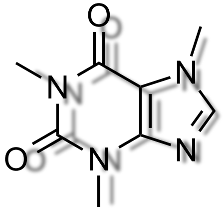


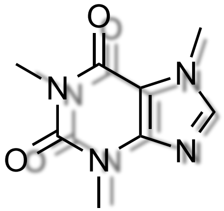
Chem 2500

Chapter 7

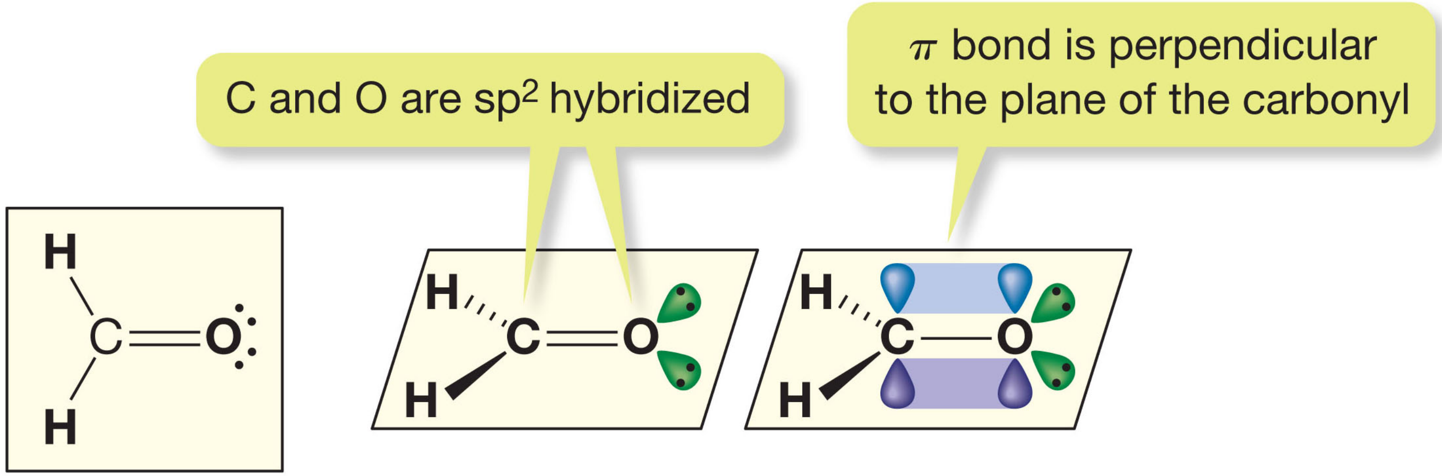
π Bonds as Electrophiles

(sections 7.1-1.11)

Carbonyls and Related Functional Groups



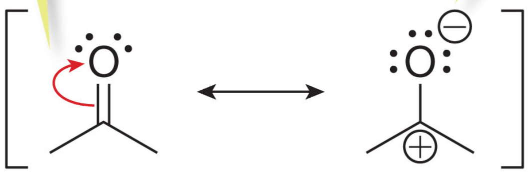
- In organic chemistry, a key component of many functional groups is the carbonyl group, which consists of a carbon atom doubly bonded to an oxygen atom.
- The carbonyl group has a permanent dipole, which is revealed by its resonance structures.
- The partial positive charge on carbon and the partial negative charge on oxygen dictate the reactivity pattern of this group.


C and O are sp^2 hybridized

π bond is perpendicular to the plane of the carbonyl

Carbonyls and Related Functional Groups

- The carbon atom is an ***electrophile***; an atom or group that tends to accept electrons to make bonds (Lewis acid).
- Electrophiles attract ***nucleophiles***; an atom or group that donate electrons to form bonds (Lewis base).
- When the carbonyl group acts as an electrophile, the π bond will ***break at the same time***, moving electrons towards the oxygen atom.



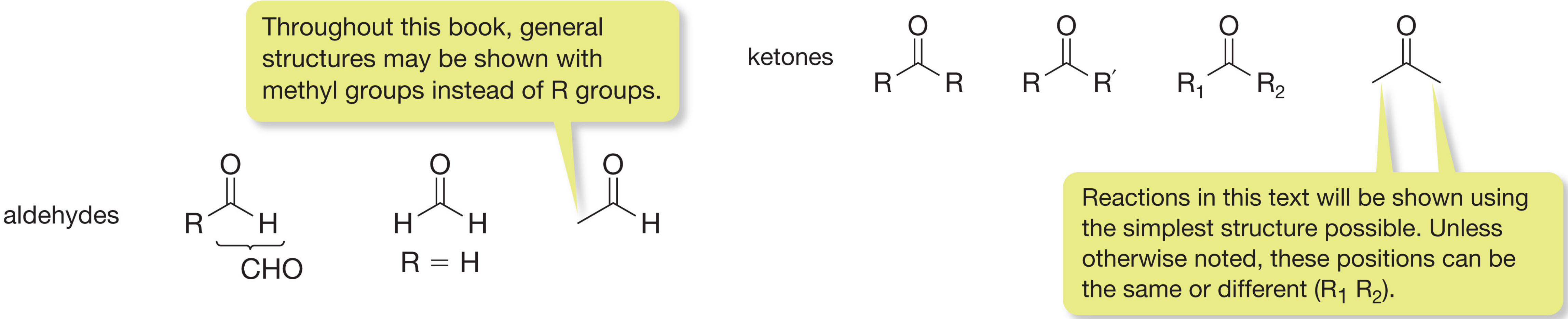
This resonance form contributes most to the overall structure and so the carbonyl group is drawn this way.

This resonance form predicts the carbonyl dipole.

A carbon in this resonance form has an incomplete octet. Nucleophiles are attracted to this carbon.

Carbonyls and Related Functional Groups

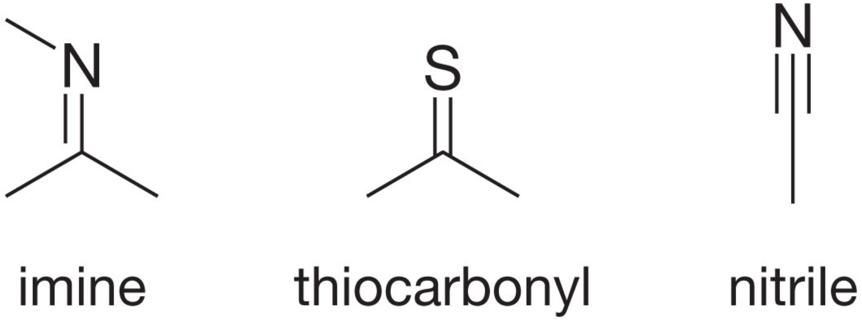
- Typical carbonyl containing functional groups:



Throughout this book, general structures may be shown with methyl groups instead of R groups.

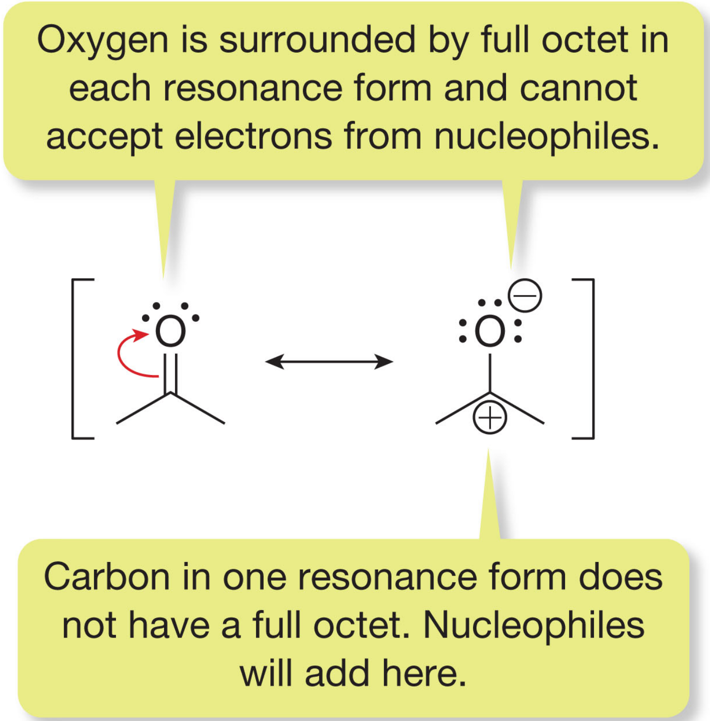
Reactions in this text will be shown using the simplest structure possible. Unless otherwise noted, these positions can be the same or different (R_1 R_2).

- Although they look different, the following functional groups ‘behave’ like a carbonyl group:

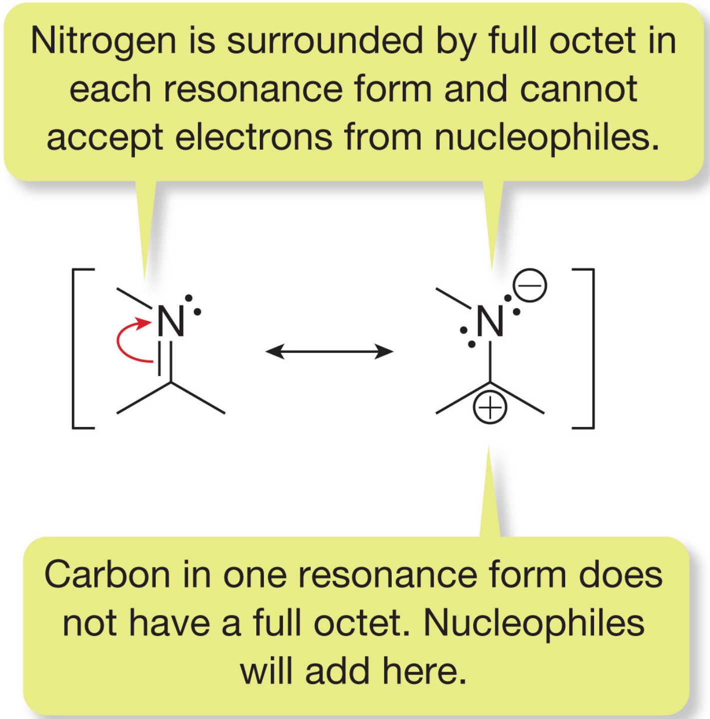


Carbonyls and Related Functional Groups

- These functional groups possess similar features and resonance forms as an aldehyde or ketone.
- Both have a resonance form where the carbon atom is electron deficient and therefore electrophilic.


Oxygen is surrounded by full octet in each resonance form and cannot accept electrons from nucleophiles.

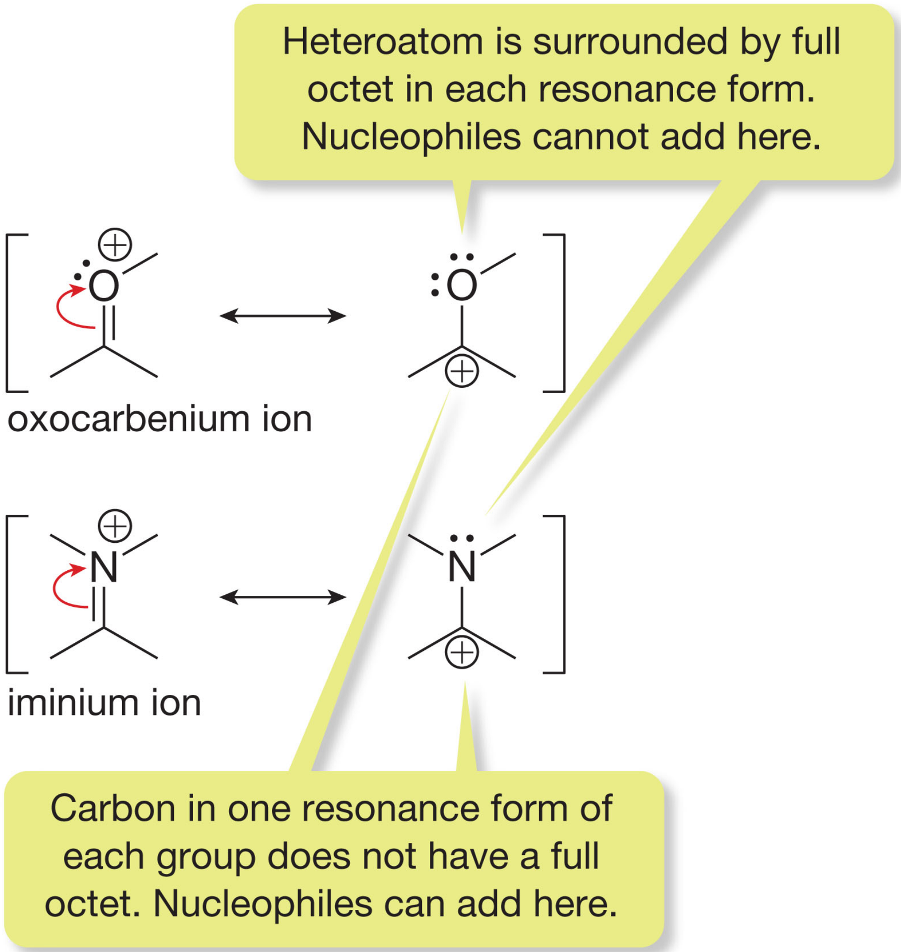
Carbon in one resonance form does not have a full octet. Nucleophiles will add here.


Nitrogen is surrounded by full octet in each resonance form and cannot accept electrons from nucleophiles.

Carbon in one resonance form does not have a full octet. Nucleophiles will add here.

Carbonyls and Related Functional Groups

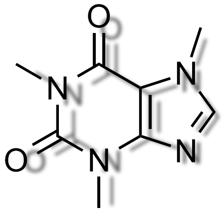
- The same analysis can be used for an oxocarbenium ion and an iminium ion.



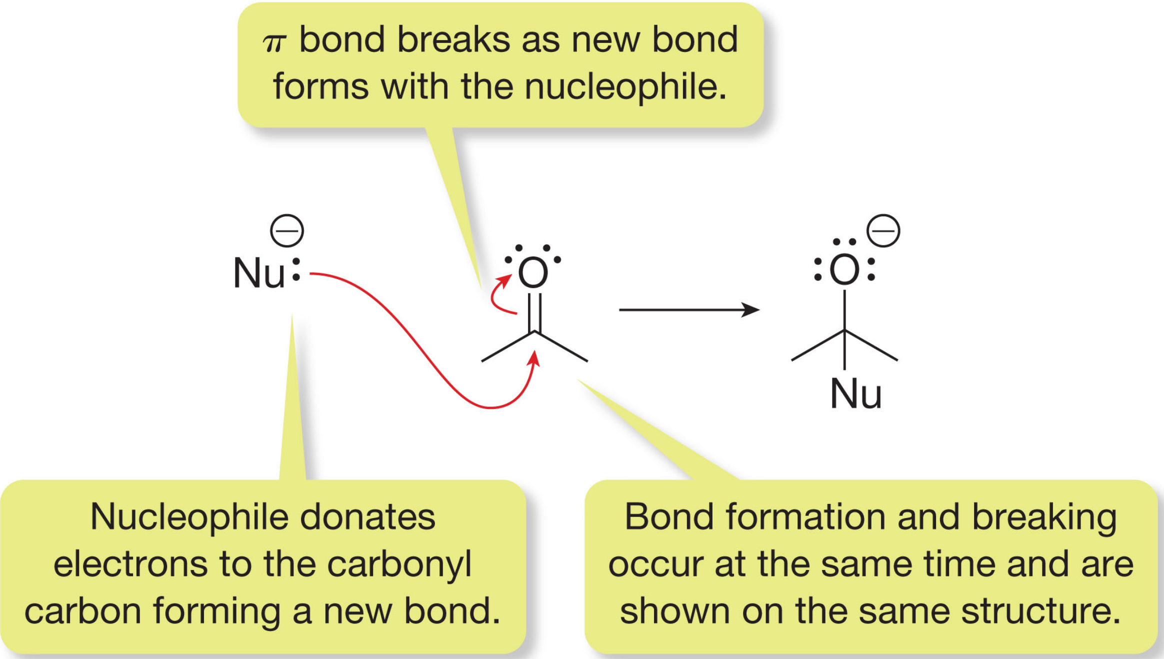
Heteroatom is surrounded by full octet in each resonance form. Nucleophiles cannot add here.

Carbon in one resonance form of each group does not have a full octet. Nucleophiles can add here.

Nucleophilic Addition to Electrophilic π Bonds



- Nucleophiles form new bonds by sharing a pair of electrons with an electrophilic site.
- This sharing of electrons between the nucleophile (Nu) and the carbonyl carbon produces a new covalent bond.
- Since the carbonyl carbon already has a full octet of electrons, the weakest bond, the π bond, breaks and puts the electrons on the oxygen atom.



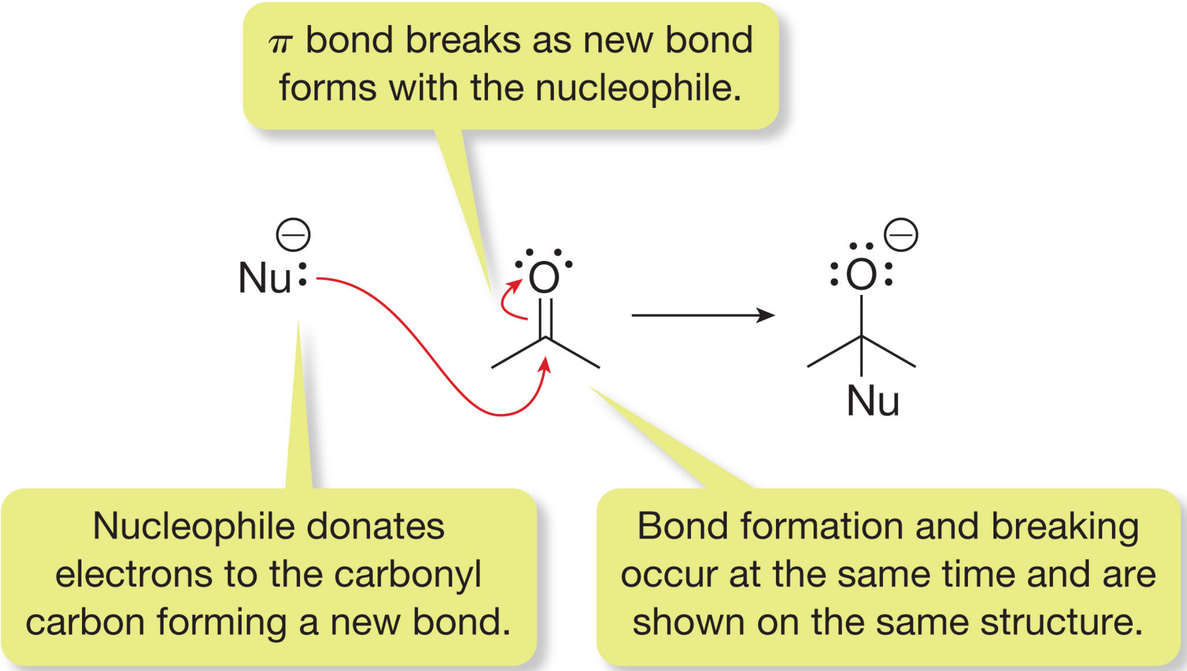
π bond breaks as new bond forms with the nucleophile.

Nucleophile donates electrons to the carbonyl carbon forming a new bond.

Bond formation and breaking occur at the same time and are shown on the same structure.

Nucleophilic Addition to Electrophilic π Bonds

- Both sequences of events are depicted as reaction arrows. Both arrows are shown on the same structure because the two electron flows happen at the same time.
- Notice how the geometry at the carbonyl carbon changes; it changes from a trigonal planar to tetrahedral.
- Also notice how the charge density changes from the nucleophile onto the oxygen atom.



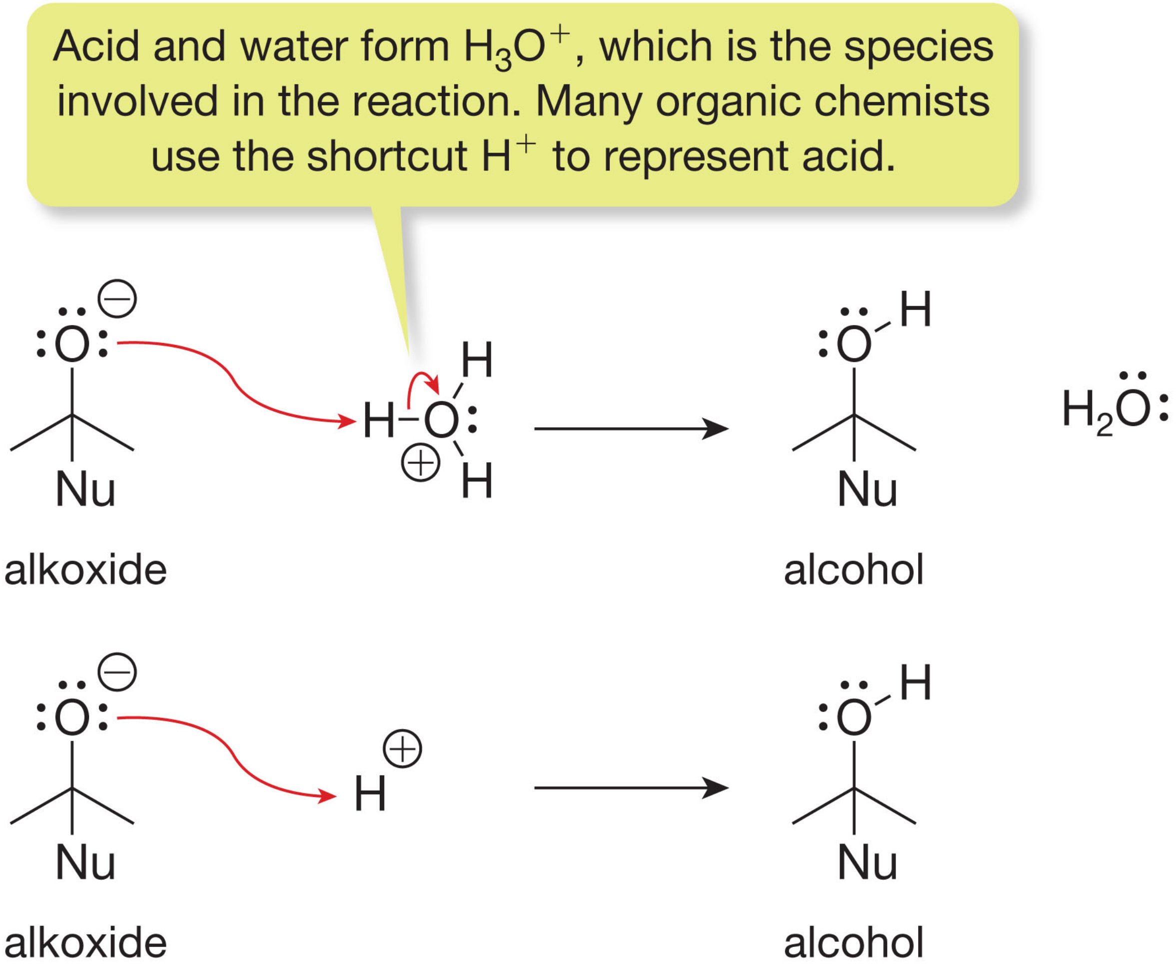
π bond breaks as new bond forms with the nucleophile.

Nucleophile donates electrons to the carbonyl carbon forming a new bond.

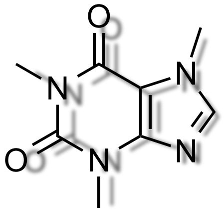
Bond formation and breaking occur at the same time and are shown on the same structure.

Nucleophilic Addition to Electrophilic π Bonds

- If a source of protons exists, the alkoxide will react with this proton to give the corresponding neutral alcohol.
- If no such proton is available, an additional step is needed, in which a proton is added (from an acid or protic solvent) to neutralize the alkoxide.

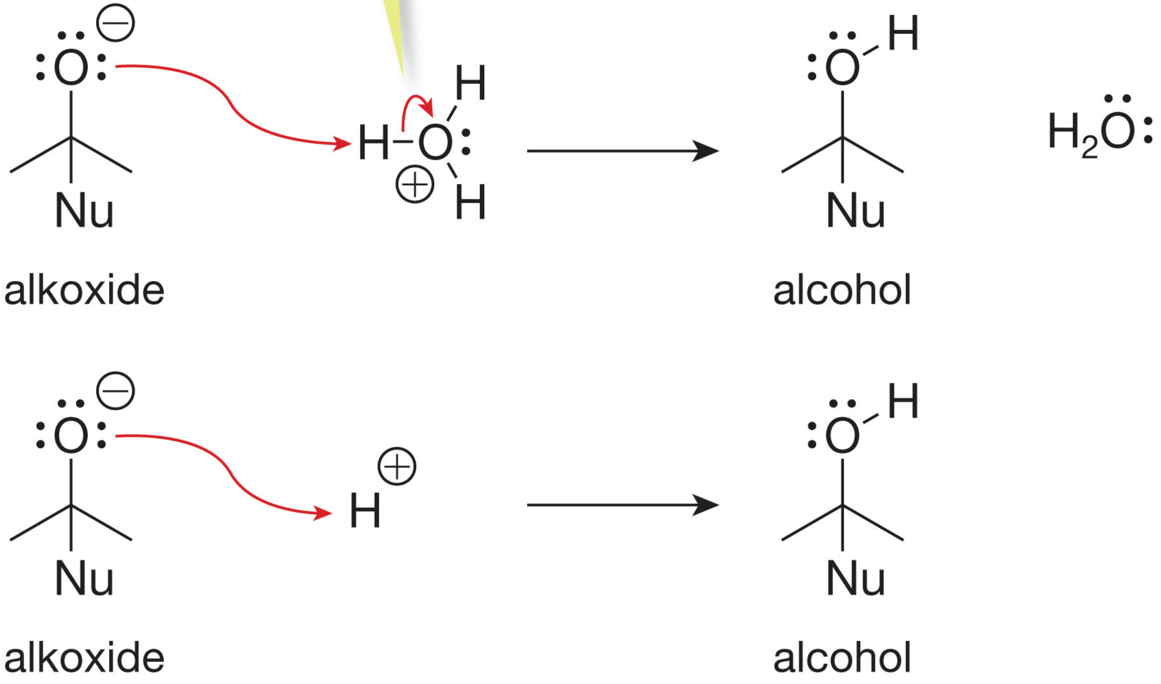

Acid and water form H_3O^+, which is the species involved in the reaction. Many organic chemists use the shortcut H^+ to represent acid.

Nucleophilic Addition to Electrophilic π Bonds



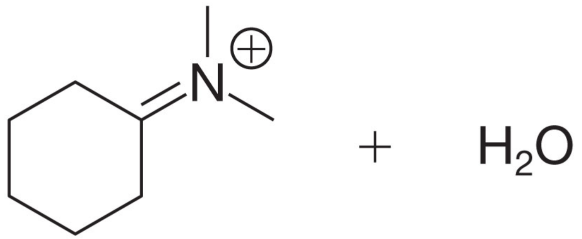
- The mechanism of neutralization is the same with either method.
- The alkoxide is now the nucleophile and donates a pair of electrons to the H+, generating a new O-H bond.
- This reaction is an acid-base process, but it can also be viewed as a nucleophile-electrophile reaction.

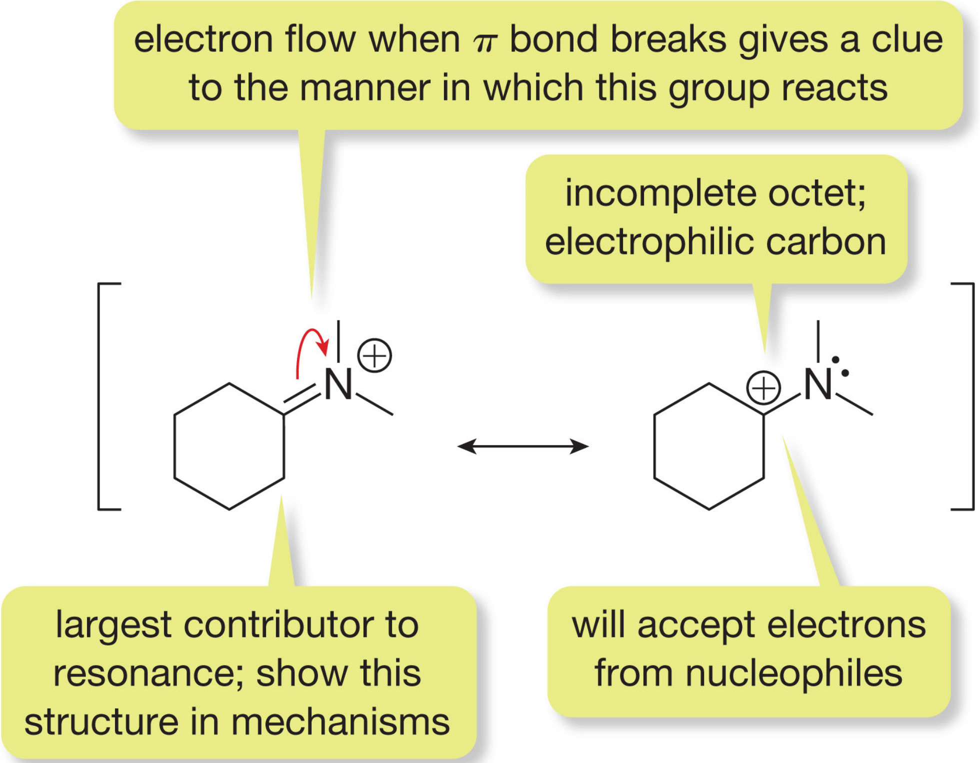
Acid and water form H_3O^+, which is the species involved in the reaction. Many organic chemists use the shortcut H^+ to represent acid.



Nucleophilic Addition to Electrophilic π Bonds

- When different resonance structures are possible, mechanisms should always use the best resonance contributors of the molecules.
- Keep in mind, however, that resonance structures often reveal ***where*** reactivity occurs.





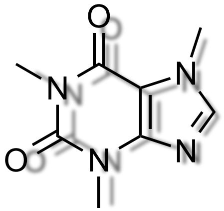
electron flow when π bond breaks gives a clue to the manner in which this group reacts

incomplete octet; electrophilic carbon

largest contributor to resonance; show this structure in mechanisms

will accept electrons from nucleophiles

Nucleophilic Addition to Electrophilic π Bonds



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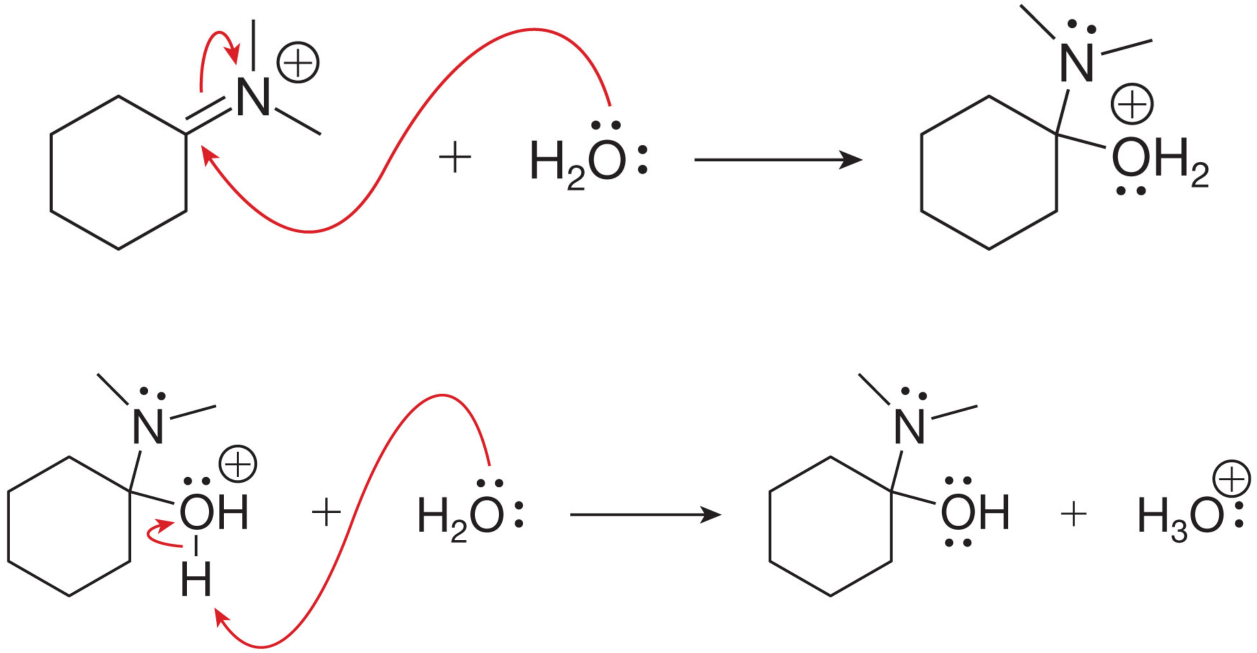
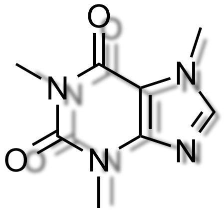
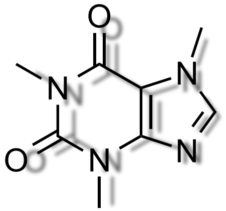


Addition of Hydrides to Carbonyl Groups

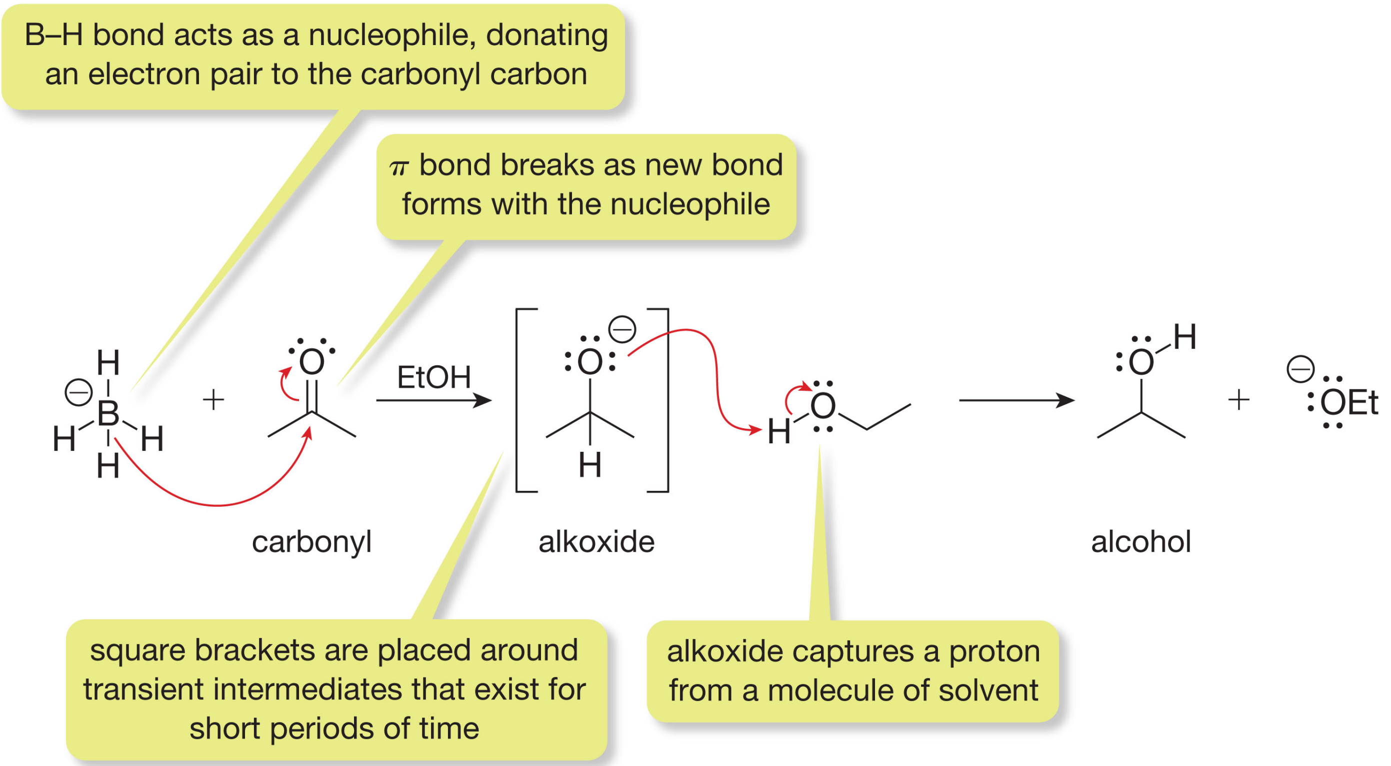


- In principle, the simplest nucleophile is the hydride ion (H:$^-$).
- For nucleophilic additions of hydride, special reagents such as $NaBH_4$ and $LiAlH_4$ must be used.
- In the anions of these reagents (BH_4^- and AlH_4^-), even though the metals carry the formal negative charge, the hydrogen atoms are more electronegative and therefore the electrons are polarized towards them.
- **Note:** NaH and KH are never used as sources of nucleophilic hydrides. Both NaH and KH are strong bases and used in acid-base reaction. Hydride itself is a very poor nucleophile.

Addition of Hydrides to Carbonyl Groups



- Reactions involving $NaBH_4$ typically use alcohol as solvent because the alcohol also participates as a reagent (acid) in the final step.
- The overall reaction happens in 2 steps, one after the other.



B–H bond acts as a nucleophile, donating an electron pair to the carbonyl carbon

π bond breaks as new bond forms with the nucleophile

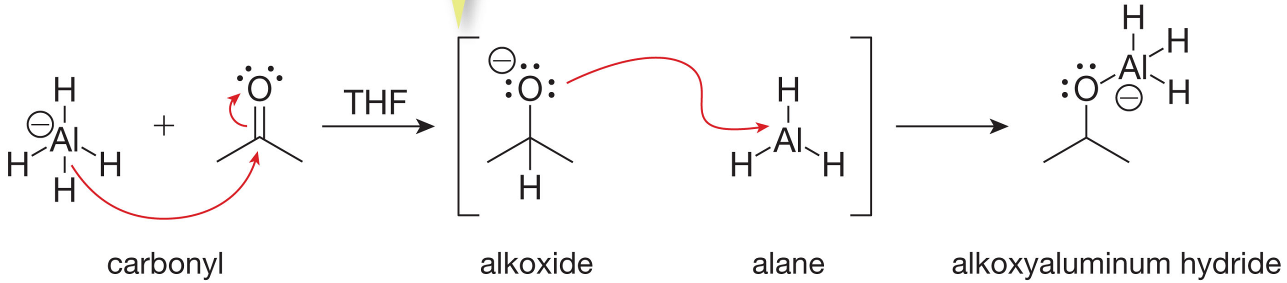
square brackets are placed around transient intermediates that exist for short periods of time

alkoxide captures a proton from a molecule of solvent

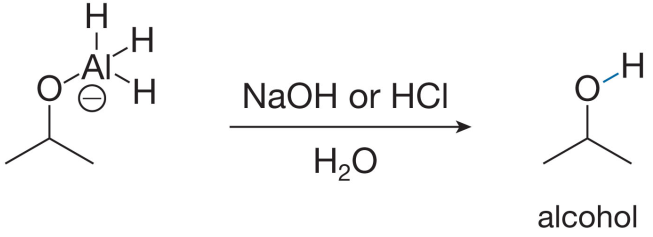
Addition of Hydrides to Carbonyl Groups

- The reaction mechanism involving $LiAlH_4$ is similar to that involving $NaBH_4$.
- Because $LiAlH_4$ is much more reactive than $NaBH_4$, the reaction conditions must be anhydrous (dry, no H^+ sources), therefore the protonation of the alkoxide is done as a separate, distinct reaction.

square brackets are placed around transient intermediates that exist only for short periods of time in a reaction



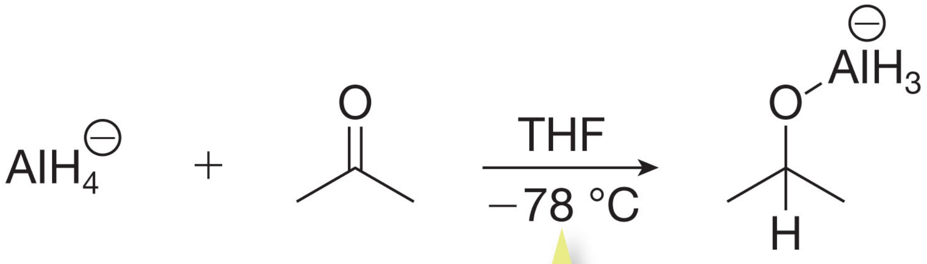
reaction 1



reaction 2

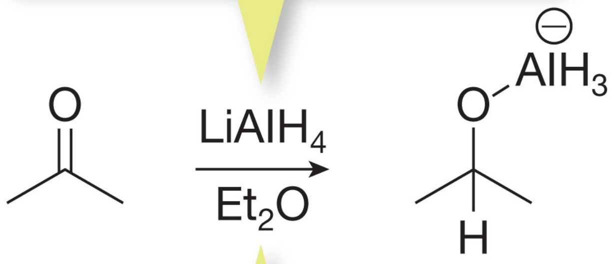
Equations: Over-the-Arrow Notation

- Organic reactions are often written in a compact notation, called over-the-arrow notation.
- Typically, the organic starting material is shown on the left side of the reaction arrow, and the organic product is shown on the right. Other reagents and/or solvents are written over the arrow.



over-the-arrow notation

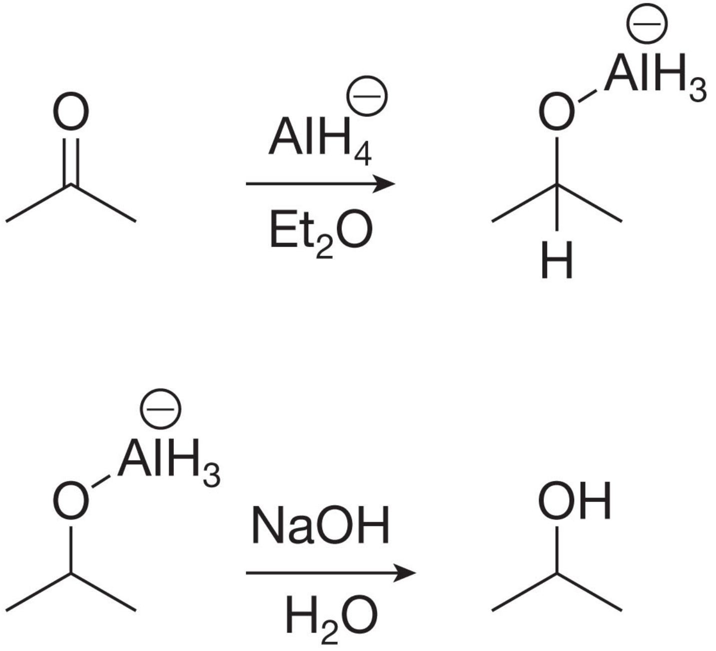
reagents are typically shown over-the-arrow



solvents and other special conditions are shown when necessary

Equations: Sequential Reactions

- Some chemical transformations are actually a set of reactions that are preformed in sequence because the reactions require incompatible reagents or different conditions.
- There are different ways to presenting these reactions.

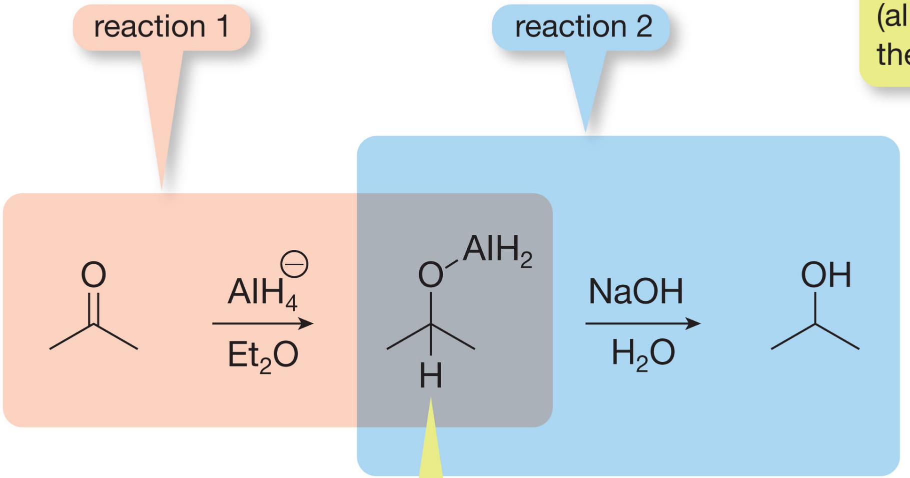


This first reaction must be performed in ether. No water can be present as it will react violently with $LiAlH_4$.

This reaction is performed in water and can only be done after the first reaction is complete.

Equations: Sequential Reactions

- Some chemical transformations are actually a set of reactions that are preformed in sequence because the reactions require incompatible reagents or different conditions.
- There are different ways to presenting these reactions.

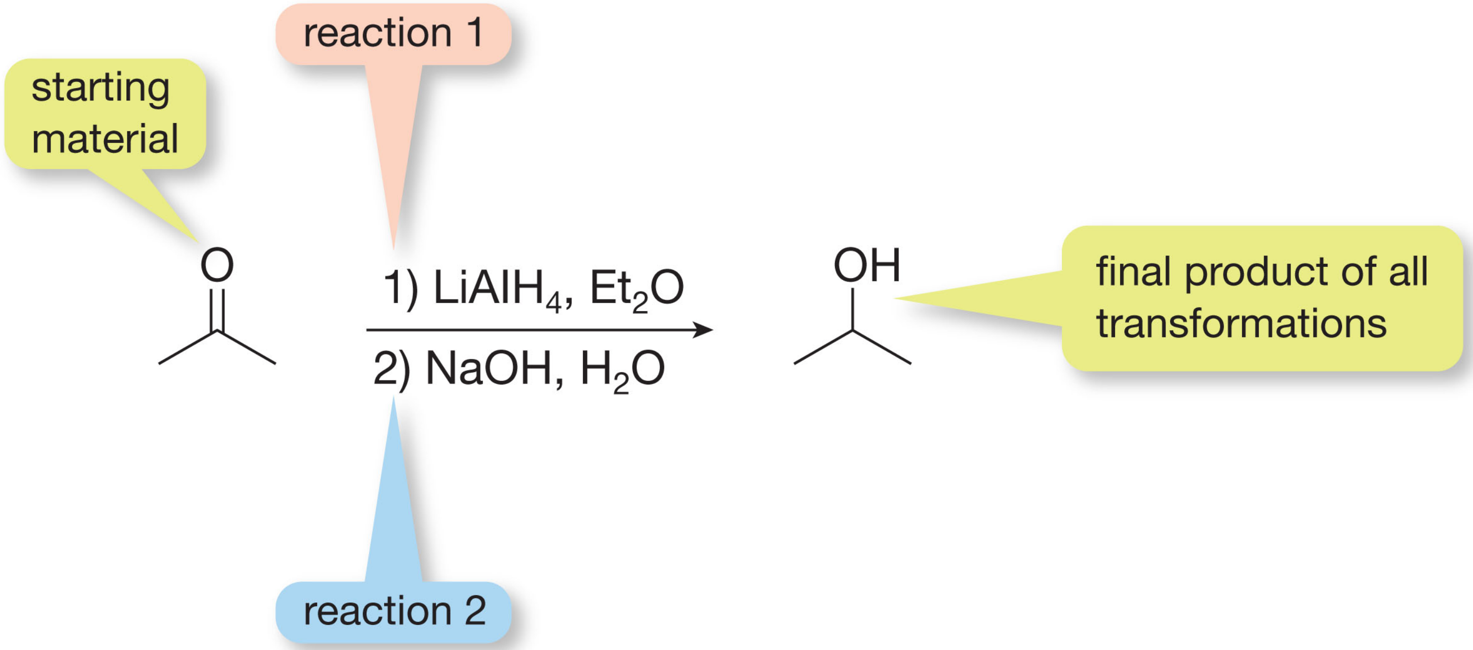


It is understood that the first reaction must be complete (all molecules reacted) before the second reaction is performed.

The product of the first reaction is the starting material for the second reaction.

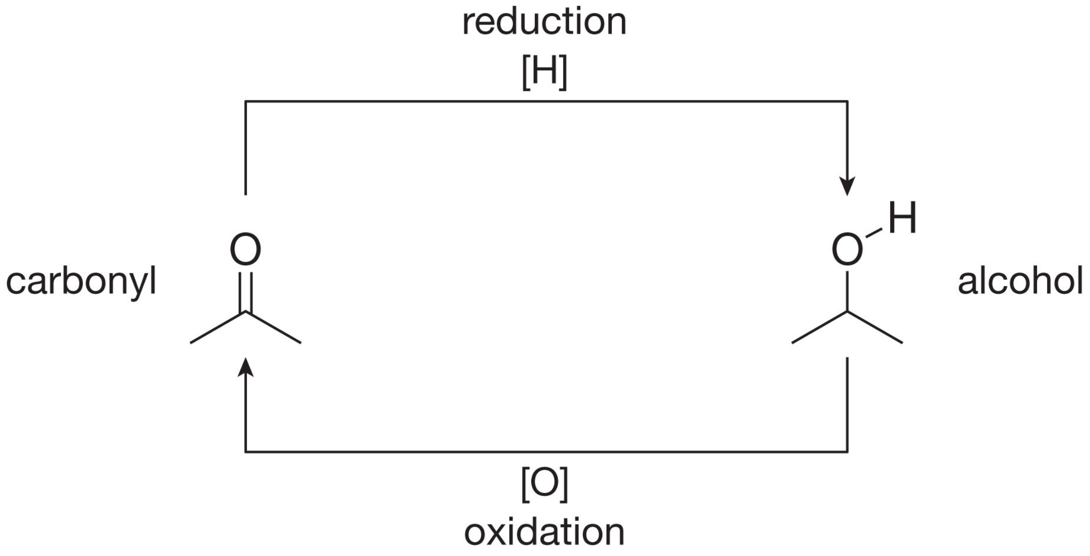
Equations: Sequential Reactions

- The most compact option is a notation that uses one arrow that points from the first starting material to the last product of the reaction, without showing the intermediate products.
- Each number represents a separate sequential reaction.



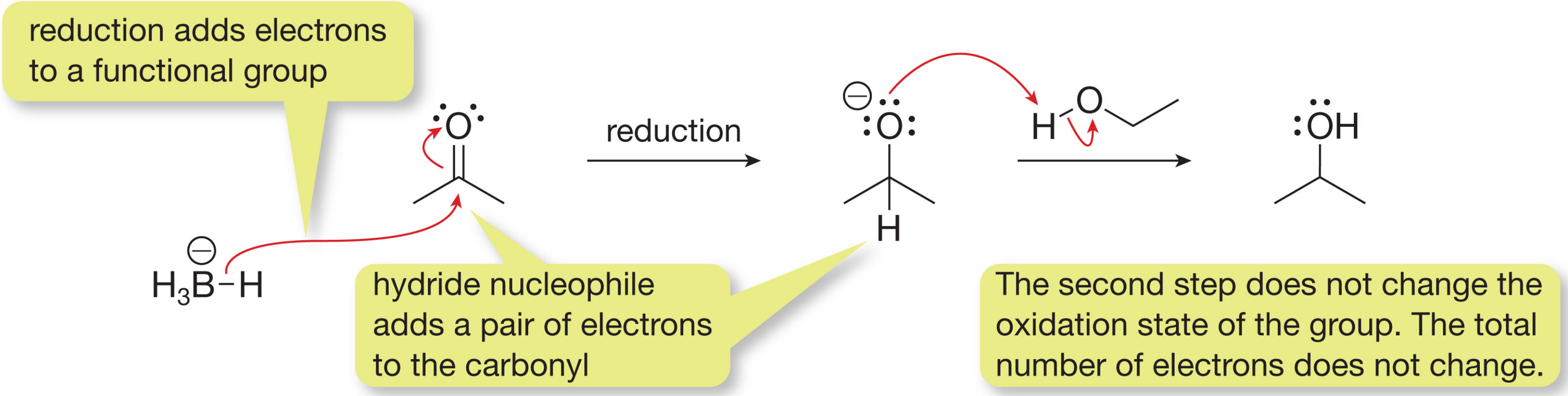
Organic Oxidations and Reductions

- Organic reactions undergo redox processes just as inorganic materials do. For organic processes, however, we typically follow the redox change of functional groups rather than that of the entire molecule.
- ***Oxidation [O]***: Addition of an oxygen atom or removal of hydrogen atoms (multiples of 2).
- ***Reduction [H]***: Addition of hydrogen atoms (multiples of 2) or removal of an oxygen atom.



Organic Oxidations and Reductions

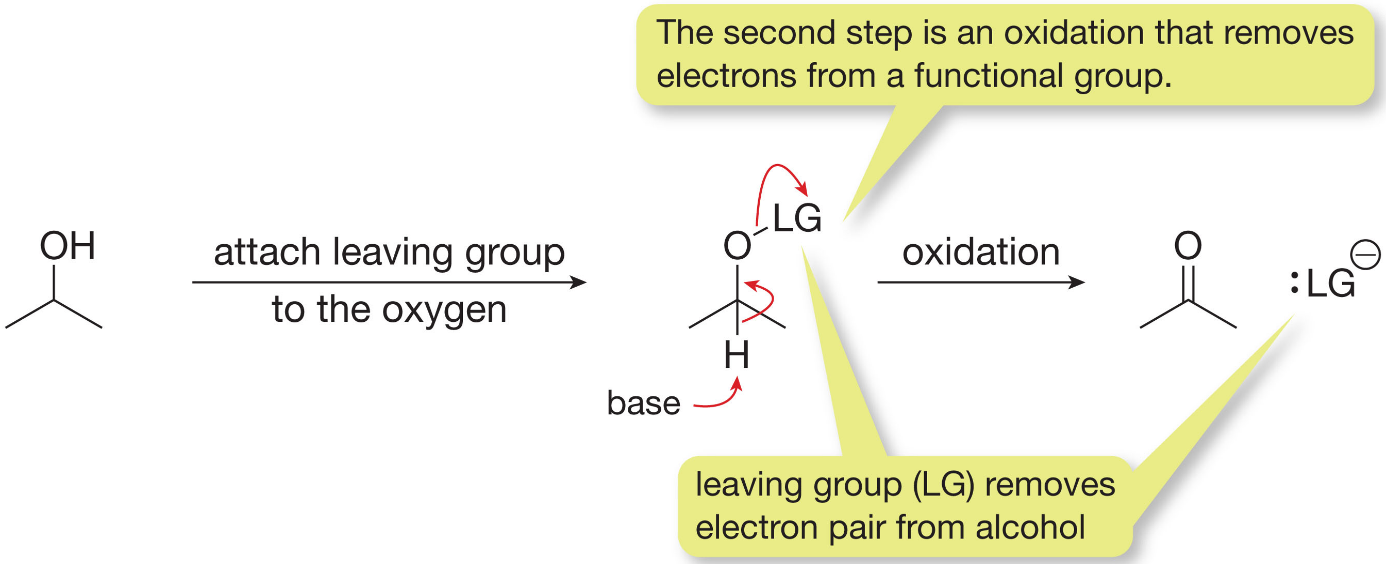
- Keep in mind that this shorthand still follows the basic definition of reduction (gaining electrons) and oxidation (losing electrons).



reduction adds electrons to a functional group

hydride nucleophile adds a pair of electrons to the carbonyl

The second step does not change the oxidation state of the group. The total number of electrons does not change.

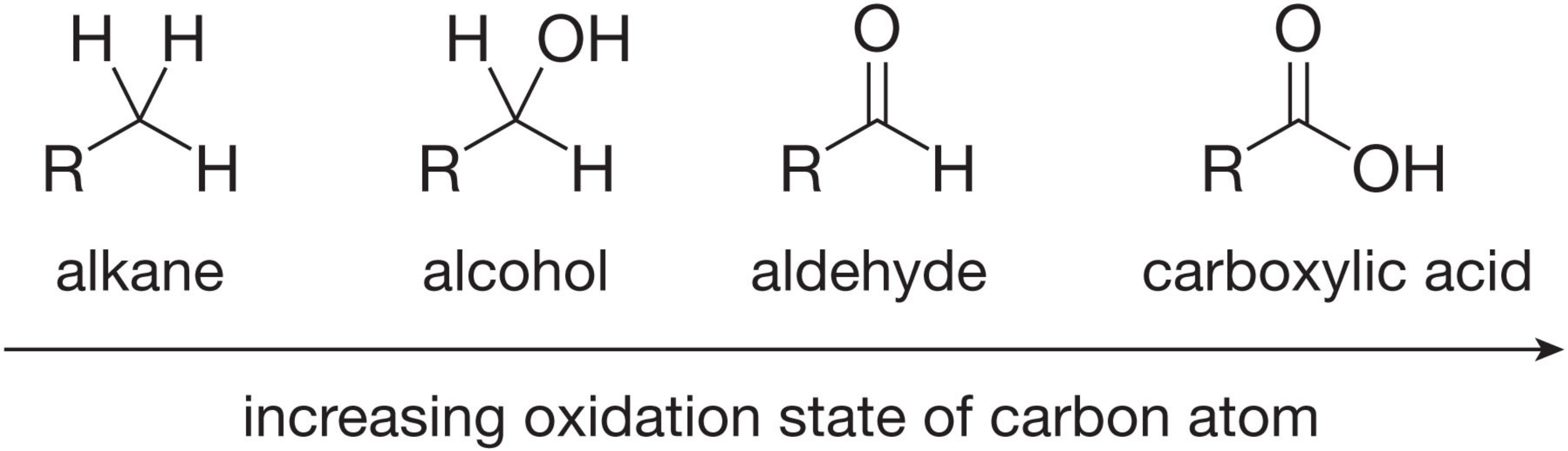


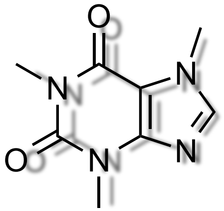
The second step is an oxidation that removes electrons from a functional group.

leaving group (LG) removes electron pair from alcohol

Organic Oxidations and Reductions

- Alkanes have the lowest oxidation state. Introducing heteroatoms or removing hydrogen atoms increases the oxidation state.

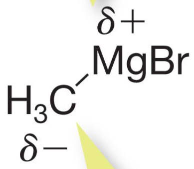




Addition of Organometallic Compounds to Electrophilic π bonds

- Organometallics are an important class of organic compounds in which ***carbon is bonded to a metal***.
- Since metals are less electronegative than carbon atoms, the carbon atoms in these bonds are nucleophilic and can be used to make new carbon-carbon bonds. Forming carbon-carbon bonds is key to the creation of new organic materials.
- Typical organometallic reagents include Grignards, organolithiums, and acetylides.

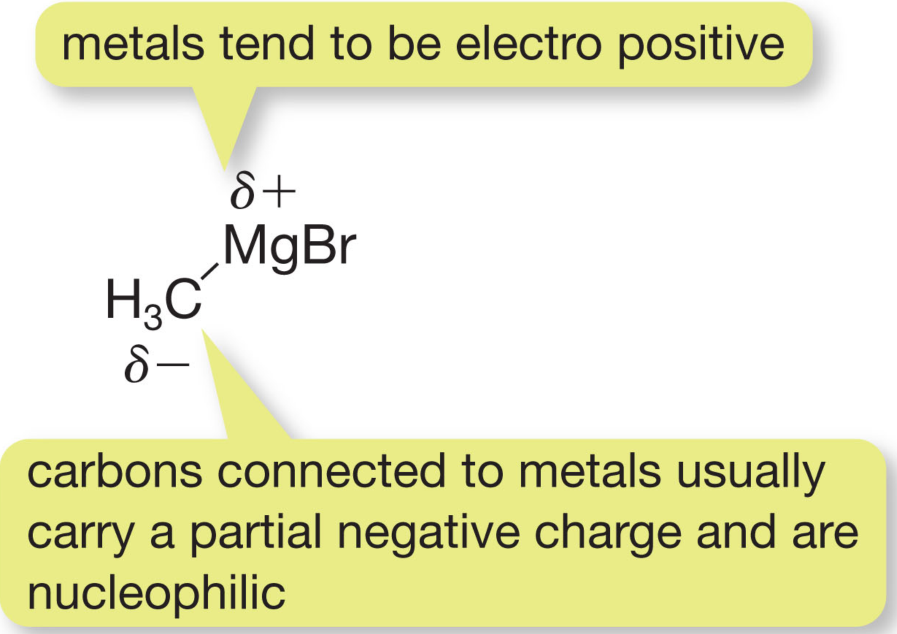
metals tend to be electro positive



carbons connected to metals usually carry a partial negative charge and are nucleophilic

Addition of Organometallic Compounds to Electrophilic π bonds

- Many organometallic reagents react violently with water, and some are even pyrophoric
- When using these organometallics; the glassware, solvents, and all reagents must be anhydrous (free of water, completely dry), and unreactive atmospheres such as N_2 and Ar are used.

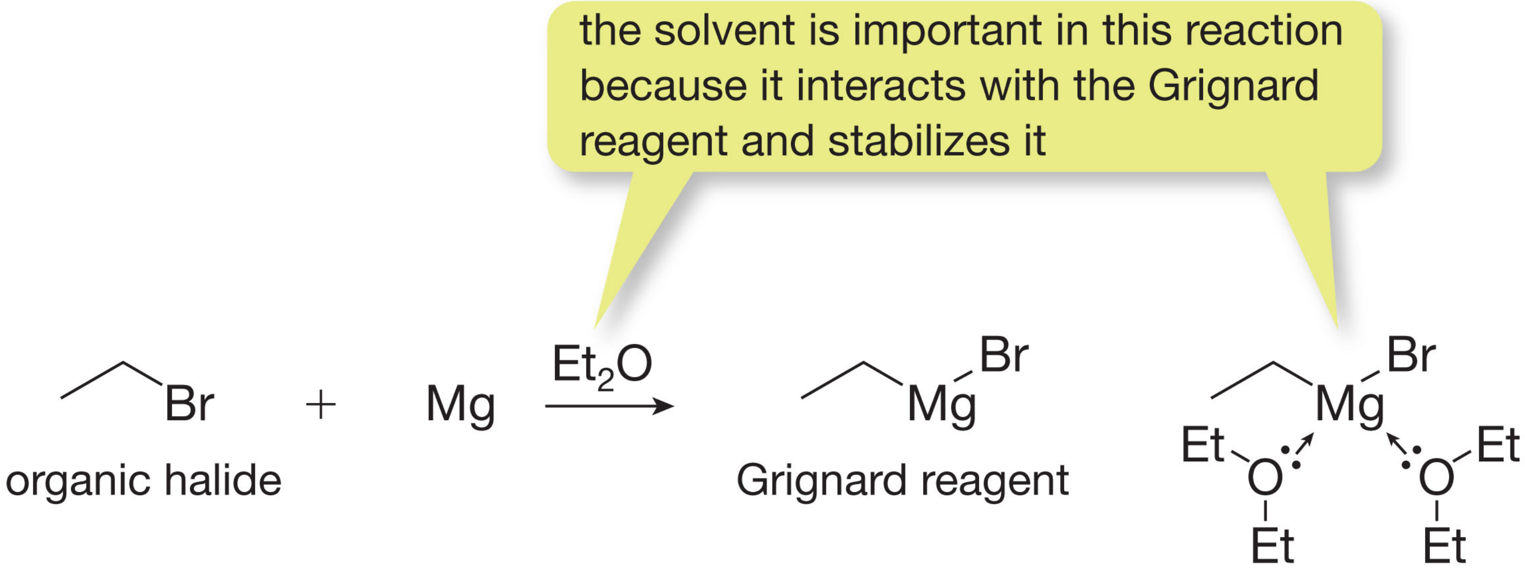


metals tend to be electro positive

carbons connected to metals usually carry a partial negative charge and are nucleophilic

Addition of Grignard Reagents

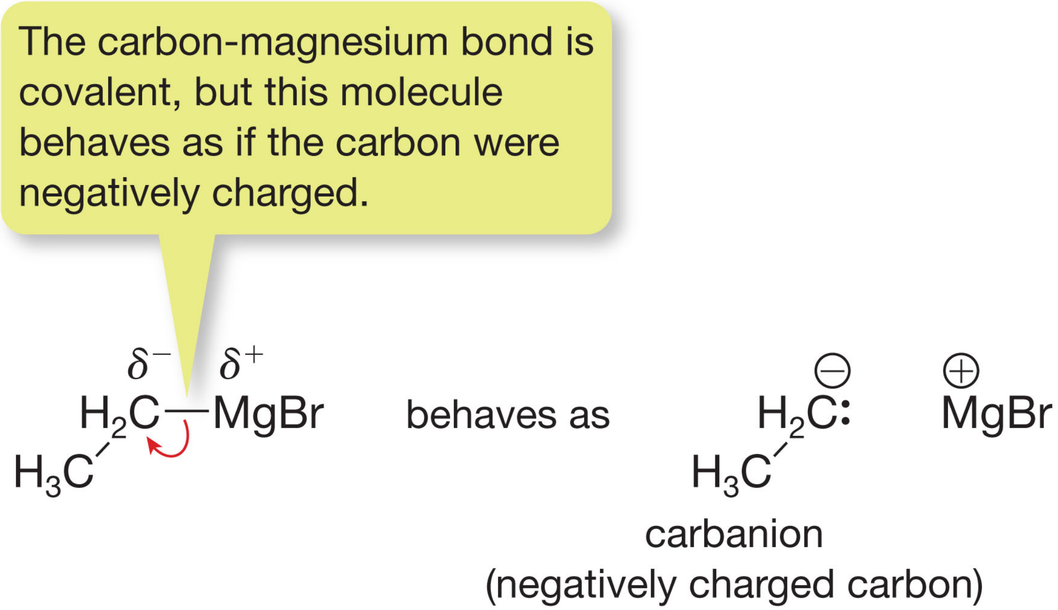
- Grignard reagents were first prepared by Victor Grignard, a French chemists, who was awarded the Noble prize for his work in 1912.
- A Grignard reagent is formed by exposing an ethereal solution of an organic halide (typically Cl, Br, or I) to magnesium metal. An ethereal solution is one in which the solvent is an ether, typically diethyl ether (ether) or tetrahydrofuran (THF).



the solvent is important in this reaction because it interacts with the Grignard reagent and stabilizes it

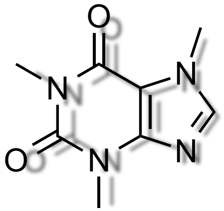
Addition of Grignard Reagents

- The polarized carbon-metal bond behaves as if there is a full negative charge on carbon – a ***carbanion***.
- Carbanions are powerful bases that have the corresponding alkane as the conjugate acid (p*K*a 45).
- Grignard reagents rapidly removes a proton from any functional group that contains a hydrogen with a p*K*a lower than that of the Grignard's conjugate acid – i.e. most functional groups!

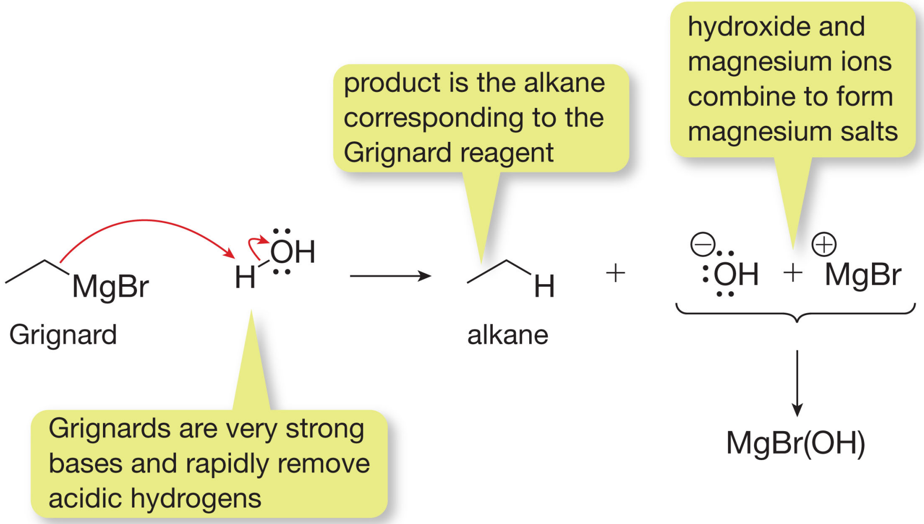

The carbon-magnesium bond is covalent, but this molecule behaves as if the carbon were negatively charged.

carbanion
(negatively charged carbon)

Addition of Grignard Reagents



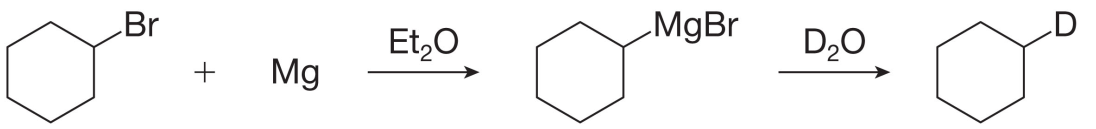
- Because acid-base reactions tend to be faster than most other processes, Grignard reagents ‘prefer’ to undergo acid-base reactions if possible.
- ***Therefore, Grignard reagents can be prepared only when functional groups containing acidic hydrogen atoms are NOT present.***
- The reaction of a Grignard with water is an acid-base reaction.



product is the alkane corresponding to the Grignard reagent

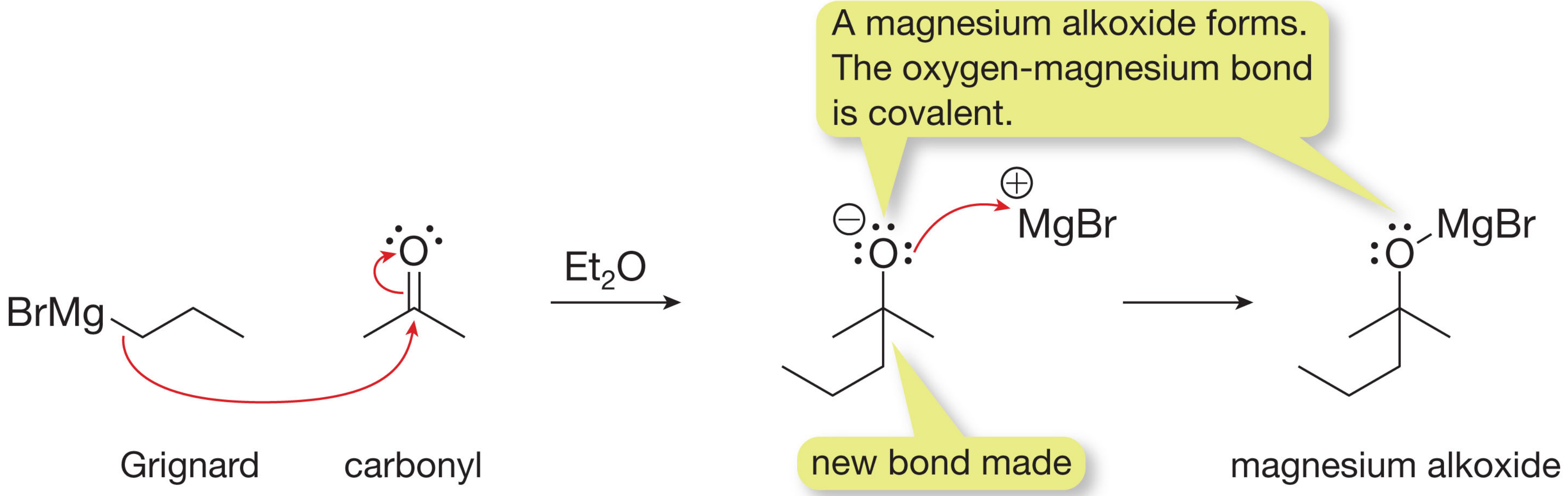
hydroxide and magnesium ions combine to form magnesium salts

Grignards are very strong bases and rapidly remove acidic hydrogens



Addition of Grignard Reagents

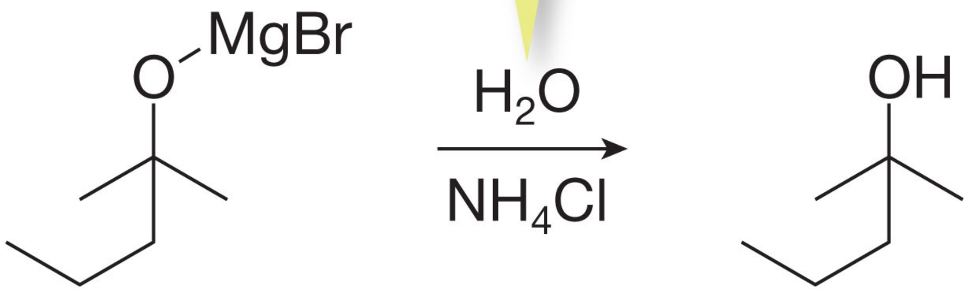
- The most useful Grignard reactions are those that create carbon-carbon bonds.
- The polarized carbon atom of a Grignard is also a powerful nucleophile and readily bonds to electrophilic carbon atoms, such as the carbon of a carbonyl group, forming a magnesium alkoxide.



Addition of Grignard Reagents

- The magnesium alkoxide then treated in a separate reaction with dilute acid in water. This breaks the magnesium-oxygen bond, producing the alcohol.
- This reaction is termed hydrolysis, because water (hydro) is breaking (lysing) a bond.

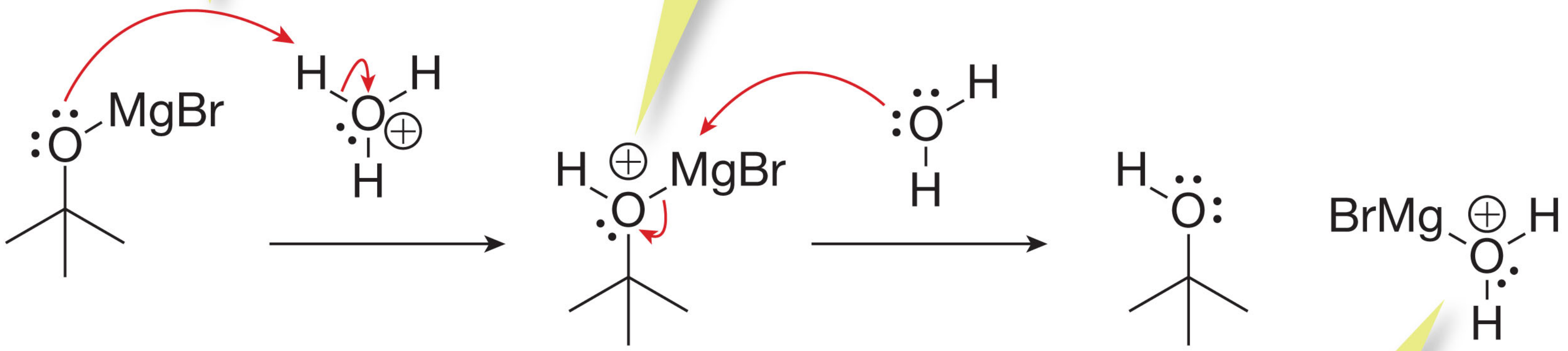
acid and water are used to hydrolyze the oxygen-magnesium bond



magnesium alkoxide

Addition of Grignard Reagents

- Hydrolysis reactions also involve electron flow, which can be described using arrow notation.

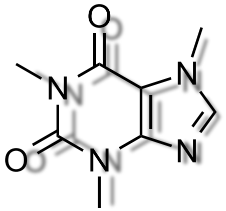


basic oxygen on product is protonated by acid

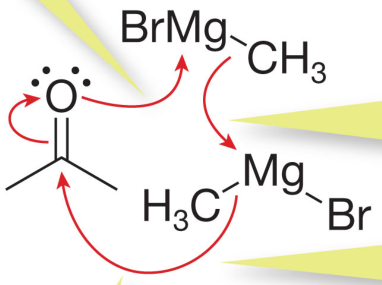
positive charge is a very strong electron attractor

by-product can transfer H^+ to another molecule of water to continue the cycle

Addition of Grignard Reagents



- Keep in mind that the exact mechanism by which Grignards add to carbonyls is not fully know.
- We do know that the Grignard reagent itself is more complex than is typically drawn.



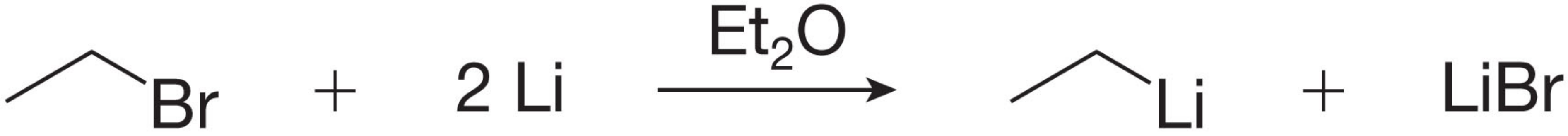
Carbonyl oxygen donates electrons to magnesium atom of one Grignard, making the carbonyl more electrophilic.

Two molecules of Grignard interact; carbon group is transferred from one Grignard to another.

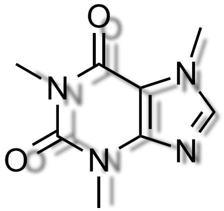
Second molecule of Grignard delivers carbon group to carbonyl.

Addition of Organolithium Reagents

- Organolithium compounds undergo nucleophilic addition to carbonyl groups in a process similar to Grignard reactions with carbonyl groups.
- Like Grignards, organolithium compounds are strong bases and react violently with water.
- Organolithium reagents are prepared by exposing the appropriate alkyl halide to lithium metal in ether.

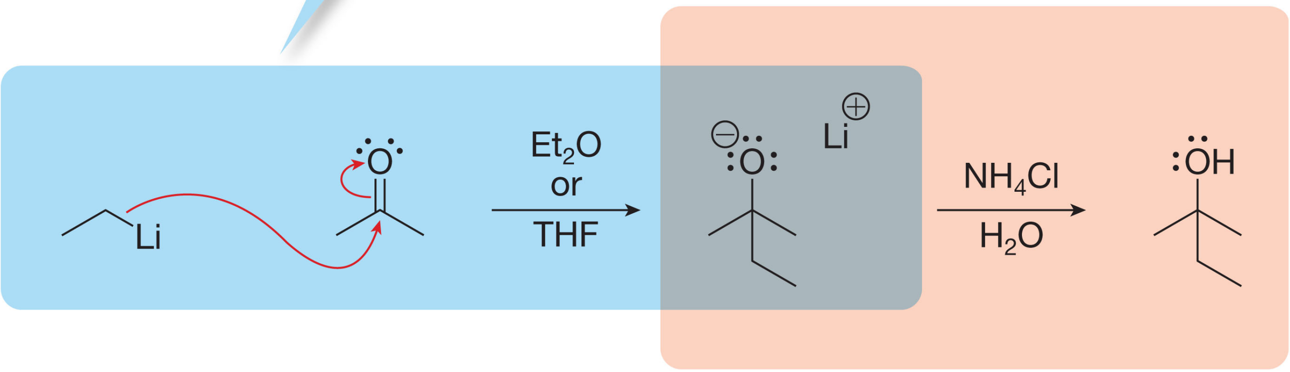


Addition of Organolithium Reagents



- As with Grignards, the carbon-metal bond in organolithium reagents is polarized towards carbon, making it strongly nucleophilic/basic.
- Organolithium reagents add to carbonyl groups to produce the alkoxide salt. In a separate reaction, the alkoxide is hydrolyzed with water and acid to produce the alcohol.

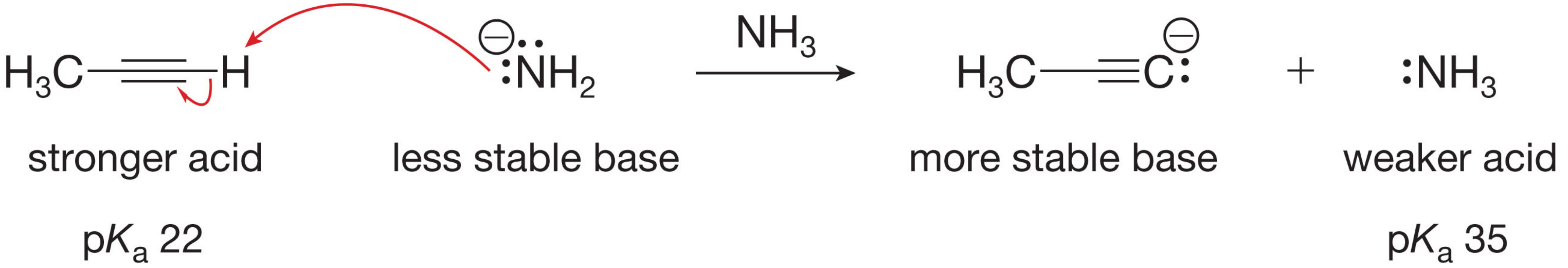
first reaction must be performed without any water present



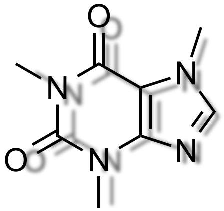
second reaction is performed once the first is complete

Addition of Acetylide Reagents

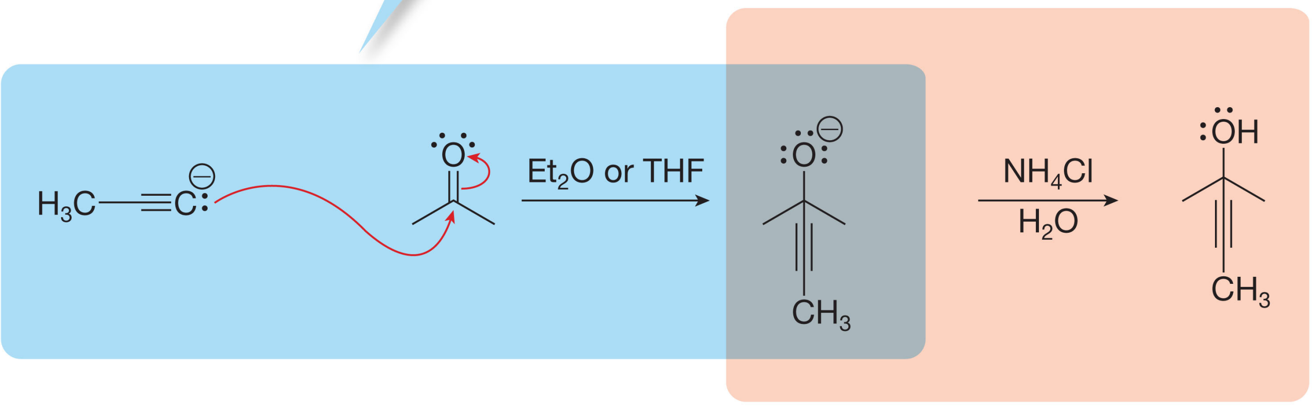
- The hydrogen atom of alkynes (acetylenes) are much more acidic than those in most other hydrocarbons.
- Acetylides (carbanions prepared from acetylenes) are very nucleophilic.
- Acetylides are usually prepared by deprotonating with a strong base such as Grignards, organolithiums, or sodium amide ($NaNH_2$).



Addition of Acetylide Reagents



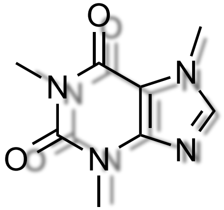
- Acetylides add to carbonyl groups in a process similar to that of Grignards and organolithiums reactions with carbonyl groups.
- Acetylides first add to carbonyl groups giving the corresponding alkoxides, which is then hydrolyzed in a separate reaction with water and acid to give the alcohol.



first reaction must be performed without any water present

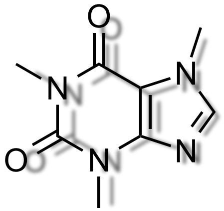
second reaction is performed once the first is complete

Using Orbitals to Analyze Reactions

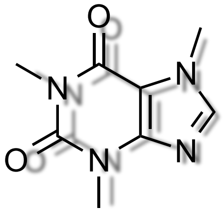


- So far, we have looked at reactivity mainly through resonance structures and electronegativity.
- Analyzing orbital interactions is another way to examine reactivity and can give deeper insights of reaction pathways.
- When analyzing nucleophiles, we tend to look at the highest occupied molecular orbitals (HOMOs).
- When analyzing electrophiles, we tend to look at the lowest unoccupied molecular orbitals (LUMOs).
- The carbonyl group almost always acts as an electrophile, specifically at the carbon atom of the carbonyl.

Using Orbitals to Analyze Reactions

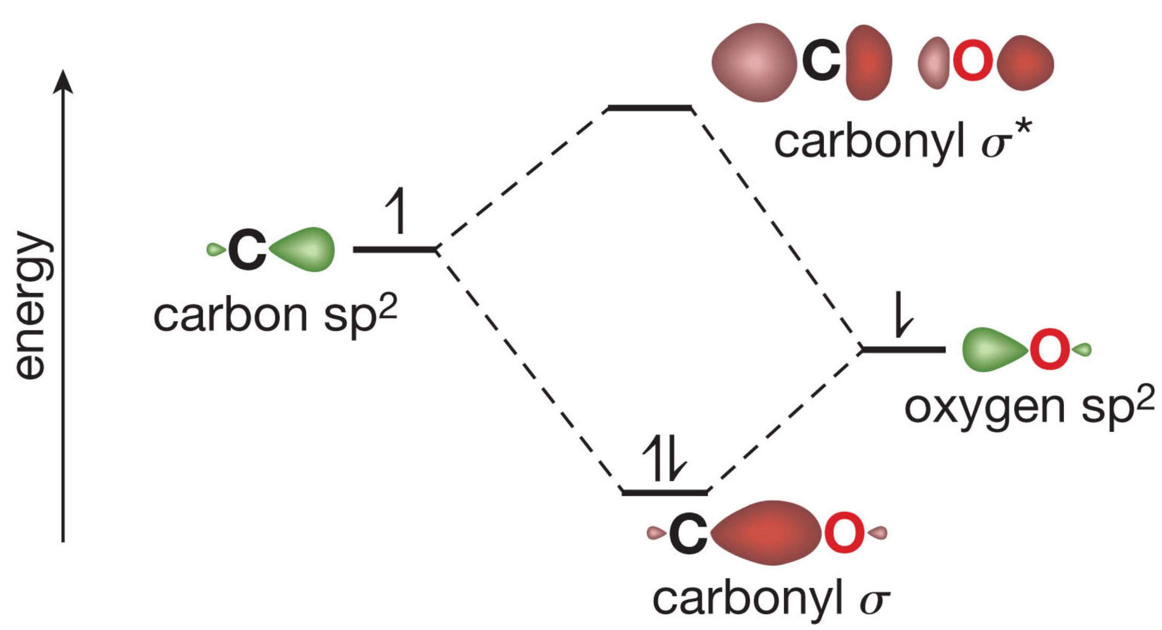


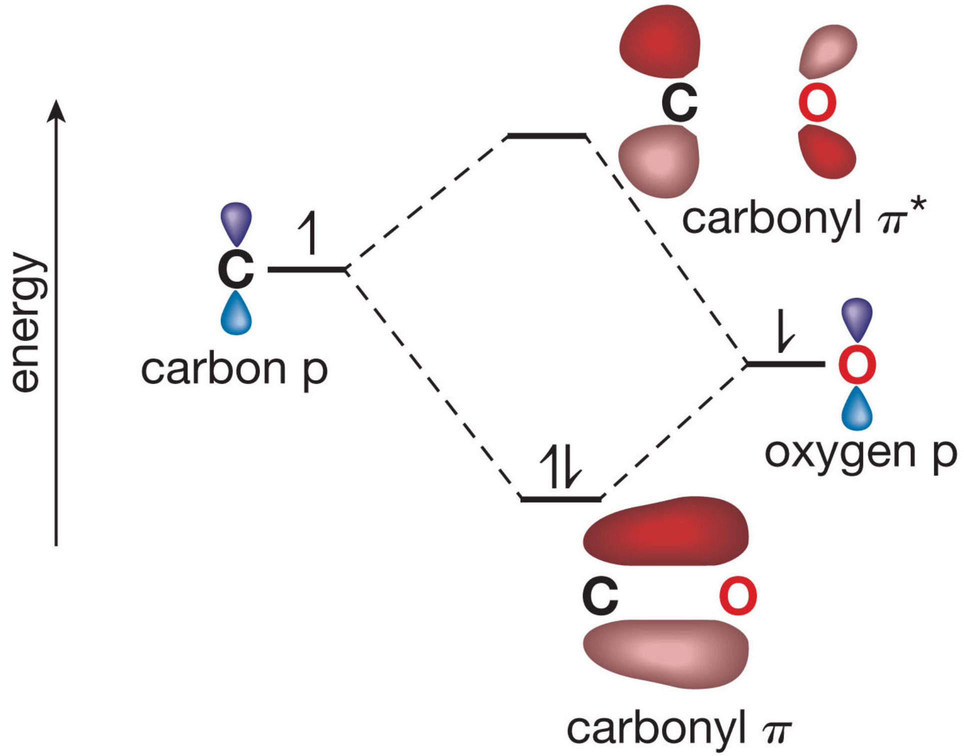
- Because the oxygen atom of the carbonyl group is more electronegative than the carbon atom, the energy of its atomic orbitals are lower in energy.
- This means that the orbital overlap is not symmetrical and that the oxygen orbital is closer in energy to the σ bond.
- Consequently, the oxygen atom contributes more to the formation of the σ bond, making the bond asymmetric: that is, the lobes are drawn larger near the oxygen.
- The size of the lobes corresponds to a factor called the ***orbital coefficient*** and indicates the relative probability of finding electrons.



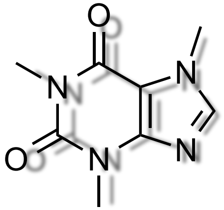
Using Orbitals to Analyze Reactions

- Because the lobes are bigger around oxygen, the electrons in this orbital are more likely to be found near the oxygen than near the carbon.
- This probability distribution gives the carbon a positive character.

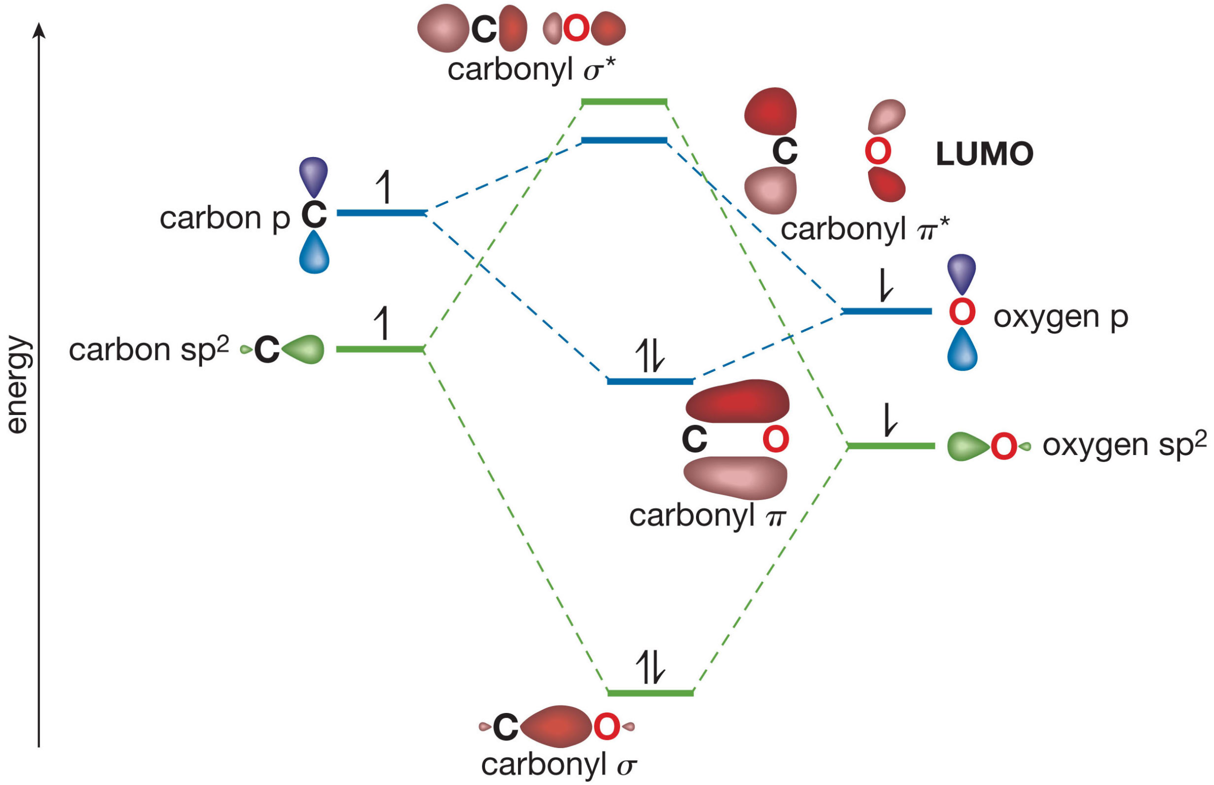




Using Orbitals to Analyze Reactions

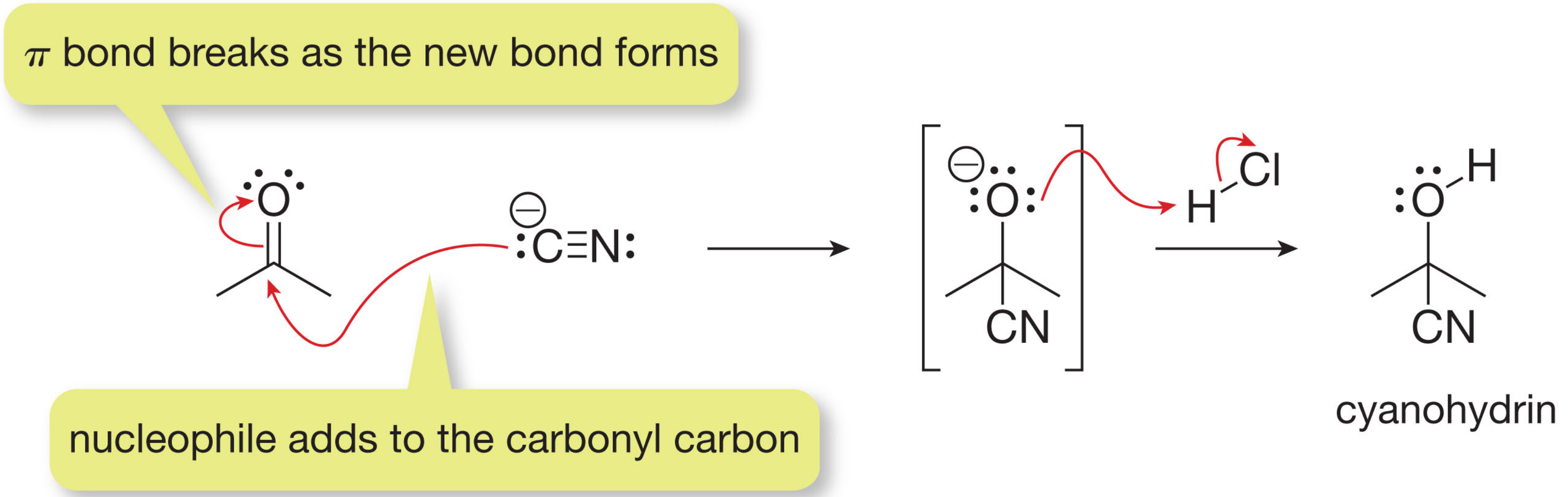


- In order for the carbonyl group to accept electrons from an incoming nucleophiles, it must have an empty orbital molecular orbital.
- Nucleophiles will typically react with the LUMO of the electrophile.
- In this case, the LUMO is the π^* orbital and is polarized towards carbon.
- Orbitals interact by overlapping the larger lobes on the nucleophile and electrophile.



Formation of Cyanohydrins from Carbonyls

- Cyanide ions are carbon nucleophiles in which both the nitrogen and carbon have full octets of and lone pairs. The carbon atom bears the formal negative charge and is the nucleophilic site of the ion.
- Cyanides add to carbonyl groups in a reaction that is similar to that of the previous nucleophiles; hydrides, Grignards, organolithiums, and acetylides.

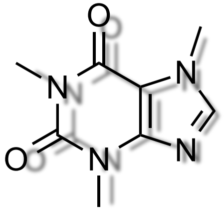


π bond breaks as the new bond forms

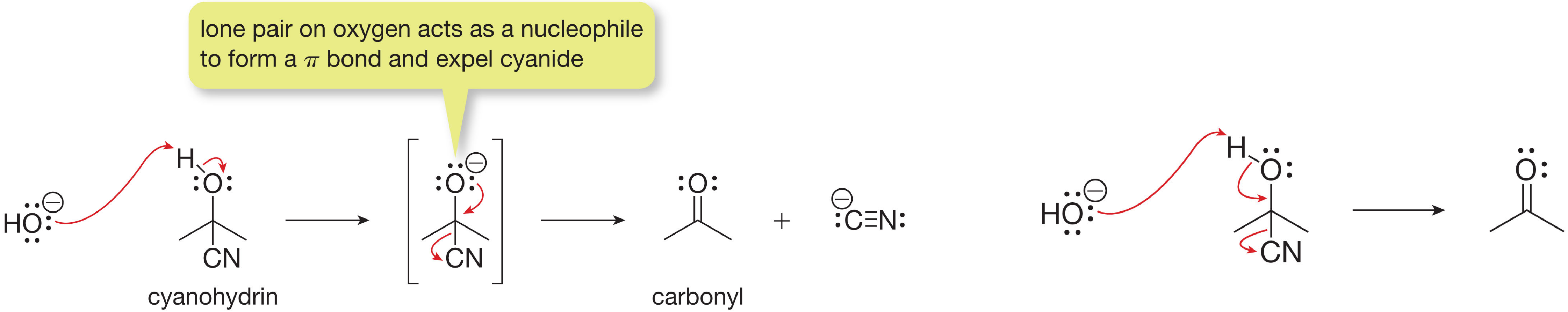
nucleophile adds to the carbonyl carbon

cyanohydrin

Formation of Cyanohydrins from Carbonyls

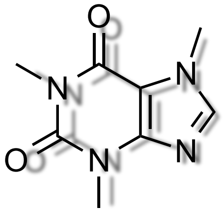


- Under basic conditions, cyanohydrins decompose back to the carbonyl group and cyanide ion.
- When a cyanohydrin decomposes, a cyanide ion is expelled from the molecule, taking a pair of electrons with it; this is known as a ***leaving group.***
- Because the alkoxide is unstable and is converted quickly to the carbonyl group, this transformation is commonly shown in 1 step.



lone pair on oxygen acts as a nucleophile to form a π bond and expel cyanide

Leaving Groups



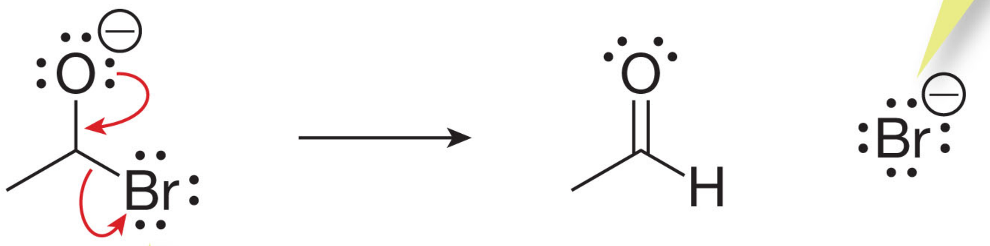
- In reaction mechanisms, groups which are expelled and take electrons with them are called ***leaving groups***.
- Typical leaving groups tend to be electronegative atoms or functional groups with can distribute charge via delocalization.
- **Good leaving groups are weak bases**.

TABLE 7.1 **Some Common Leaving Groups and Their Conjugate Acids**

Strong Acid	**Conjugate Base (weak base, excellent leaving group)**
HI	I^-
HBr	Br^-
HCl	Cl^-
H_2SO_4	HSO_4^-
H_3O^+	H_2O

Leaving Groups

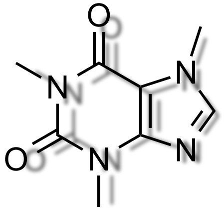
- **<u>Good leaving groups are weak bases</u>**.
- The methods for estimating acid/base strength can be applied to predict the ability other potential leaving groups.



Good leaving groups stabilize negative charges well. The conjugate bases of strong acids make excellent leaving groups.

$Br^{\ominus}$ is a leaving group. It leaves with a pair of electrons.

Catalysis of Addition Reactions to Electrophilic π bonds

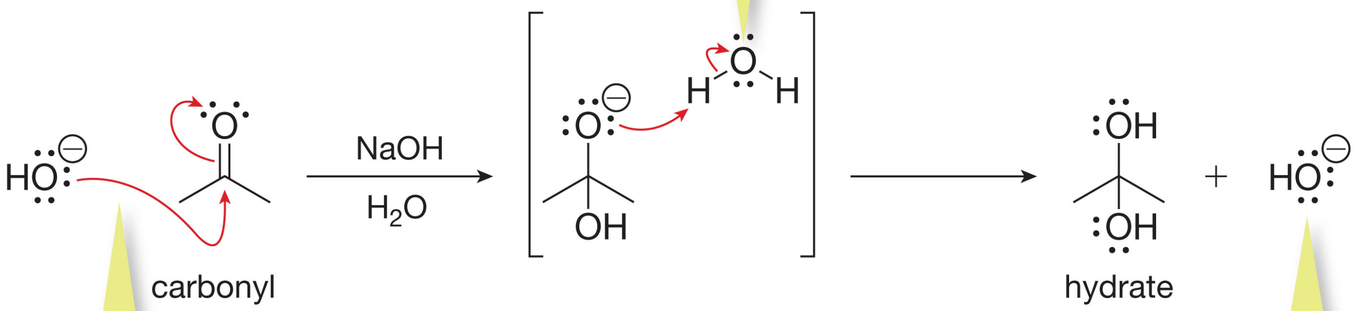


- A catalyst, typically an acid or base, can be used to accelerate a nucleophilic addition to a carbonyl group.
- A catalyst is a species added to a reaction, usually in trace amounts, in order to accelerate the reaction.
- Catalyst accelerate reactions by lowering the activation energy of that reaction.
- Catalyst are not consumed during a reaction

Catalysis of Addition Reactions to Electrophilic π bonds

- Water is a poor nucleophile and only adds slowly to carbonyl groups. Under basic conditions, the addition of water is very fast, and a ***hydrate*** is the final product.
- Hydroxide is a much better nucleophile than water. It has 3 lone pairs and a negative charge, making it a much better electron donor.

water as an acid to protonate the intermediate

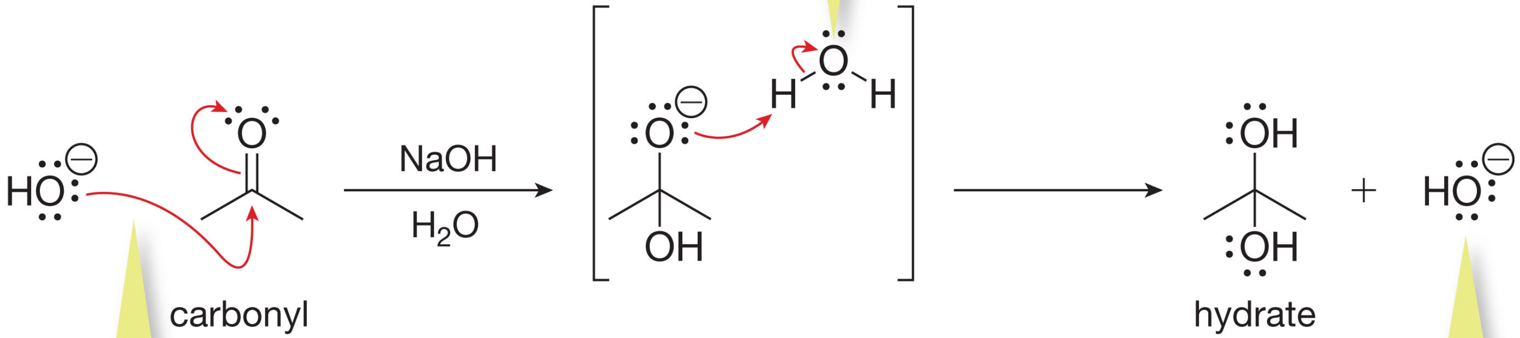


hydroxide nucleophile adds to carbonyl as the π bond breaks

OH^- is a catalyst; the total amount present does not change during the reaction.

Catalysis of Addition Reactions to Electrophilic π bonds

- Notice how the concentration of hydroxide, the catalyst, does not change.
- Although the hydroxide ion produced is not the one that began the sequence, there is no overall consumption of hydroxide.

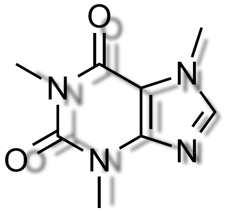


water as an acid to protonate the intermediate

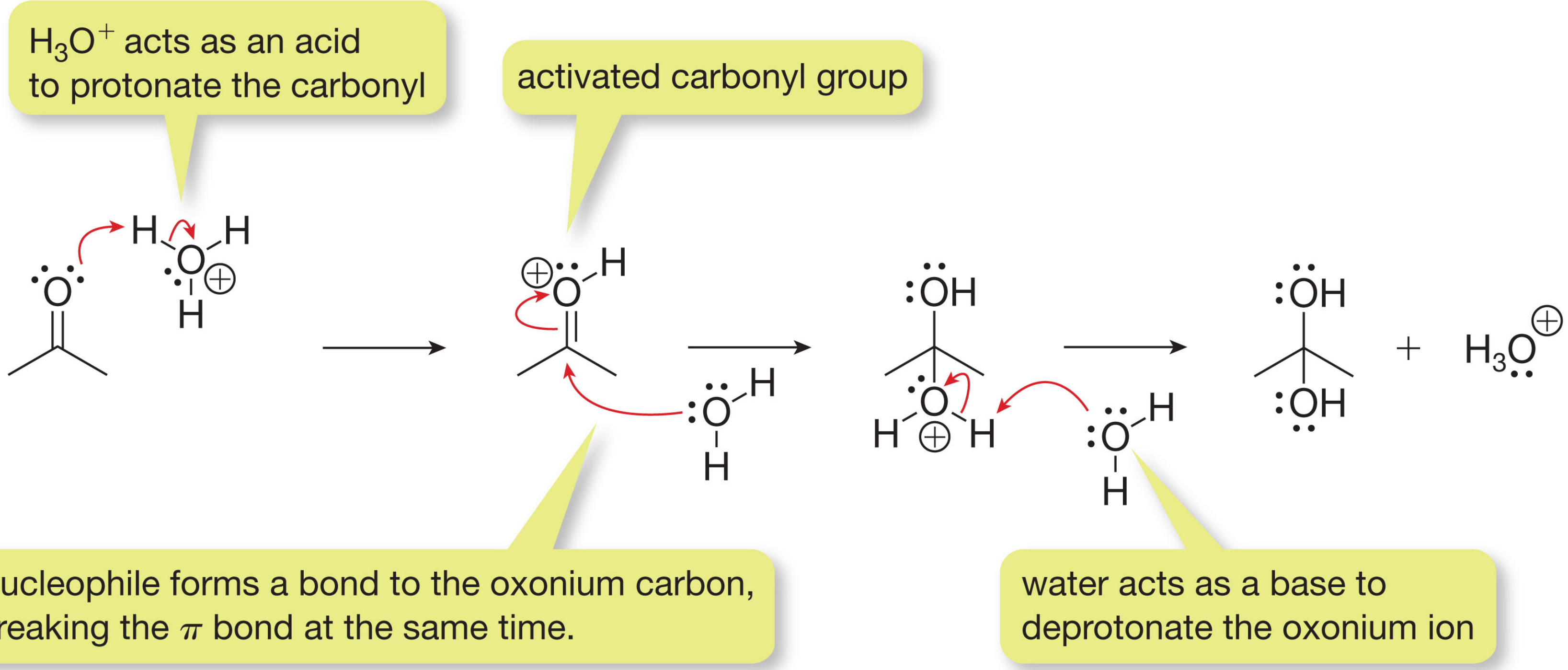
hydroxide nucleophile adds to carbonyl as the π bond breaks

OH^- is a catalyst; the total amount present does not change during the reaction.

Catalysis of Addition Reactions to Electrophilic π bonds



- Under acidic conditions, the addition process begins with the protonation of the carbonyl group.
- The activated carbonyl group, an oxonium ion, is a powerful electrophile to which the poor nucleophile can add.



H_3O^+ acts as an acid to protonate the carbonyl

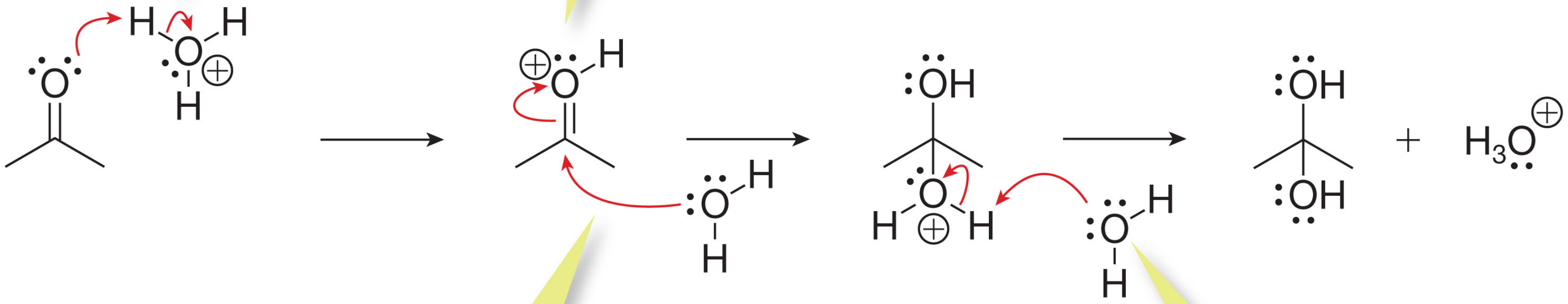
activated carbonyl group

Nucleophile forms a bond to the oxonium carbon, breaking the π bond at the same time.

water acts as a base to deprotonate the oxonium ion

Catalysis of Addition Reactions to Electrophilic π bonds

- Again, notice how the concentration of the catalyst, the hydronium ion, does not change.
- It is consumed at the beginning of the reaction but regenerated at the end of the reaction.


H_3O^+ acts as an acid to protonate the carbonyl

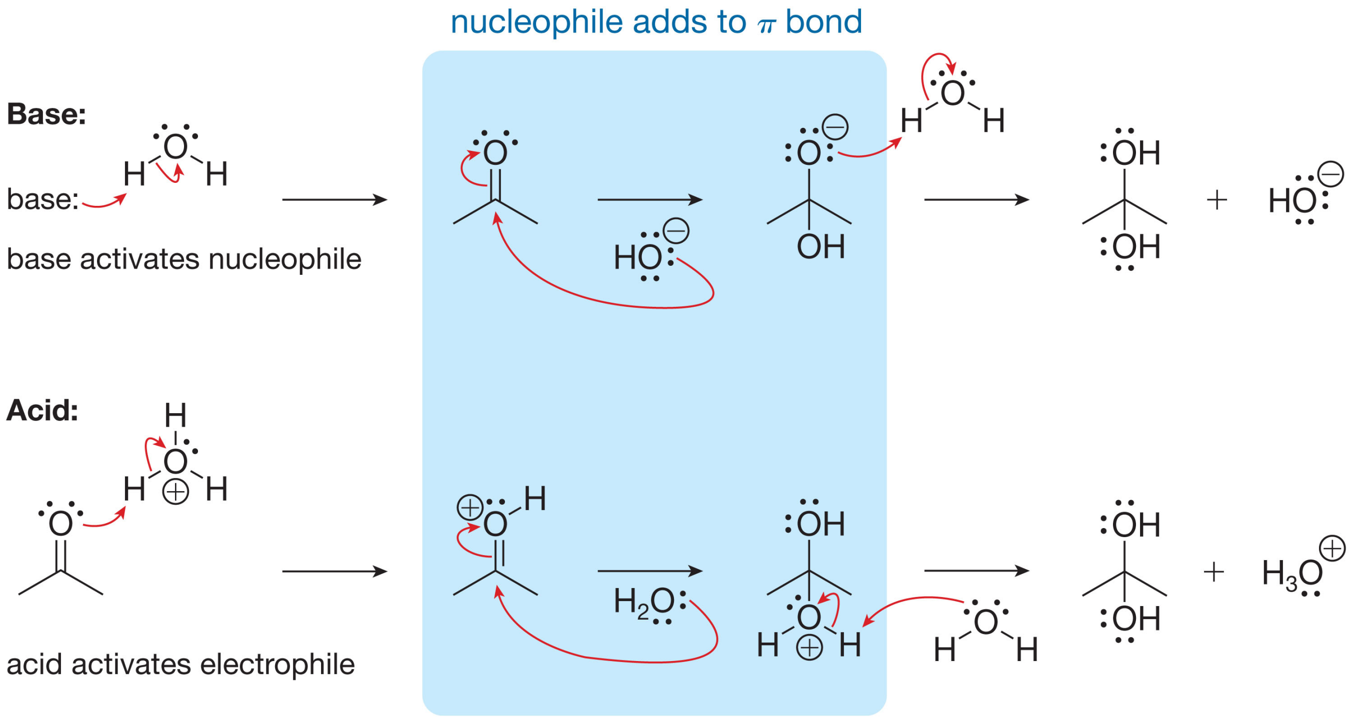
activated carbonyl group

Nucleophile forms a bond to the oxonium carbon, breaking the π bond at the same time.

water acts as a base to deprotonate the oxonium ion

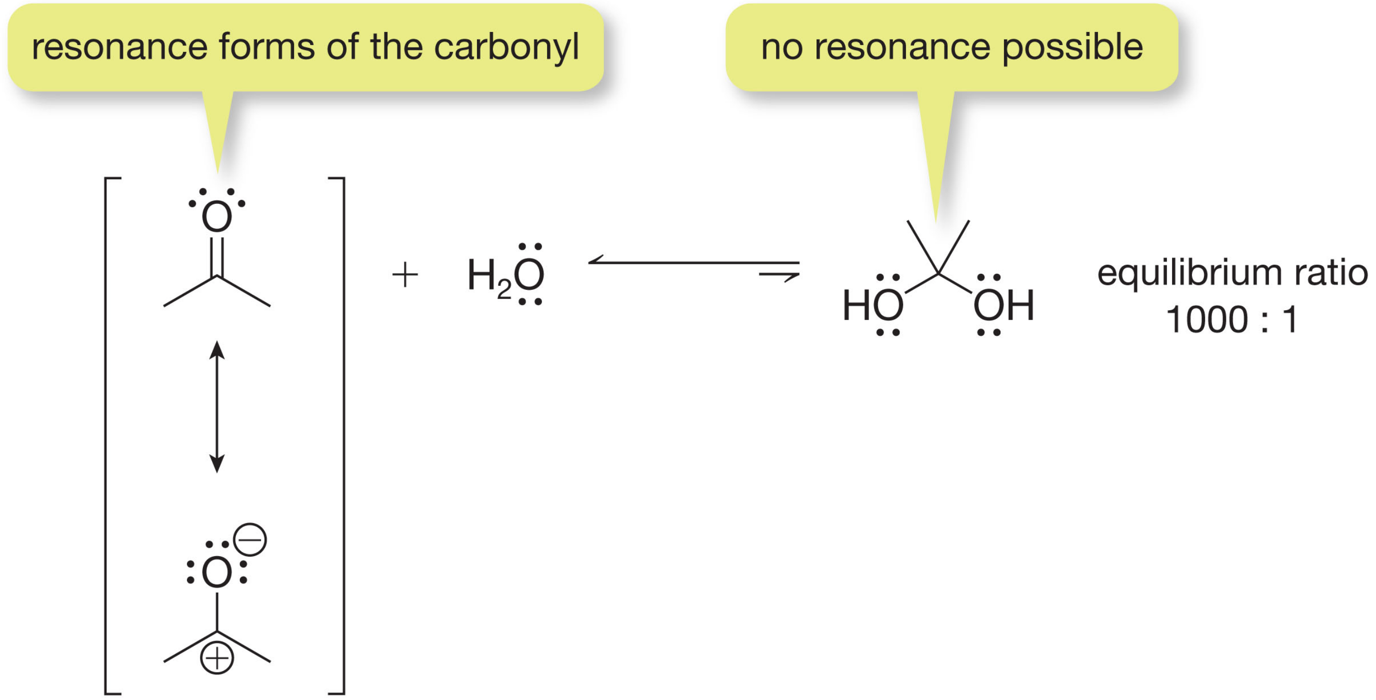
Catalysis of Addition Reactions to Electrophilic π bonds

- The reactions of both acid and base catalyst have a step involving the addition of a nucleophile to the carbonyl group.
- The difference between the catalytic sequences is simply the order of protonation or deprotonation.



The Hydrates of Aldehydes and Ketones

- The reaction between water and carbonyl groups is a very fast process. The reaction is reversible and therefore in equilibrium.
- The position of the equilibrium is dependent on the relative energies of the carbonyl and hydrate forms of the molecule.


resonance forms of the carbonyl

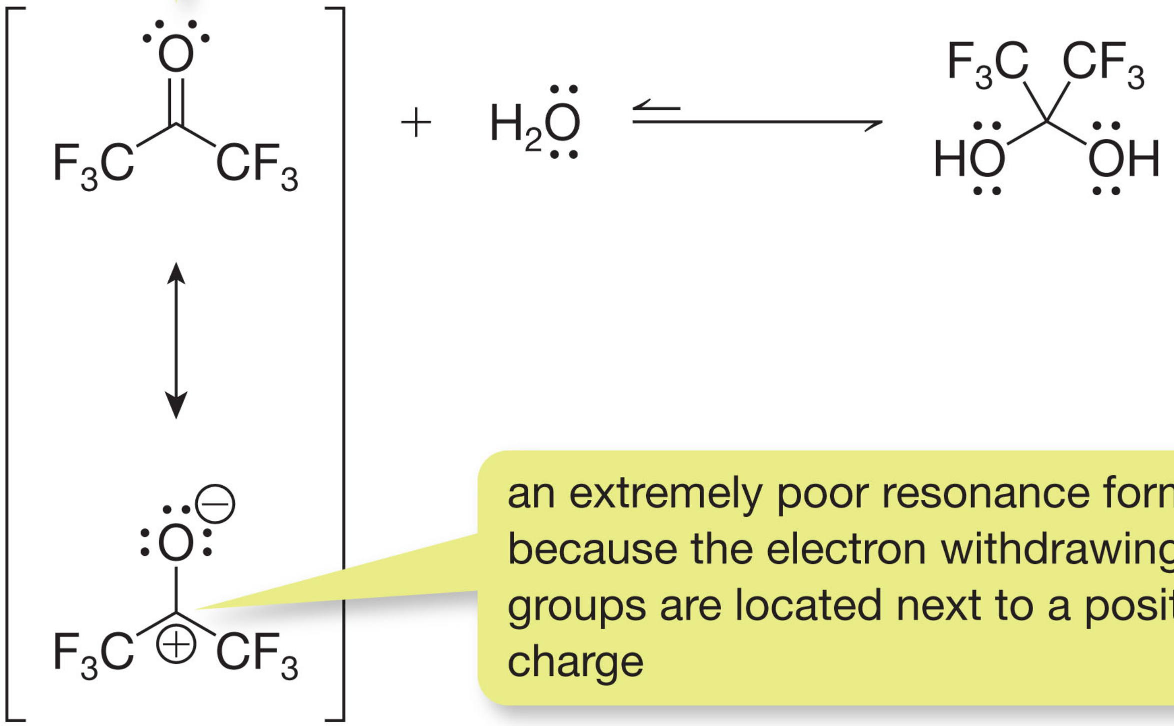
no resonance possible

equilibrium ratio
1000 : 1

The Hydrates of Aldehydes and Ketones

- In general, aldehydes are typically more hydrated than ketones.

carbonyl form is *destabilized* by inductive effects

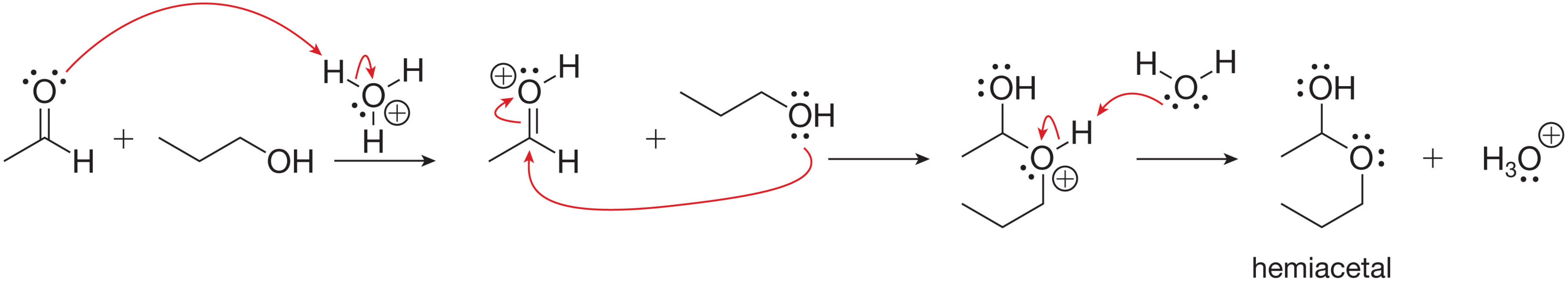


equilibrium ratio 1 : 10^6

an extremely poor resonance form because the electron withdrawing CF_3 groups are located next to a positive charge

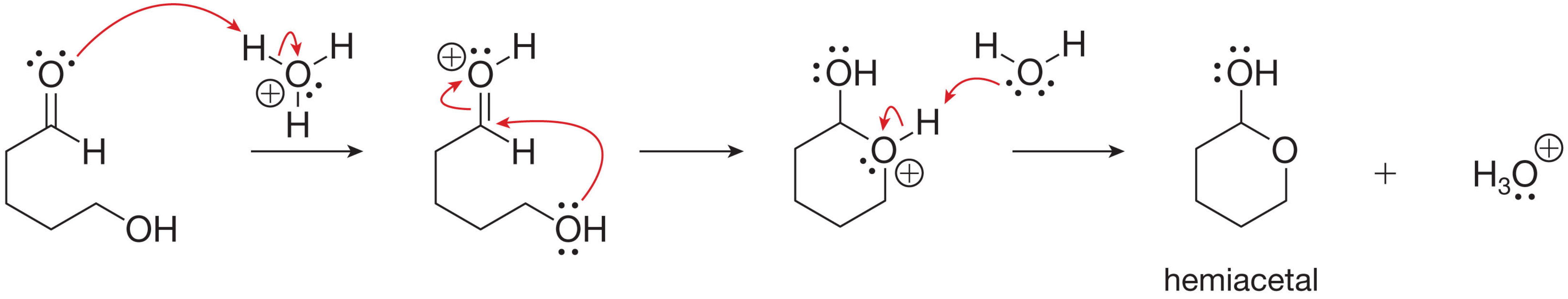
Hemiacetals

- The acid catalyzed addition of alcohols to carbonyl groups produce ***hemiacetals***.
- This reaction is identical to that of hydration, the only difference being that the nucleophile added is an alcohol (ROH) rather than water (HOH).



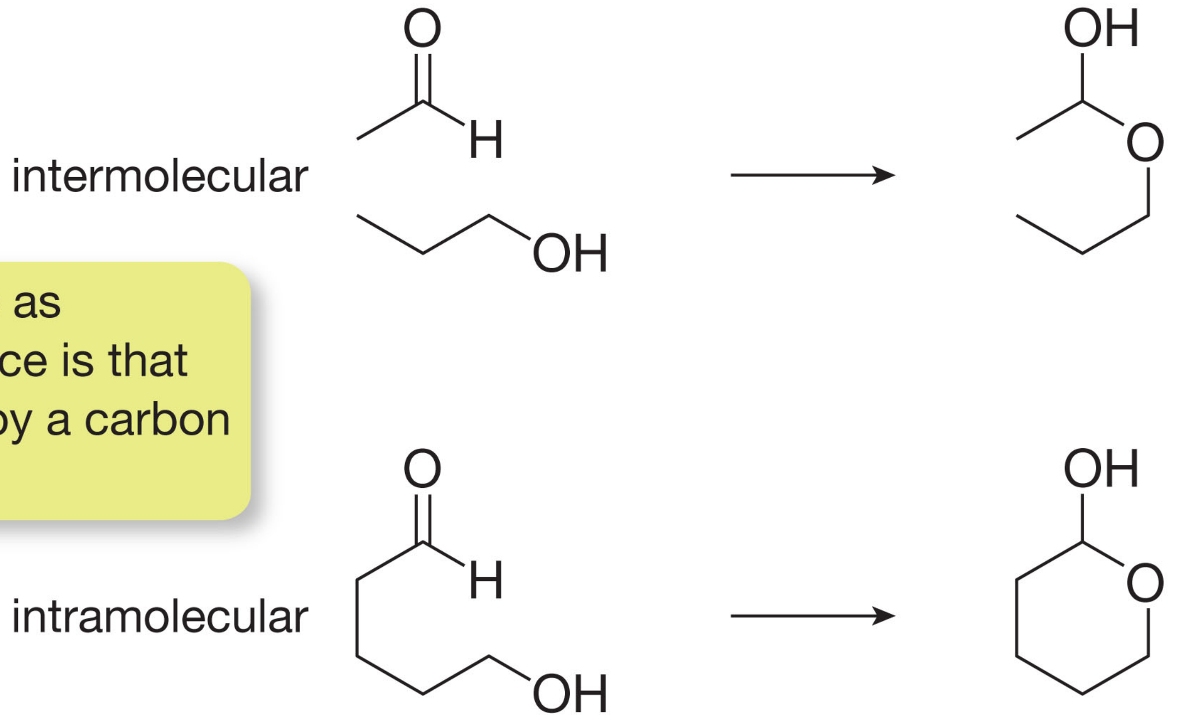
Hemiacetals

- The formation of hemiacetals can also occur via an intramolecular reaction.



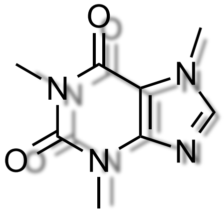
Hemiacetals

- Intermolecular and intramolecular forms of this reaction are essentially the same.
- The only difference is that the two reacting groups are linked together by a carbon chain in the intermolecular version.



Intramolecular reactions are the same as intermolecular ones. The only difference is that the functional groups are connected by a carbon chain in an intramolecular reaction.

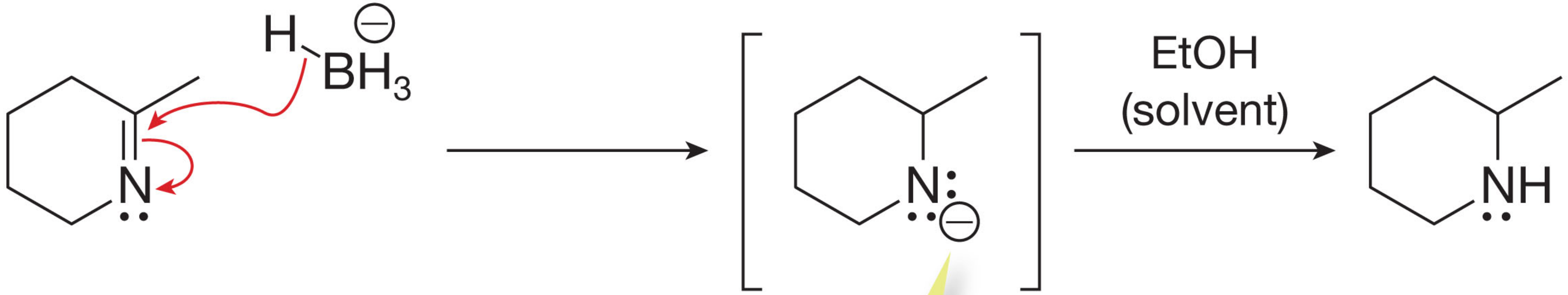
Catalysis of Reduction Reactions



- We have seen how both acids and bases can be used to catalyze organic reaction.
- The selection of an acid or base as a catalyst depends on the reactivity of the molecules and of the operating mechanism.
- In general, bases accelerate a reaction by increasing the reactivity of the operating nucleophile.
- Acids accelerate a reaction by increasing the reactivity of the operating electrophile.

Catalysis of Reduction Reactions

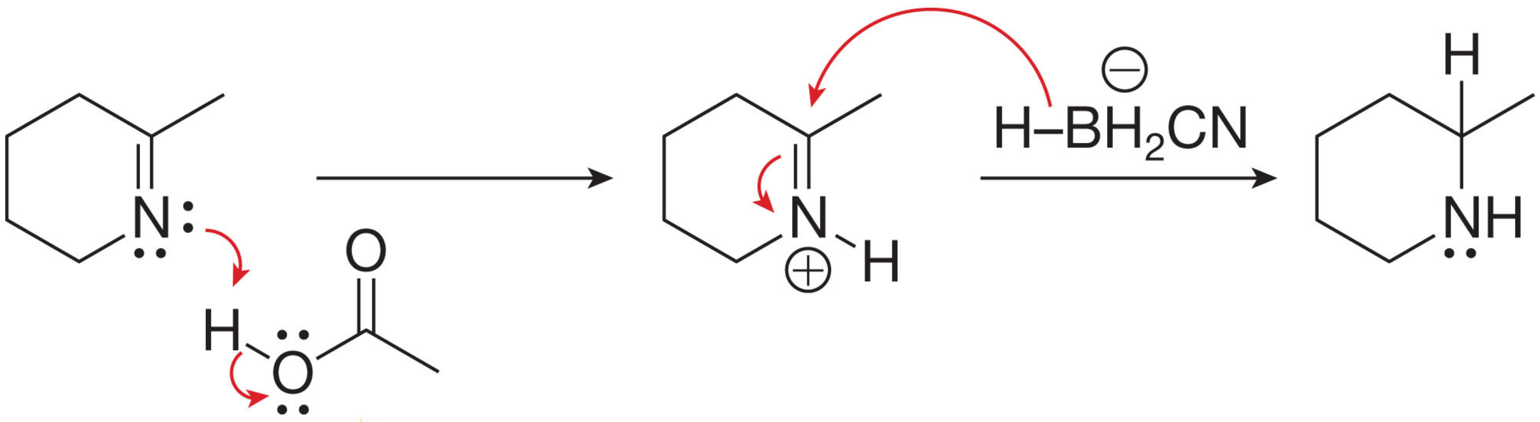
- The reduction of imines is usually slow because:
  - imines are not very electrophilic
  - direct addition of the hydride produces a negative charge on nitrogen
  - $NaBH_4$ is not a strong nucleophile



The pK_a of the amine NH is approximately 35, meaning that N^- is very unstable and difficult to form.

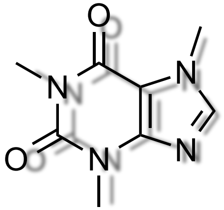
Catalysis of Reduction Reactions

- The reduction of imines can be accelerated two ways:
  - use a stronger nucleophile (such as $LiAlH_4$)
  - use an acid catalyst
- Under acidic conditions, a different reducing agent (such as $NaCNBH_3$) must be used as $NaBH_4$ reacts with acid.



acetic acid is a common solvent for imine reductions

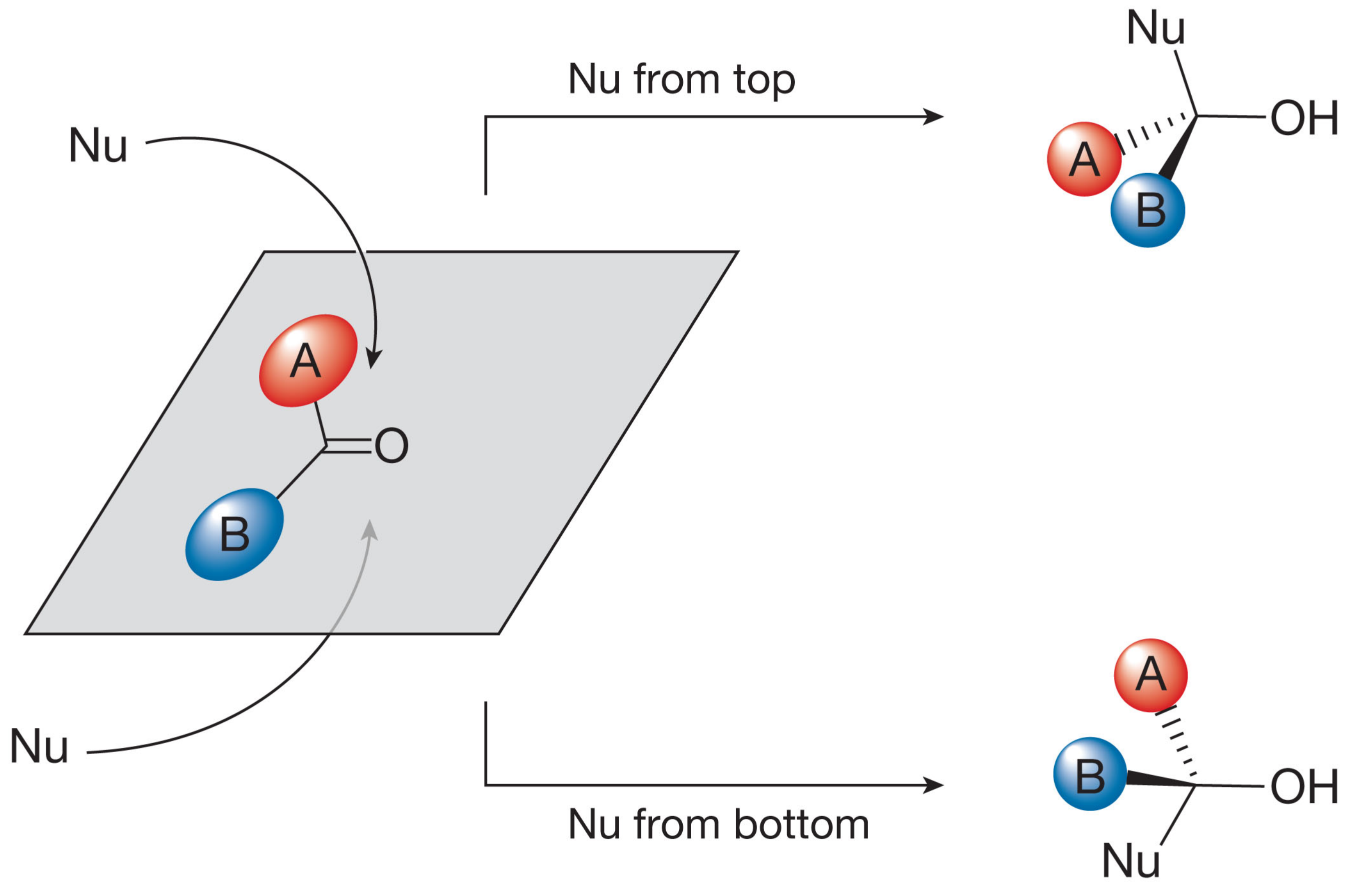
Stereochemistry of Nucleophilic Additions to π Bonds



- During the addition of a nucleophile to carbonyl group, the geometry of the electrophilic carbon atom changes from trigonal planar (sp^2) to tetrahedral (sp^3).
- This has the potential of creating stereogenic centres if the carbon atom has 4 different substituents.
- Because the carbonyl group is flat, the nucleophile and attack the carbon atom either from above or below.
- Two product stereoisomers are possible.

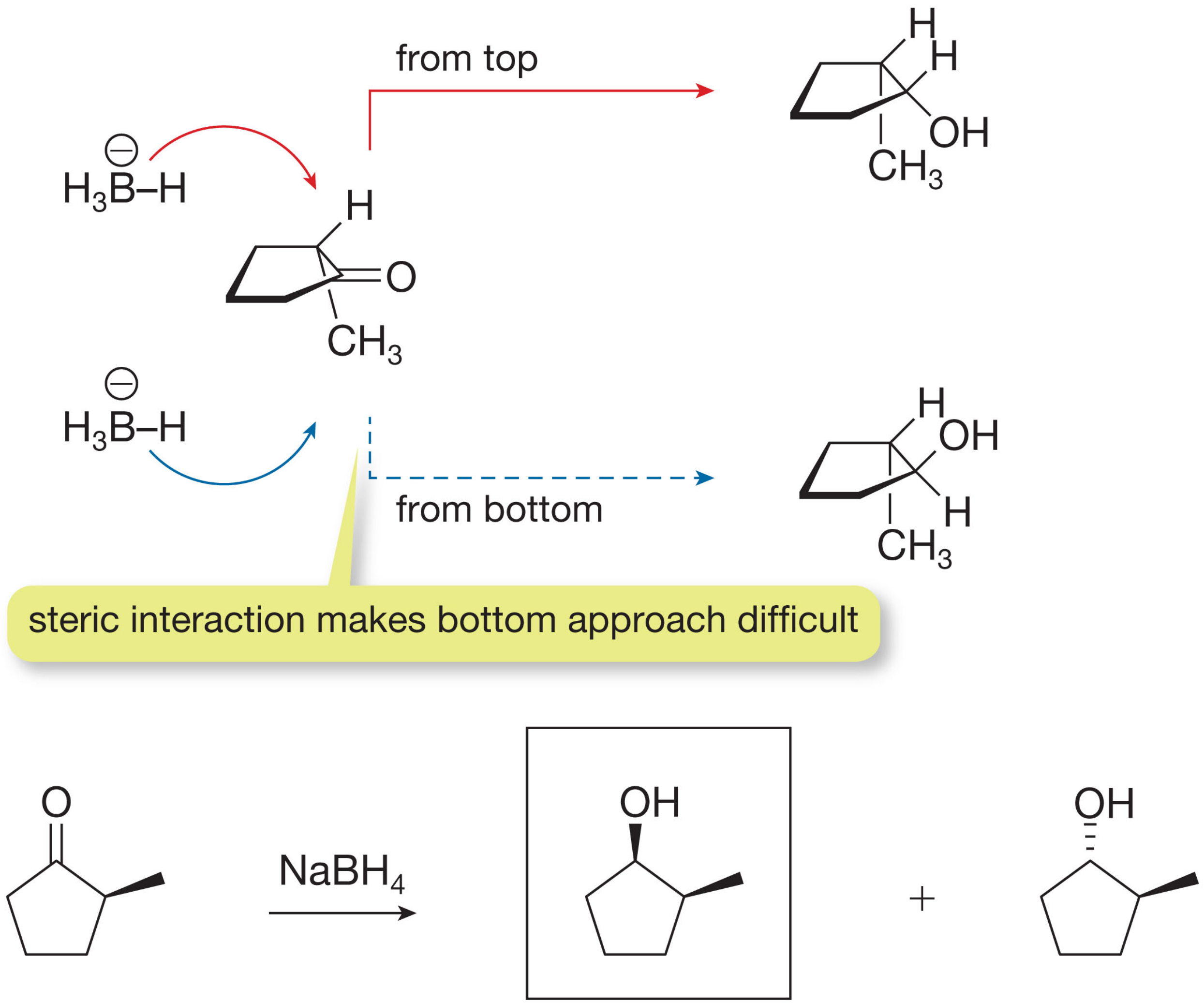
Stereochemistry of Nucleophilic Additions to π Bonds

- If the carbonyl group is symmetrical about the plane, the nucleophile can approach either face with equal probability.



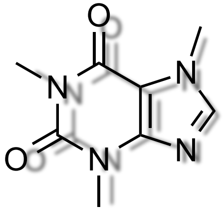
Stereochemistry of Nucleophilic Additions to π Bonds

- Often times, the carbonyl group is not symmetrical about the plane. This asymmetry can make the reaction ***stereoselective***; that is, one stereoisomer is favoured over the other stereoisomer.



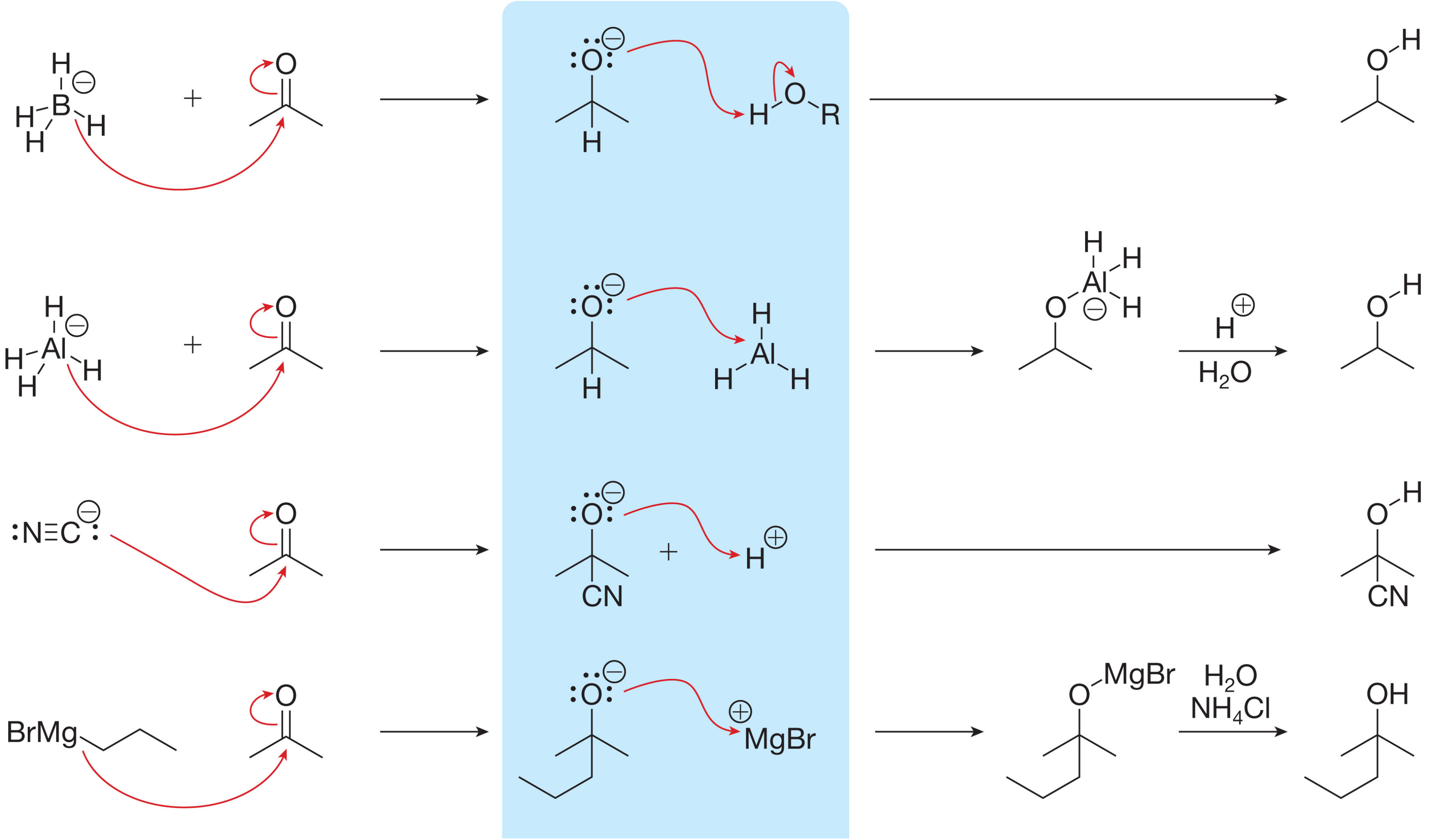
steric interaction makes bottom approach difficult

Patterns in Nucleophilic Additions to π Bonds

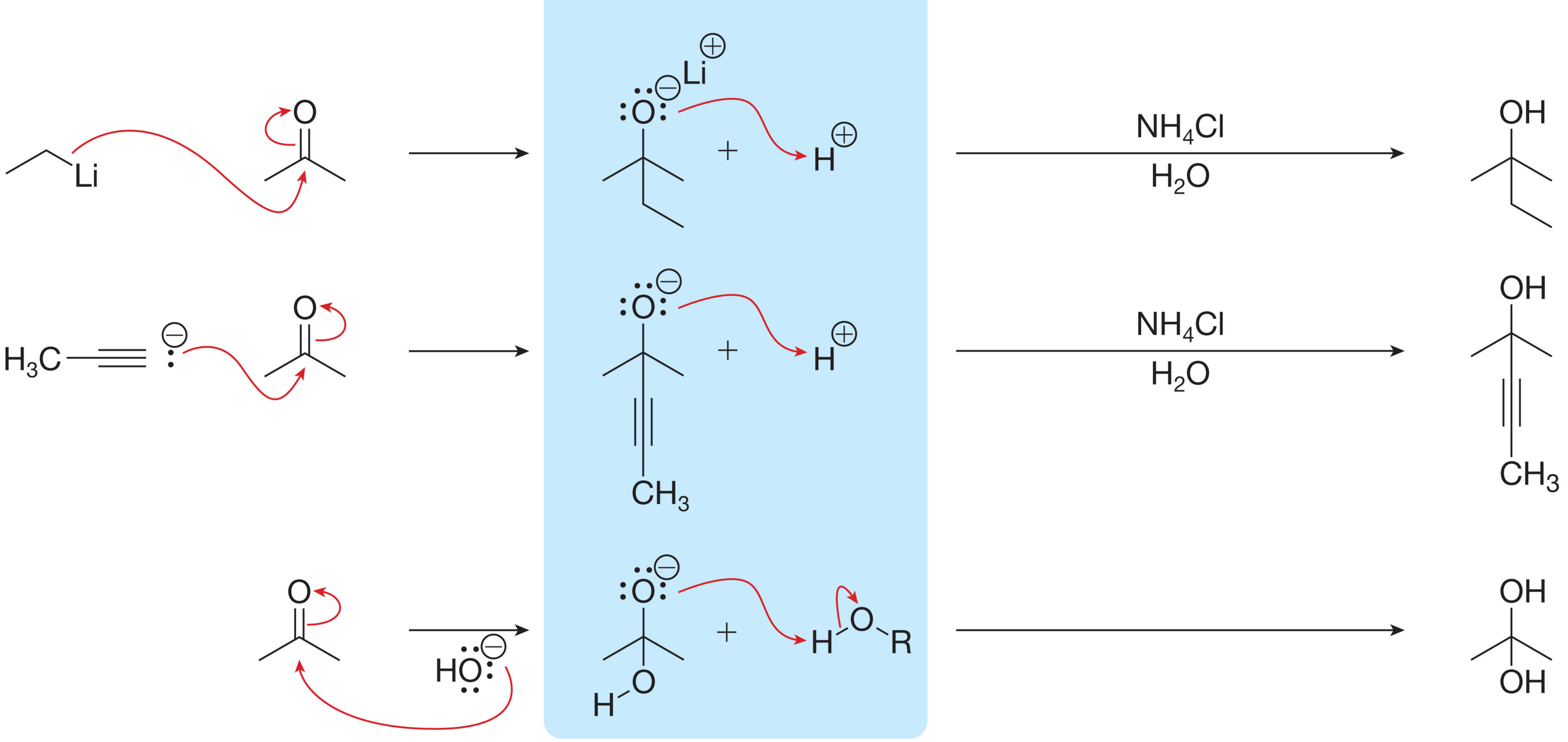


- Nucleophilic additions to electrophilic π bonds (π bonds involving at least one heteroatom; e.g. C=O, C=N) follow similar patterns.
- The pathway involves attack of the nucleophile at the electrophilic atom while the π bond simultaneously breaks, adding electrons to the other atom as a lone pair.
- This step is usually followed by the addition of an electrophile (usually H^+).

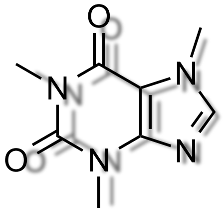
Patterns in Nucleophilic Additions to π Bonds



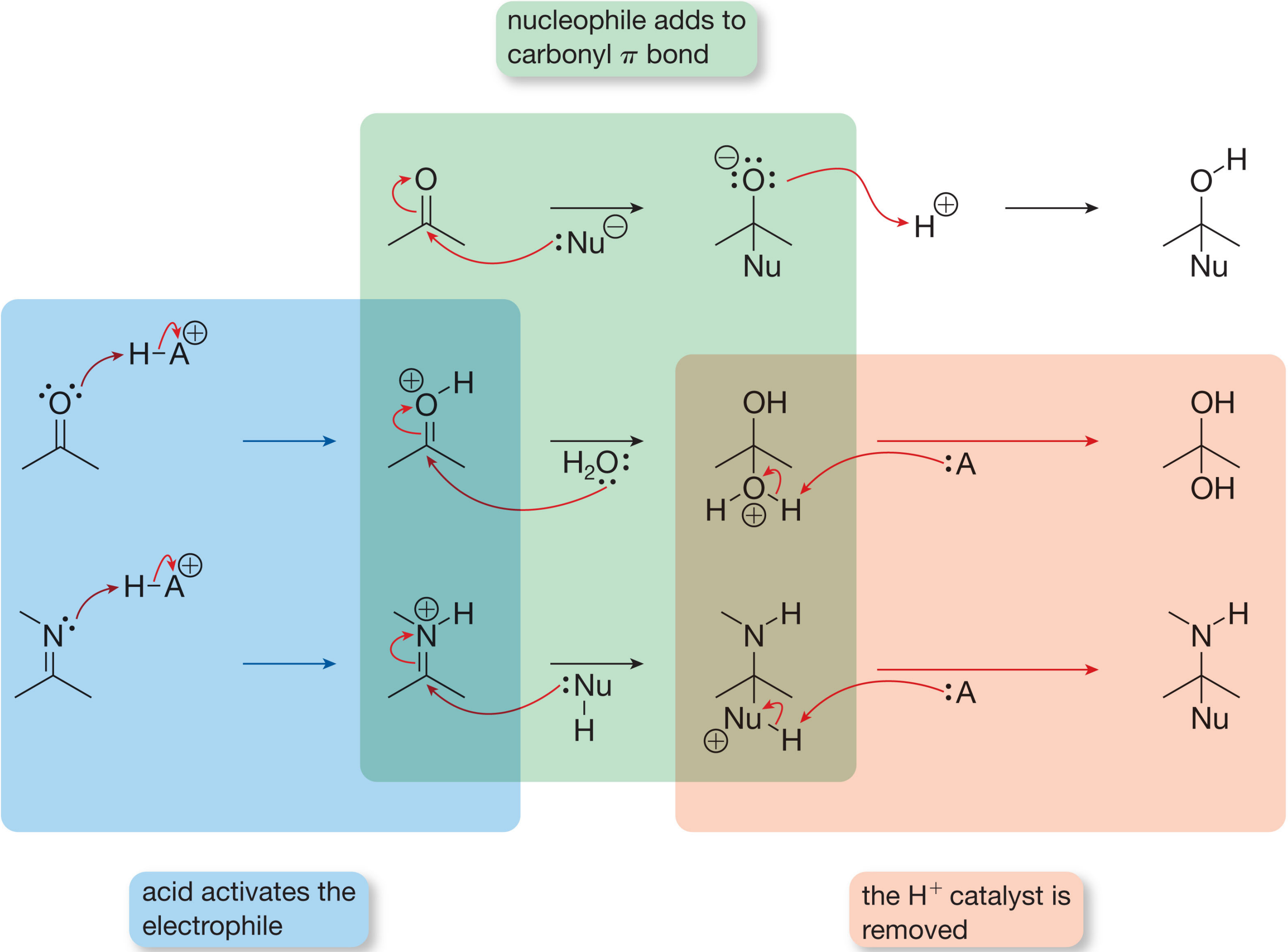
Patterns in Nucleophilic Additions to π Bonds



Patterns in Nucleophilic Additions to π Bonds



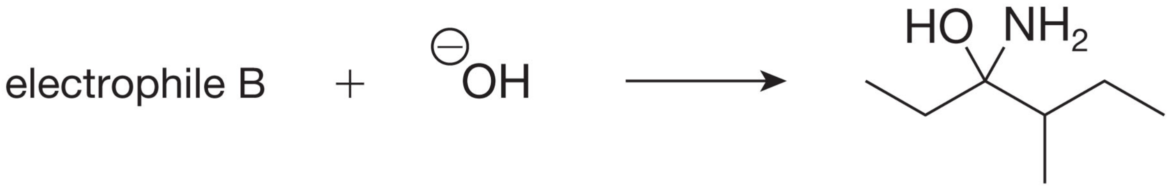
- In acidic conditions, the same process occurs, but the order of the protonation is reversed.
- This reactivity can be applied to all electrophilic π bond functional groups.



Questions

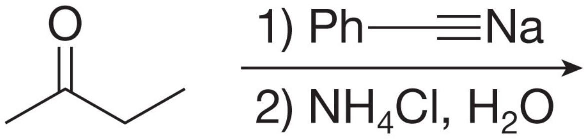
7.2

b)



7.9

c)



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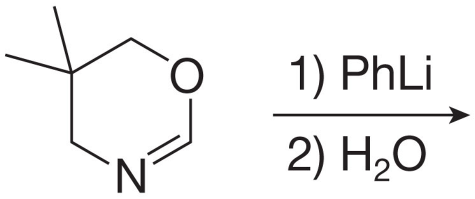


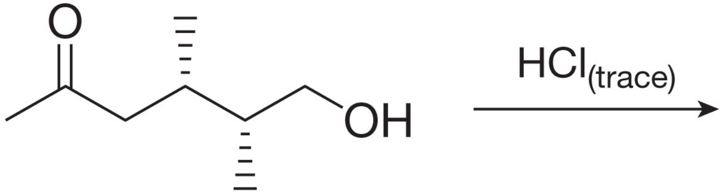
7.15

b)

Questions

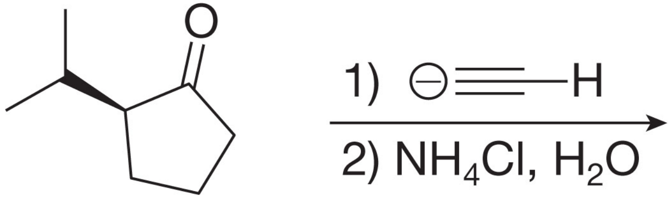
7.17

b)



7.19

a)



e)