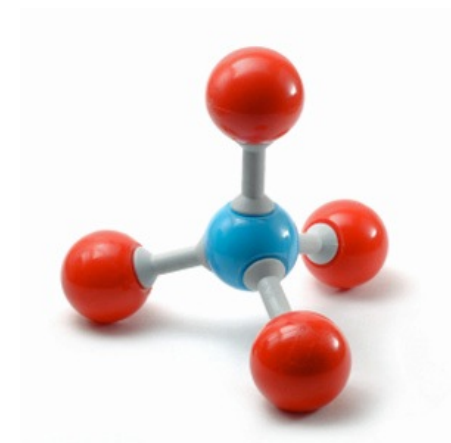


Ch12

Carbonyls

The carbonyl functional group.
Exploring ketones, aldehydes and their reactions.

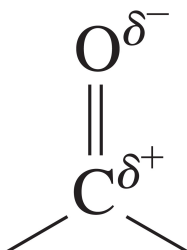


Carbonyls & Red-Ox Reactions



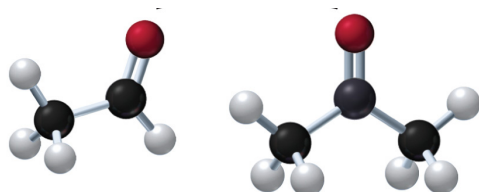
The carbonyl group

- ▶ Structure
 - ▶ sp² trigonal planar
- ▶ Partial charge



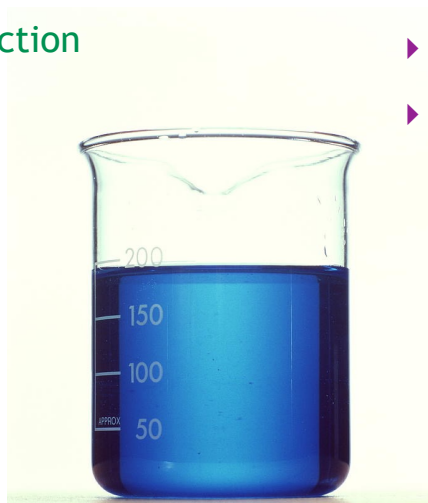
Substances with carbonyl groups

- ▶ Aldehydes
- ▶ Ketones
- ▶ Carboxylic Acids

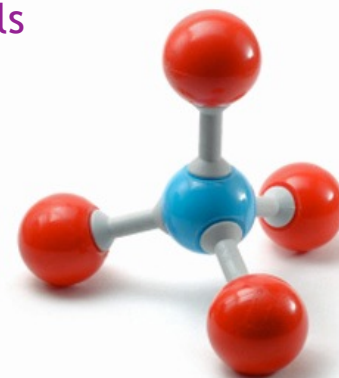


Oxidation-Reduction

- ▶ For organics, focus on carbon
 - ▶ Adding O-C bonds is oxidation
 - ▶ Adding H-C bonds is reduction



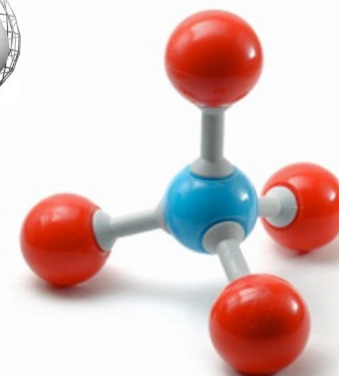
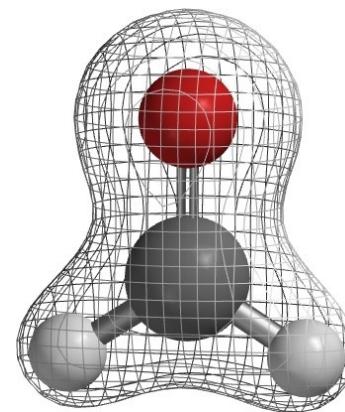
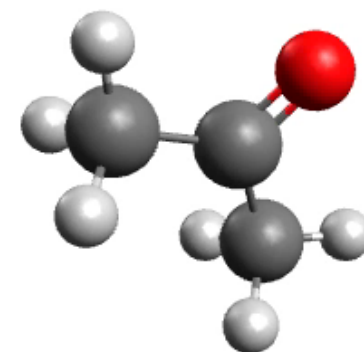
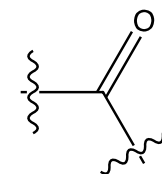
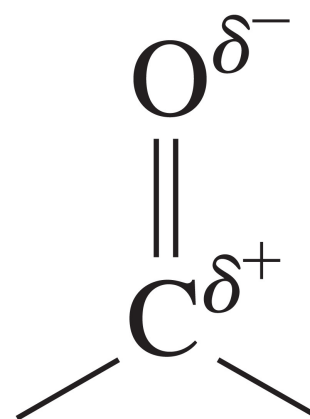
- ▶ Reactions of Alcohols
 - ▶ Combustion reactions
 - ▶ Dehydration reactions
 - ▶ structural & stereoisomers
- ▶ Reactions of Thiols
 - ▶ Oxidation to disulfides
- ▶ Oxidation of Carbonyls
 - ▶ Tests for aldehydes
 - ▶ Tollens' Test
 - ▶ Benedict's Test
- ▶ Reduction of Carbonyls
 - ▶ Aldehydes to 1° alcohols
 - ▶ Ketones to 2° alcohols



The Carbonyl Group

- ▶ A **carbonyl** group is an oxygen double bonded to a carbon skeleton.
- ▶ The the carbonyl group is present in and responsible for the chemistry of many classes of organic compound including:
 - ▶ Ketones
 - ▶ Aldehydes
 - ▶ Carboxylic Acids... and more we'll talk about in Chapter 13 and 14.

- ▶ The carbon in a carbonyl group is sp^2 .
- ▶ The bonds to it form a trigonal planar shape.
- ▶ The double bond allows electron density to shift more easily between the oxygen and carbon.



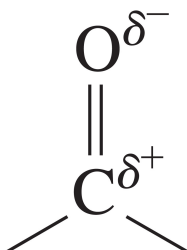
Carbonyls & Red-Ox Reactions

▶ The carbonyl group

▶ Structure

▶ sp^2 trigonal planar

▶ Partial charge

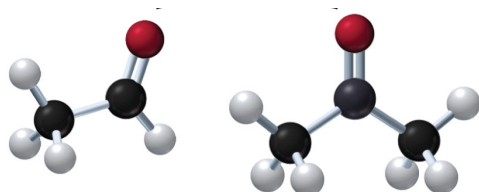


Substances with carbonyl groups

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▶ Ketones

▶ Carboxylic Acids



▶ Oxidation-Reduction

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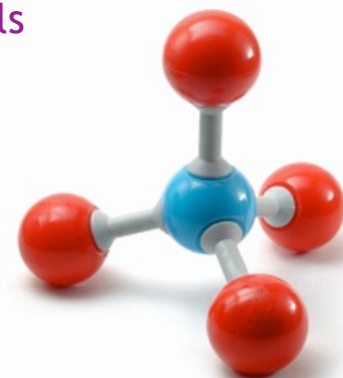
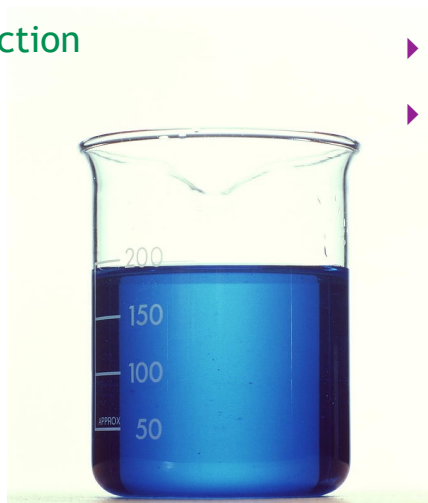
▶ Tollens' Test

▶ Benedict's Test

▶ Reduction of Carbonyls

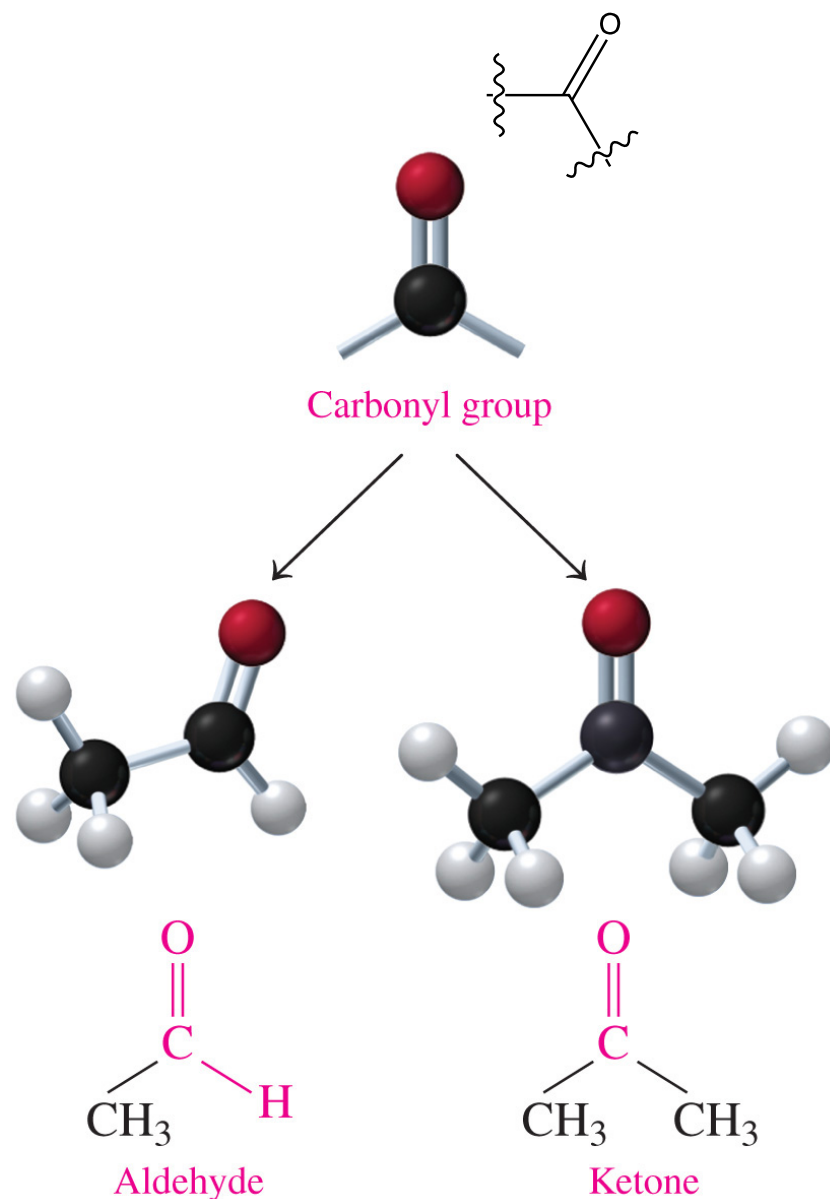
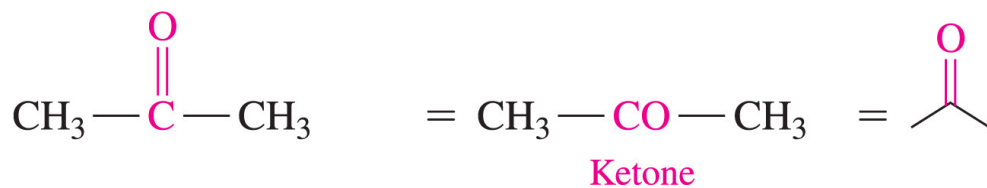
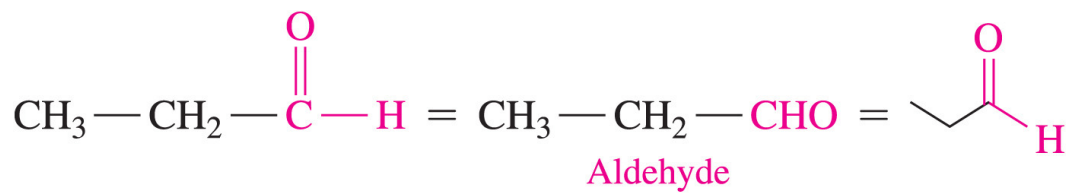
▶ Aldehydes to 1° alcohols

▶ Ketones to 2° alcohols



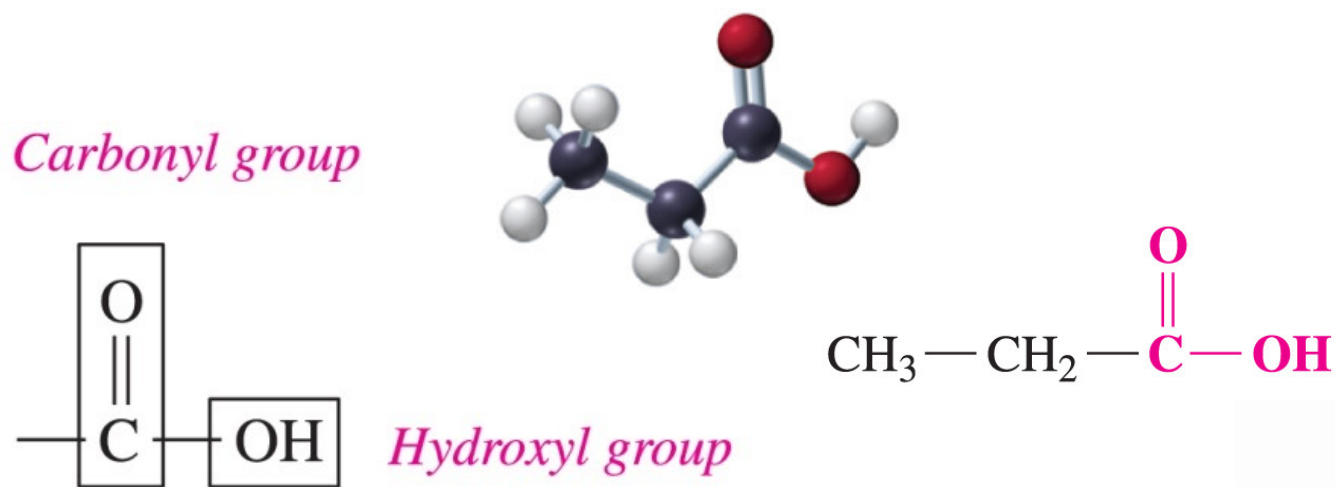
Ketones & Aldehydes

- ▶ The **ketone** family includes any substances that have a carbonyl group attached to two carbons.
- ▶ The **aldehyde** family includes any substances that have a hydrogen atom attached to the carbonyl group.



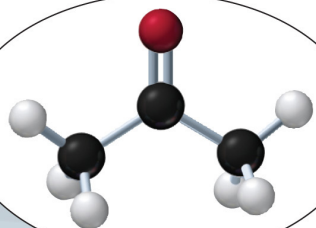
Carboxylic Acid

- ▶ **Carboxylic acids** are substances that have a hydroxyl group attached to a carbonyl group.
- ▶ We will discuss carboxylic acids in more detail in chapter 14.
(including how to name them).

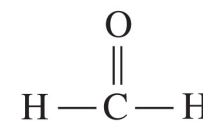
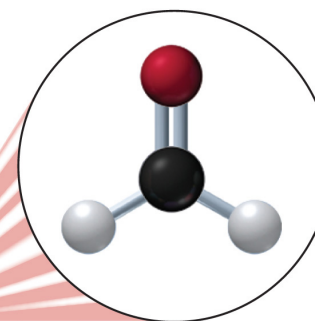


Some uses of Aldehydes & Ketones

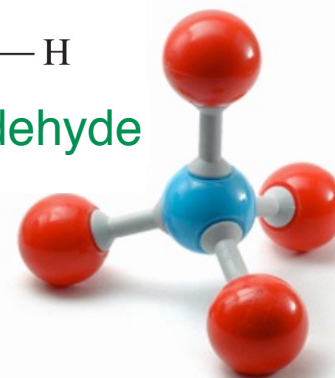
- ▶ Acetone ($\text{CH}_3)_2\text{CO}$ is the simplest ketone. Acetone and other ketones make good organic solvents, able to dissolve both polar and non-polar substances.
- ▶ Formaldehyde (H_2CO) is a gas at room temperature. The simplest aldehyde possible, it's used in many manufacturing processes. As an aqueous solution (40%) it's used to preserve biological specimens.



Acetone

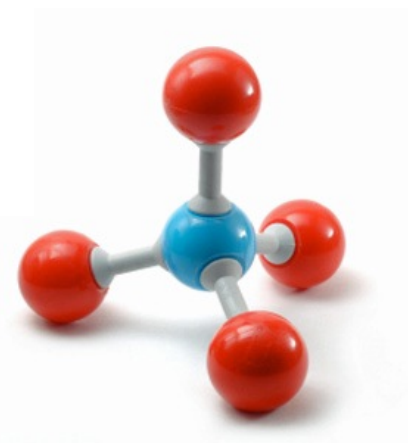
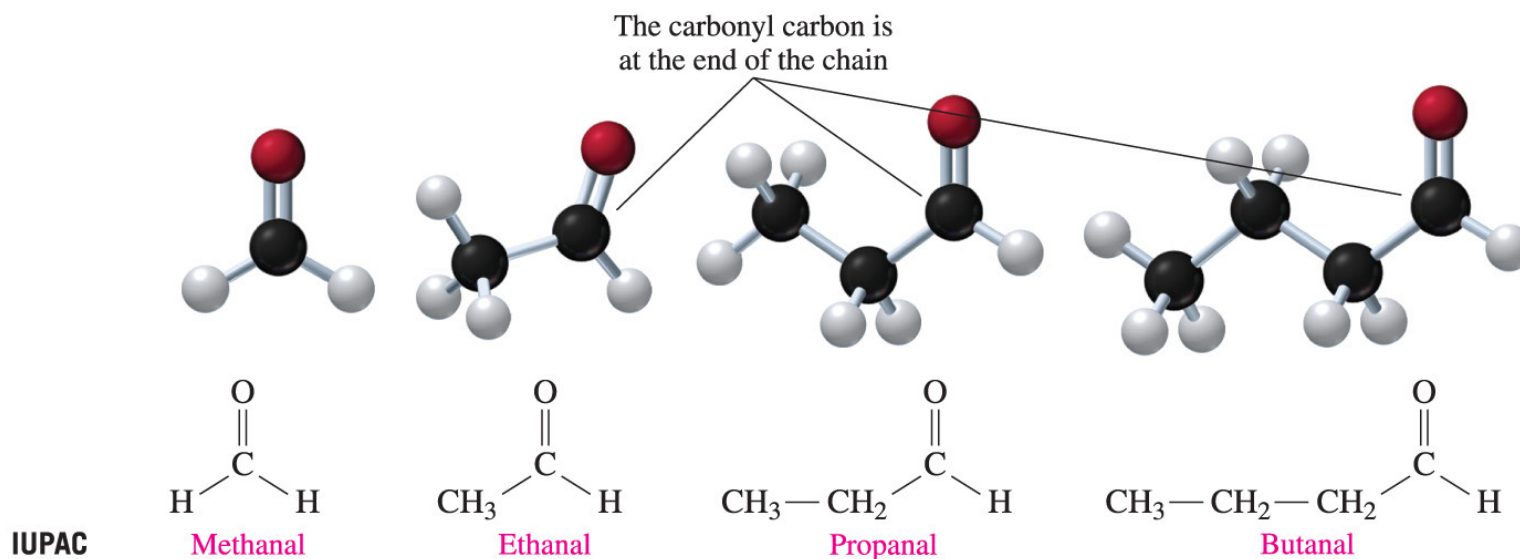


Formaldehyde



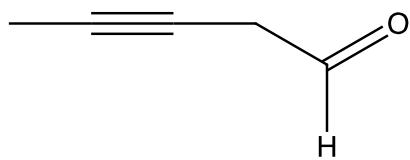
Naming Aldehydes

- ▶ You do not need to know the common names of aldehydes.
- ▶ To name aldehydes using IUPAC use the family suffix **-al**.
- ▶ You do not need to indicate the address of the aldehyde, because it is always in one one end of the chain.
- ▶ The carbonyl in an aldehyde is always carbon #1.

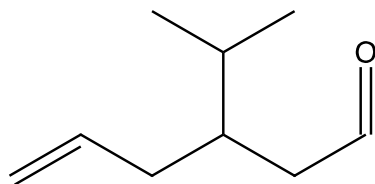


Naming Aldehydes

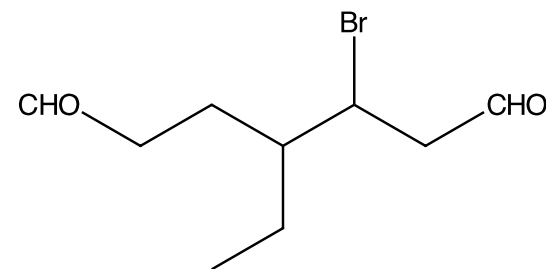
- ▶ You do not need to know the common names of aldehydes.
- ▶ To name aldehydes using IUPAC you use the family suffix **-al**.
- ▶ You do not need to indicate the address of the aldehyde, because it is always terminal.
- ▶ In an aldehyde carbon #1 is always a carbonyl.



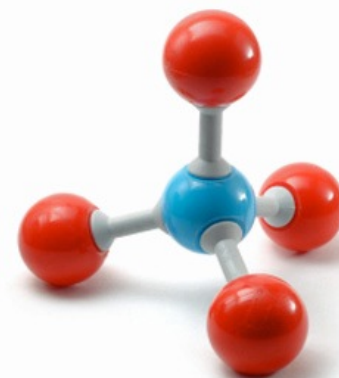
3-Pentynal



3-Isopropyl-5-hexenal

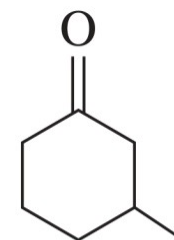


3-Bromo-4-ethylheptanal

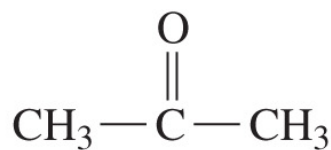


Naming Ketones

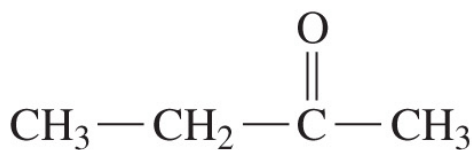
- ▶ Common names for ketones are made by listing the two chains attached to the carbonyl in alphabetical order (like you do for the common name of ethers).
- ▶ To name ketones using IUPAC use the family suffix **-one**.
 - ▶ Giving the ketone(s) the smallest address numbers is the first priority.
- ▶ Ketones can have a cyclic backbone.



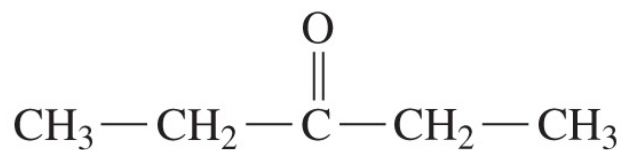
3-Methylcyclohexanone



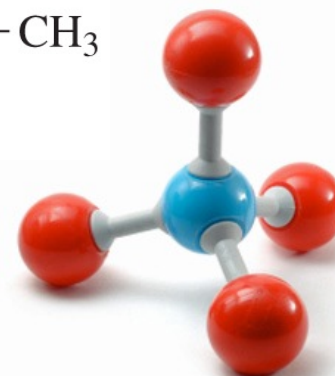
Propanone
(dimethyl ketone; acetone)



Butanone
(ethyl methyl ketone)

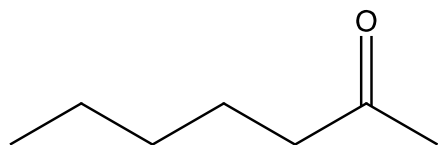


3-Pentanone
(diethyl ketone)

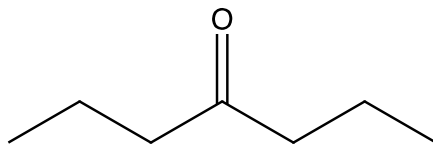


Common Names for Ketones

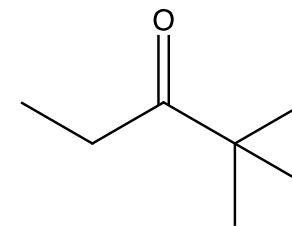
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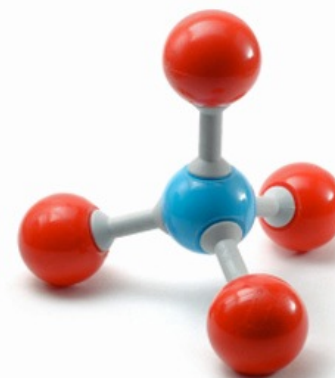
Methyl pentyl ketone



Dipropyl Ketone

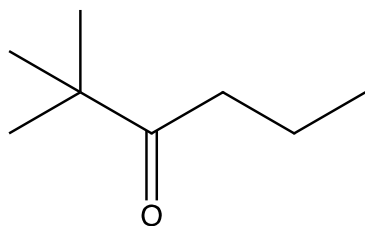


tert-Butyl Ethyl Ketone

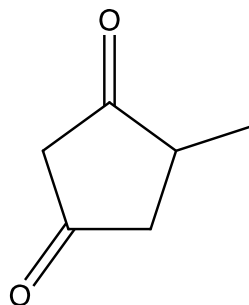


IUPAC Naming Ketones

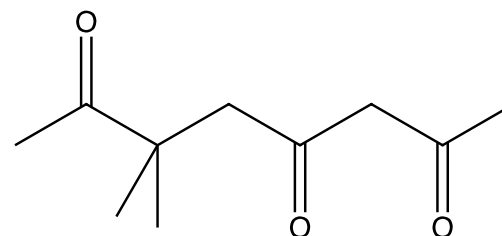
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- ▶ To name ketones using IUPAC use the family suffix **-one**.
 - ▶ Giving the ketone(s) the smallest address numbers is the first priority.
- ▶ Ketones can have a cycle backbone.



tert-butyl propyl ketone
or
2,2-Dimethyl-3-hexanone



4-Methyl-1,3-cyclopentanedione



6,6-Dimethyl-2,4,7-octanetrione



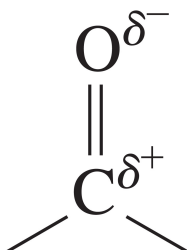
Carbonyls & Red-Ox Reactions

▶ The carbonyl group

▶ Structure

▶ sp^2 trigonal planar

▶ Partial charge

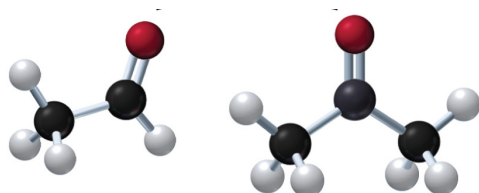


▶ Substances with carbonyl groups

▶ Aldehydes

▶ Ketones

▶ Carboxylic Acids



▶ Reactions of Alcohols

▶ Combustion reactions

▶ Dehydration reactions

▶ structural & stereoisomers

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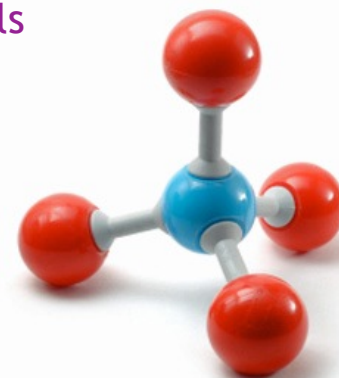
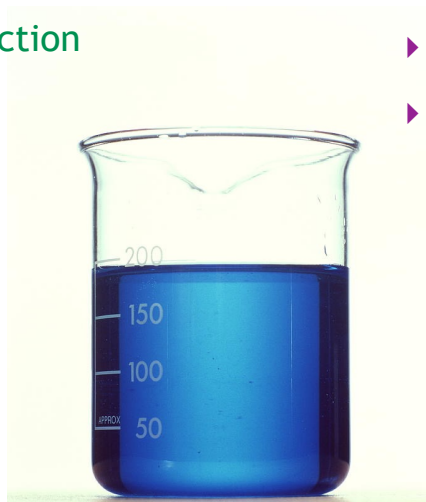


Oxidation-Reduction

▶ For organics, focus on carbon

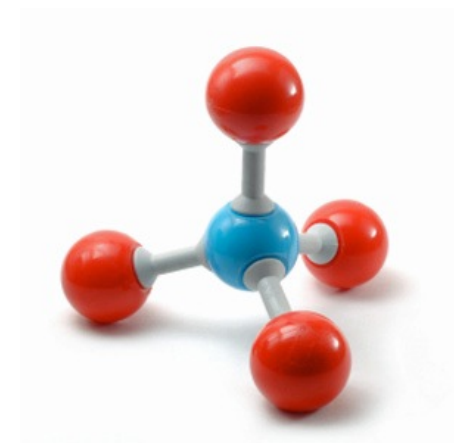
▶ Adding O-C bonds is oxidation

▶ Adding H-C bonds is reduction



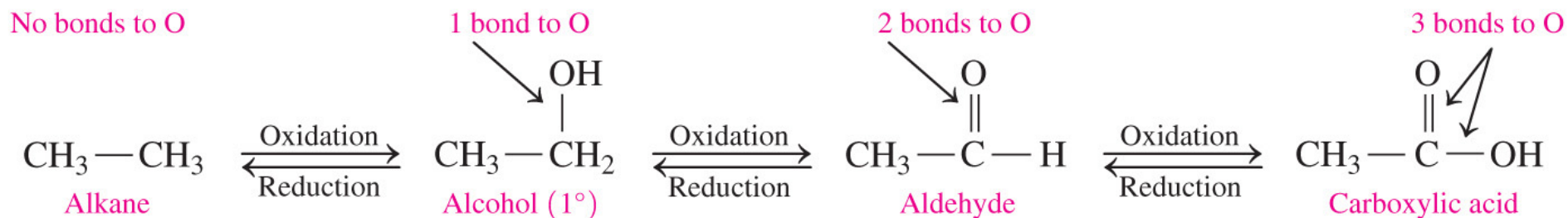
Oxidation-Reduction Reactions

- ▶ **Oxidation** is the process of **removing electrons**.
- ▶ **Reduction** is the process of **adding electrons**.
- ▶ For organic molecules, we will focus on the oxidation state of carbon.
- ▶ It can be complicated to calculate what happened to the carbon atoms in an organic reaction, but there is a short cut.
 - ▶ **Adding O-C bonds** or **losing H atoms** **oxidizes** the organic molecule.
 - ▶ **Adding H-C bonds** or **losing O atoms** **reduces** the organic molecule.

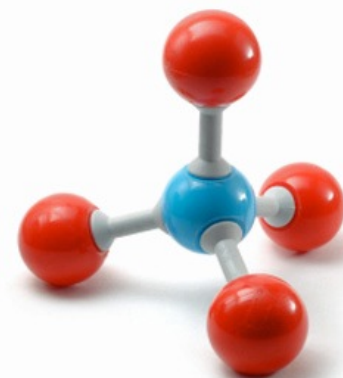


Oxidation-Reduction Reactions

- ▶ Oxidation is the process of removing electrons.
- ▶ Reduction is the process of adding electrons.
- ▶ For organic molecules, we focus on the oxidation state of carbon.
- ▶ It can be complicated to calculate what happened to the carbon atoms in an organic reaction, but there is a short cut.
 - ▶ Adding O-C bonds or losing H atoms oxidizes the organic molecule.
 - ▶ Adding H-C bonds or losing O atoms reduces the organic molecule.

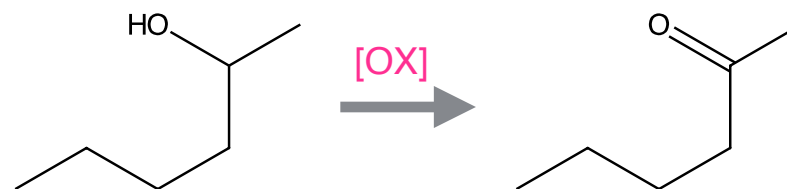
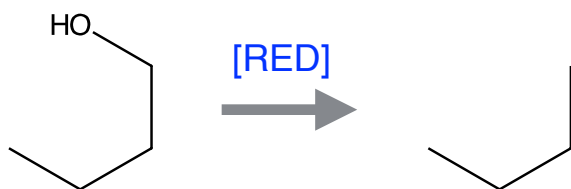


- ▶ Oxidizing reagents can be used to convert a primary alcohol into an aldehyde.
- ▶ Reducing agents can convert an aldehyde into an alcohol into an alkane...

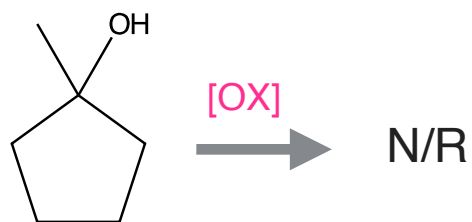


Oxidation-Reduction Reactions

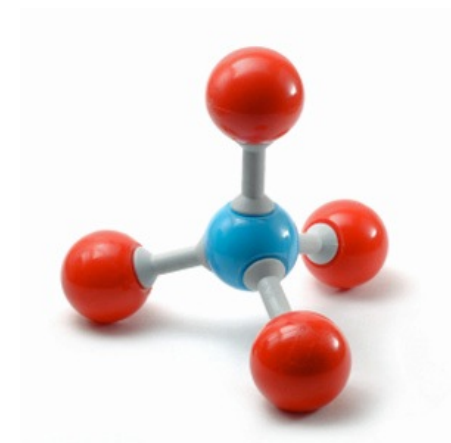
- ▶ Are these reactions oxidations or reductions?



- ▶ What would happen if the alcohol was tertiary?



Breaking Carbon bonds is more than oxidation/reduction, tertiary alcohols are very stable.



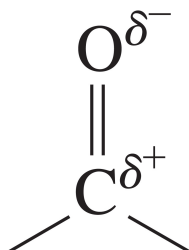
Carbonyls & Red-Ox Reactions

▶ The carbonyl group

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Reactions of Alcohols

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▶ Dehydration reactions

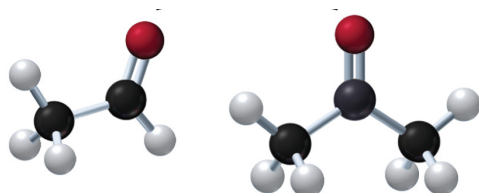
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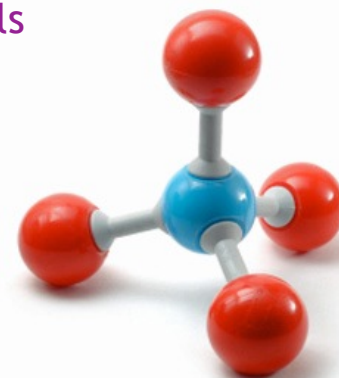
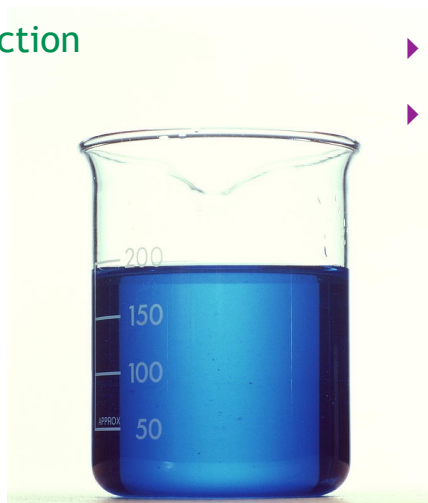
▶ Adding O-C bonds is oxidation

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▶ Reduction of Carbonyls

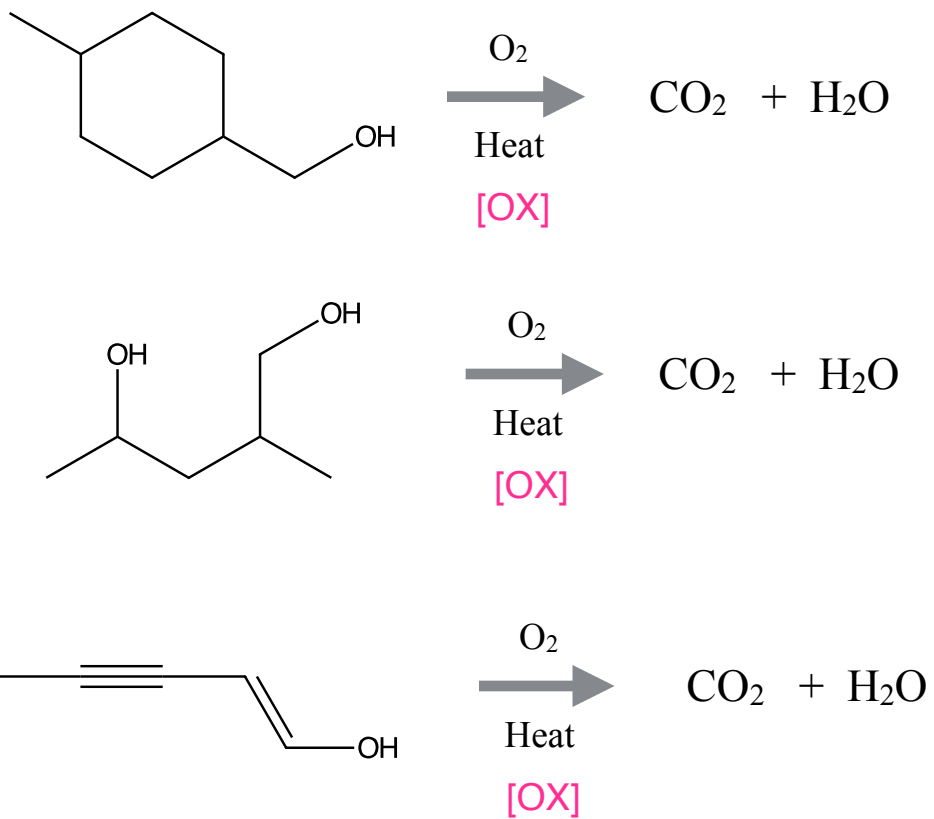
▶ Aldehydes to 1° alcohols

▶ Ketones to 2° alcohols



Combustion Reactions

- ▶ Alcohols burn easily.
- ▶ Combustion is an **oxidation** reaction.

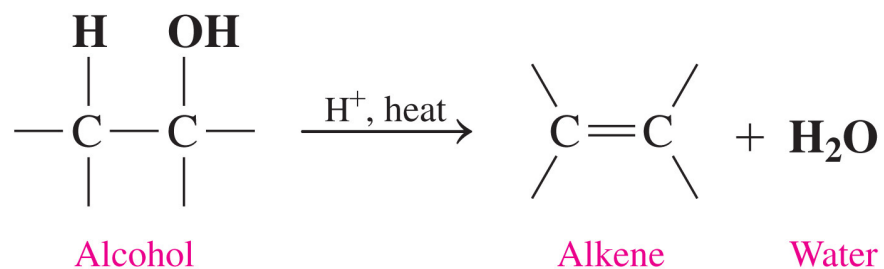


Unsaturated hydrocarbons burn hotter!

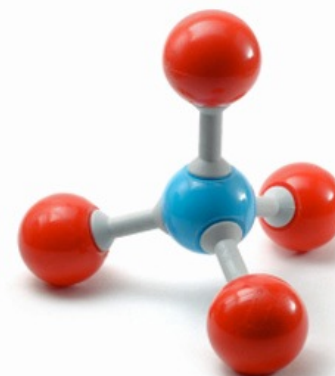


Dehydration Reactions

- ▶ Alcohols heated with an acid catalyst can dehydrate (lose water).
- ▶ This reaction has moderate selectivity in the kinds of alcohols that react.
 - ▶ Tertiary alcohols react more readily, than secondary, react more readily than primary.
 - ▶ Selectivity can be achieved with temperature control.

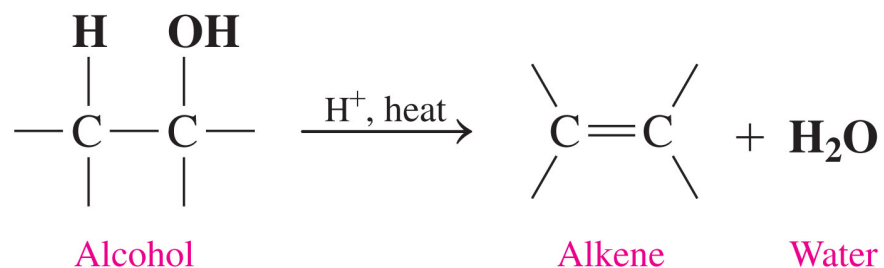


1° alcohols: 170° - 180 °C
2° alcohols: 100° - 140 °C
3° alcohols: 25° - 80 °C

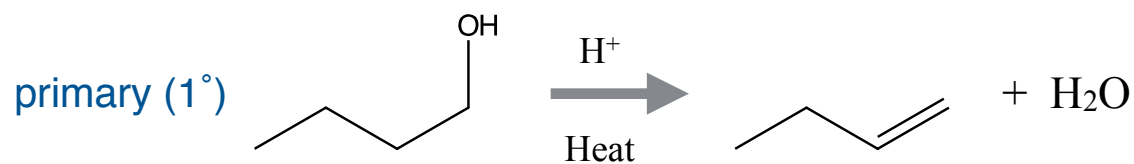
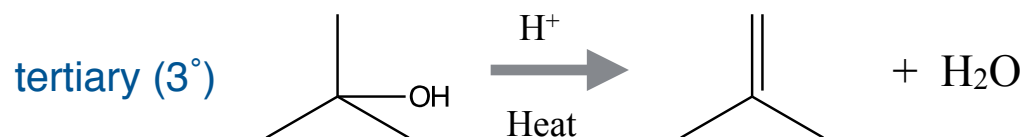
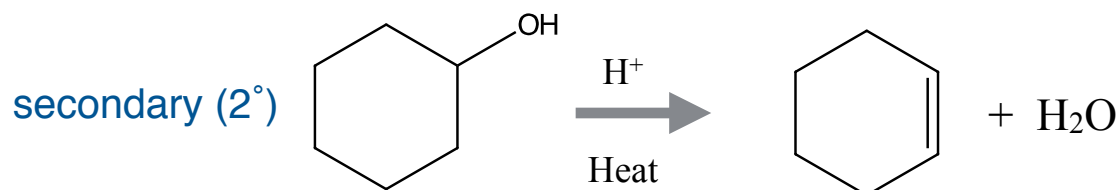


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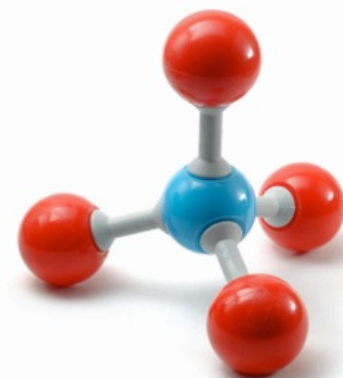
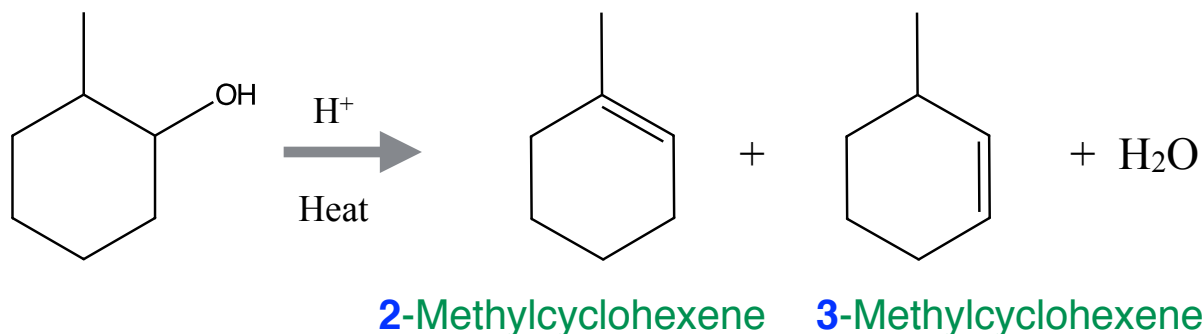
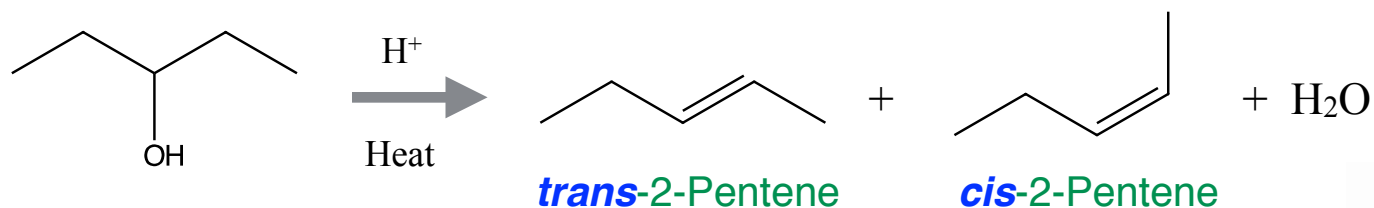
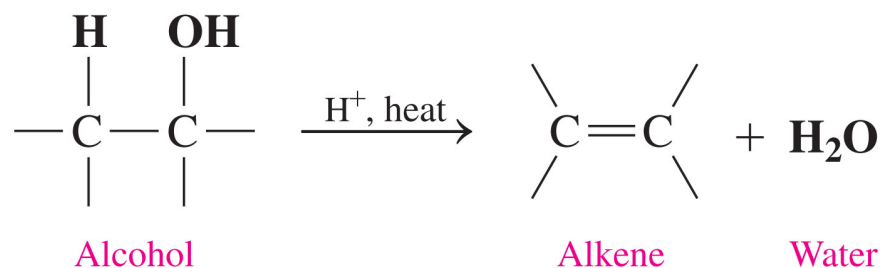


1° alcohols: 170° - 180 °C
 2° alcohols: 100° - 140 °C
 3° alcohols: 25° - 80 °C



Dehydration Reactions

- ▶ Alcohols heated with an acid catalyst can dehydrate (lose water).
- ▶ This reaction has **poor selectivity** in the products it forms.
- ▶ Depending on the structure of the starting material, it may produce:
 - ▶ Stereoisomers
 - ▶ (these are different products)
 - ▶ Structural isomers
 - ▶ (these are different products)



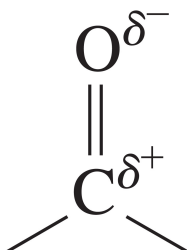
Carbonyls & Red-Ox Reactions

▶ The carbonyl group

▶ Structure

▶ sp^2 trigonal planar

▶ Partial charge

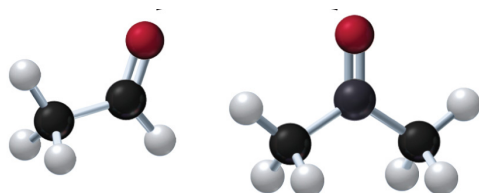


▶ Substances with carbonyl groups

▶ Aldehydes

▶ Ketones

▶ Carboxylic Acids



▶ Oxidation-Reduction

▶ For organics, focus on carbon

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▶ Oxidation to disulfides

▶ Oxidation of Carbonyls

▶ Tests for aldehydes

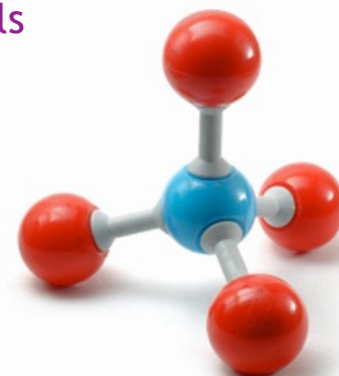
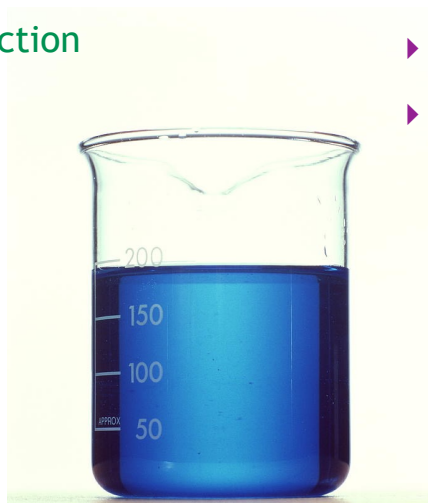
▶ Tollens' Test

▶ Benedict's Test

▶ Reduction of Carbonyls

▶ Aldehydes to 1° alcohols

▶ Ketones to 2° alcohols

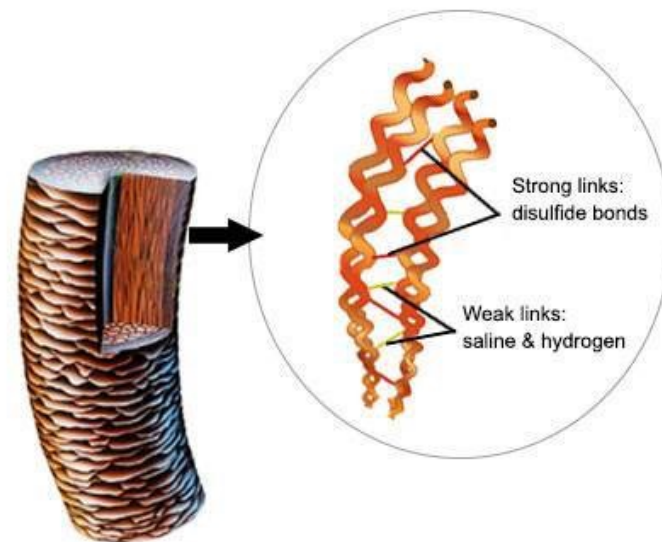
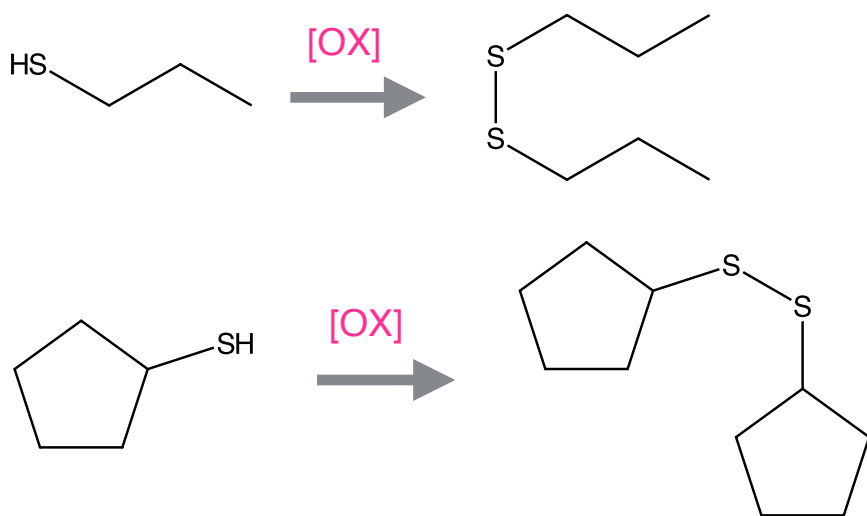


Oxidation of Disulfides

- ▶ Sulfides form disulfides when exposed to oxidation.
- ▶ Reminder:
 - ▶ Adding O-C bonds or losing H atoms oxidizes the organic molecule.
- ▶ These disulfide bonds between and within hairs are what cause it to curl when oxidized (permed).
- ▶ PCC or KMnO_4 can be used.



Hair structure, strong links and weak links



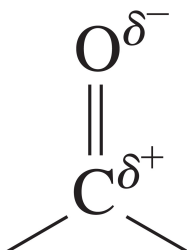
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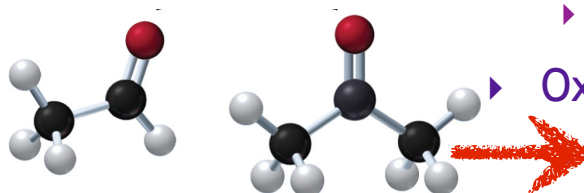


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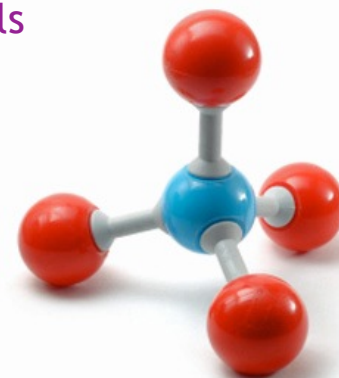
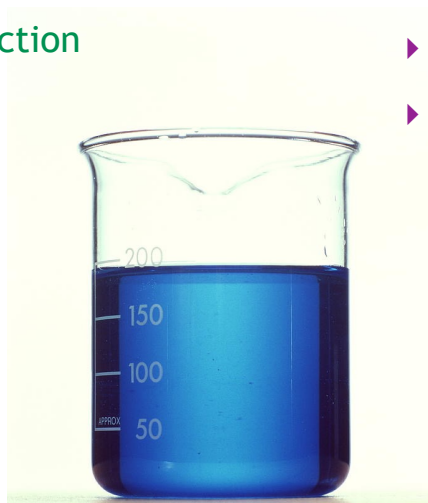
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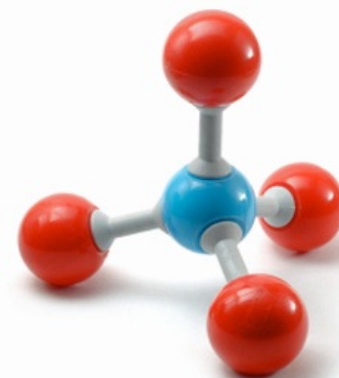
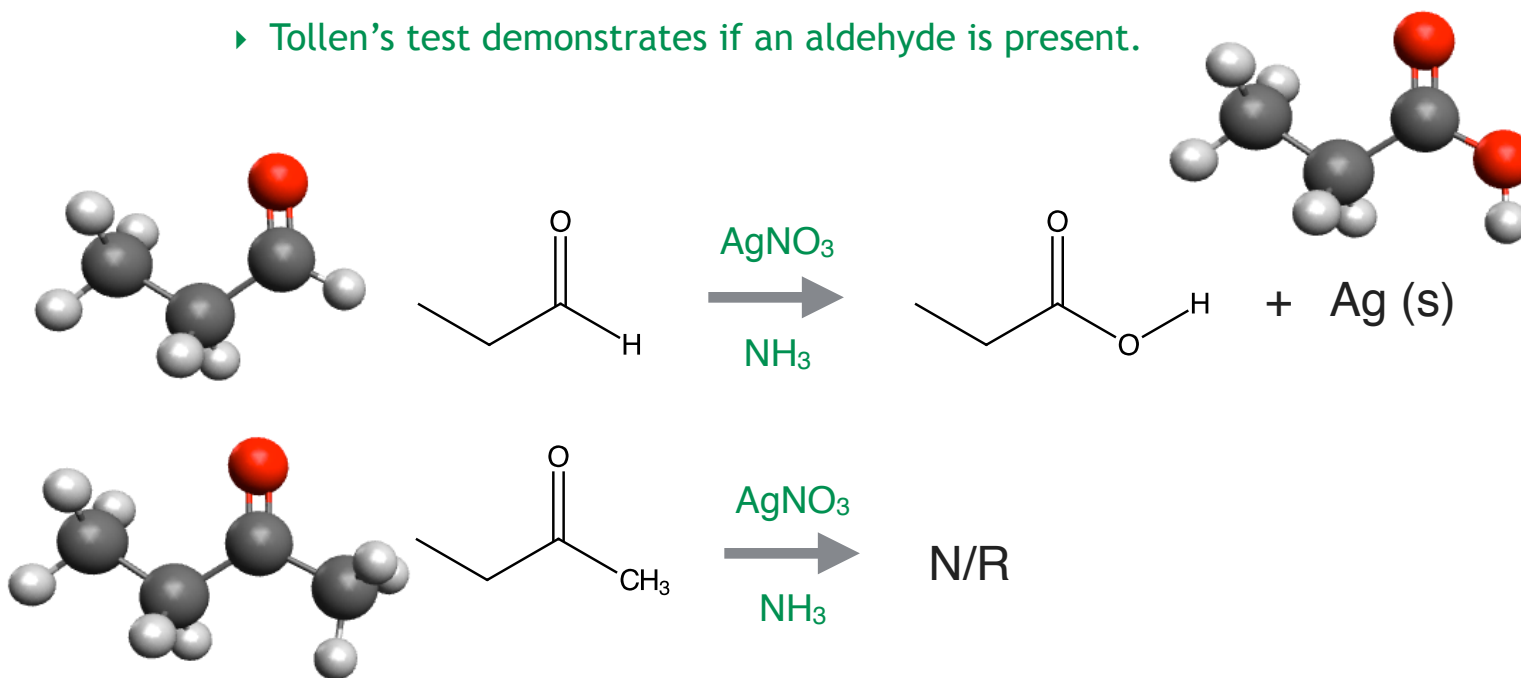
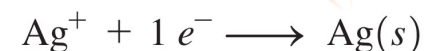
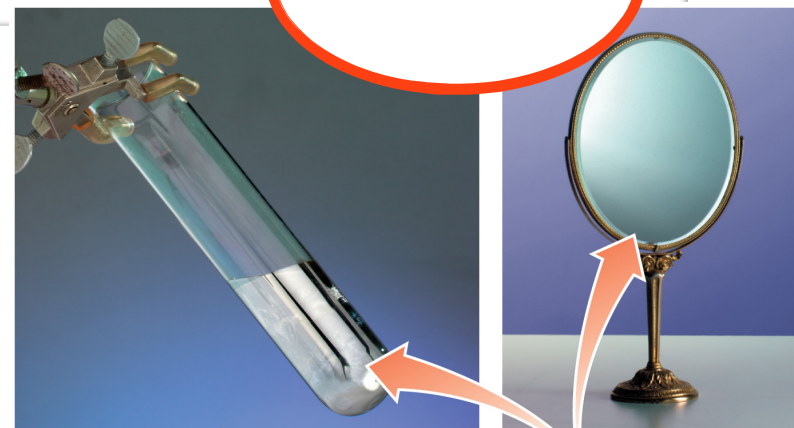
▶ Ketones to 2° alcohols



Testing for Aldehydes

Tollen's Test

- ▶ When something gets oxidized, something else gets reduced.
- ▶ One way to test for the presence of aldehydes, is to try and reduce them with copper or silver ions.
 - ▶ Tollen's solution (AgNO_3 & NH_3) oxidizes aldehydes to carboxylic acids but has no effect on ketones.
 - ▶ Tollen's solution will produce silver metal when exposed to an aldehyde, but nothing will happen in the presence of a ketone.
 - ▶ Tollen's test demonstrates if an aldehyde is present.



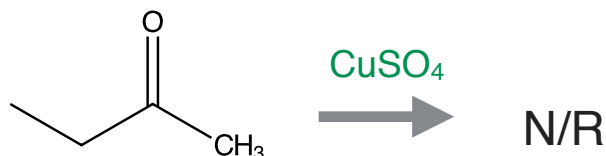
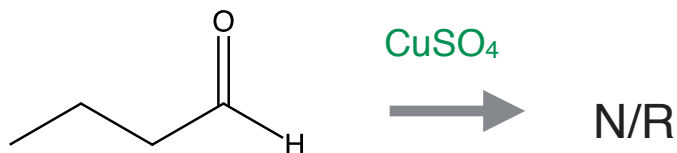
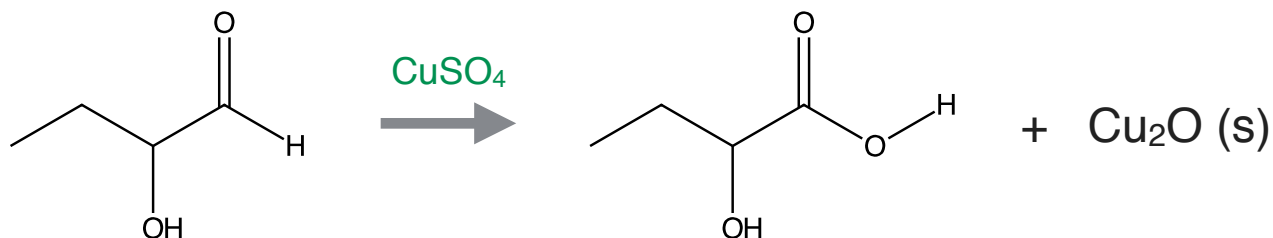
Testing for Aldehydes

- ▶ When something gets oxidized, something else gets reduced.
- ▶ One way to test for the presence of aldehydes, is to try and reduce them with copper or silver ions.
 - ▶ Benedict's test is even more specific.
 - ▶ CuSO_4 (Cu^{2+}) will reduce an aldehyde only if there is an adjacent hydroxyl group.
 - ▶ Benedict's Test demonstrates if an aldehyde with an adjacent hydroxyl group is present.

Benedict's Test

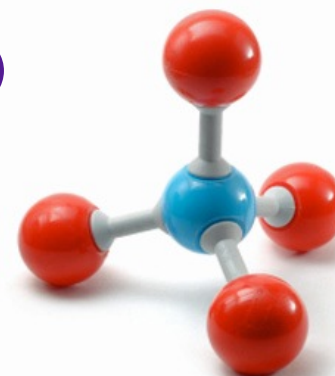


Cu^{2+} $\text{Cu}_2\text{O}(s)$



Note: If you add heat, you can convert an aldehyde even without the alcohol.

But you'll never get reaction with a ketone.



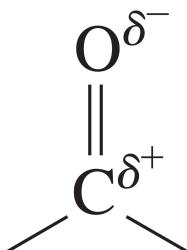
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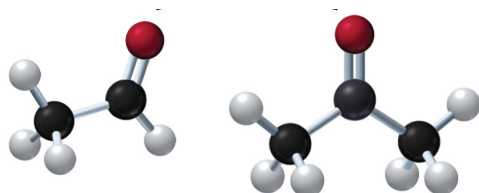


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▶ Tollens' Test

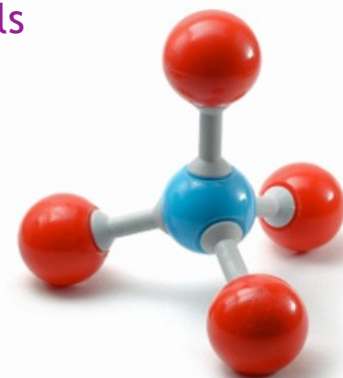
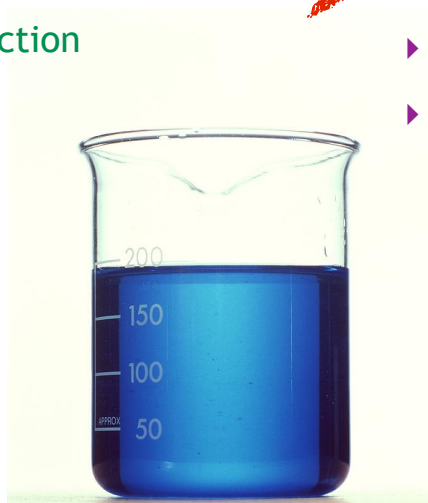
▶ Benedict's Test



▶ Reduction of Carbonyls

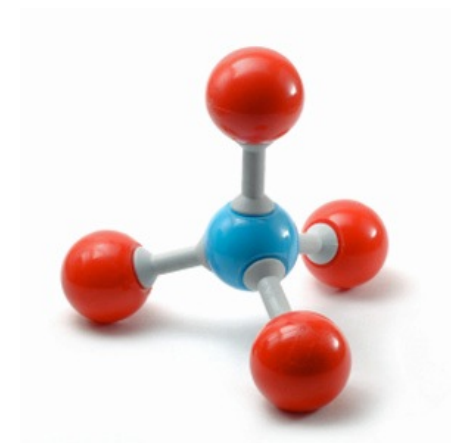
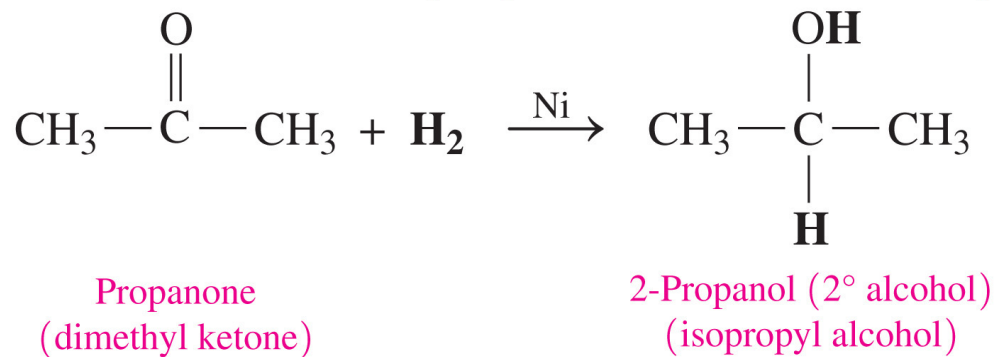
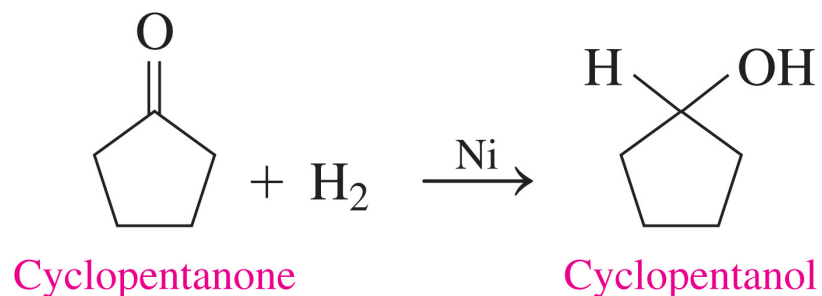
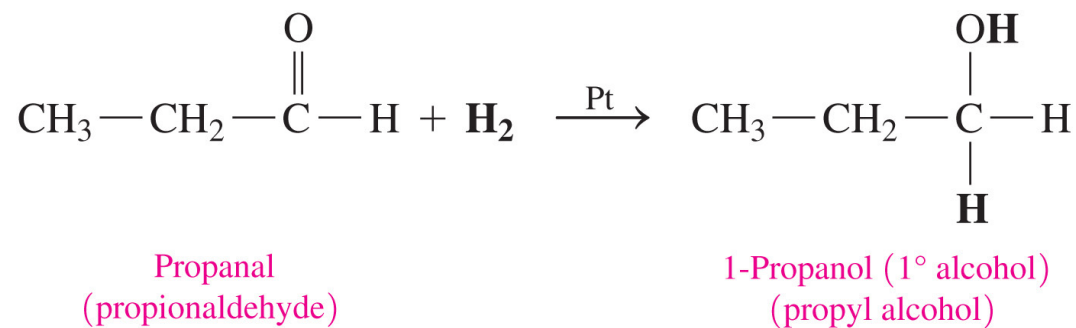
▶ Aldehydes to 1° alcohols

▶ Ketones to 2° alcohols



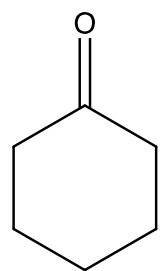
Reducing Carbonyls

- Carbonyls can be **reduced** to alcohols with H_2 and catalyst (Ni, Pd, or Pt).

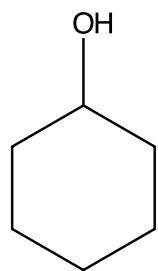
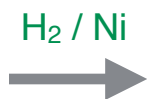


Reducing Carbonyls

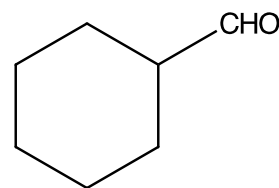
- ▶ Carbonyls can be **reduced** to alcohols with H_2 and catalyst (Ni, Pd, or Pt).



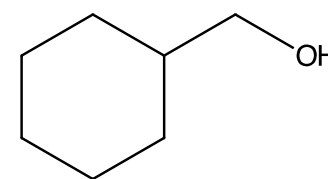
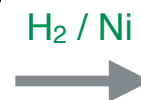
(ketone)



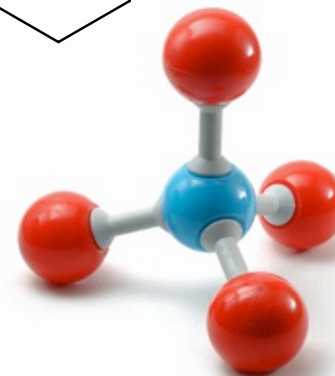
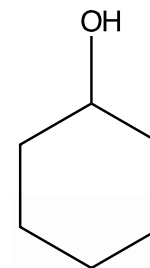
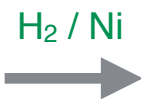
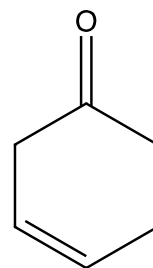
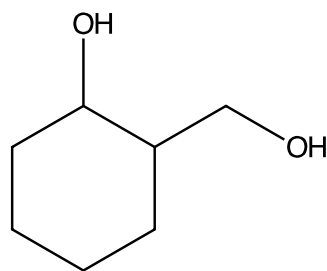
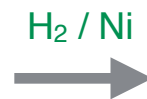
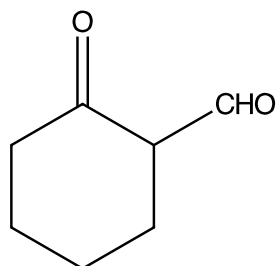
(2° alcohol)



(aldehyde)

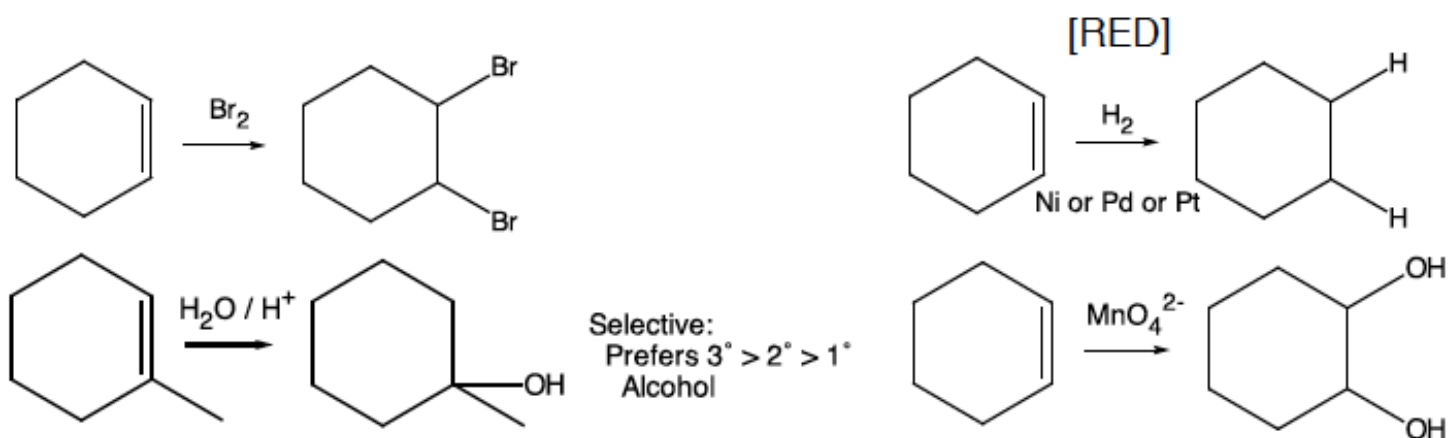


(1° alcohol)

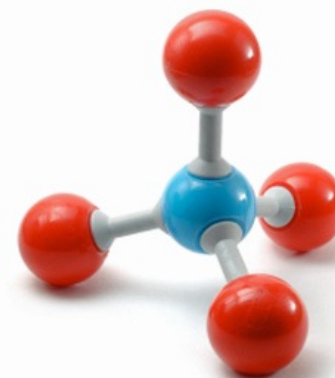


Summary of Reactions

Alkenes

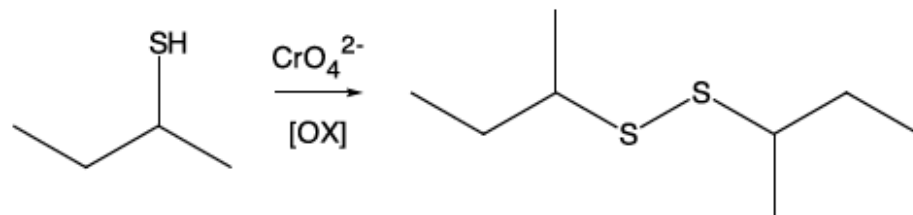


(reference handout on the website summarizes all reactions Ch11-12)

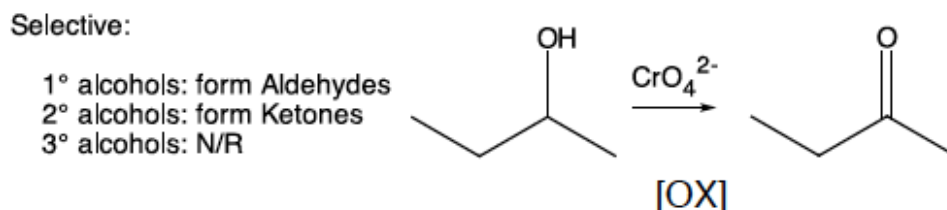
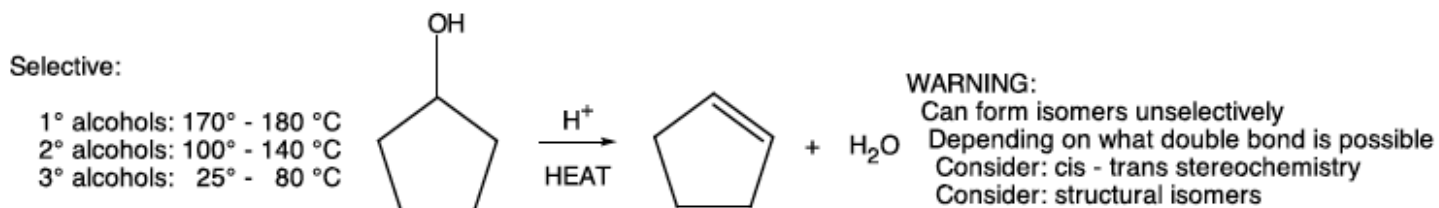


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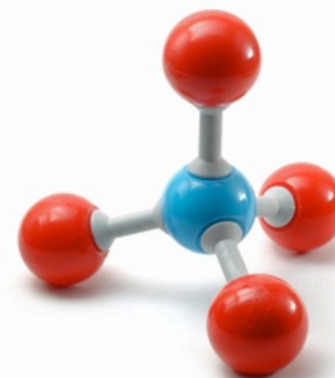
Thiols



Alcohols

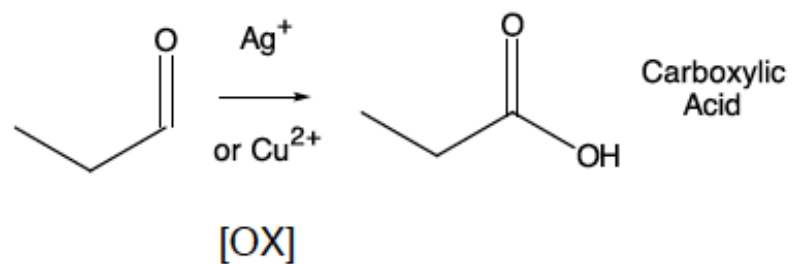
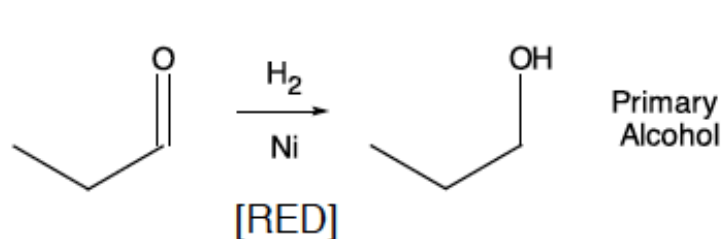


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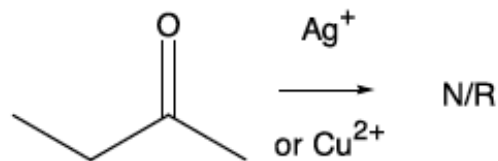
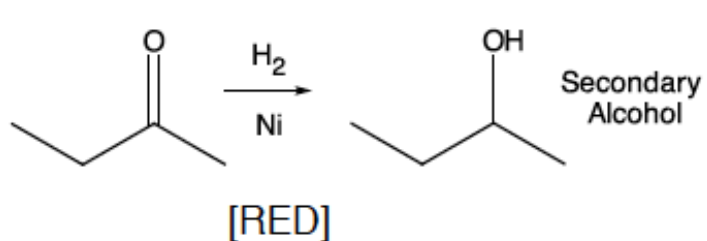


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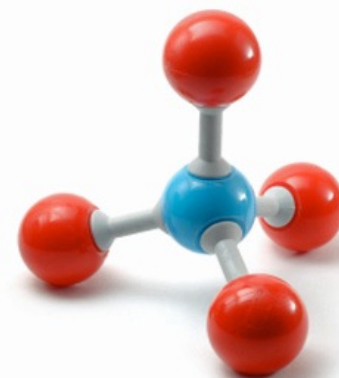
Aldehydes



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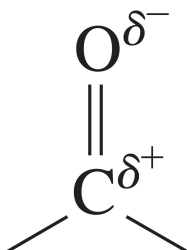
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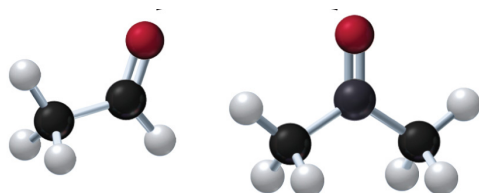


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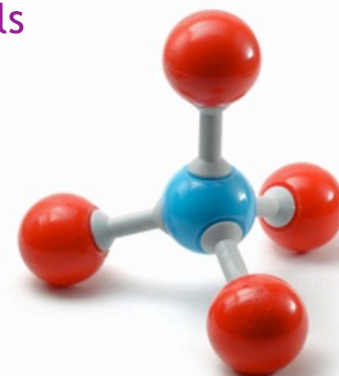
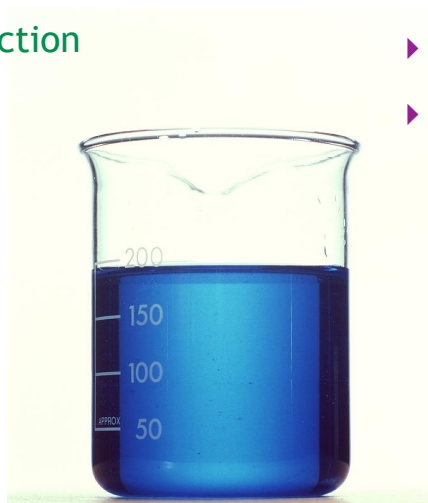
▶ Tollens' Test

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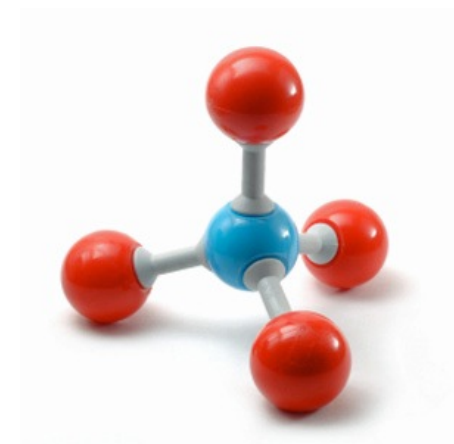
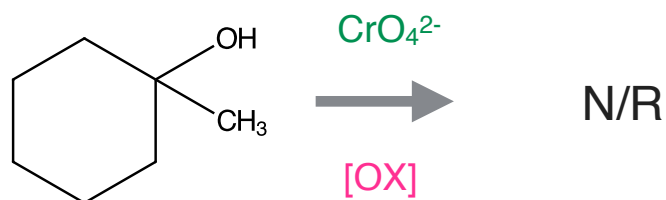
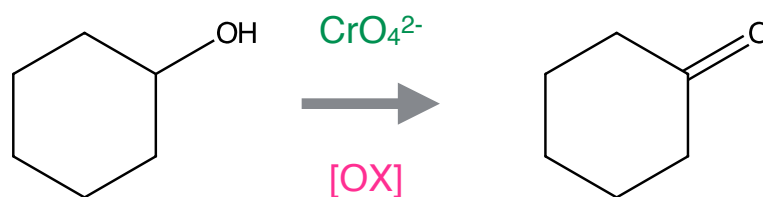
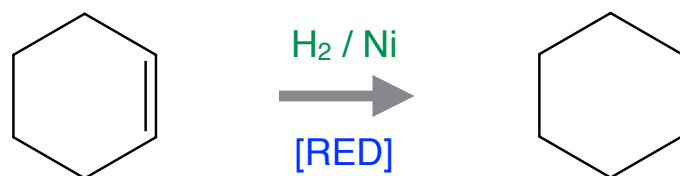
▶ Aldehydes to 1° alcohols

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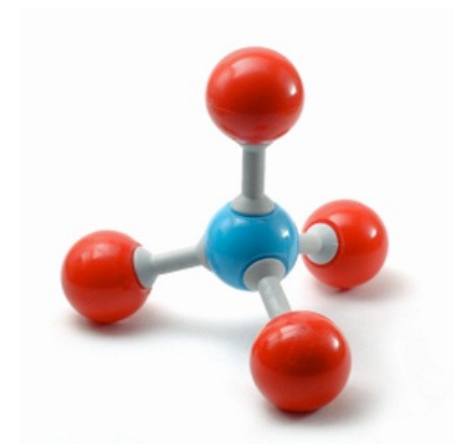
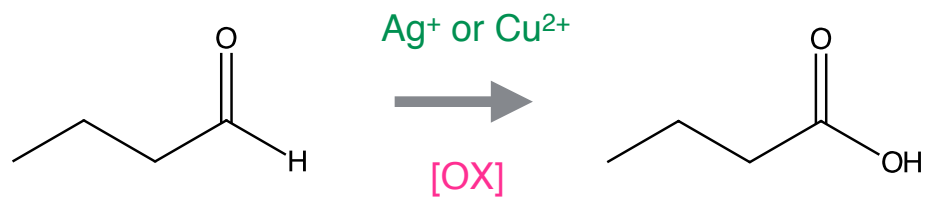
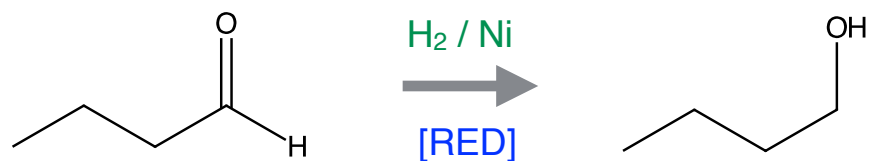
Predict the Product

- Each reaction below is a reduction or oxidation, predict the product.



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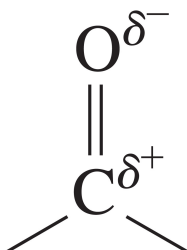
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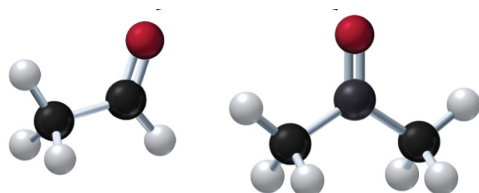


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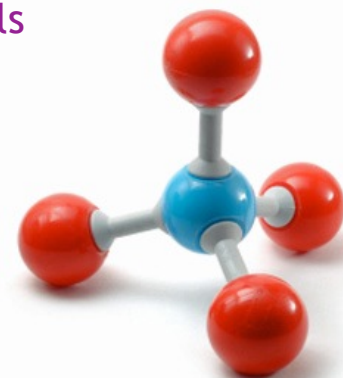
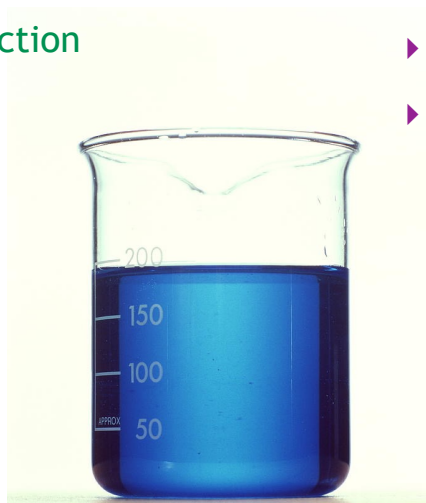
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Questions?

