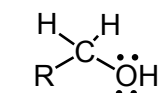
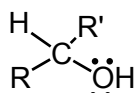


1 Nomenclature

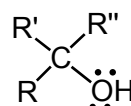
Notation: Recall the following notation (primary, secondary etc.)



1°, primary



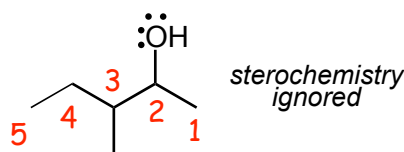
2°, secondary



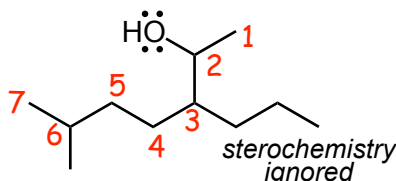
3°, tertiary

- IUPAC naming priority, **alcohol** > alkene ~ alkyne > halide (more oxidized functional groups have higher priority)
- Alcohols use the suffix "**-ol**".
- Number to give the -OH the lowest number, and if this is the same numbering from both "ends", **then** (and only then), number to give the first alkene the lowest number.
- Number to give the first substituent the lowest number **only if all else is equal**.

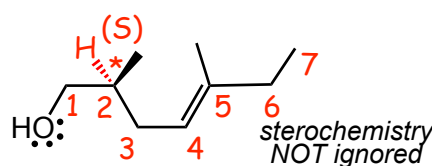
Examples



3-methyl-2-pentanol or 3-methylpentan-2-ol

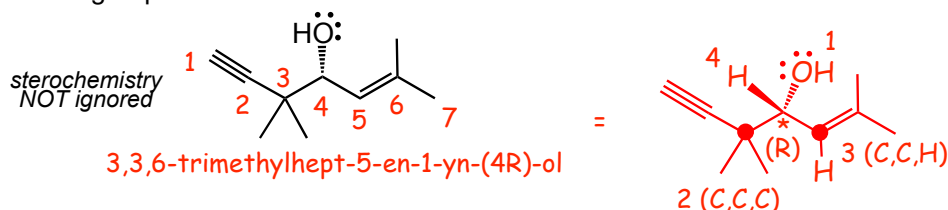


6-methyl-3-propyl-2-heptanol



(2S,5)-dimethylhept-(4E)-en-1-ol

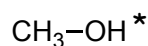
- Numbering is performed to give the **alcohol the lowest number**, not the substituents.
- For more than one functional group (above right), put the number that refers to the functional group immediately in front of the functional group.



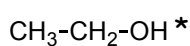
3,3,6-trimethylhept-5-en-1-yn-(4R)-ol

- In this example (b), the -OH group is #4 numbering from **either** end, therefore it is numbered from the left end to give the alkyne the lowest number, but **only** because the alcohol is #4 from either end, **in all cases number to give the alcohol the lowest number unless there is a special case such as this one**.
- Note the use of number directly before the functional group in the examples above, used when we have multiple functional groups.
- When we have **multiple functional groups** they are included in the name in the order: **first -ene (if there is one), then -yne (if there is one) followed by -ol**.

In addition to IUPAC names, many organic structures have "common" names, that are often historical, but are still widely used, more than the IUPAC names. Some common alcohols with common names:



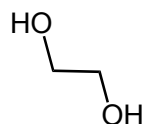
methanol



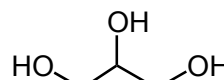
ethanol



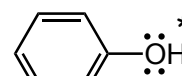
iso-propanol



ethylene glycol



glycerol



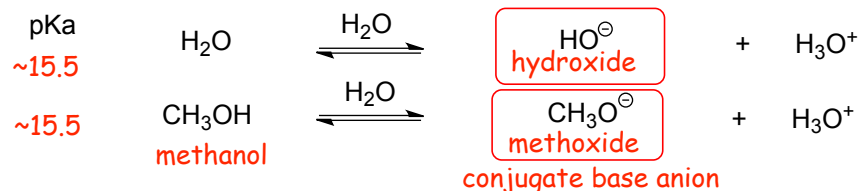
phenol

- Those with the * symbol you should know.

2 Alcohol Acidity, Return to Substituent Effects

- Alcohols are weak acids, the -OH bonds are similar to those in water.

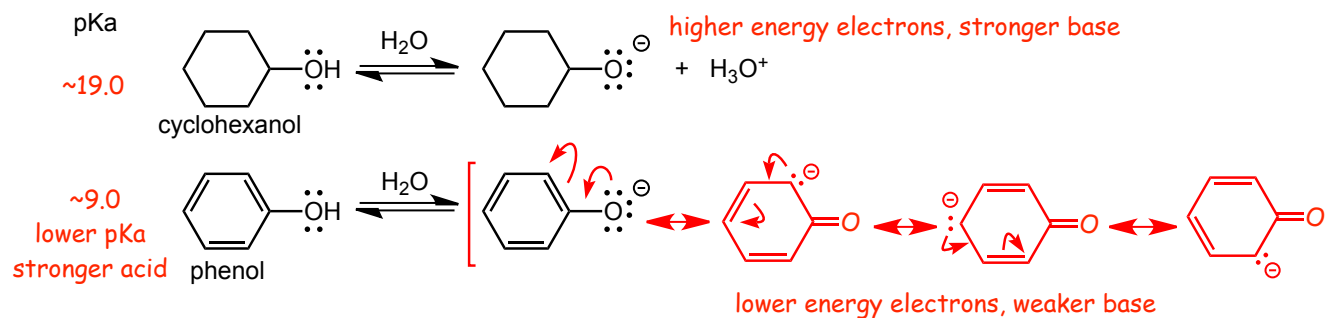
Example: The simplest alcohol methanol:



conjugate base anion

RO^\ominus = generically alkoxide anion

- The conjugate base anion of water is the hydroxide anion.
- The conjugate base anion of an alcohol is generically an alkoxide anion, i.e. the conjugate base anion of **methanol** is the **methoxide** anion, the conjugate base of **ethanol** is the **ethoxide** anion etc.
- In general we will find that the acidity of alcohols is determined by the energy of the electrons in the conjugate base anion, the lower the electron energy in the base, the weaker the base, the stronger acid is the alcohol.
- For Example: Simple Resonance effects significantly influence alcohol Bronsted acidity.



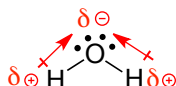
- The energy of the non-bonding electrons in the conjugate base anion of phenol are lower compared to cyclohexanol due to resonance delocalization/stabilization, phenol is the stronger acid, has the smaller pKa.

2.1 Substituent Effects: An Important New General Concept

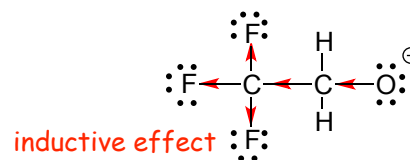
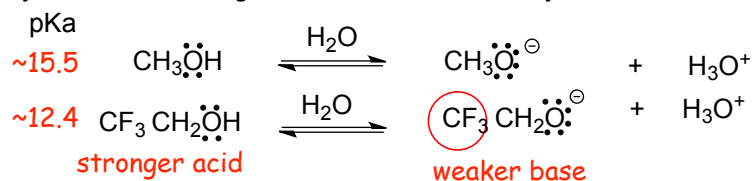
- There are **three** main kinds of substituent effects, **inductive** effect substituents, **alkyl** substituent effects and **resonance** effect substituents.
- Substituent effects primarily influence the **energies** of the **electrons** that are involved in Bronsted acidity, and therefore influence this simple chemical reaction in ways that we are already familiar with.
- A complicating factor in Bronsted acidity is that because liberation of a proton generates ions (the proton and the conjugate base anion), we will also sometimes need to take into account ionic **solvation effects**.

1. Recall the Inductive Substituent Effect:

- Inductive Effect:** This is the polarization of electrons in sigma-Bonds due to electronegative elements.
- We previously saw this effect as being responsible for generating **bond dipole moments**.

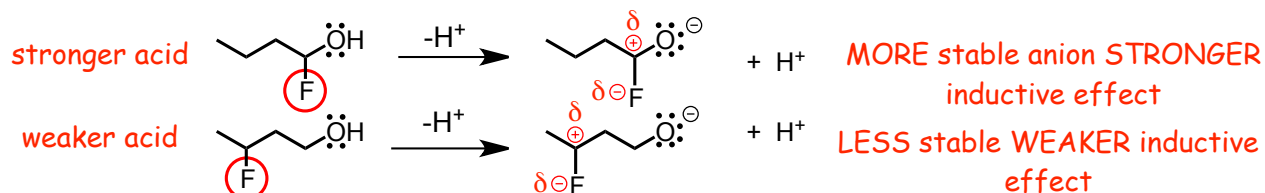


- Electron polarization occurs because the electrons are **stabilized** by proximity to electronegative elements.
- Electronegative elements are electronegative because they have more concentrated positive charges on the nucleus that are not highly shielded by electrons, which lowers the energy (increases the stability) of electrons not only on the electronegative atom but also on adjacent atoms that are connected via σ -bonds.



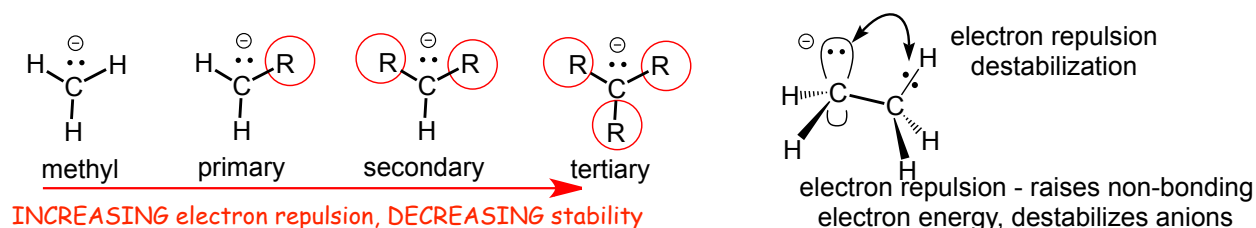
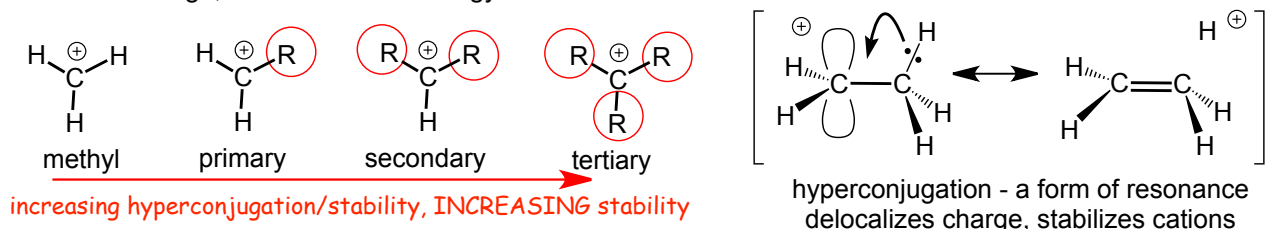
- The inductive effect normally stabilizes the conjugate base alkoxide anion.

- The inductive effect decreases rapidly with increasing distance between the electronegative element and the electrons of the base anion, here is an example from earlier in the course.

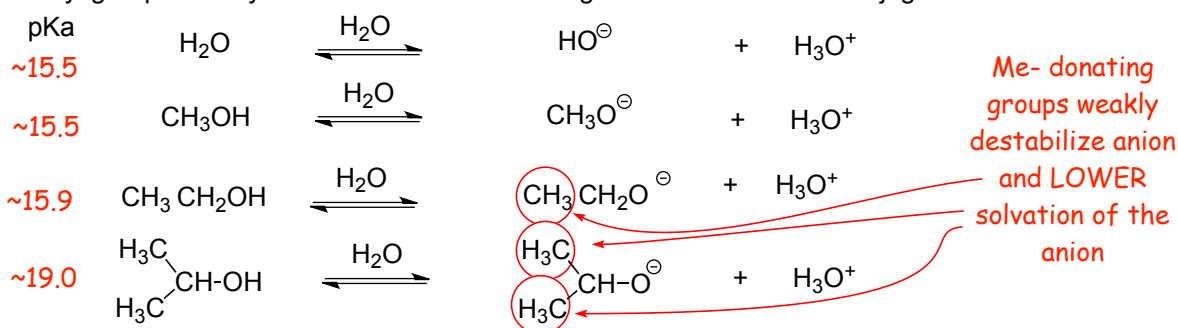


2. Alkyl groups as substituents:

- Alkyl groups stabilize cations by **hyperconjugation**, and destabilize anions due to electron repulsion.
- Alkyl groups stabilize carbocations by hyperconjugation, a form of resonance, hyperconjugation delocalizes electrons and charge, lowers the total energy of the electrons in the cation:

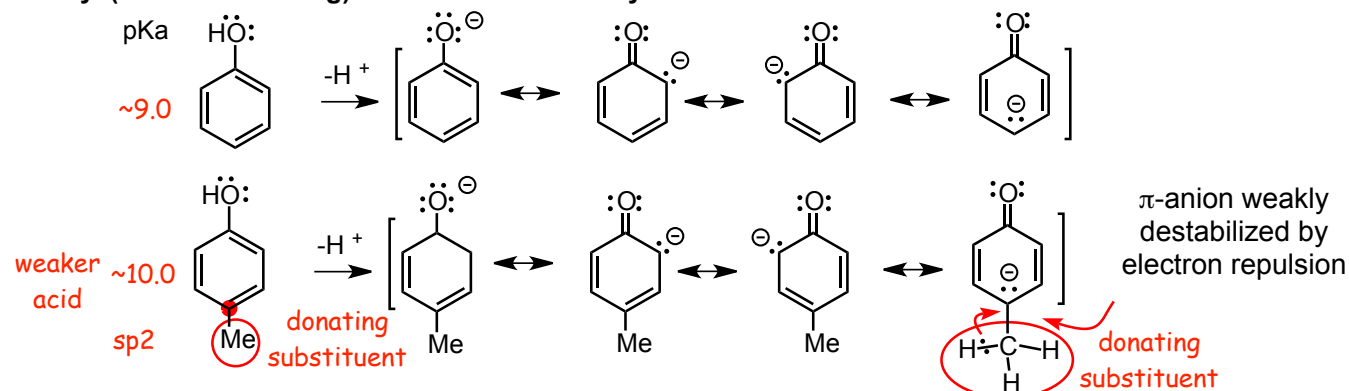


- Extra methyl groups weakly destabilize the non-bonding electrons in alcohol conjugate base anions.



- The electron donation effect is actually **pretty weak** in this case, **and**, probably more important is that the extra methyl groups also decrease solvation of the conjugate base anions, lowering the propensity of the alcohols to ionize in water, decreasing their acidity.

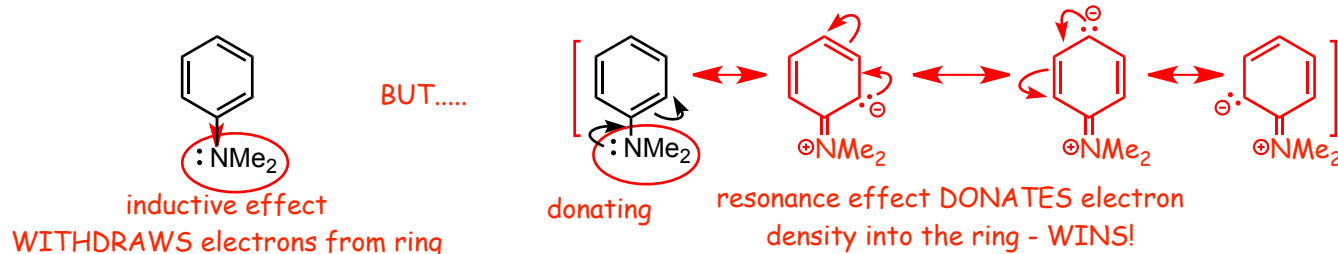
3. Alkyl (electron donating) substituents on a π -System.



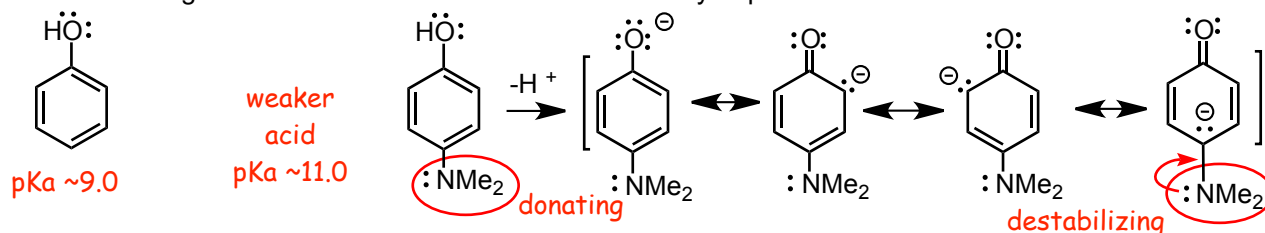
- Simple Alkyl substituents weakly **donate** electron density into the ring as a result of **hyperconjugation**.
- The conjugate base anion is thus weakly destabilized by the methyl group. Alkyl groups are **weakly** donating, because hyperconjugation is a much less effective form of electron donation compared to conventional resonance (below), because the donated electrons are already in a strong σ -bond.

4. Stronger Electron Donating substituents on a π -System:

- Minor resonance contributors show how substituents **donate** electrons into a π -system, e.g. benzene ring:



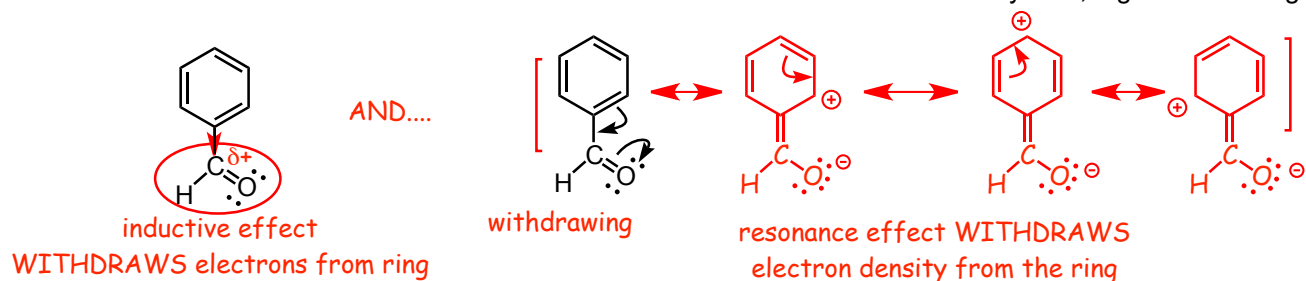
- The -NMe_2 substituents withdraws electron density via the inductive effect, **but**, the inductive effect is overwhelmed by the resonance donating effect, -NMe_2 is overall **electron donating**.
- Electron donating substituents **decrease** the Bronsted acidity of phenols:



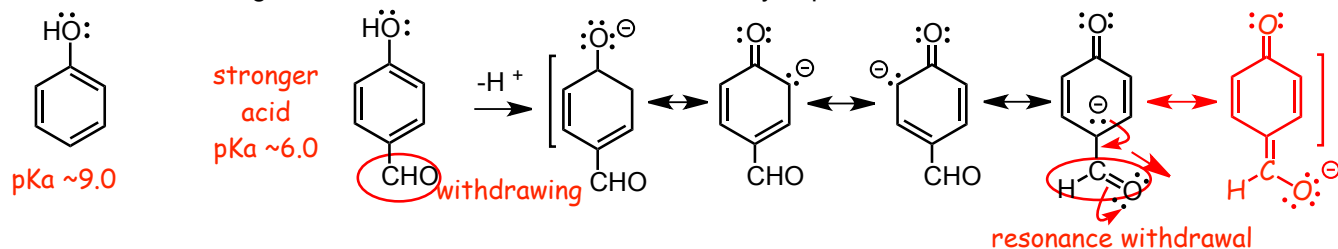
- The conjugate base π -anion is resonance **destabilized** by the electron **donating** -NMe_2 group. The resonance donating effect is **stronger than any inductive stabilization by the electronegative nitrogen**.

5. Electron Withdrawing substituents on a π -System.

- Minor resonance contributors show how substituents **withdraw** electrons from a π -system, e.g. benzene ring:



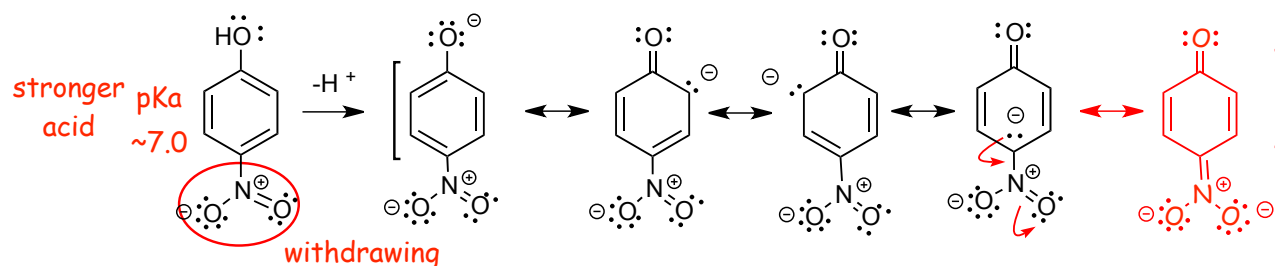
- The -CHO substituent withdraws electron density via the inductive effect, **and** via the resonance effect illustrated by the minor resonance contributors, -CHO is overall **electron withdrawing**.
- Electron withdrawing substituents **increase** the Bronsted acidity of phenols:



- The conjugate base π -anion is resonance **stabilized** by the electron **withdrawing** -CHO group.
- The -CHO group is electron withdrawing on a π -system, electron withdrawal occurs by **both resonance and inductive effects**.

6. The Position of a Substituent on a π -System Matters.

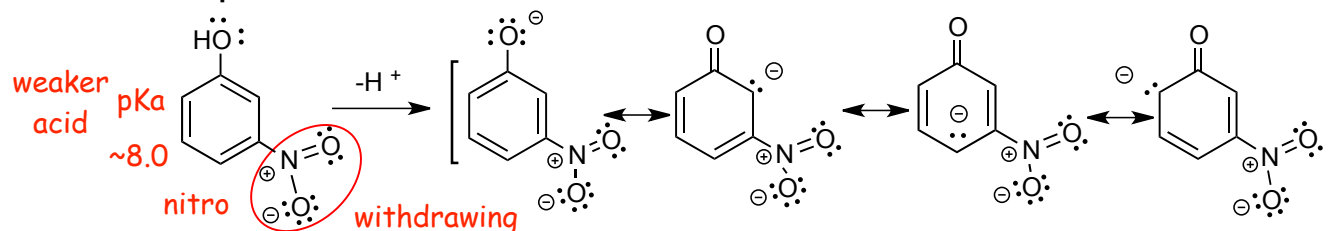
- The pK_a of unsubstituted phenol is ca. 9.0.
- Consider **4-nitrophenol**:



• The conjugate base anion of 4-nitrophenol is directly stabilized by the inductive **and** resonance effect of the nitro (-NO₂) substituent, the formal negative charge is delocalized onto the carbon that the -nitro group is attached, the negative charge is further resonance stabilized by the nitro group, the base anion is stabilized and the acid is thus stronger.

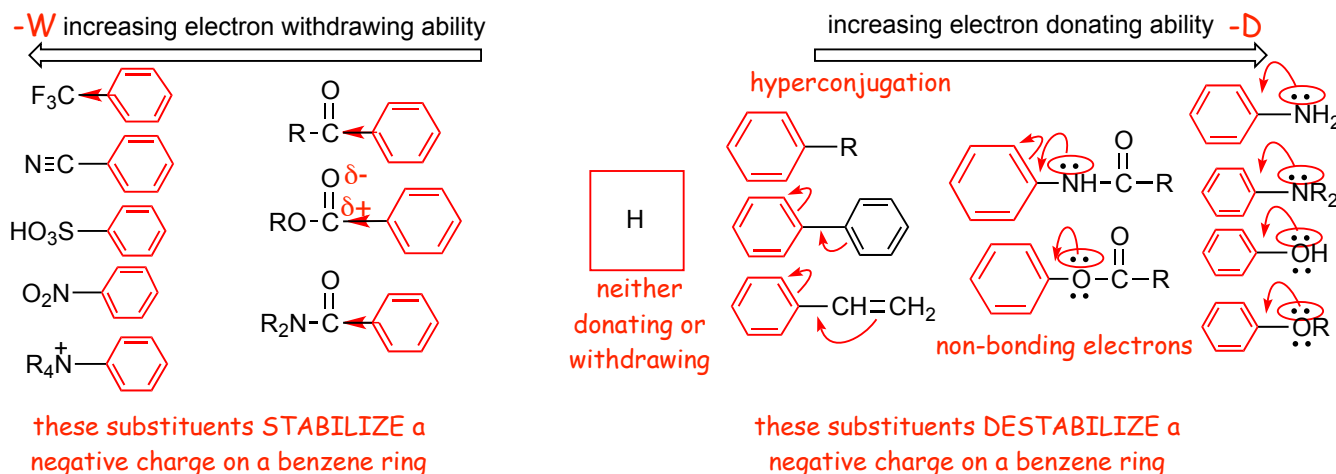
• The pKa of unsubstituted phenol is ca. 9.0.

• Consider **3-nitrophenol**:



• The conjugate base anion is **not directly** stabilized by the nitro (-NO₂) substituent because the formal negative charge is not delocalized onto the carbon that the substituent is attached to, there is no resonance stabilization although there is still some inductive stabilization of the conjugate base anion, 3-nitrophenol is more acidic than phenol but less acidic than 4-nitrophenol.

Summary of Electron Withdrawing/Donating Substituents when attached to π -Systems



- Donating and withdrawing ability is measured **relative to hydrogen (H)**.
- **Distinguishing the D- and W- groups is easier than it looks (no memorization!).**
- The donating groups have non-bonding electrons or electrons in π -bonds that can be used to **donate** to the attached π -system.
- Just about every other substituent is withdrawing due to the presence of electronegative elements, W- groups do **not** have non-bonding electrons on the atoms that is connected to the π -system.

3 Oxidation/Reduction: Definition

- The General Chemistry Definition of oxidation and reduction is the addition and subtraction of electrons.
- Counting electrons in **organic** structures is difficult because the electrons are mainly shared in covalent bonds.
- There are formal ways of counting electrons in bonds that require learning rules, so we will skip this
- There is also a slightly less formal way that we **will** use, that focuses attention on the **atoms** that are involved in the bonds that are made and are broken for the organic structure in question.

- When a new bond is made (for example) from a carbon atom to a **more electronegative** atom (usually oxygen), that is **oxidation** (the more electronegative element "takes" an electron from the carbon).
- When a new bond is made (for example) from carbon atom to a **less electronegative** atom (usually hydrogen), that is **reduction** (the more electronegative element "gives" an electron to the carbon).

Oxidation: Making **new bonds** to more electronegative elements, usually oxygen

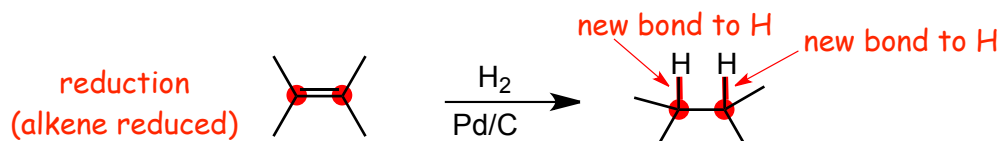
Oxidation: Breaking **old bonds** to (removing or replacing) less electronegative elements, usually hydrogen

Reduction: Making **new bonds** to less electronegative elements, usually hydrogen

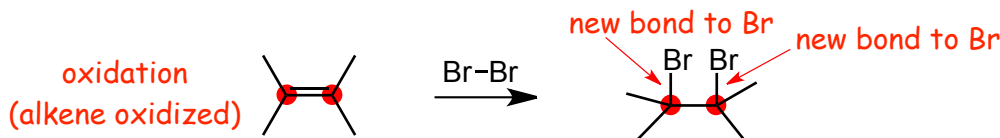
Reduction: Breaking **old bonds** to (removing or replacing) more electronegative elements, usually oxygen

Attention is focused on the atoms that are involved in the **bonds that are made and broken**, other atoms are not important.

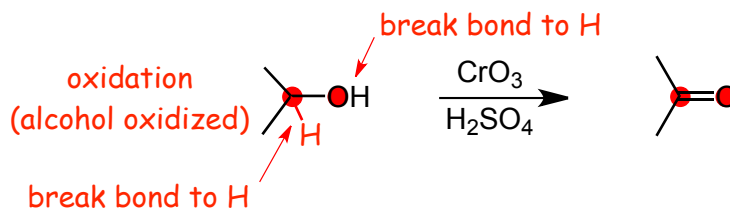
Examples:



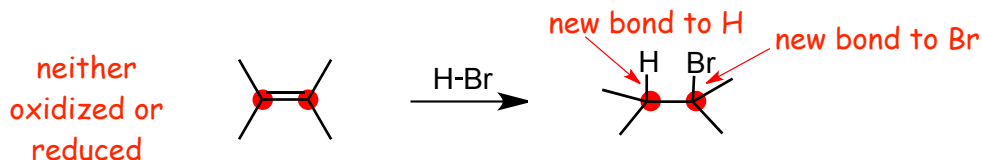
- For the starting organic structure, the new bonds are to both to the less electronegative hydrogen (2 x H added), thus, overall **reduction** of the organic structure.



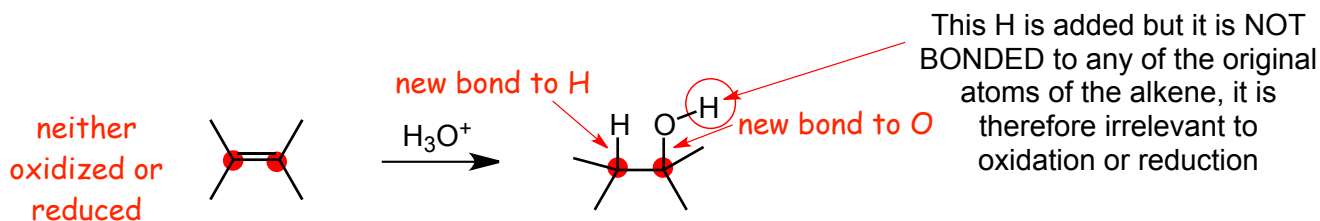
- For the starting organic structure, the new bonds are to both to the more electronegative bromine (2 x Br added), thus, overall **oxidation** of the organic structure.



- For the starting organic structure, bonds are broken to less electronegative H atoms (2 x H are removed), thus, overall **oxidation** of the organic structure.



- For the starting organic structure, the new bonds are to the more electronegative bromine **and** to the less electronegative H (1 x Br and 1 x H added), thus, overall **neither** oxidation or reduction of the organic structure.

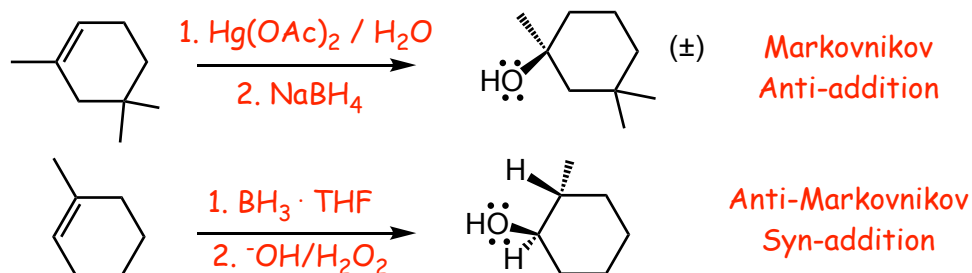


- For the starting organic structure, the new bonds are to the more electronegative oxygen **and** to the less electronegative H (1 x O and 1 x H added), thus, overall **neither** oxidation or reduction of the organic structure.
- Note the fact that a H atom is also added to the structure via the -OH group is irrelevant, it is only the atoms that are involved in forming bonds to the organic structure that are important.

4 Preparation of Alcohols

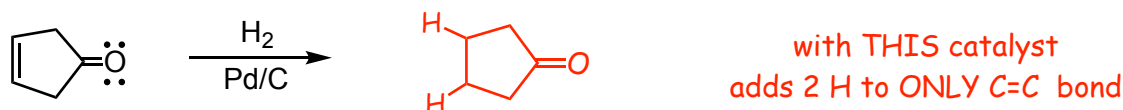
4.1 Review of Reactions We Have Already Seen

Recall:

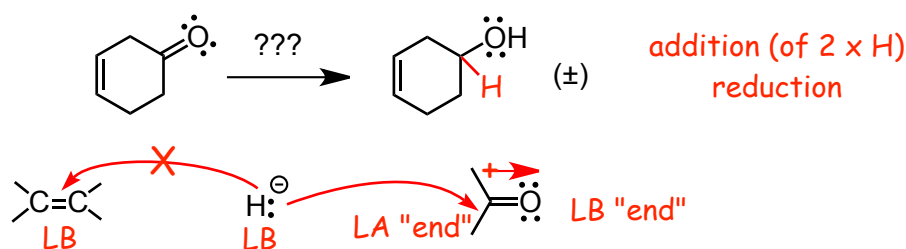


4.2 Hydride Reduction of the Carbonyl Group

Catalytic hydrogenation can actually get quite subtle, with different catalysts, one functional group can be reduced in the presence of another, e.g.:

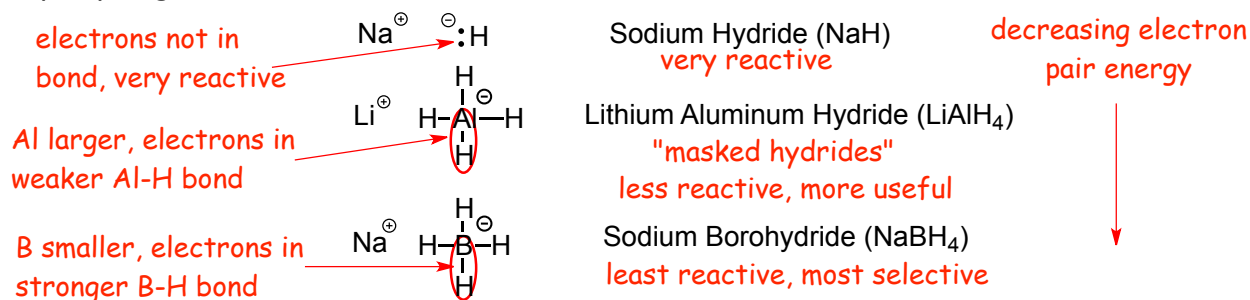


To prepare an alcohol, however, we need to do **selective reduction** of only the C=O bond, **How?**

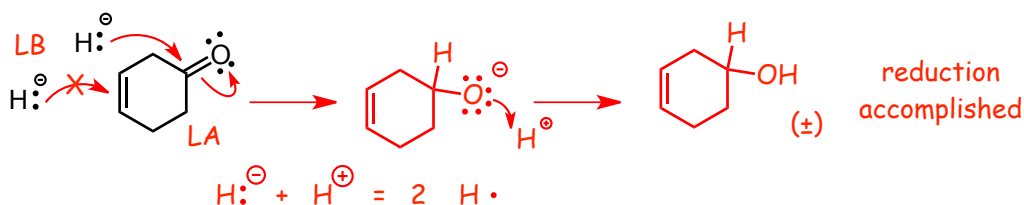


• A Lewis base (e.g. hydride anion) tends not to react with another Lewis base, and so does not react with the alkene, but **does** react with the carbonyl (C=O) group, which can act as a Lewis acid.

Some (new) reagents:



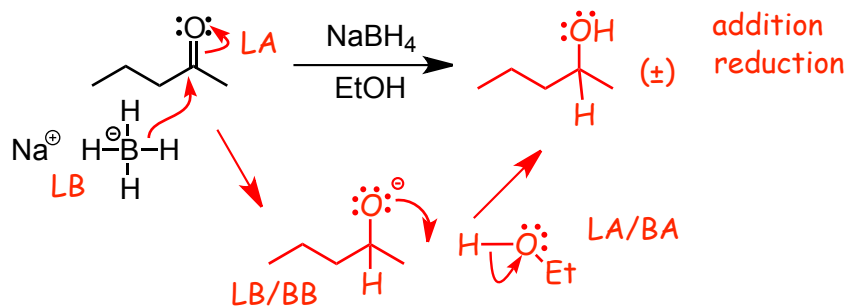
In Principle:



- Both hydride anion and the alkene are nucleophiles (Lewis bases), thus no reaction there.
- A hydride anion (H^-) and a proton (H^+) are equivalent to 2 hydrogen atoms (2 H).

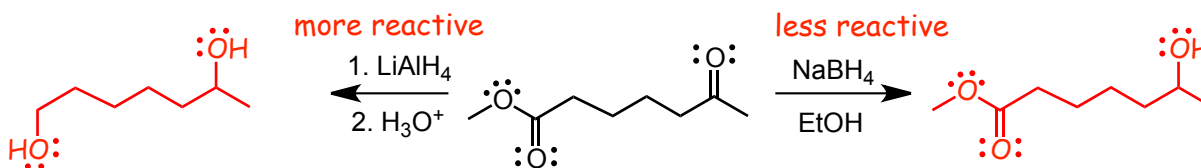
In Practice:

- NaH is too reactive and too strong a Bronsted base (less selective), NaH will usually deprotonate an aldehyde/ketone rather than add to the $\text{C}=\text{O}$ bond, LiAlH_4 or NaBH_4 used instead:

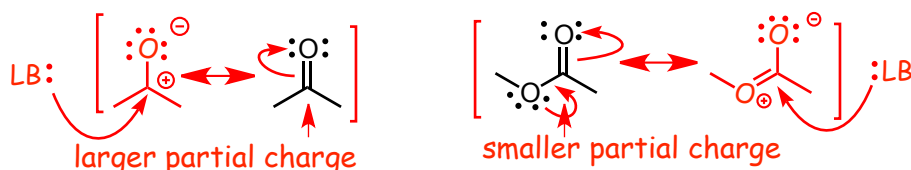


- The BH_4^- anion is less reactive than H^- because the electrons are in a bond, therefore lower in energy.
- Overall, BH_4^- supplies H^- , EtOH supplies H^+ . Together H^- and H^+ make H_2 .

Example: (stereochemistry ignored)

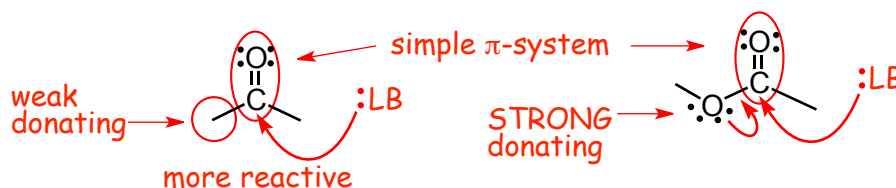


- Why does the **NaBH_4 reduce the ketone and not the ester, and the LiAlH_4 reduce both?**
- The less reactive NaBH_4 reduces aldehydes and ketones but not esters.
- The more reactive LiAlH_4 also reduces esters (and acids).
- The **$(\text{H}_3\text{Al}-\text{H})^-$ bond is weaker than the $(\text{H}_3\text{B}-\text{H})^-$ bond**, and so is more reactive.
- **Esters and acids are less reactive than aldehydes and ketones** due to better resonance stabilization.



- Minor resonance structures **emphasize the Lewis acid character and partial positive charge** on the carbonyl carbon in a **ketone**, a **LB will react faster with an aldehyde and ketone**.
- Minor resonance structures show why there is a **much smaller partial positive charge** on the carbonyl carbon in an **ester**, a **LB will react slower with an ester**.

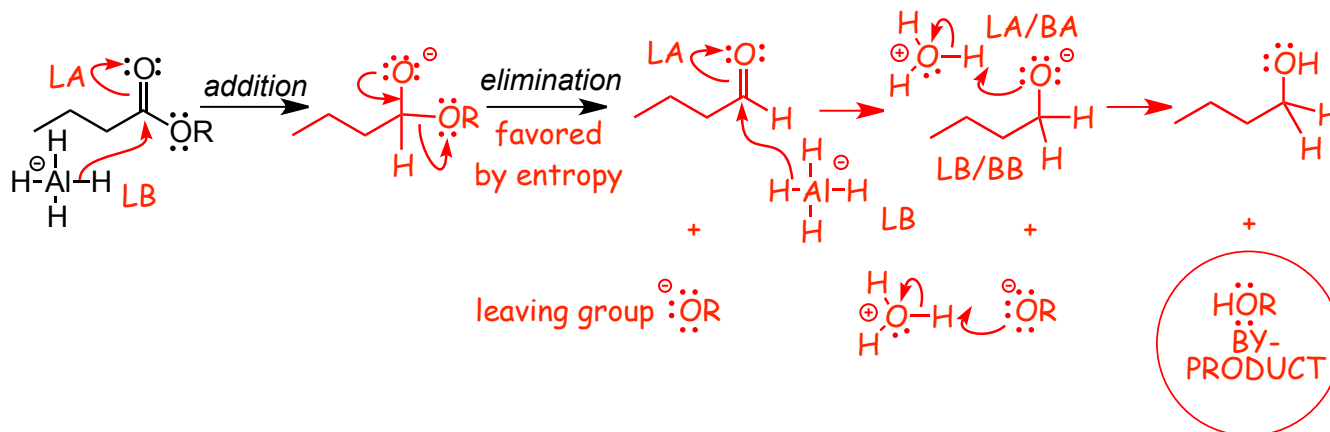
Alternatively:



- We can consider that $\text{C}=\text{O}$ to be a simple π -system (the same way that a benzene ring is a larger π -system), and the ester has a strong donating group attached to the carbon of the $\text{C}=\text{O}$, which decreases its reactivity towards a Lewis base/nucleophile, aldehydes/ketones have only weak donating groups attached to the carbon of the $\text{C}=\text{O}$ group, they are more reactive.
- To reduce the less reactive esters, the more reactive LiAlH_4 is required.

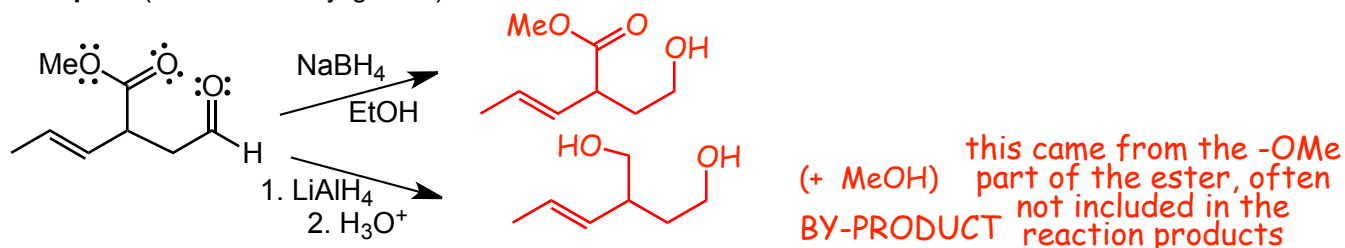
More on LiAlH_4 :

- The AlH_4^- ion will react violently with water and alcohols, so the proton has to be added in a second **acid workup** step, hence the notation: 1. LiAlH_4 ... 2. H_3O^+
- In this second acid workup step, just enough dilute acid is used to "complete" the reaction.
- The protonation is essentially instantaneous, i.e. this is **not** the same as acid catalyzed addition of water to an alkene (for example), which requires higher concentrations of acid, a lot of time and usually some heat.



- This is our first example of an **addition/elimination mechanism**, we will see this again later.....
- Note complete **removal of the OR^- group** of the ester in the elimination step.
- Elimination occurs because the OR^- is a reasonable leaving group (but not great!), **and** elimination is favored by entropy, **and**, occurs because the species that is eliminating already has a negative charge on oxygen.
- Note that the OR^- leaving group will get protonated in the acid step to form usually a simple alcohol (HOR) that is often not included in the products since it is not part of the main organic structure, it is a **by-product**.
- A negatively charged oxygen **can be** a leaving group, but only if the reaction **starts** with high chemical potential reactants that provide the energy to allow an oxygen anion to leave, for example a strong Lewis base that is an anion, e.g. the aluminum hydride anion (AlH_4^-).

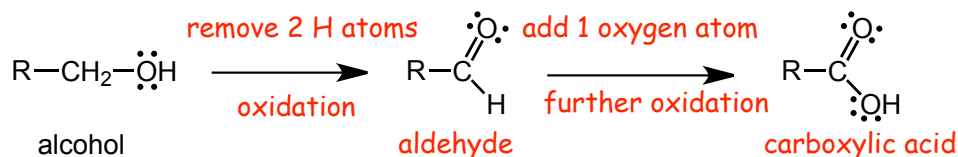
Examples: (stereochemistry ignored)



- NaBH_4 reacts **only** with the aldehyde, the ester is less reactive and the alkene is also a Lewis base.
- LiAlH_4 reacts with the aldehyde **and** the carboxylic acid (the acid reaction proceeds via addition/elimination).
- The H_3O^+ in the LiAlH_4 reaction does **not** react with the alkene, because in this context, H_3O^+ means an "acid workup step", which in turn means "add just enough dilute aqueous acid to protonate the negatively charged oxygen atoms". When acid catalyzes water addition to the $\text{C}=\text{C}$ bond of an alkene the acid concentrations are high, the reaction time is long and the temperature has to be high, the context defines the meaning of H_3O^+ .

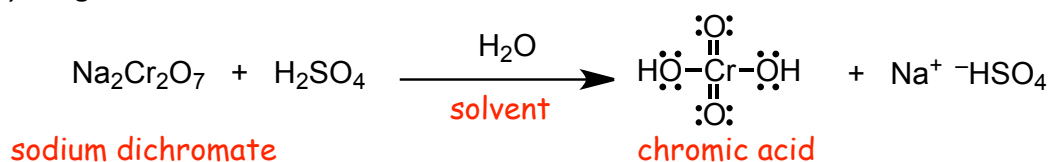
5 Oxidation Reactions of Alcohols

Here are a couple of oxidation reactions:



- These reactions can be **controlled** by appropriate choice of reagent/conditions.

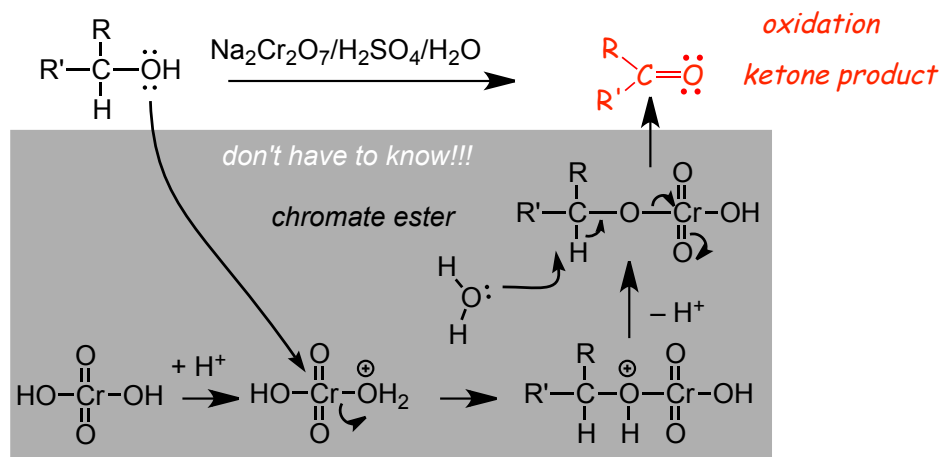
A New Cr(VI) Reagent #1:



- The reagent is sodium dichromate and sulfuric acid dissolved in water, this generates chromic acid "in situ".

Example with a secondary alcohol:

- Oxidation to form a **ketone**:

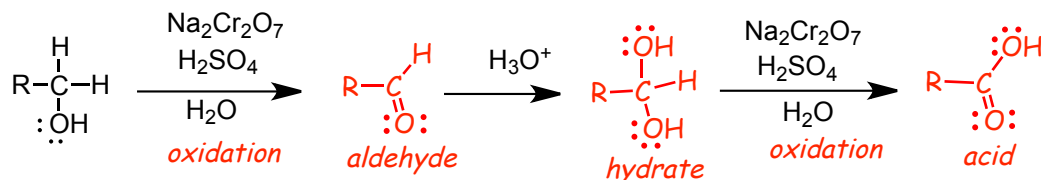


- Mechanisms involving oxidation/reduction of metals do not follow the usual patterns of Lewis acid/base Bronsted acid/base reactions, **and** they tend to be specialized and specific, for this reason you do not have to know this mechanism.

Example with a primary alcohol:

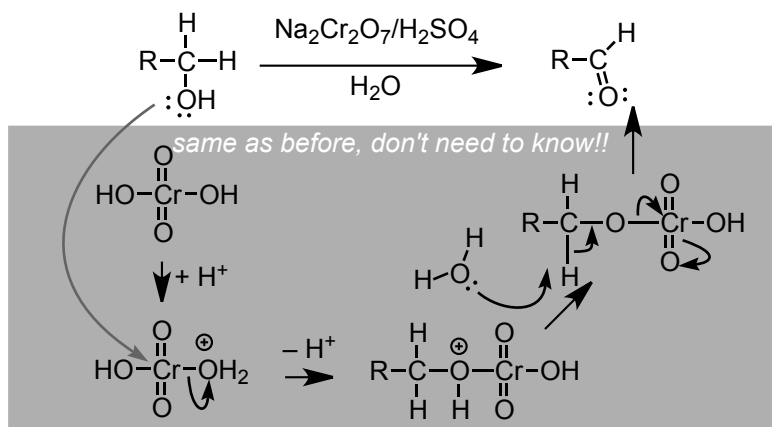
- Oxidation to form a **carboxylic acid**.

The overall process is as follows:

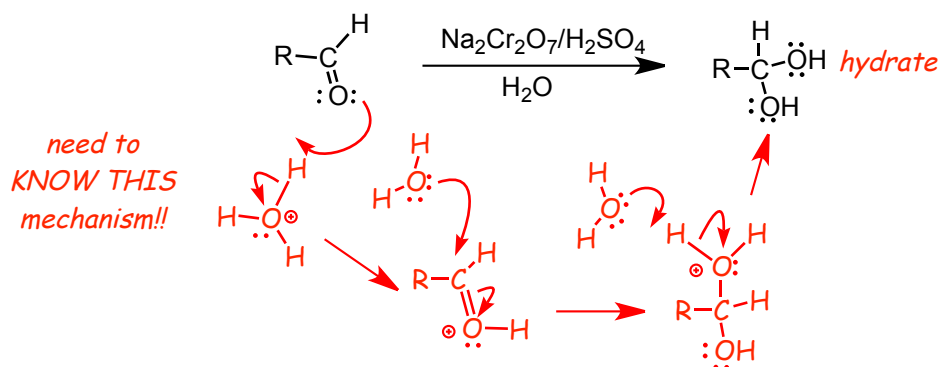


- Note that formation of the aldehyde from the alcohol is oxidation (removes 2 H atoms).
- Note that formation of the acid from the hydrate is oxidation (removes 2 H atoms).
- Note that formation of the hydrate from the aldehyde is **neither** oxidation or reduction.

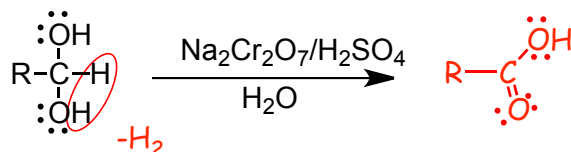
Details: First, formation of the aldehyde via the same mechanism as above:



Details: Second, conversion of the aldehyde into the hydrate in the presence of water and an acid catalyst, **you do need to know this mechanism.** Remember, the reaction conditions involve sulfuric acid in water, the next step is simply acid catalyzed addition of water to the aldehyde:

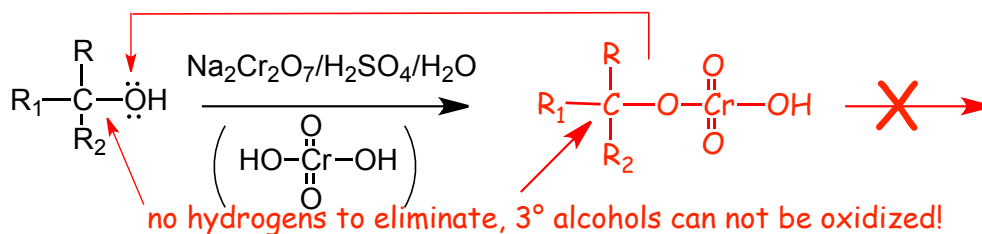


Final Detail: Third, conversion of the hydrate (a geminal di-alcohol) into a carboxylic acid, via the same mechanism as before, the chromic acid removes 2 hydrogen atoms from the hydrate, which forms the carboxylic acid, the mechanism by which chromic acid does this is the same as formation of the aldehyde from the primary alcohol, you don't need to know this and it is not shown again here:

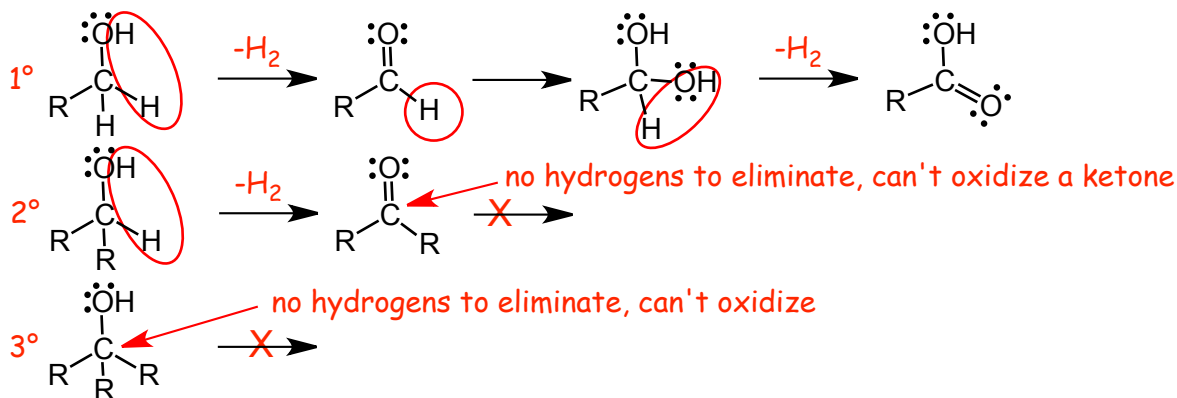


- The hydrate gets oxidized to a carboxylic acid because it is now a (di)alcohol.

Example with a tertiary alcohol:

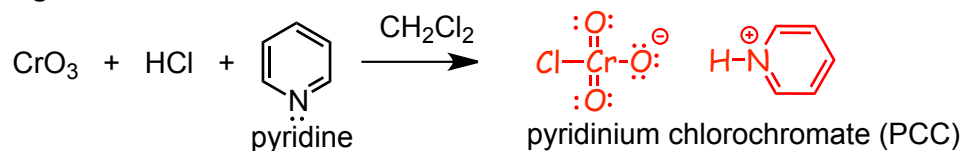


- Tertiary alcohols **cannot be oxidized**, the necessary hydrogen atom is missing!



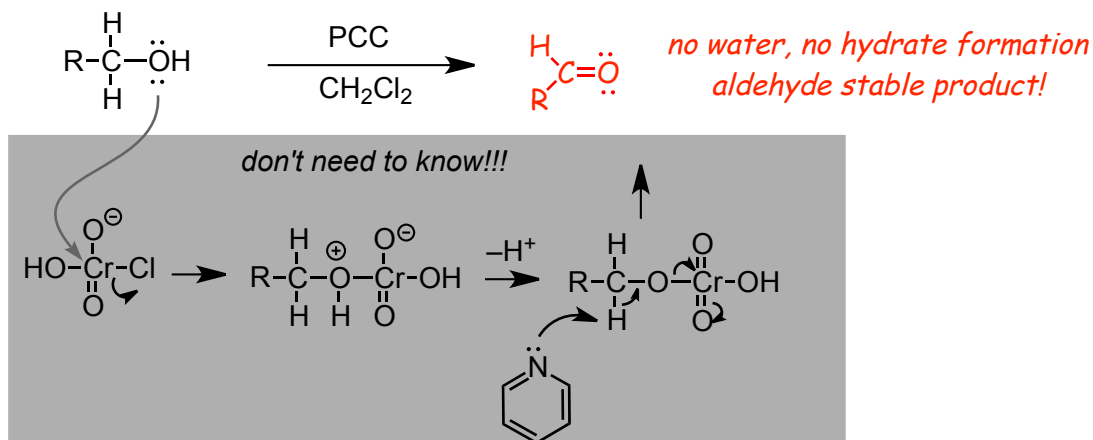
- For the same reason, ketones cannot be oxidized, the necessary hydrogen atom is missing.

A New Cr(VI) Reagent #2:



• CH_2Cl_2 is the **solvent**, therefore there is **no water here**, so any aldehydes that are formed **cannot make a hydrate**, so further oxidation to a carboxylic acid will not occur.

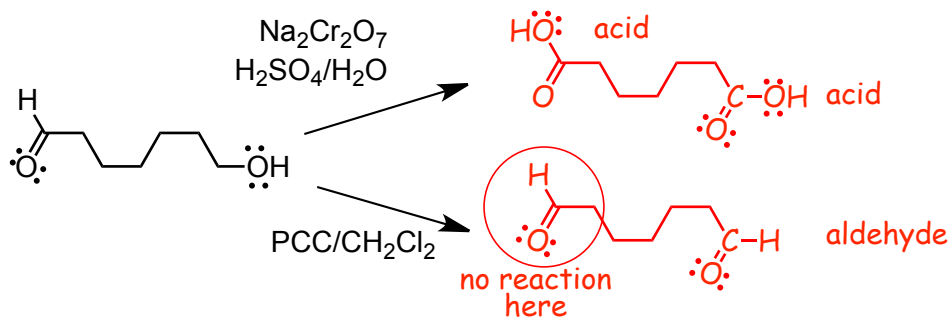
PCC with a primary alcohol:

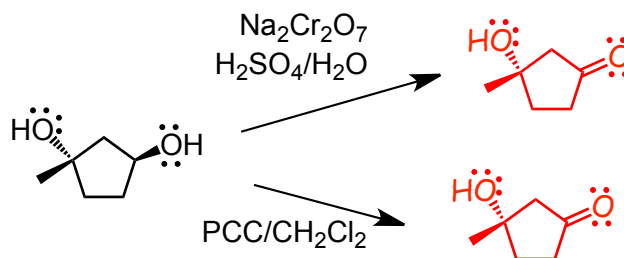


Summary of Oxidation Reactions

		$\text{Na}_2\text{Cr}_2\text{O}_7$ $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$	PCC/ CH_2Cl_2
$\text{R}-\text{CH}_2-\text{OH}$	1° alcohol	Carboxylic Acid	Aldehyde
$\text{R}-\overset{\text{R}'}{\underset{ }{\text{CH}}}-\text{OH}$	2° alcohol	Ketone	Ketone
$\text{R}-\overset{\text{R}'}{\underset{\text{R}''}{\underset{ }{\text{C}}}}-\text{OH}$	3° alcohol	no reaction!	no reaction!
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	aldehyde <i>via the hydrate</i>	Carboxylic Acid	no reaction!

Examples:

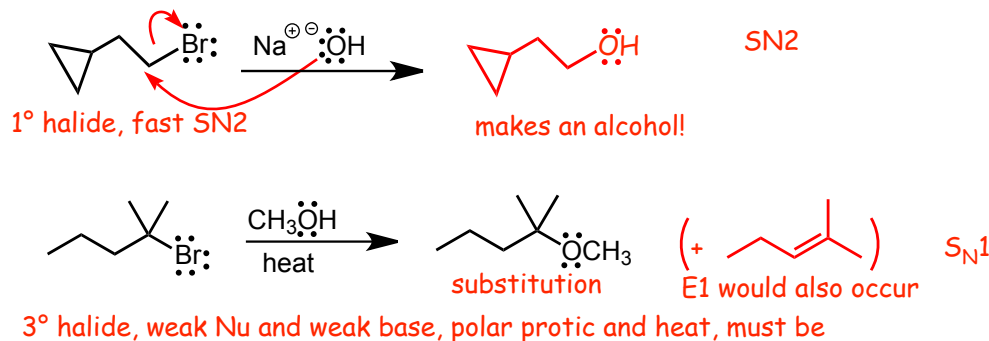




6 Substitution Reactions of Alcohols (SN1 and SN2) : Water, and other species as Good Leaving Groups

6.1 Recall: SN1 and SN2 Reactions of Alkyl Halides

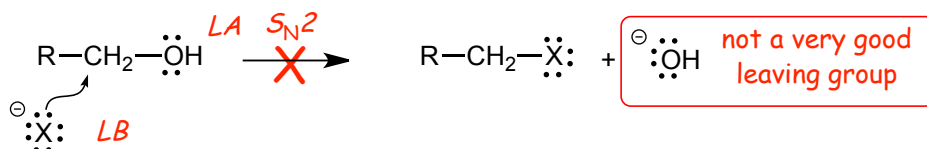
Substitution reactions of alkyl halides (SN1 and SN2)



- Substitution via SN2 is a very important substitution mechanism.
- We will try to avoid SN1 if we can since it involves a carbocation intermediate that can rearrange and/or eliminate, **although there will be some cases where it will not be possible to avoid SN1.**

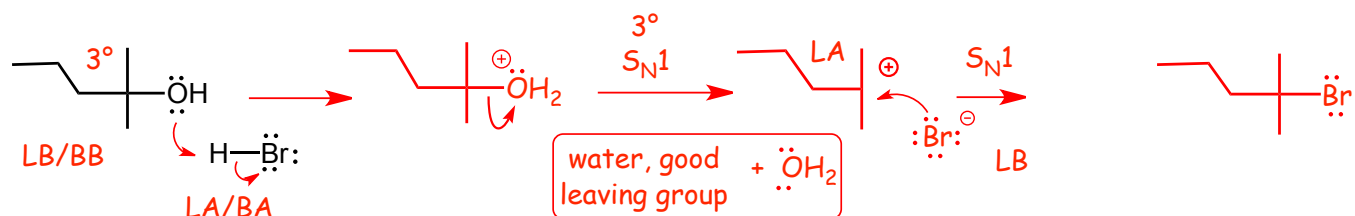
6.2 Substitution of Alcohols (SN1 and SN2) : Formation of Alkyl Halides

Consider the following substitution reaction, is it possible?



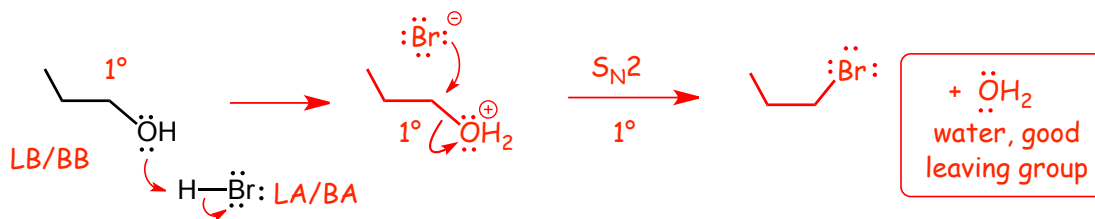
- It doesn't work! in fact, this reaction goes in the **opposite** direction.
- OH^- is a good nucleophile and will substitute for a halide, which is a good leaving group (think about standard SN2 reactions).

Reactions with Haloacids: HCl, HBr, HI, etc.



- This works because **water is an excellent leaving group.**
- This is a **really important** principle, if good leaving groups have low energy electrons in the anions, then leaving groups that are neutral, stable small molecules that don't even have a charge are even better!
- Note the tertiary (3°) alcohol and water being an excellent leaving group, substitution by SN1, SN1 is unavoidable here because the carbon is tertiary.

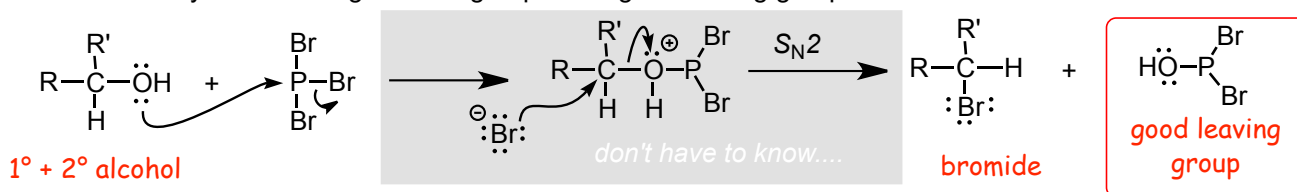
Compare



- The alcohol is now on a primary carbon, therefore only $\text{S}_{\text{N}}2$ is possible (it is not possible to form a carbocation on a primary carbon).
- This reaction goes even though the bromide anion is a poor nucleophile because water is such a good leaving group.
- These previous two mechanisms are **important**, we will see mechanistic step such as these several times.
- However, the **$\text{S}_{\text{N}}1$ mechanism still prevails for 2° and 3° alcohols**, thus, there is still the usual problem with the cation intermediates such as elimination and rearrangements.
- For 1° alcohols we have the $\text{S}_{\text{N}}2$ mechanism**, but still, the halide anions are poor nucleophiles, something better is needed.

Compare: Reaction with PBr_3 (phosphorous tribromide).

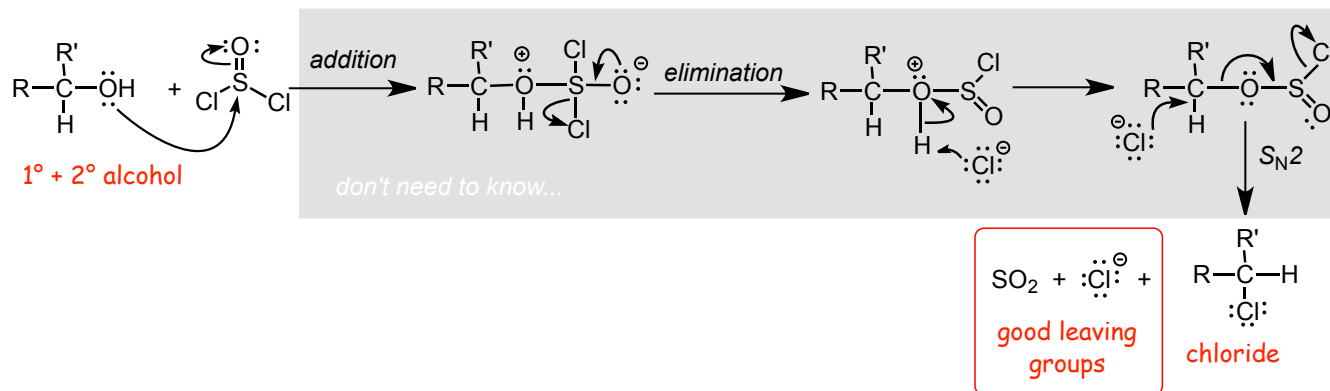
- An alternate way of converting an $-\text{OH}$ group into a good leaving group



- In the first step the leaving group is bromide, in the second step it is the neutral and stable HOPBr_2 .
- An $\text{S}_{\text{N}}2$ mechanism works well with both 2° and 1° alcohols due to the good leaving group, this is a good reaction.
- The mechanism is not quite as straightforward as standard $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$, and it a bit specific for PBr_3 , therefore you don't need to know the details of this mechanism.
- The only problem is 3° halides, which still don't work well for steric reasons (recall, no $\text{S}_{\text{N}}2$ at 3° centers!).
- (Another issue is the stereochemistry of the reaction, if it is $\text{S}_{\text{N}}2$ there should be inversion at a chiral center, but the stereochemical outcome of this reaction is less reliable than other $\text{S}_{\text{N}}2$ reactions, therefore, we will ignore it!)*

Compare: Reaction with SOCl_2 (thionyl chloride):

- Another way of converting an $-\text{OH}$ group into a good leaving group:



- Here we have addition/elimination, followed by deprotonation, followed by an $\text{S}_{\text{N}}2$ reaction to make an alkyl chloride.
- In the $\text{S}_{\text{N}}2$ reaction the leaving groups are Cl^- (a good leaving group), and SO_2 (a very good leaving group).
- An $\text{S}_{\text{N}}2$ mechanism works well with both 2° and 1° alcohols due to the good leaving group, this is a good reaction.
- The mechanism is not quite as straightforward as standard $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$, and it a bit specific for SOCl_2 , therefore you don't need to know the details of this mechanism.
- The only problem is 3° halides, which still don't work well for steric reasons (recall, no $\text{S}_{\text{N}}2$ at 3° centers!).

(As with PBr_3 , another issue is the stereochemistry of the reaction, if it is $\text{S}_\text{N}2$ there should be inversion at a chiral center, but the stereochemical outcome of this reaction is less reliable than other $\text{S}_\text{N}2$ reactions, therefore, we will ignore it again!)

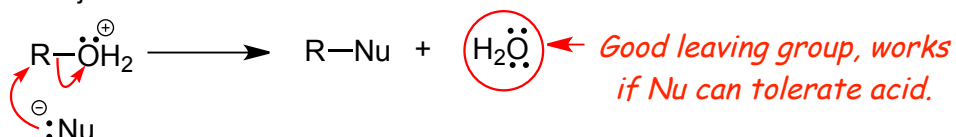
Reaction Summary				
Preferred Reagents	Chloride		Bromide	
1° alcohol	SOCl_2	" $\text{S}_\text{N}2$ "	PBr_3	use THESE for 1° & 2° alcohols
2° alcohol	SOCl_2	" $\text{S}_\text{N}2$ "	PBr_3	
1°, 2°, 3° alcohol	HCl	$\text{S}_\text{N}1$ & $\text{S}_\text{N}2$	HBr	

- The mechanisms for PBr_3 and SOCl_2 are a bit complicated, you don't need to know these, but you **do need to know** the mechanisms of the HCl and HBr reactions, even when they are not the preferred reagents.

6.3 Substitution of Alcohols : Formation of Tosylate Esters (better leaving group)

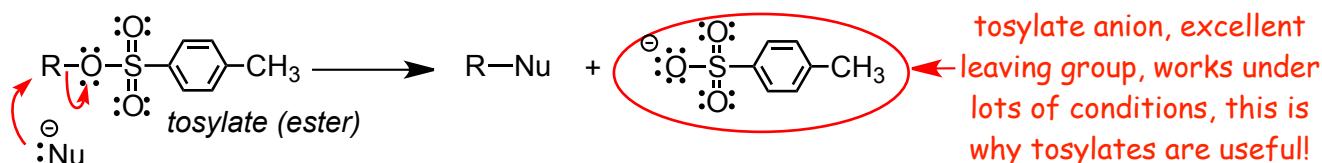
Why are Tosylates Useful?

- They are yet **another** even **more** versatile way of converting $-\text{OH}$ from a poor leaving group into a good leaving group.
- This is what we have just learned:

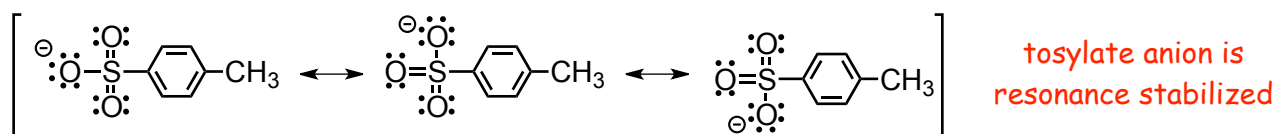


- This is OK, except that is rarely useful beyond HCl , HBr , H_2SO_4 , etc. because you need to protonate the $-\text{OH}$ first, **then** add the nucleophile (which is a Lewis base and often a reasonable Bronsted base) and hope that the nucleophile doesn't just get protonated, hmmm, something better is really needed....

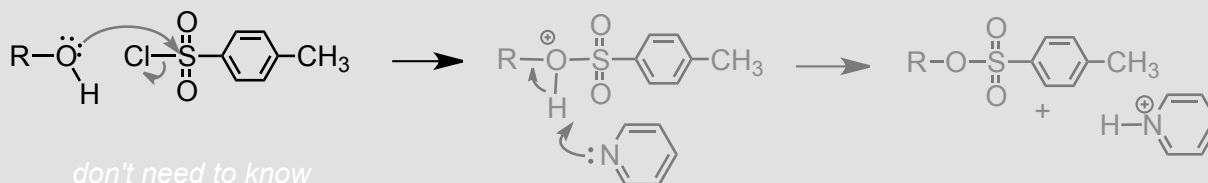
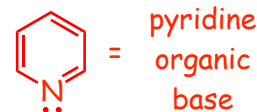
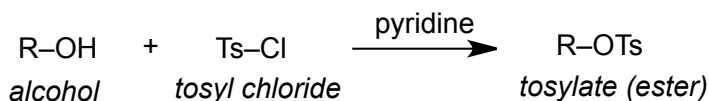
- This reaction looks a lot more complicated (but it isn't) and it **fixes this problem**.



- The tosylate anion is highly resonance stabilized, it is low energy non-bonding electrons, which is why it is such a good leaving group.

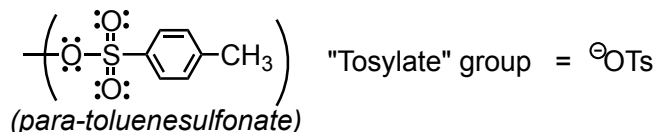
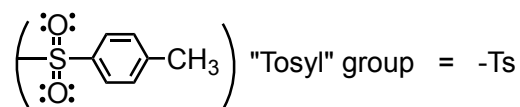


Where do tosylate (esters) come from?

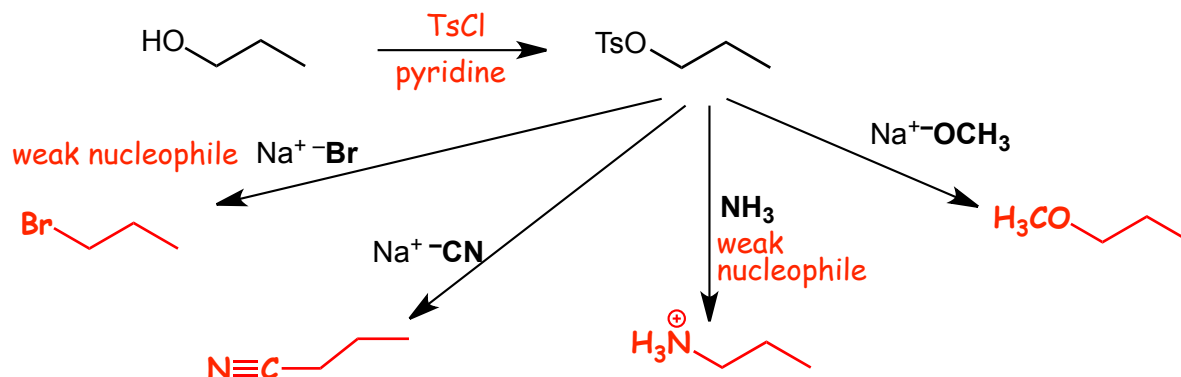


- You don't need to know the mechanism, but you **do** need to know that you need pyridine to remove the proton.

Some clarification on notation and structure.....

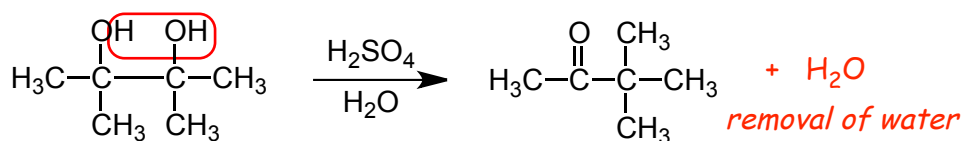


Examples: Useful reactions:



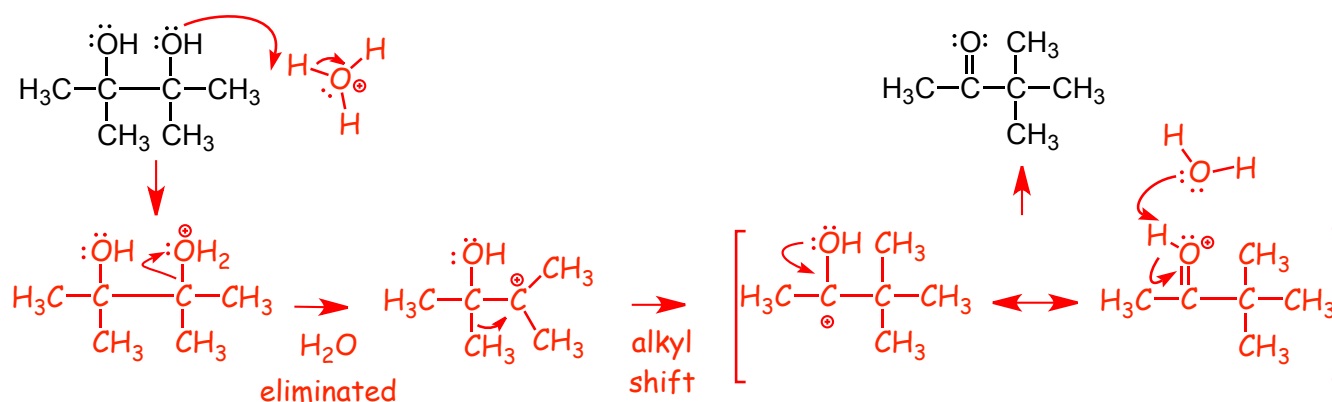
6.4 A Different E1 Elimination: The Pinacol Rearrangement Mechanism

The Pinacol Rearrangement: (another kind of alcohol dehydration)



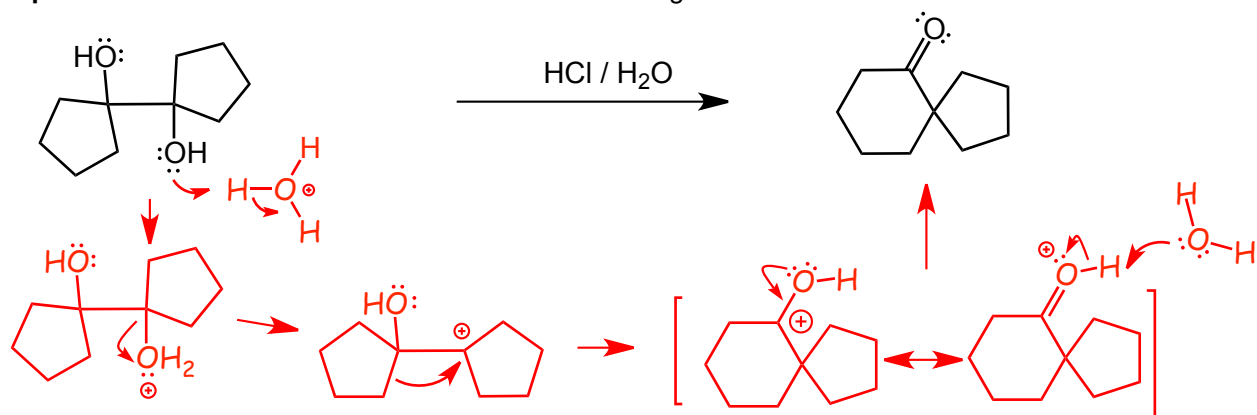
- Let's treat this as a mechanism problem, how to solve it and what basic principles can we use to guide us?
- Look carefully at the reagents/conditions (in this case, acid in water).
- Look for differences in start and end structures.
- Need to remove -H and -OH and do an alkyl shift.
- Acid catalyzed, therefore protonate first, **no anionic intermediates in presence of acid.**

The Mechanism:



- Protonate to make a good leaving group (H₂O)
- We have a usual carbocation rearrangement to make a more stable (resonance stabilized) cation intermediate.
- Deprotonation at the end regenerates the acid catalyst.

Example Mechanism Problem: A "Hidden" Pinacol rearrangement



6 Alcohols : Summary of Reactions

