG
LA/Elec

often
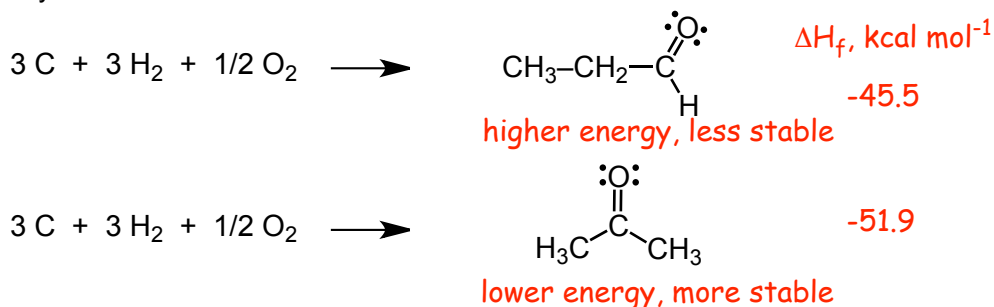reversible

OH
|
C
|
Nu

Weak Nu= ROH

H_2O

NR_3

etc

• **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).

3.2 Relative Reactivities of Aldehydes and Ketones

• The 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.

simple π-system

D-substituent on a
π-system

alkyl groups donate and "stabilize", "spread
out" the positive charge by hyperconjugation

Increasing Reactivity

Decreasing
Stability

electrophilic carbon stabilized by 2 weak donating groups

electrophilic carbon stabilized by 1 weak donating group

electrophilic carbon not stabilized

electrophilic carbon destabilized by withdrawing group

Aldehydes and Ketones : Page 2

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

$$3\,C + 3\,H_2 + 1/2\,O_2 \longrightarrow$$

CH₃–CH₂–C(=O)H

ΔH_f, kcal mol^{-1}

-45.5

higher energy, less stable

$$3\,C + 3\,H_2 + 1/2\,O_2 \longrightarrow$$

H₃C–C(=O)–CH₃

-51.9

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.

Comparing Donating Groups on Different π-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 π-system) **deactivate** it, make it less reactive, because the C=O group is the Lewis Acid in most of its reactions.

donating alkyl ACTIVATES

Lewis BASE

R

E⁺

:O: Lewis ACID

donating alkyl DEACTIVATES

R'—C—R

Nu:⁻
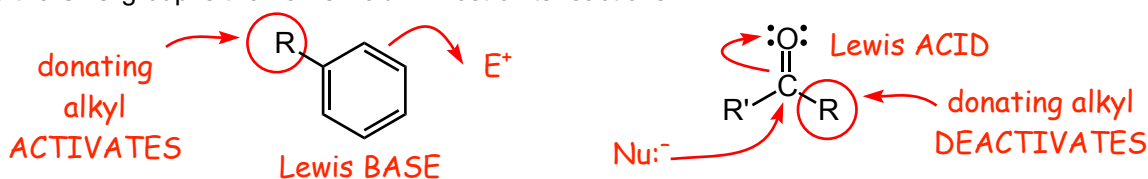
3.3 Reactions with Strong Nucleophiles Review: Hydride, Grignard and Acetylide Reagents
Examples with Hydride Reducing Agents: (stereochemistry ignored)

1. LiAlH₄
2. H₃O⁺

NaBH₄
EtOH

ester harder to reduce
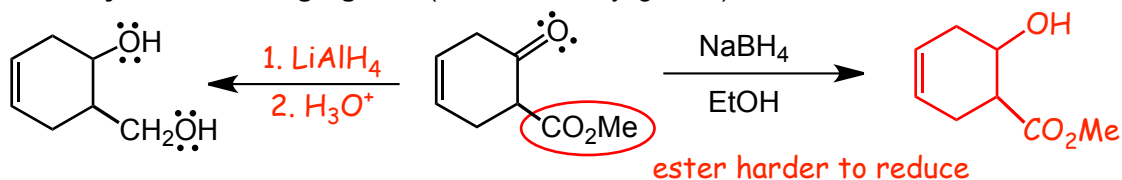
• **Recall**: LiAlH₄ is the stronger reducing agent because the Al-H bond is weaker than the B-H bond, the energy of the electrons in the bond are higher, more reactive.
• Neither reagent reduces the C=C bond.

Examples with Acetylide Anions:

Ph—C≡CH

NaNH₂

Ph—C≡C:⁻ Na⁺

Ph—C≡C—C(CH₃)(CH₃)—O⁻ Na⁺

H₃O⁺

Ph—C≡C—C(CH₃)(CH₃)—OH
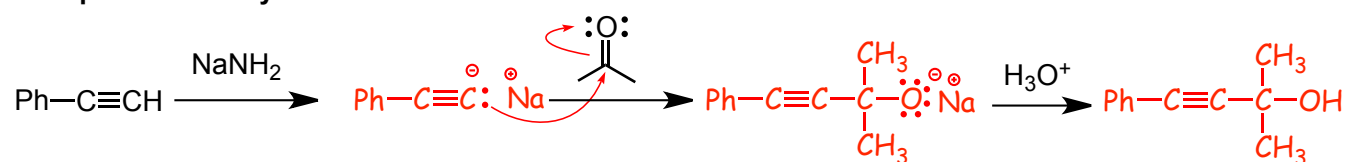
• **Recall**: Deprotonation of a terminal alkyne with sodium amide (NaNH₂) forms an acetylide anion that can do nucleophilic addition to the C=O bond of an aldehyde or ketone.
• The second step of the reaction is acid workup (H₃O⁺).

An Intramolecular Example with a Grignard Reagent:

Mg, THF

INTRAmolecular reaction

INTERmolecular

H₃O⁺

OH
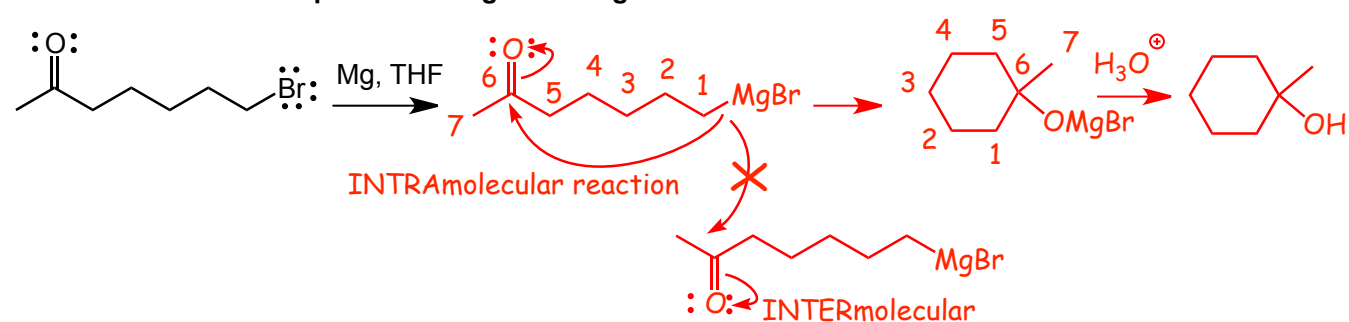
• The competition between bimolecular **inter**molecular reaction and unimolecular **intra**molecular reaction can be controlled by concentration, at higher concentrations the intermolecular reaction often dominates.
• But what concentration do you need to make intermolecular reaction compete with intramolecular reaction? It often turns out to be quite high, often around 1 - 5M!
• Therefore **intra**molecular reactions usually "wins" over a competing **inter**molecular 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.

3.4 Hydrate Formation : Water as a Weak Nucleophile

• **Recall**: 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:
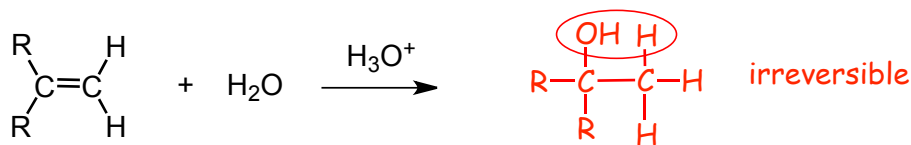

• **Compare:** Acid or base catalyzed addition of water to a C=O bond, however, is **not** as exothermic, and is often **reversible** at room temperature:
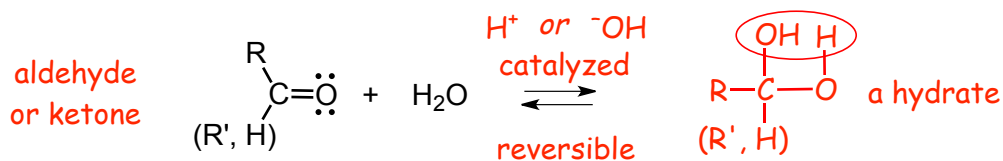

• The reasons for this is that the C=O bond is stronger than the C=C bond (oxygen is more electronegative).
• Addition to C=O still converts a pi bond and a sigma bond into two sigma-bonds, but the enthalpy decrease due to forming stronger bonds in this case may not be enough to overcome the entropy 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.
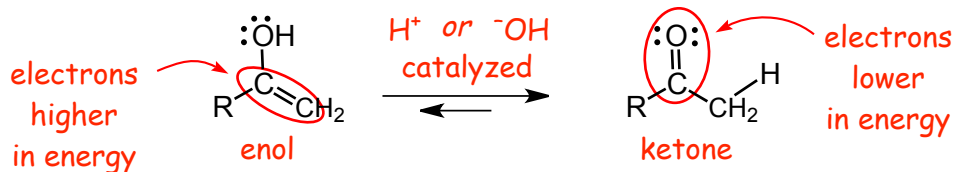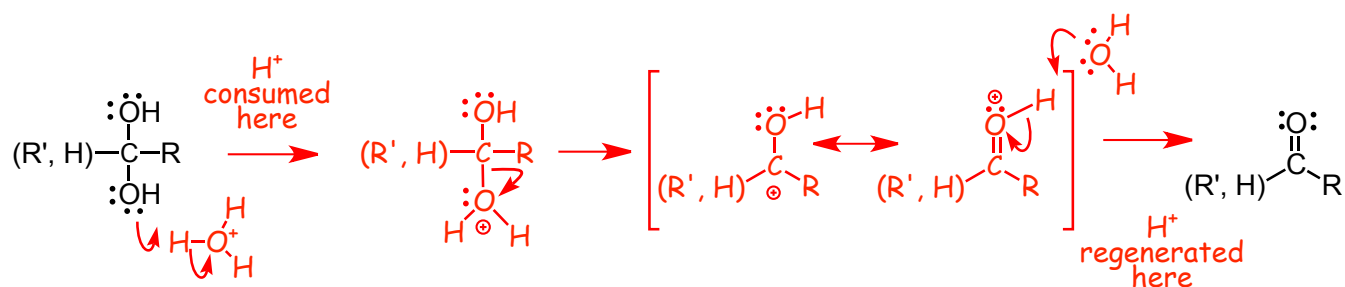

• We have seen hydrates previously…..
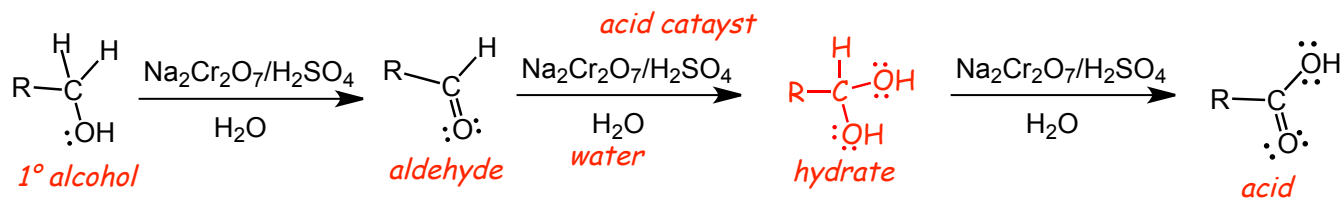
Addition of Water: The Acid catalyzed mechanism.
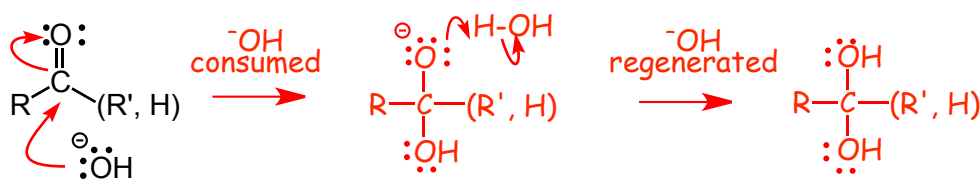

Aldehydes and Ketones : Page 4
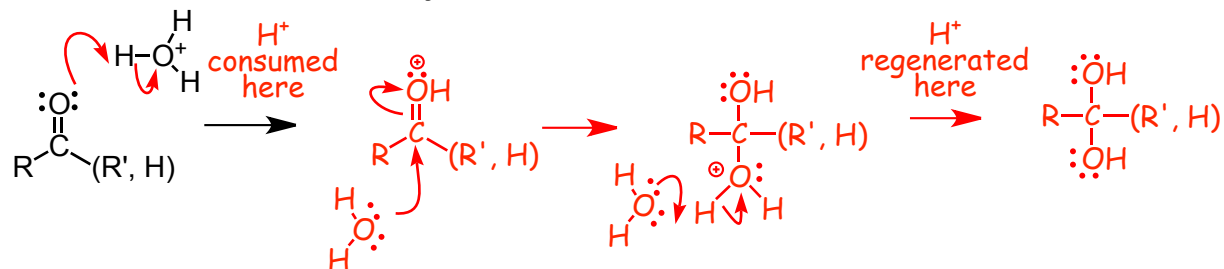
• H+ is not consumed overall, it is a true catalyst.
• The principle of **microscopic reversibility** says that the reverse mechanism must be exactly reversed!


• Note the inclusion of the resonance contributor (it is actually optional).
• Conventionally, the curved arrow pushing will be drawn for the **major** resonance contributor (as shown here), but that is also optional.

Addition of Water: The Base catalyzed mechanism.

• ⁻OH is not consumed overall, a true catalyst, **and**, base catalyzed mechanisms are often simpler.
• Again, the principle of **microscopic reversibility** says that the reverse mechanism must be exactly reversed!
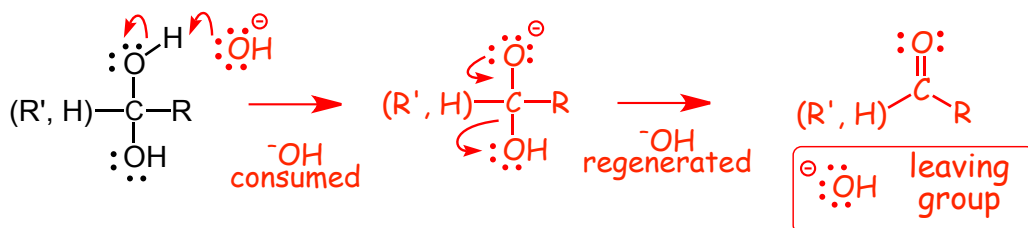
• Note, something important, we just had an anion, hydroxide as the **leaving group**!
• Wasn't it the case that an oxygen anion is a poor leaving group?
• We **can** have an oxygen anion as a leaving group is we **supply** plenty pf chemical potential energy as a reactant, we **added** a high energy oxygen anion to make the reaction go.
• And so we just learned that we **can** have an oxygen anion as a leaving group if we also **start** with an oxygen anion, hydroxide in this case.

3.5 Reactivity of Aldehydes/Ketones in Additions of Water and Other Weak Nucleophiles
• As above, reactions of weak nucleophiles/weak bases with C=O bonds are often reversible:

$$K_{eq} = \frac{k_1}{k_2} = \frac{[Hydrate]}{[Carbonyl]} = \text{Equilibrium Constant}$$
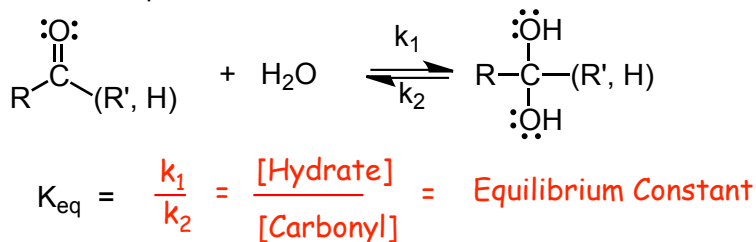
• Larger Keq (>1) means the hydrate is favored.
• Smaller Keq (<1) means the carbonyl is favored.

Increasing Reactivity

$$\left[\text{H}_3\text{C}-\overset{\overset{\displaystyle :\text{O}:}{\|}}{\text{C}}-\text{CH}_3 \longleftrightarrow \text{H}_3\text{C}-\overset{\overset{\displaystyle :\ddot{\text{O}}:^{\ominus}}{|}}{\overset{\oplus}{\text{C}}}-\text{CH}_3\right]$$ K_{eq} ~10^{-3}-10^{-4}

$$\left[\text{H}-\overset{\overset{\displaystyle :\text{O}:}{\|}}{\text{C}}-\text{CH}_3 \longleftrightarrow \text{H}-\overset{\overset{\displaystyle :\ddot{\text{O}}:^{\ominus}}{|}}{\overset{\oplus}{\text{C}}}-\text{CH}_3\right]$$ ~1

$$\left[\text{H}-\overset{\overset{\displaystyle :\text{O}:}{\|}}{\text{C}}-\text{H} \longleftrightarrow \text{H}-\overset{\overset{\displaystyle :\ddot{\text{O}}:^{\ominus}}{|}}{\overset{\oplus}{\text{C}}}-\text{H}\right]$$ ~2000

$$\left[\text{H}-\overset{\overset{\displaystyle :\text{O}:}{\|}}{\text{C}}-\text{CF}_3 \longleftrightarrow \text{H}-\overset{\overset{\displaystyle :\ddot{\text{O}}:^{\ominus}}{|}}{\overset{\oplus}{\text{C}}}-\text{CF}_3\right]$$ ~5000
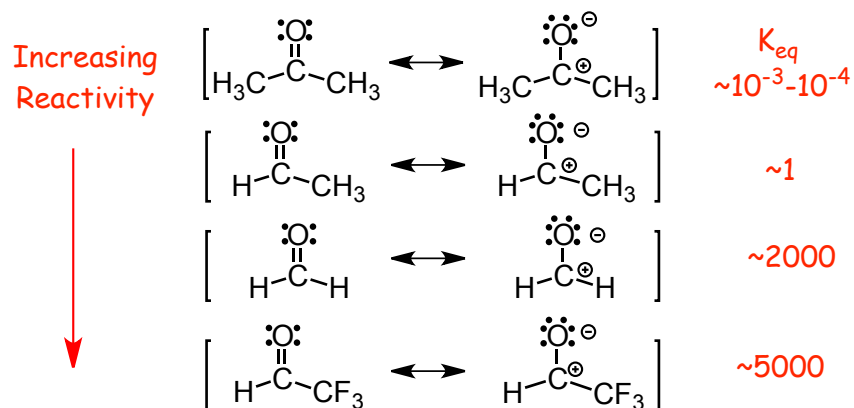
• Decreasing stability of the carbonyl increases the equilibrium constant and the propensity to form the hydrate.

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

Acid catalyzed Reaction: Alcohols as weak nucleophiles, for the example of methanol (CH_3OH):

hemiacetal → acetal
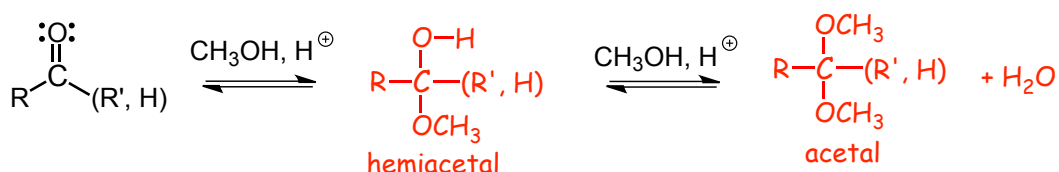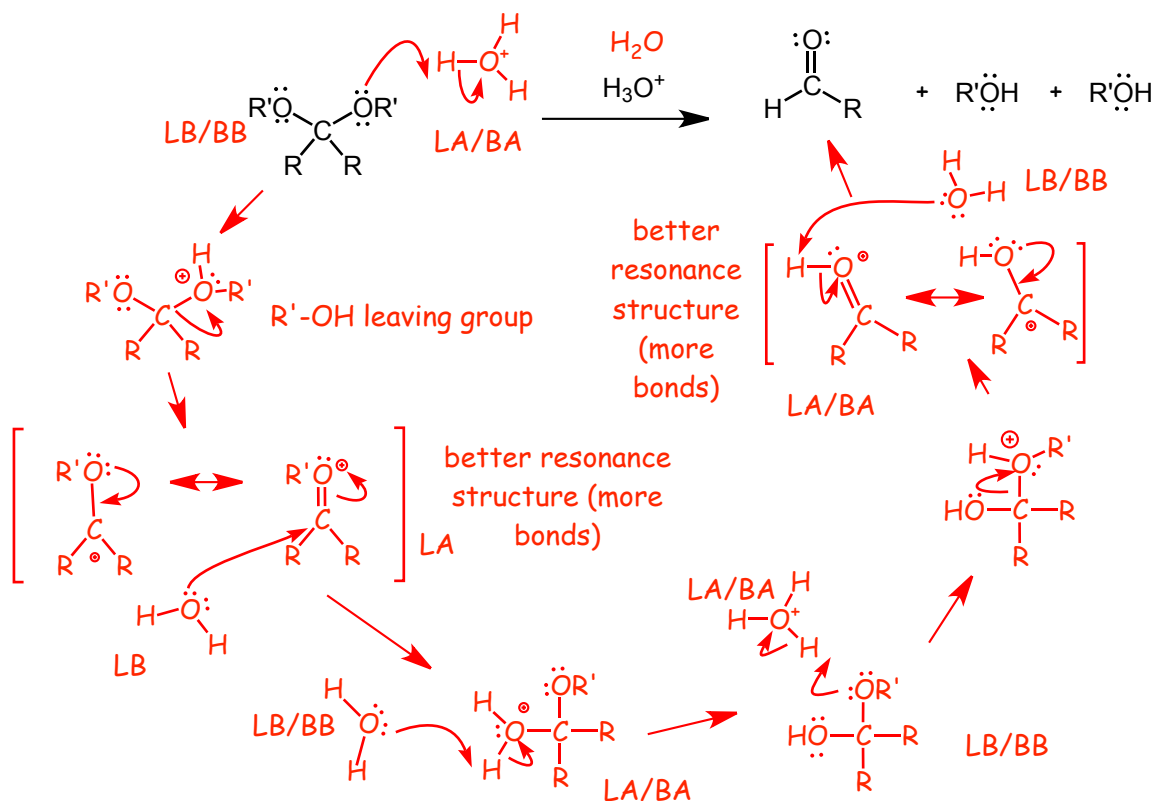
• The reaction requires acid catalysis, **the acid may be HCl or TsOH, or CF₃CO₂H etc., but not H₃O⁺** since H_2O is in the products and a high water concentration pushes the reaction **back** to aldehyde/ketone and alcohol.

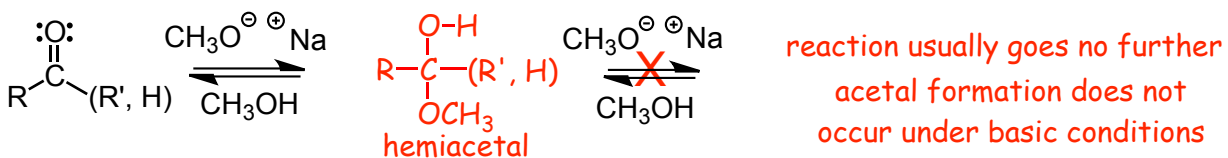**The mechanism of Acid catalyzed Formation of an Acetal - No water, no H₃O⁺**
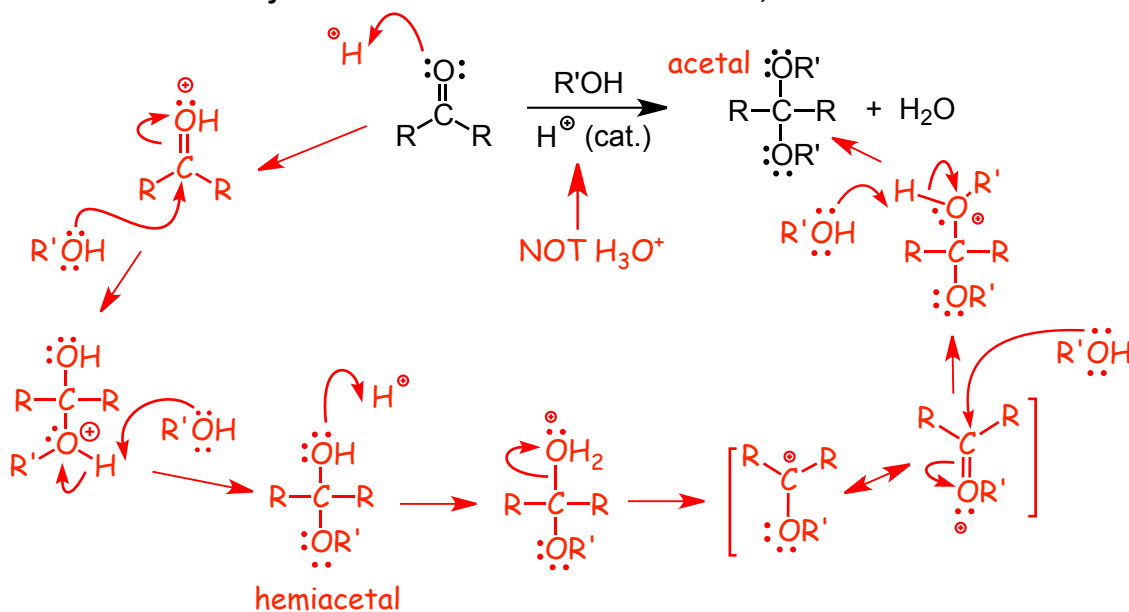
• These reactions are **reversible**, in each case the reaction is hydrolysis of the acetal or the hemiacetal (hydrolysis means bond breaking (lysis) with water (hydro)).
• The **Mechanism** of acetal hydrolysis of an acetal is just the reverse of acetal formation above:
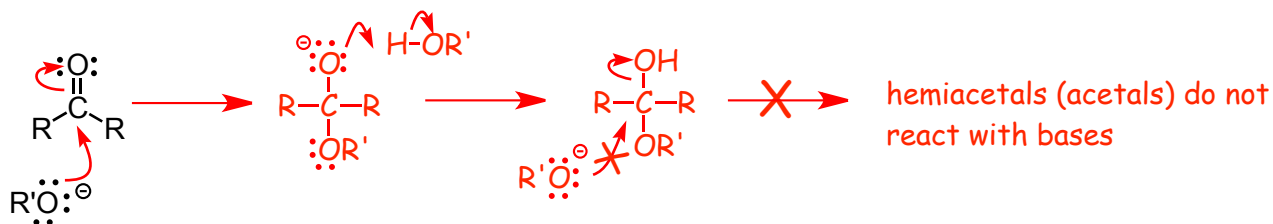
LB/BB R'O–C(R)(R)–OR' H–O⁺(H)(H) **LA/BA** H_2O, H_3O^+ → O=CH–R + R'ÖH + R'ÖH

R'–OH leaving group

better resonance structure (more bonds) **LA/BA**

LA better resonance structure (more bonds)

LB H–Ö–H

LB/BB H–Ö–H   **LA/BA**

LA/BA H–O⁺H

LB/BB

• Note, the **formation** of the acetal requires an acid but it **must be** an **organic acid**, not H_3O^+, since H_3O^+ means the presence of water, H_2O, which would **hydrolyze** the acetal back to the aldehyde not ketone.
• Note, the acetal **hydrolysis requires H_3O^+** because water is need to provide the oxygen atom that becomes the oxygen in the aldehyde or ketone.

Base catalyzed Reaction: Alkoxide as strong nucleophile, for the example of methanol (CH_3OH).
• 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 this observation lies in the mechanisms:

O=C(R)(R', H) $CH_3O^⊖$ $^⊕Na$ / CH_3OH ⇌   R–C(O–H)(R', H)–OCH₃ hemiacetal $CH_3O^⊖$ $^⊕Na$ ✗ / CH_3OH reaction usually goes no further acetal formation does not occur under basic conditions

The Corresponding Base catalyzed mechanism

:O:=C(R)(R) R'O:⊖ → R–C(R)(R)–Ö:⊖ , :OR' H–OR' → R–C(R)(R)–OH , :OR' R'Ö:⊖ ✗ ✗→ hemiacetals (acetals) do not react with bases

• 'RO⁻ cannot attack 2nd time because there is no good leaving group.
• Hemiacetals (and acetals) do not react with bases.
• Compared this to the acid catalyze mechanism, where protonation makes a good leaving group.
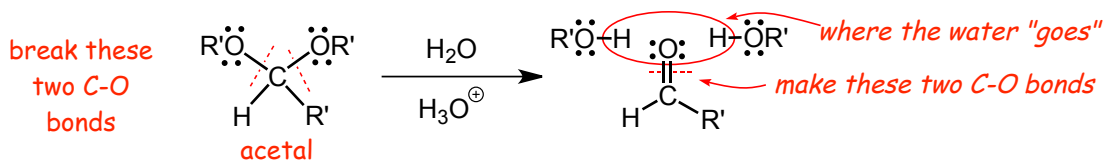
Hydrolysis of the hemiacetal via base catalysis proceeds via the reverse mechanism:
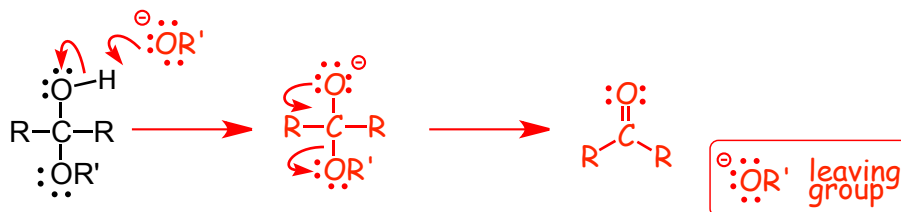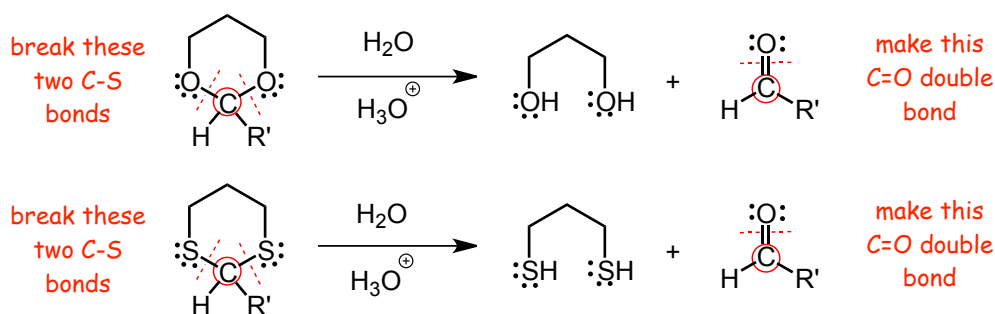

• **Again**, an oxygen anion is a **leaving group**!
• **Again**, we **can have** an oxygen anion as a leaving group if we also **start** with an oxygen anion, an alkoxide (-OR') in this case.
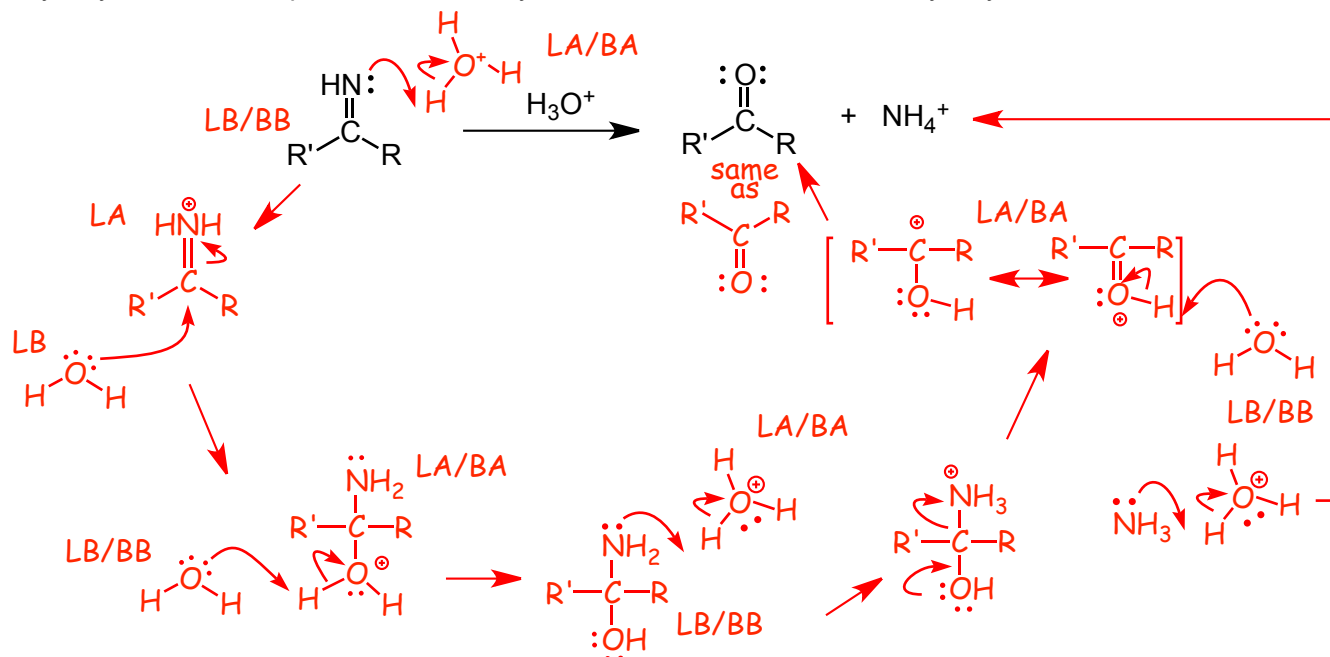
3.7 Hydrolysis Reactions

Hydrolysis: bond breaking (-lysis) using water, we have just seen this with acetals:

• Hydrolysis of C-O bonds can come in many forms:

• In general, hydrolysis can break 2 C-O bonds, 2 C-S bond 2 C-N bonds, even a C=N double bond.
• Hydrolysis of an imine proceeds via exactly the same mechanism as acetal hydrolysis:
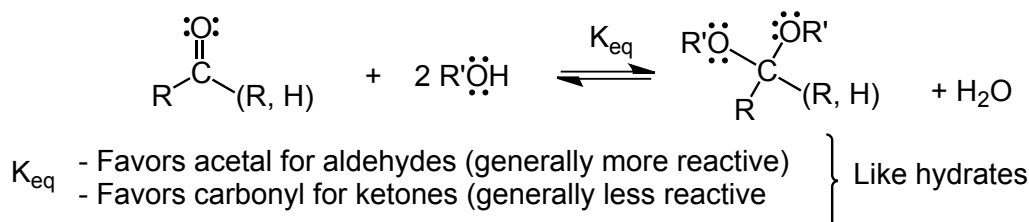

Aldehydes and Ketones : Page 8

• In the imine, the two C-N bonds are part of a C=N double bond, 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:
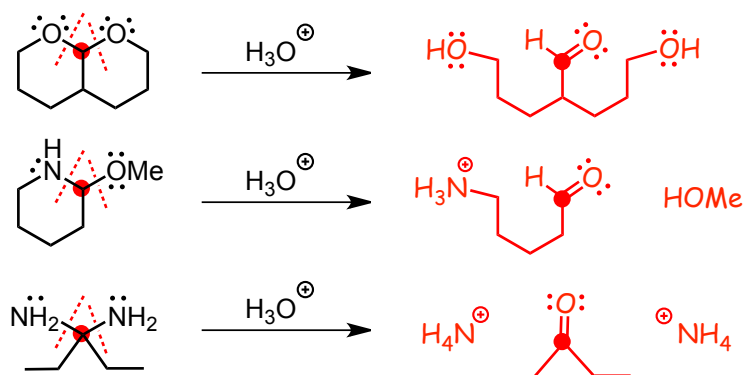
• **Remember**: H_3O^+ means, some strong acid (such as HCl) dissolved in water as the solvent.

3.8 Controlling Reversibility in Acetal Formation : Introduction to Protecting Groups

•Alcohols are weak nucleophiles/Lewis bases, and their addition reactions to C=O bonds (remember they are stringer than C=C bonds) are often reversible:


K_{eq} - Favors acetal for aldehydes (generally more reactive)   } Like hydrates
      - Favors carbonyl for ketones (generally less reactive

• For this reaction, the equilibrium can be controlled in two ways.

1) Solvent as a Controlling Factor:
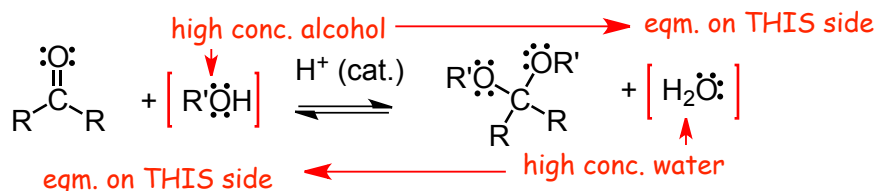
• A high concentration of **alcohol**, e.g. it is the solvent, equilibrium pushed **towards the acetal.**
• high concentration of **water**, e.g. it is the solvent, equilibrium pushed **back towards the carbonyl** + alcohol
• This is why H_3O^+ cann**ot** be used as the acid catalyst to form an acetal from an aldehyde/ketone, an organic acid such as TsOH or TFA must be used instead.

2) Entropy as a Controlling Factor:
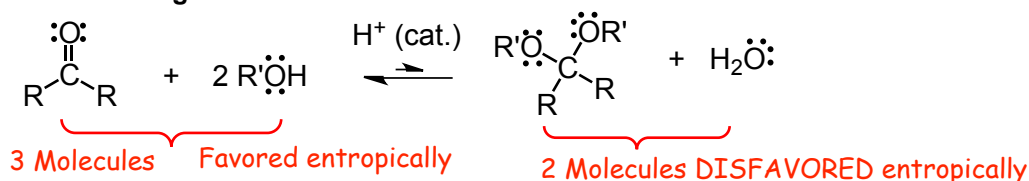
• There is an entropy cost associated with formation of acetal + water because 3 molecules become 2 molecules (the products have fewer degrees of freedom).
• Enthalpy usually **dominates** chemical reactivity, enthalpy is equivalent to electron energy, we can usually get away with describing organic 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.

Aldehydes and Ketones : Page 9

Fixing the Entropy "Problem"

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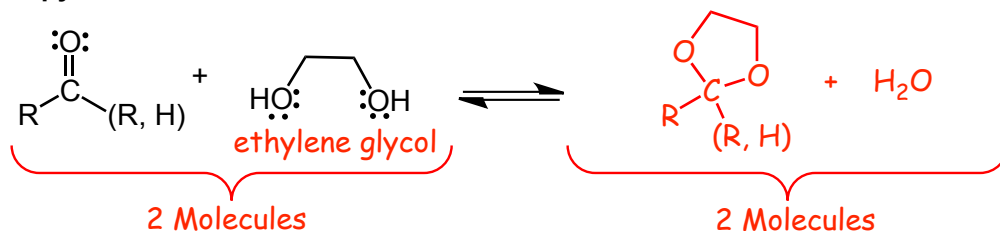
• **This** reaction now is entropically neutral (there is no entropy cost to make the acetal in this case) because 2 molecules become 2 molecules.
• Ethylene glycol can thus be used to favor acetal formation.

Making use of equilibrium: Protecting Groups, a 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

No reaction
(compare lack of formation of acetal in base catalyzed reaction above)

Example problem

Desired product **NOT FORMED**

Dimer, wrong product
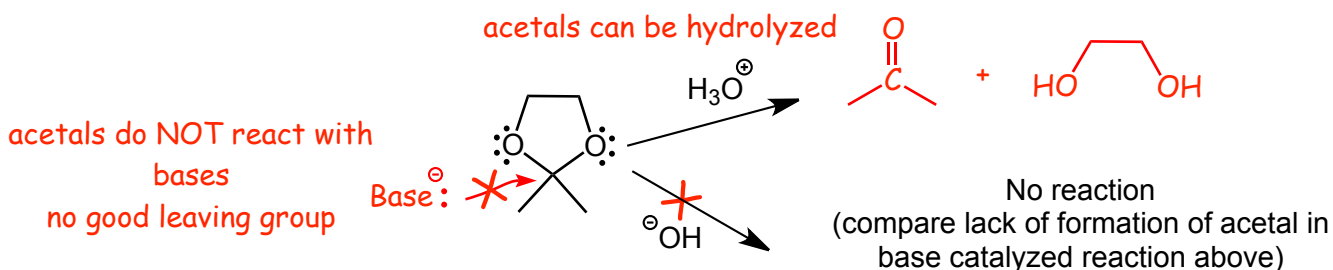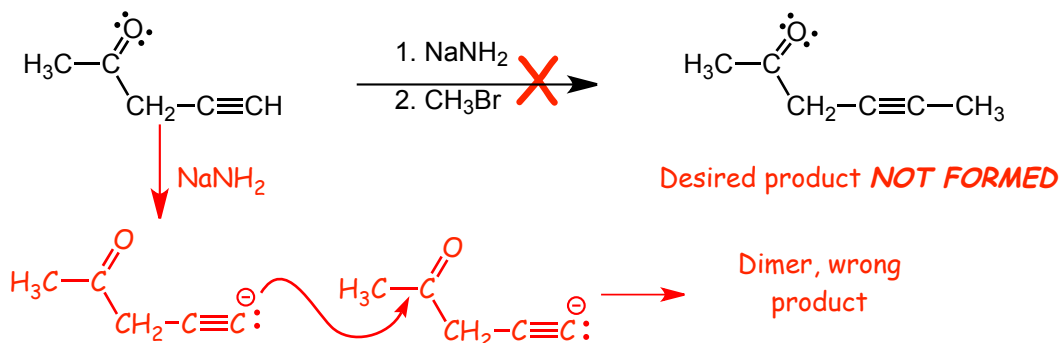
Solution: "Protect" the carbonyl group!

protect

NaNH₂

SN2

deprotect

Aldehydes and Ketones : Page 10
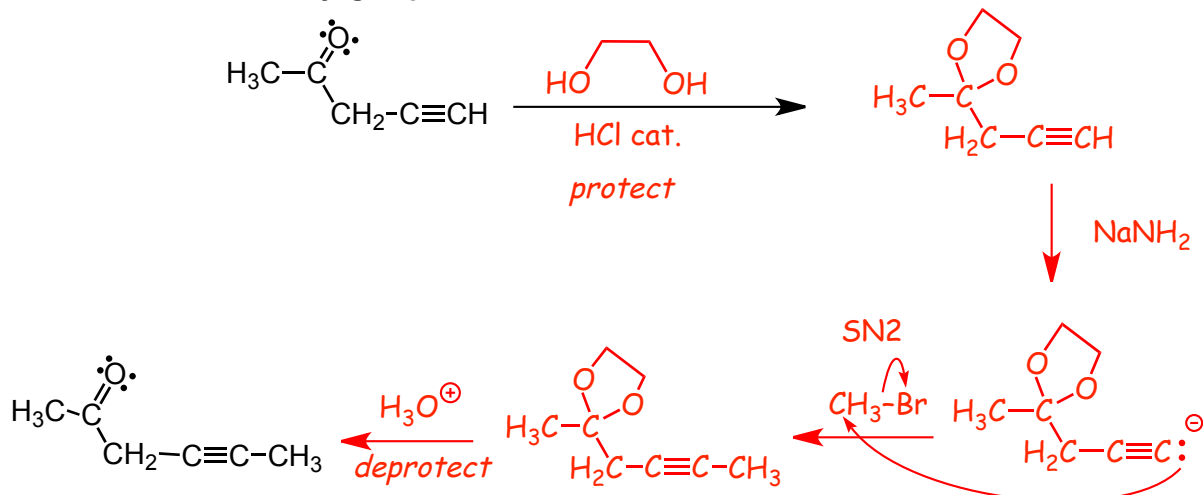
Example

• Aldehydes make acetals more readily than ketones (because as we saw above, they are more reactive).

1. 1 Equiv. MeMgBr
2. H_3O^+

HO ⌢ OH /HCl
1 Equivalent

1 Equiv. MeMgBr

$H_3O^{\oplus}$
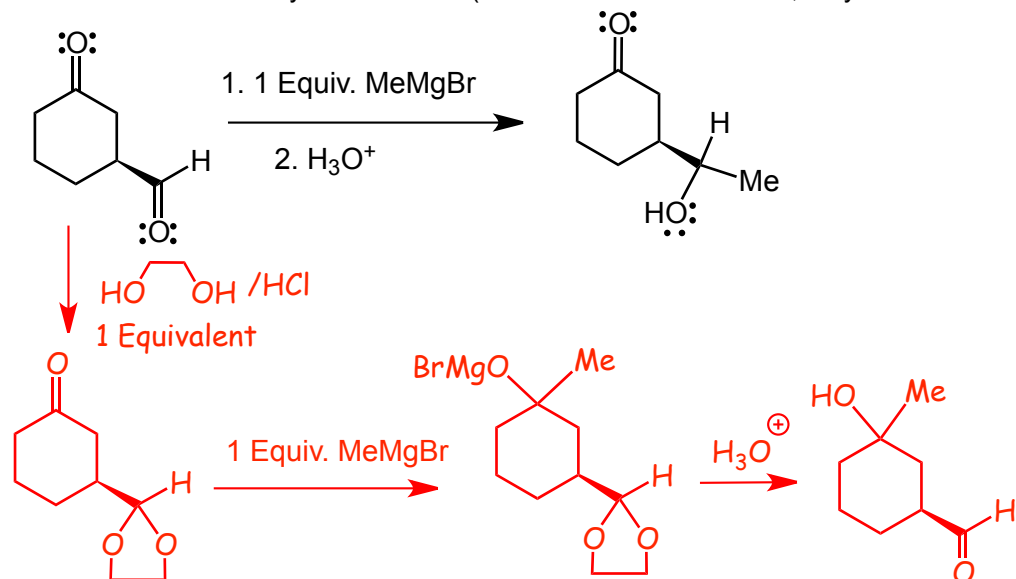
• The ketone can react with the Grignard ketone reduced in presence of aldehyde by use of protecting group.
• Note that the H_3O+ **both** hydrolyzes the O-Mg bond **and** hydrolyzes the acetal back to the aldehyde.

Example

protected

HCl cat.

Mg.THF

$H_3O^{\oplus}$

H_3O^+ hydrolyzes both the acetal (deprotects the aldehyde) and also the O-MgBr bond.
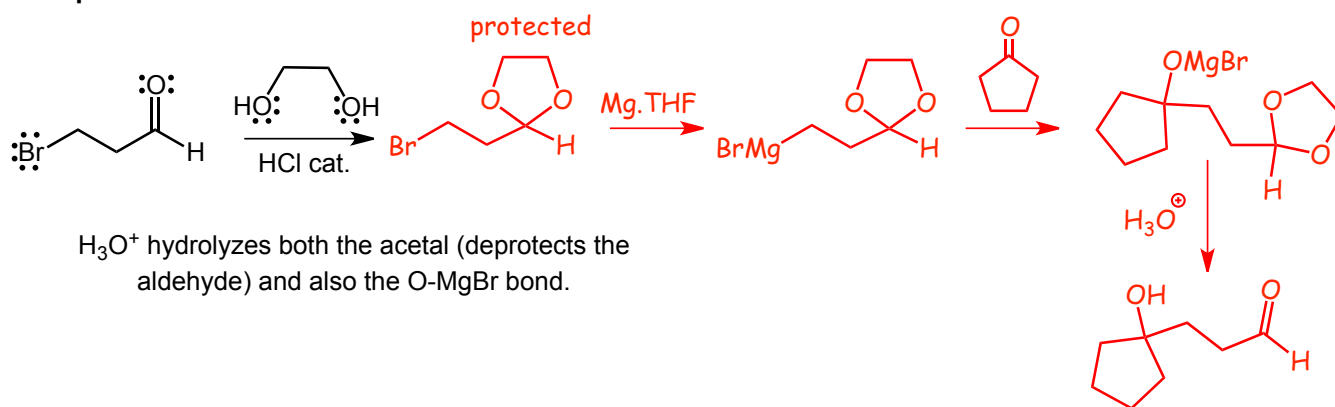
3.10 Amines as Intermediate Nucleophiles : Mechanisms start to get a bit ambiguous!

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

RNH_2
1° amine

Imine
(Schiff Base)
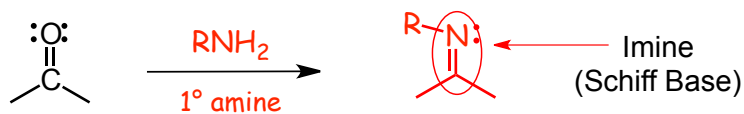
• Reactions with 2° amines makes **enamines**:

R_2NH
2° amine

enamine   enol

• Both reactions are acid catalyzed - but this is now tricky, because:

Aldehydes and Ketones : Page 11

harder to protonate

$$:O: \quad + \quad H_3O^{\oplus} \quad \rightleftharpoons \quad {}^{\oplus}\ddot{O}{-}H \quad + \quad H_2O$$

pKa ~ – 8

$$:\ddot{N} \quad + \quad H_3O^{\oplus} \quad \rightleftharpoons \quad {}^{\oplus}N{-}H \quad + \quad H_2O$$

pKa ~ 8 — Not a nucleophile at all!
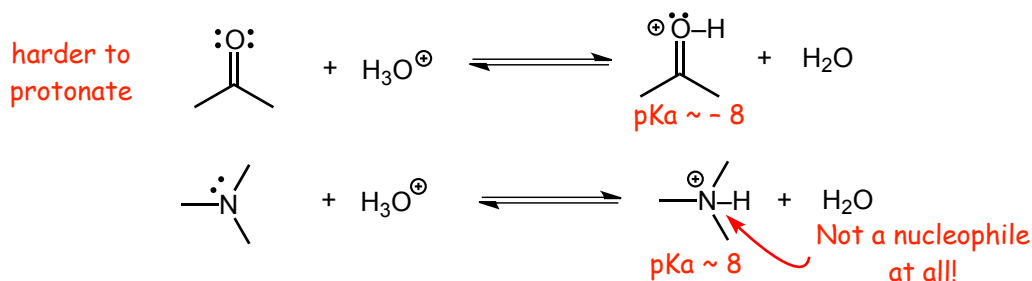
• It is harder to protonate a ketone than amine, and so we need just enough acid to catalyze the reaction, but not too much otherwise the amine becomes protonated and thus non-nucleophilic (not reactive).
• In fact, amines are better nucleophiles than water/alcohols, and protonation is not even required in the **first** step of the mechanism (although an acid catalyst is still needed overall, see below):
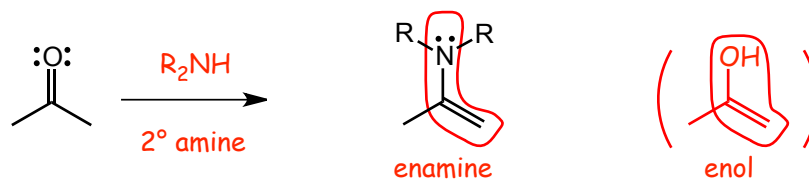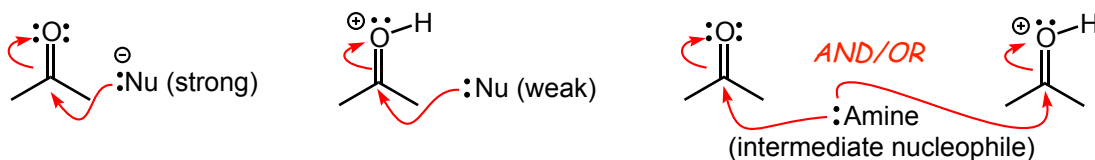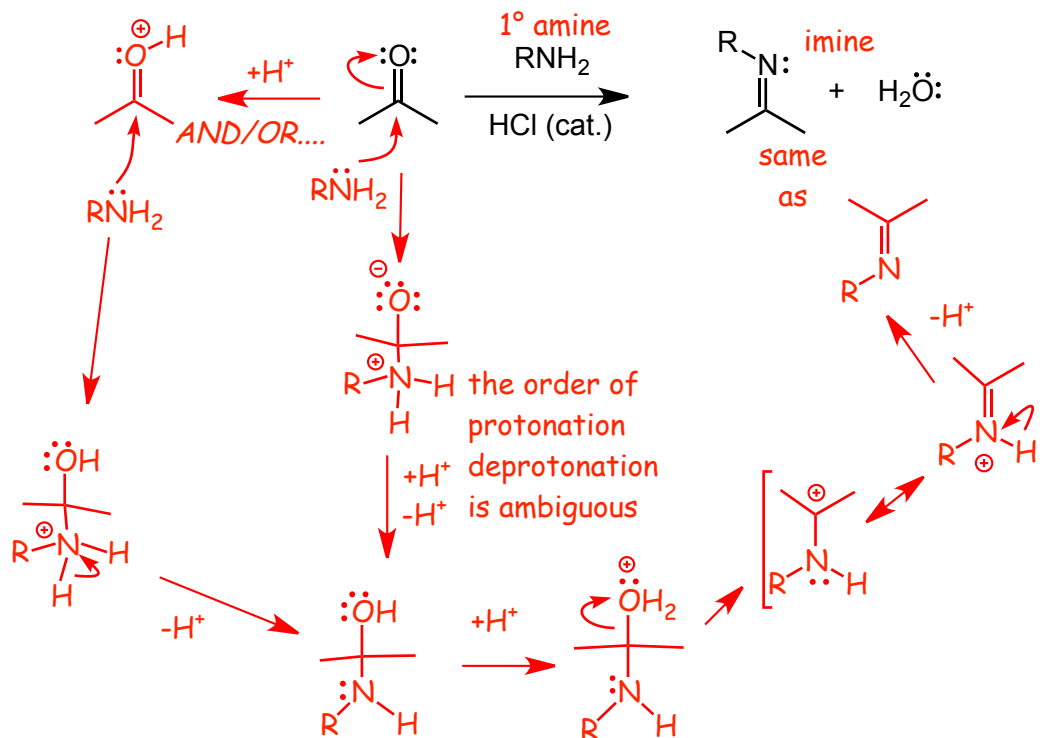
:O: + :Nu (strong) ${}^{\oplus}\ddot{O}{-}H$ + :Nu (weak)   :O: *AND/OR* ${}^{\oplus}\ddot{O}{-}H$ + :Amine (intermediate nucleophile)

• Strong nucleophiles (e.g. Grignards) react directly with C=O bonds, weak nucleophiles (e.g. ROH) require acid protonation of the C=O before reaction takes place.
• Amines are "intermediate nucleophiles", reaction may occur directly without the C=O (i.e. without protonation first), **or**, after protonation of the C=O similar to the reaction with alcohols and other weak nucleophiles, depending upon the acid concentration, the particular reactants etc., which means you can draw **either** mechanism and be correct.

Mechanism of formation of Imines: Reaction with 1° amines (acid catalyzed):

1° amine RNH₂, HCl (cat.) → imine $R{-}N{=}$ + $H_2\ddot{O}:$

same as (imine structures shown)

the order of protonation deprotonation is ambiguous

+H⁺ / −H⁺

+H⁺ / −H⁺   −H⁺   +H⁺

• **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 equilibrium favors imine

Ketone equilibrium favors carbonyl compound
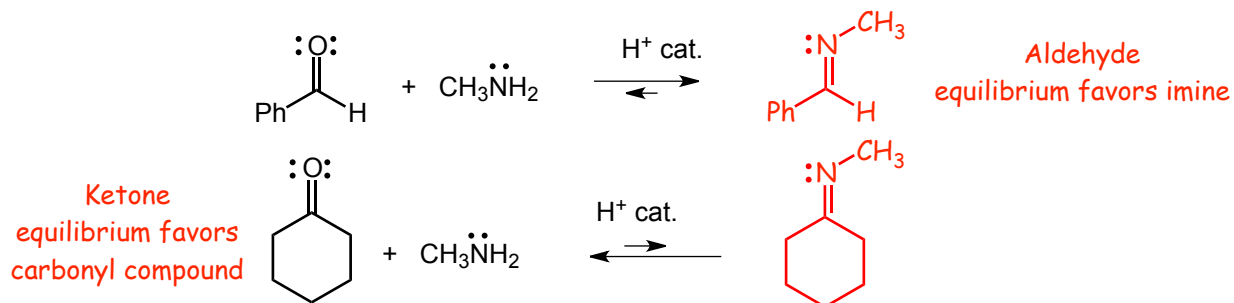
Imines are used in **synthesis**, we will **need this chemistry again** later in the course:

- The amine product of the reaction sequence above is crystal meth, and this sequence is the one used by the infamous **Walter White** in **Breaking Bad** in his synthesis (cooking) of crystal meth. Walter didn't use these exact reagents, we modified them here to ones that you know. Just like Walter, you will really need to know how to make imines later in the course.

Mechanism of Formation of Enamines
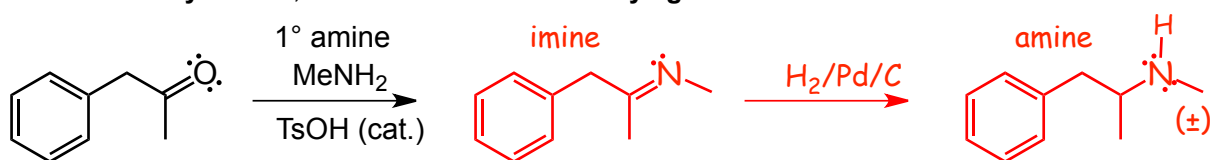- Reaction with 2° amines (acid catalyzed):

No hydrogen on N deprotonation must occur at α-carbon

IMINIUMN SALT

- Note the use the new abbreviated +H$^+$/-H$^+$+ notation, which is 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.

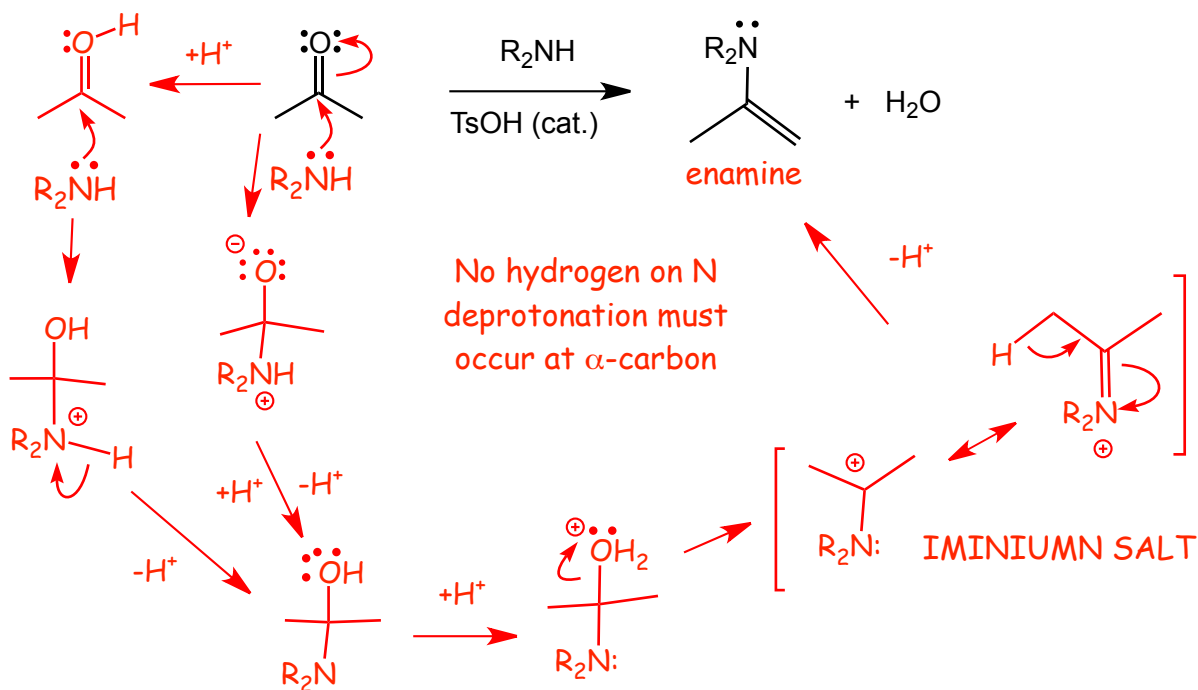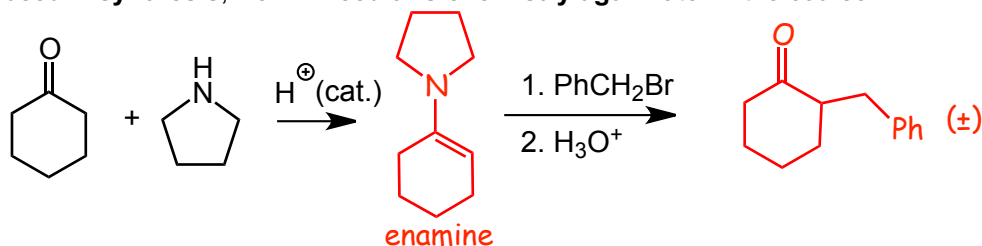**Enamines** are used in **synthesis**, we will **need this chemistry again** later in the course:

enamine

• The reaction sequence above is the **Gilbert Stork enamine synthesis** (this one is **not** illegal), it will be one of our final carbon-carbon bond forming reactions. Just like Gilbert, you will really need to know how to make enamines later in the course.
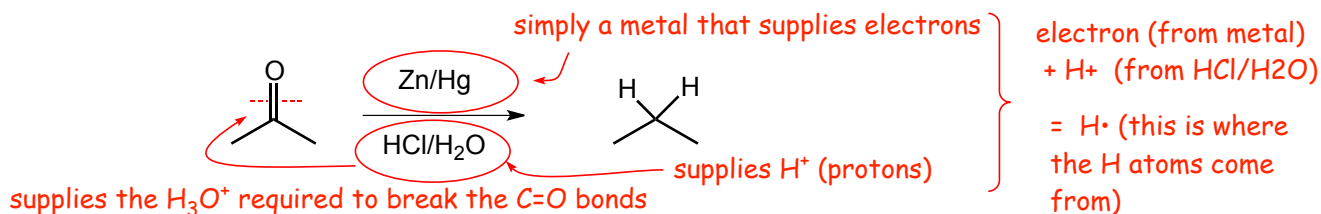
3.11 Complete Reduction of Carbonyl Groups: Clemmensen and Wolff-Kishner Reactions
Clemmensen Reduction: We have already seen this reaction in the benzene reactions section of the notes.

The mechanism of the Clemmensen reduction is actually complex and not well known!
• We *can* write some useful principles that may *help you understand/remember*
1. We need to break the 2 C=O bonds, this is done the usual way by protonating the oxygens using H_3O^+.
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:

simply a metal that supplies electrons

electron (from metal)
+ H+ (from HCl/H2O)

= H· (this is where
the H atoms come
from)

supplies H⁺ (protons)

supplies the H_3O^+ required to break the C=O bonds

• 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
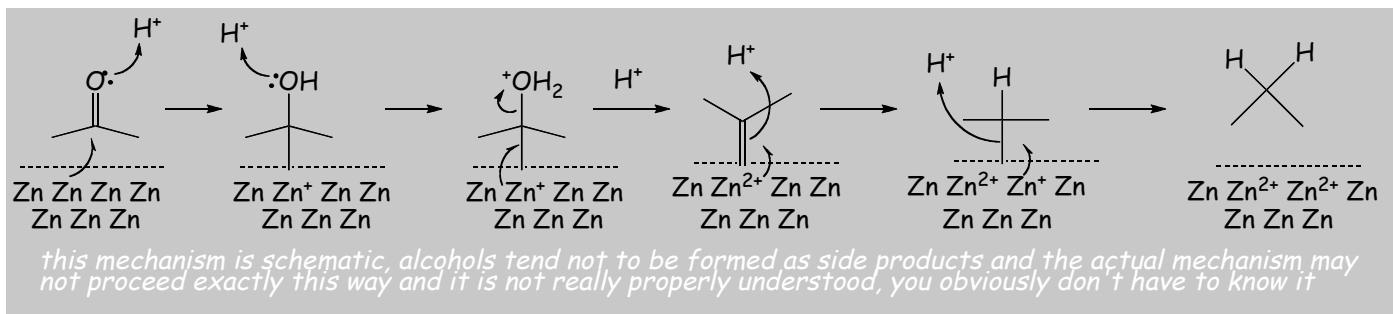
• The Clemmensen reaction represents an example of a "dissolving metal" reduction, since as the metal is oxidized (by giving the electron to the substrate), it dissolves in the form of an ionic metal salt.

Na (supplies electrons)
EtOH (supplies protons)
you don't have to know!!!

dissolving
metal
reductions

Na (supplies electrons)
NH₃ (supplies protons)

you DO have to know!!!
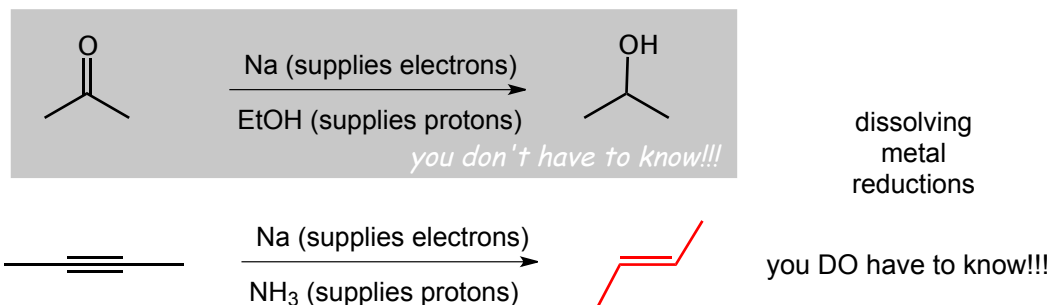
• Other examples of a dissolving metal reducing agents are sodium in ethanol (Na/EtOH) that can reduce a C=O to an alcohol, and also sodium in liquid ammonia, $Na/NH_3(I)$, which reduces an alkyne to a trans-alkene. Walter White almost certainly used a dissolving metal reduction in his crystal meth synthesis in Breaking Bad.

2. Wolff-Kishner Reduction
The Reaction:

Wolf-Kischner Reduction

• This does the same thing as the Clemmensen reduction, complete reduction of the C=O bond using **but using basic reagents and conditions** (not acid as in the Clemmensen).
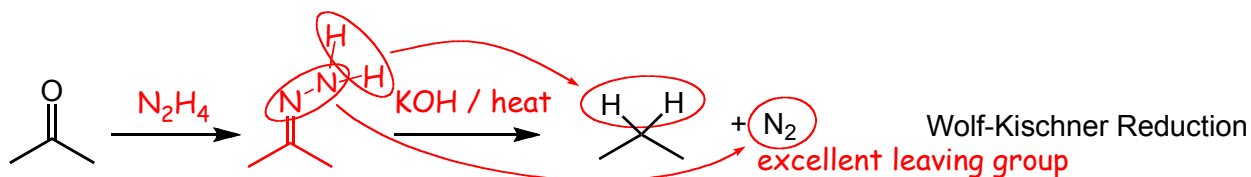• The oxygen of the C=O bond is removed when the hydrazone (imine) is formed, and the hydrogen atoms from the imine are then transferred to the carbon with overall loss of molecular nitrogen;
The mechanism of the Wolff-Kishner reduction:
• Starts off with formation of a hydrazone (a special kind of imine), we already know **this** part.
• The rest involves deprotonations and reprotonations that the facilitate loss of molecular nitrogen and overall transfer of hydrogen atoms to carbon, you don't have to know this mechanism.

Don't Need to Know!!!!
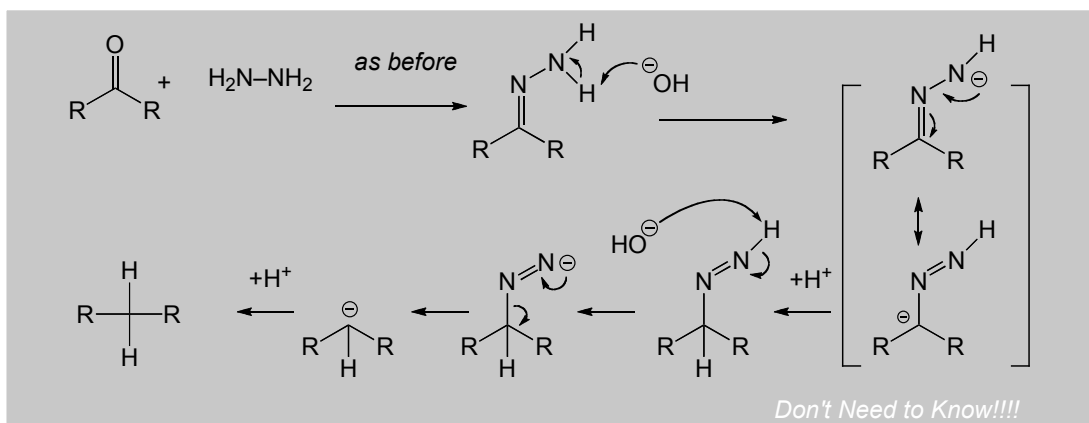
• We need to choose reduction conditions carefully......

Clemmenson

Wolff-Kichner

Clemmenson

Wolff-Kishner
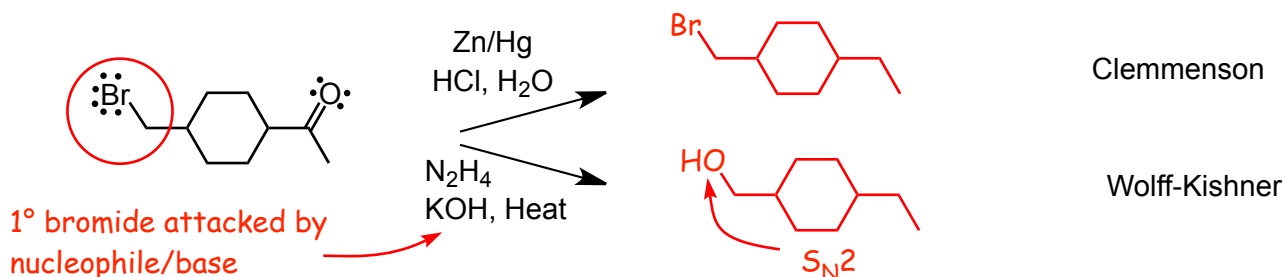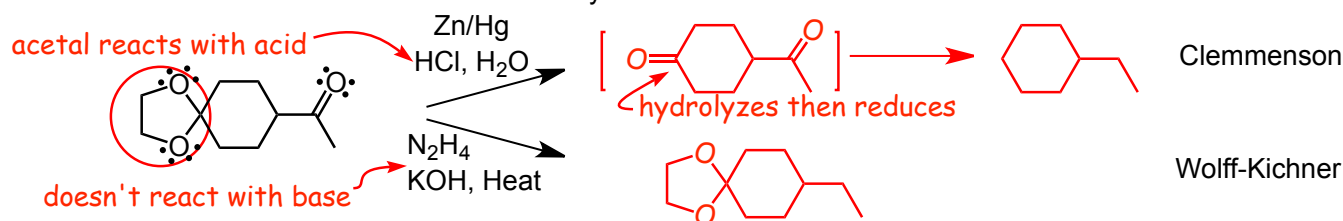
• There are many examples in organic chemistry in which there are more ways of performing a specific reaction, this is only one of them.
• There are different reasons for having more than one reaction that does the same thing, in this case it is so that you can do **chemistry on one functional group in the presence of another one**.

5 Summary of Aldehyde and Ketone Reactions

Reactions that make aldehydes/ketones from alcohols

Ph–C(OH)(H)–Me	$\xrightarrow[\text{CH}_2\text{Cl}_2\ \text{(solvent)}]{\text{PCC}}$ Y / N *seen previously*	Ph–C(=O)–Me
cyclohexyl-CH$_2$OH	$\xrightarrow[\text{CH}_2\text{Cl}_2\ \text{(solvent)}]{\text{PCC}}$ Y / N *seen previously*	cyclohexyl-C(=O)H
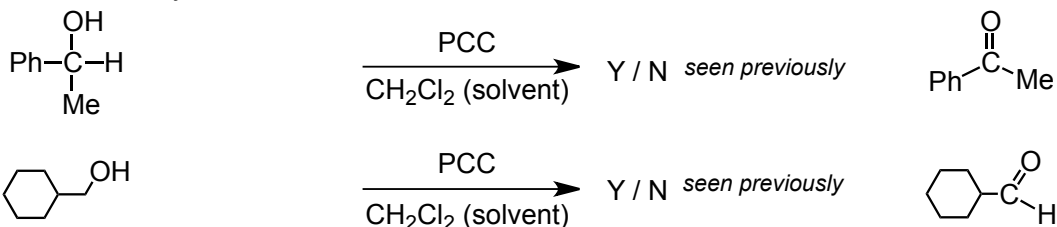
Reactions involving aldehydes/ketones

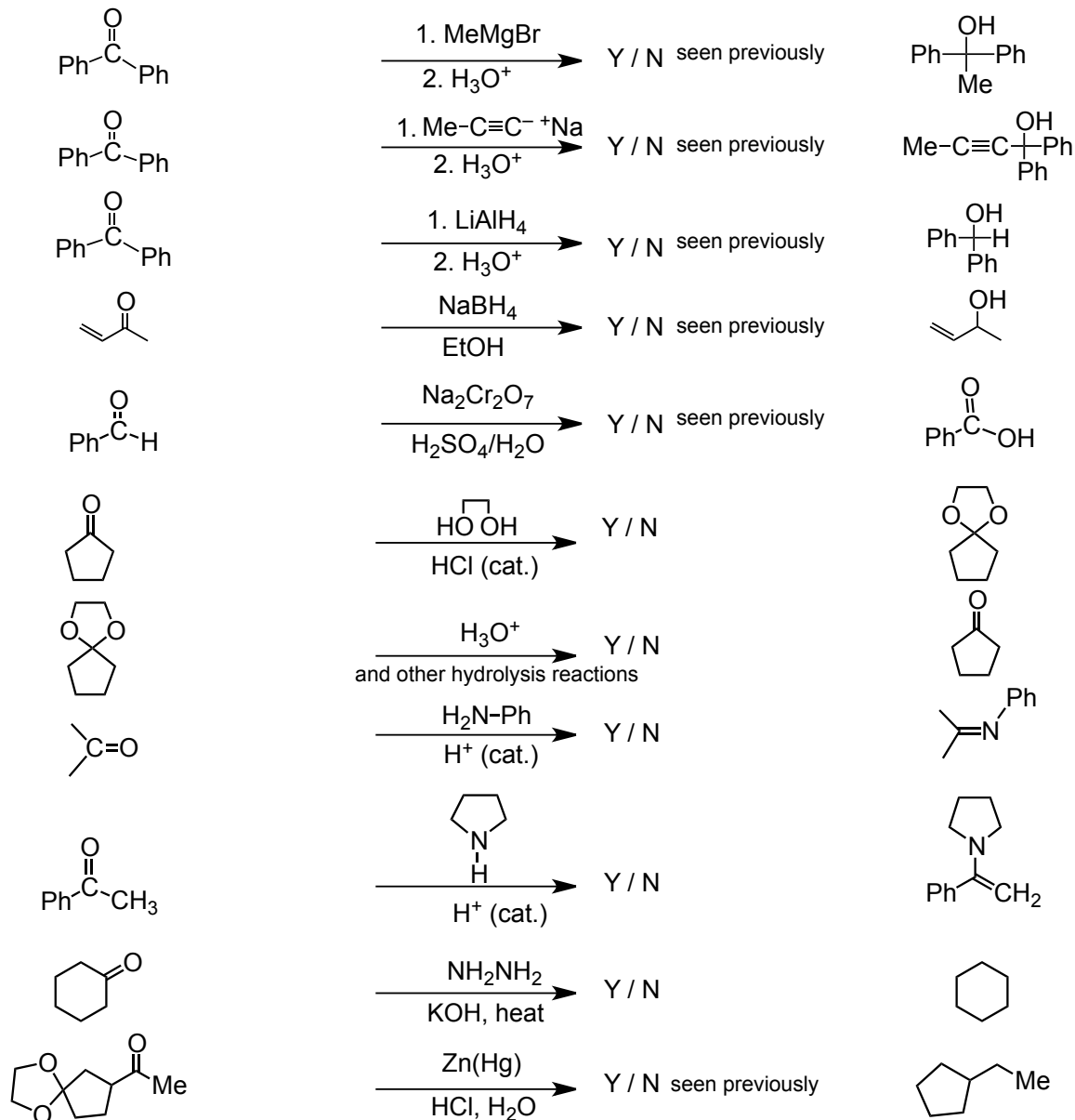|		
Ph–C(=O)–Ph	$\xrightarrow[\text{2. H}_3\text{O}^+]{\text{1. MeMgBr}}$ Y / N *seen previously*	Ph–C(OH)(Me)–Ph
Ph–C(=O)–Ph	$\xrightarrow[\text{2. H}_3\text{O}^+]{\text{1. Me–C≡C}^-\ {}^+\text{Na}}$ Y / N *seen previously*	Me–C≡C–C(OH)(Ph)–Ph
Ph–C(=O)–Ph	$\xrightarrow[\text{2. H}_3\text{O}^+]{\text{1. LiAlH}_4}$ Y / N *seen previously*	Ph–C(OH)(H)–Ph
(but-3-en-2-one)	$\xrightarrow[\text{EtOH}]{\text{NaBH}_4}$ Y / N *seen previously*	(but-3-en-2-ol)
Ph–C(=O)–H	$\xrightarrow[\text{H}_2\text{SO}_4/\text{H}_2\text{O}]{\text{Na}_2\text{Cr}_2\text{O}_7}$ Y / N *seen previously*	Ph–C(=O)–OH
(cyclopentanone)	$\xrightarrow[\text{HCl (cat.)}]{\text{HO OH}}$ Y / N	(cyclopentanone dioxolane)
(dioxolane spiro)	$\xrightarrow[\text{and other hydrolysis reactions}]{\text{H}_3\text{O}^+}$ Y / N	(cyclopentanone)
(CH$_3$)$_2$C=O	$\xrightarrow[\text{H}^+\text{ (cat.)}]{\text{H}_2\text{N–Ph}}$ Y / N	(CH$_3$)$_2$C=N–Ph
Ph–C(=O)–CH$_3$	$\xrightarrow[\text{H}^+\text{ (cat.)}]{\text{pyrrolidine}}$ Y / N	Ph–C(N-pyrrolidine)=CH$_2$
(cyclohexanone)	$\xrightarrow[\text{KOH, heat}]{\text{NH}_2\text{NH}_2}$ Y / N	(cyclohexane)
(dioxolane)–C(=O)–Me	$\xrightarrow[\text{HCl, H}_2\text{O}]{\text{Zn(Hg)}}$ Y / N *seen previously*	cyclopentyl-CH$_2$–Me

Not really useful reactions of aldehydes/ketones, but ones you should know

Cl$_3$C–C(=O)–H	$\xrightarrow[\text{H}^+\ or\ {}^-\text{OH}]{\text{H}_2\text{O}}$ Y / N	Cl$_3$C–C(OH)(OH)–H
Cl$_3$C–C(=O)–H	$\xrightarrow[\text{CH}_3\text{OH}]{\text{Na}^+\ {}^-\text{OCH}_3}$ Y / N	Cl$_3$C–C(OH)(OCH$_3$)–H