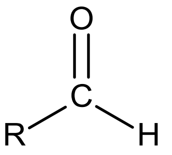
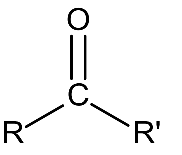


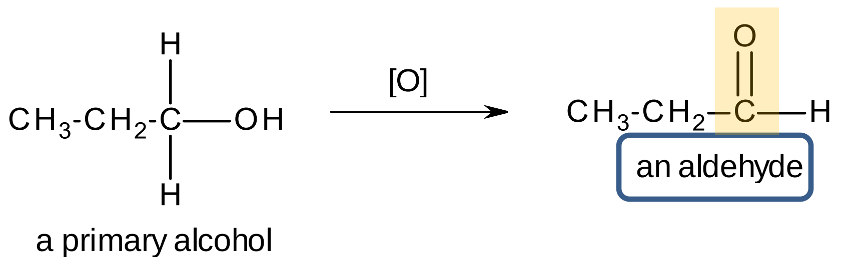


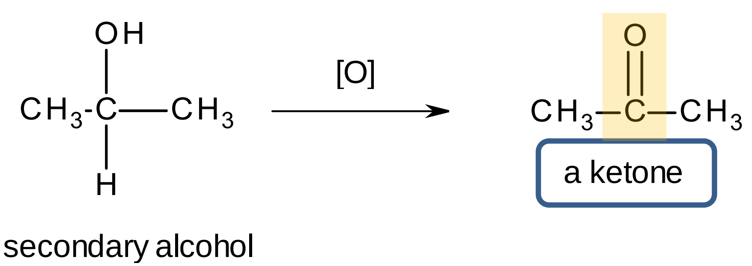
Aldehydes and ketones

Chapter 15

Aldehydes and ketones

- In Chapter 14, we saw a reaction that converts an alcohol (1° or 2°) into a new kind of molecule that possesses a C=O double bond

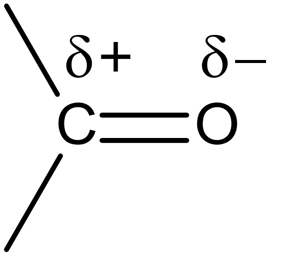




mild oxidizing agent = [O]

The carbonyl group

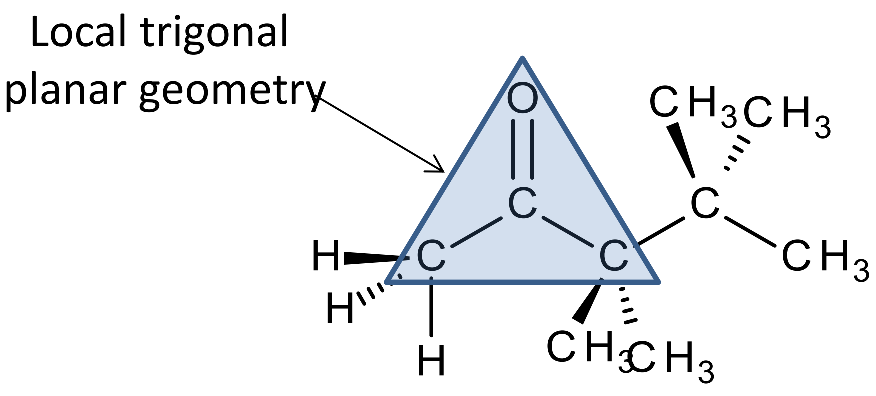
- Aldehydes and ketones are among the first examples of compounds that possess a C-O double bond that we've seen (oxidation of alcohols section, Ch-14).
- This group is called a carbonyl group, and it has very different chemical properties than a C=C double bond in alkenes:



- Because oxygen is more electronegative than carbon, the bond is **polar**.
- Bond angles are about 120^{o} around the carbon atom (see VSEPR theory).

The carbonyl group

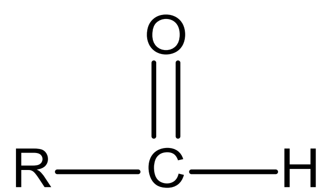
- The local geometry around the carbonyl group is trigonal planar. The rest of the molecule doesn't have to be planar:

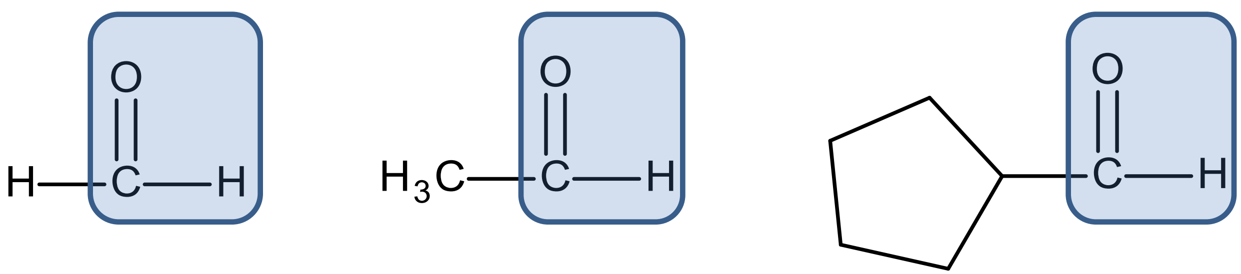


Compounds containing the carbonyl group

- **The following classes of organic compounds involve the carbonyl group**:
  - **Aldehydes** have a H-atom or a carbon substituent (alkyl, cycloalkyl, aromatic) bound to a CHO group (carbonyl group bound to a H-atom):

General formula for aldehyde:



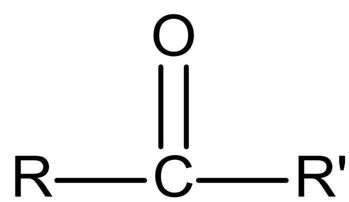


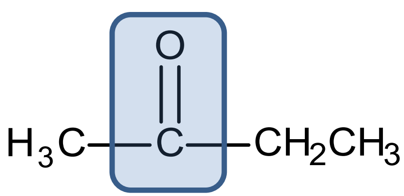
Compounds containing the carbonyl group

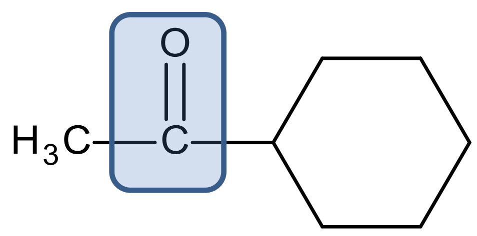
- **Ketones** have two carbon substituents (alkyl, cycloalkyl, aromatic and *not necessarily the same*)

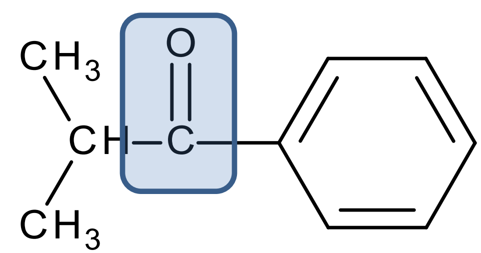
This is why one of them is called “R” and the other “R’”

General formula for ketones:





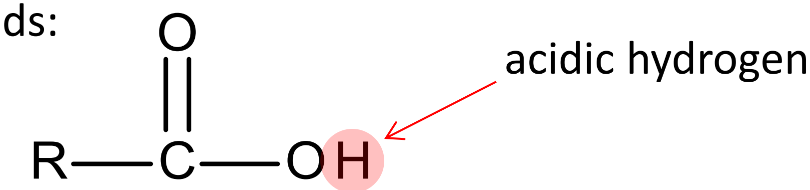


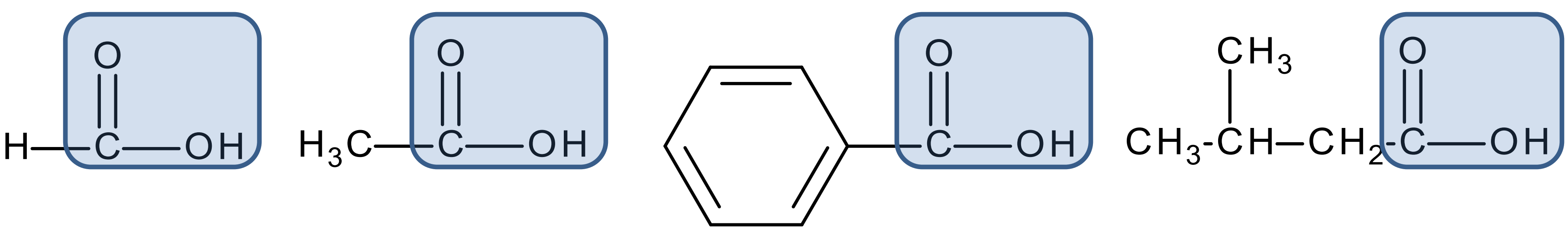


Compounds containing the carbonyl group

- **Carboxylic acids** have an OH (hydroxyl) group bound to the carbonyl carbon, in addition to either a H-atom or a carbon group (alkyl, cycloalkyl, aromatic):

General formula for carboxylic acids:

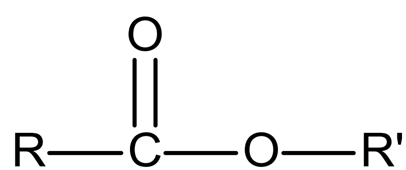


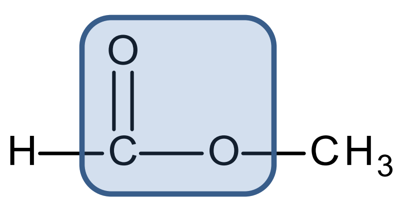


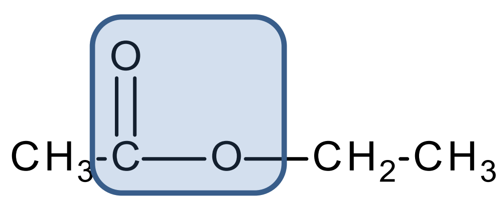
Compounds containing the carbonyl group

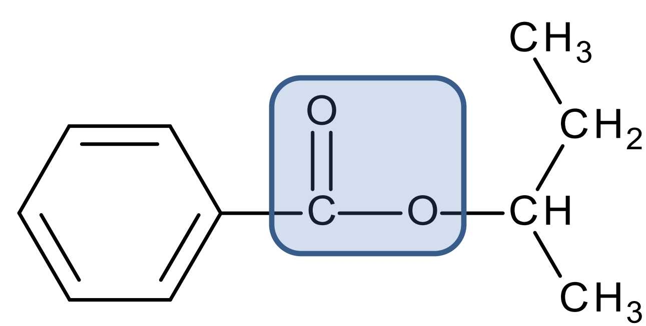
- **Esters** have a carbonyl group singly bound to an oxygen, which in turn is bound to a carbon group (alkyl, cycloalkyl, or aromatic). The other bond to the carbonyl is either to a H-atom or another carbon group:

General formula for an ester:





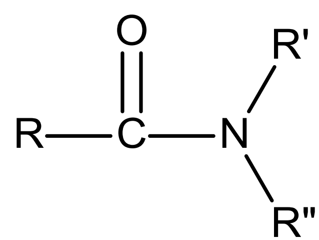


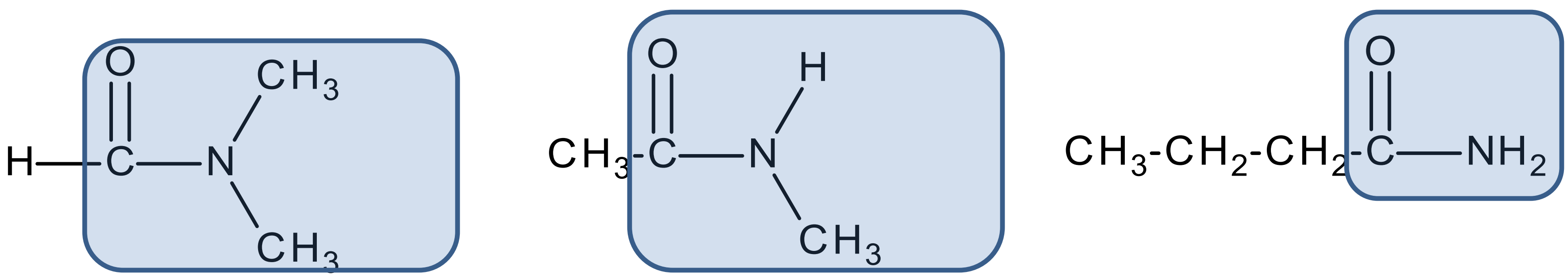


Compounds containing the carbonyl group

- **Amides** are the first nitrogen-containing organic compounds we've seen. In these compounds, the carbonyl group is bound to a nitrogen (an amino group), in addition to either a H-atom or a carbon group (alkyl, cycloalkyl, aromatic). The R' and R" groups of the amino group may either be H or carbon groups:

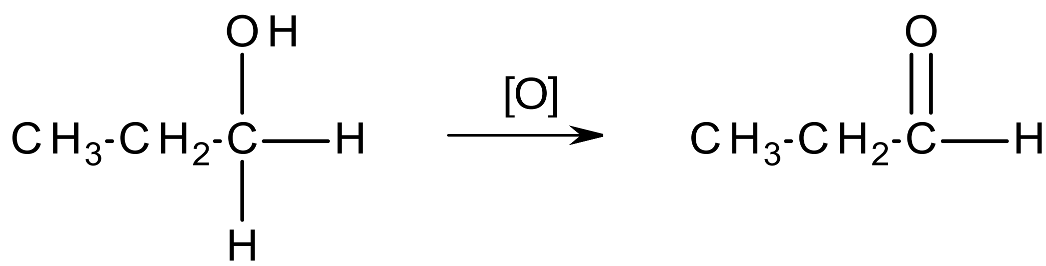
General formula for an amide:



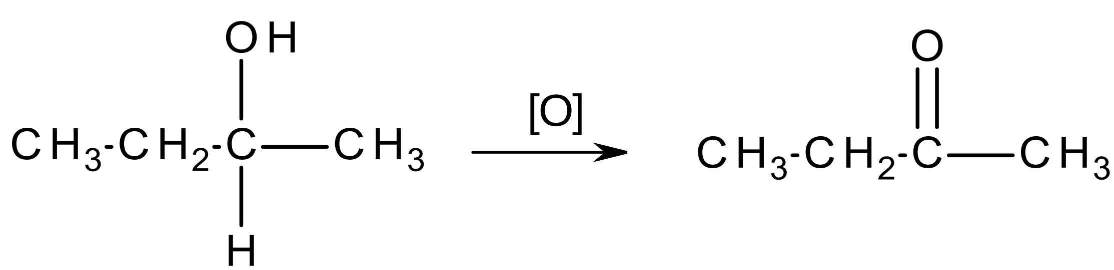


Aldehyde and ketone functional group

- As we saw, alcohols can be used to create aldehydes and ketones. Oxidation of a primary alcohol yields an aldehyde:

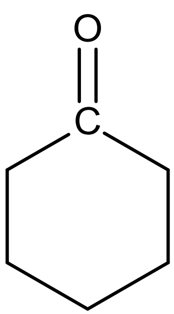


- And oxidation of a secondary alcohol yields a ketone:

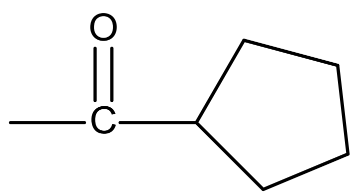


Aldehyde and ketone functional group

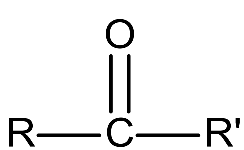
- Aldehyde groups may be bound to ring structures, but can't, themselves, be part of a ring structure. Ketones can form part of a ring structure.
- Also, note that cyclic ketones aren't heterocyclic compounds (have non-carbon atoms within the ring structure)

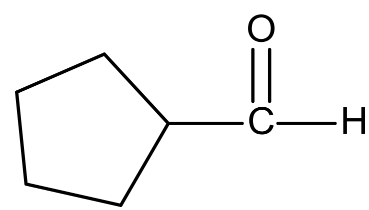


a cyclic ketone

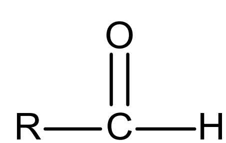


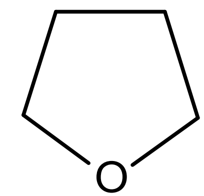
a ketone incorporating a cyclic compound





an aldehyde incorporating a cyclic compound

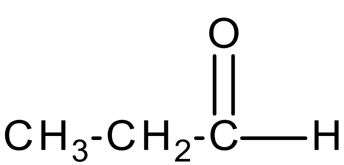




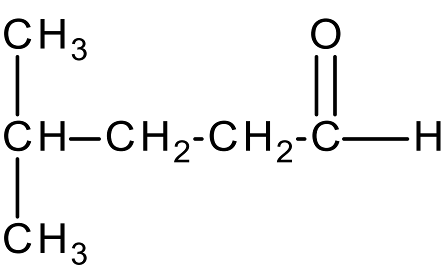
tetrahydrofuran,
a cyclic ether
(example of a heterocyclic compound)

Nomenclature for aldehydes

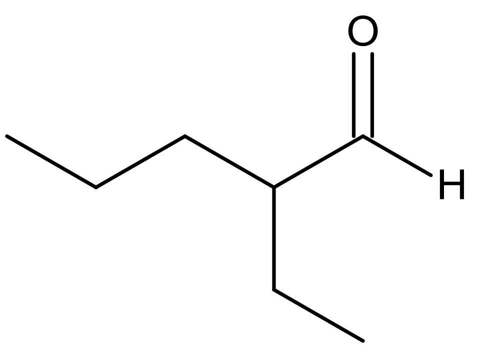
- IUPAC rules:
  - Select as the parent chain the longest continuous chain that includes the carbon of the carbonyl group
  - Name the parent chain by changing the corresponding alkane name (ending with “e”) to an ending with “al”
  - Number the parent chain assuming the carbonyl carbon is C-1
  - Identify substituents on the parent chain as before, at the beginning of the compound’s name.



Propanal



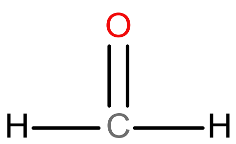
4-Methylpentanal

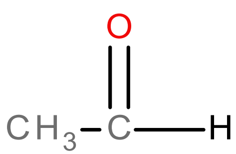


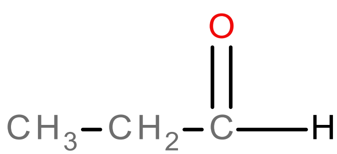
2-Ethylpentanal

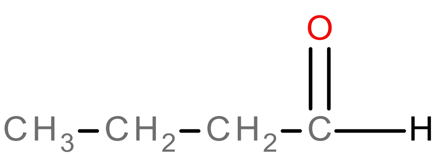
Nomenclature for aldehydes

- For aldehydes having short carbon chains, the following common names are usually encountered:





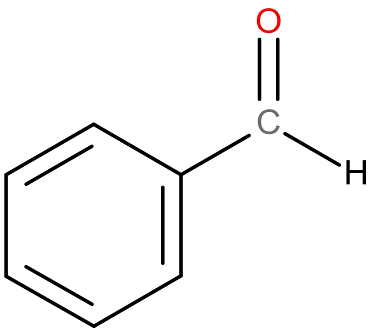




IUPAC

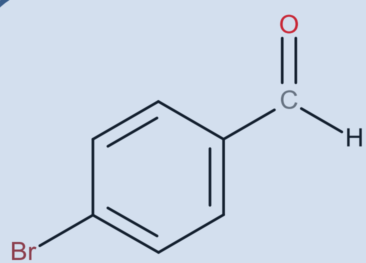
Formaldehyde (Methanal)	Acetaldehyde (Ethanal)	Propionaldehyde (Propanal)	Butyraldehyde (Butanal)

- The following aromatic aldehyde is called benzaldehyde:



Benzaldehyde

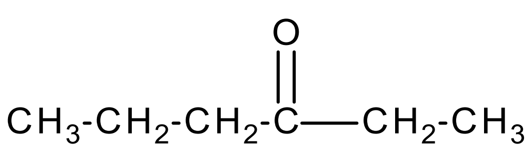
An example of a benzaldehyde derivative:



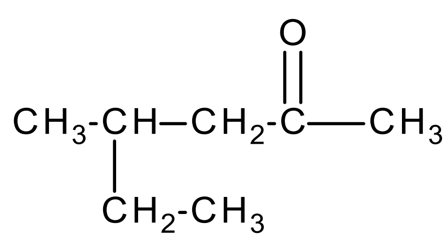
4-Bromobenzaldehyde

Nomenclature for ketones

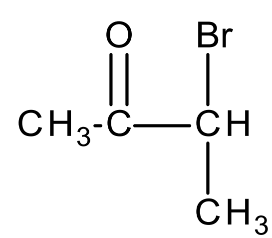
- IUPAC:
  - Select as the parent chain the longest continuous chain that involves the carbon of the carbonyl group
  - Name the parent chain by removing the “e” from the corresponding alkane name and adding “one”
  - Number the chain to give the carbonyl group the lowest numbering. The number goes before the parent chain name
  - Determine the number and location of substituents and number them accordingly



3-Hexanone



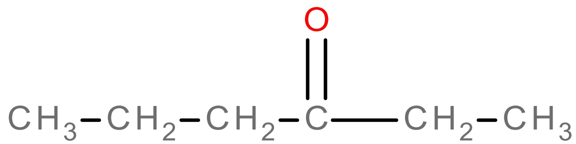
4-Methyl-2-hexanone



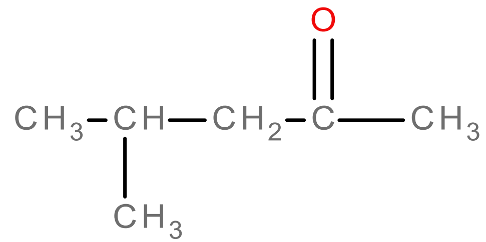
3-Bromo-2-butanone

Nomenclature for ketones

- The *common* (non-IUPAC) system of naming ketones is similar to what we saw for ethers:



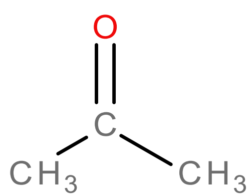
Ethyl propyl ketone



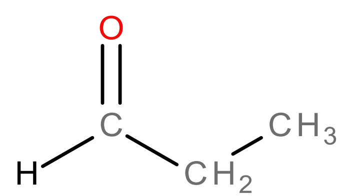
Isobutyl methyl ketone

Isomerism for aldehydes and ketones

- Aldehydes and ketones that have a given number of carbon atoms are another example of *functional group isomers*. (same applied to alcohols/ethers with the same number of C-atoms)



Propanone

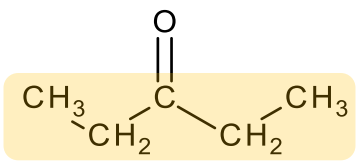


Propanal

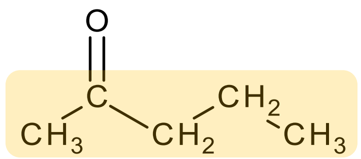
a ketone | C_3H_6O | an aldehyde

Isomerism for aldehydes and ketones

- *Positional isomers* are possible for ketones (but not aldehydes)



3-Pentanone

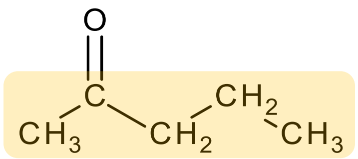


2-Pentanone

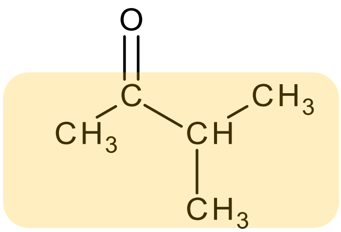
$C_5H_{10}O$

Positional isomers: functional group is in different positions on same carbon skeleton

- And *skeletal isomers* are possible for both



2-Pentanone



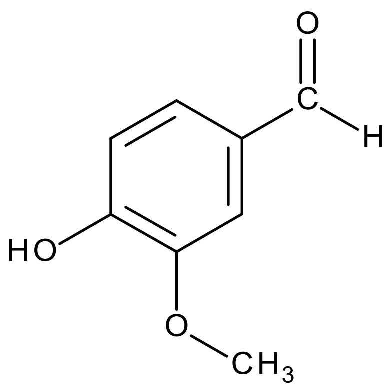
3-Methyl-2-butanone

$C_5H_{10}O$

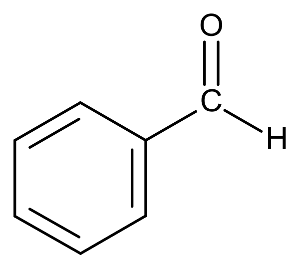
Skeletal isomers: have different carbon skeletons

Common aldehydes and ketones

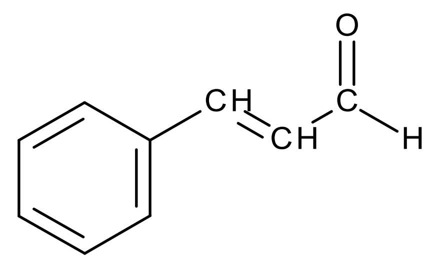
- Aldehydes are often recognizable by their "sweet" smells:



Vanillin
(vanilla flavoring)



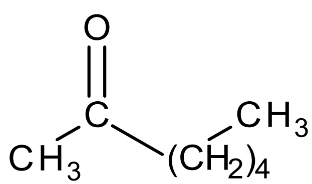
Benzaldehyde
(almond flavoring)



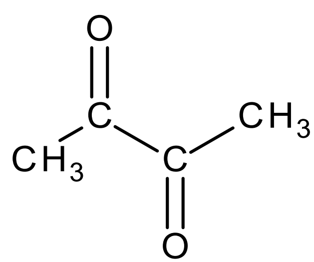
Cinnamaldehyde
(cinnamon flavoring)

Common aldehydes and ketones

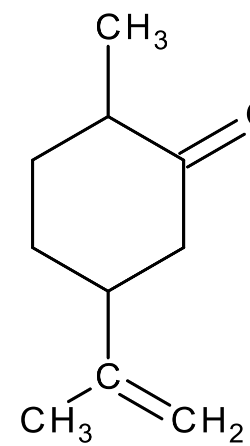
- Some ketones (e.g. acetone) have a “sweet” smell also). Other examples are:



2-Heptanone
(clove flavoring)



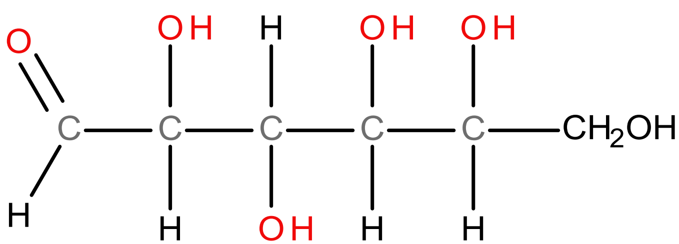
Butanedione
(butter flavoring)



Carvone
(spearmint flavoring)

Naturally occurring aldehydes and ketones

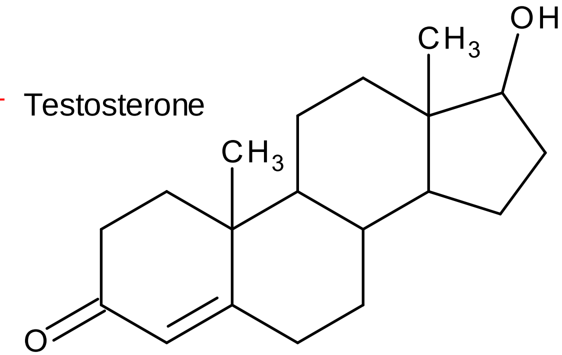
- A wide variety of biologically relevant molecules possess aldehyde and/or ketone functional groups:



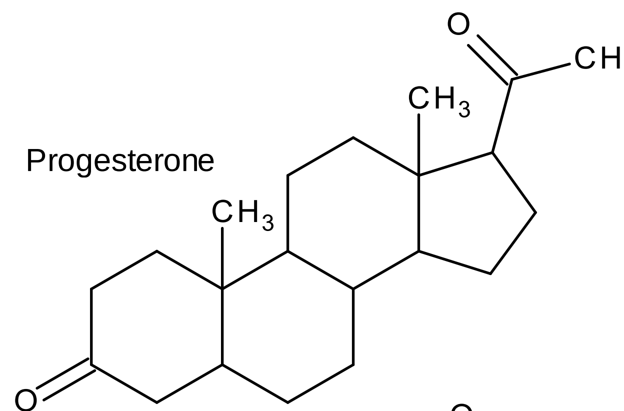
D-Glucose

horomones

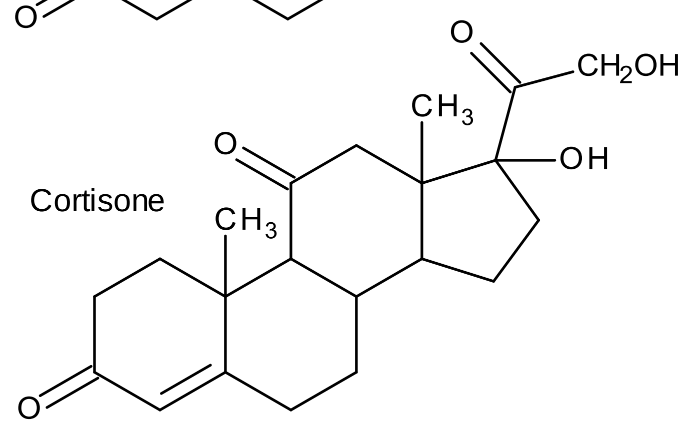
Testosterone



Progesterone



Cortisone



Physical properties of aldehydes and ketones

Boiling points and water solubility

- To understand boiling point trends, need to look at how identical molecules interact. The stronger the attractions between them, the higher the boiling point.
- To understand water-solubility, need to understand how molecules interact with H_2O (e.g. can they H-bond with H_2O?)

Intermolecular forces

Increasing strength ↑

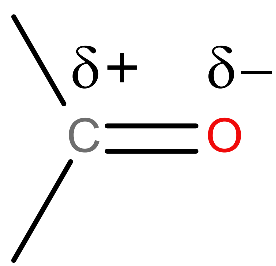
H-bonding

Dipole-dipole ← (the more polar the molecule, the stronger these are)

London forces ← (the heavier the molecule, the stronger these become)

Physical properties of aldehydes and ketones

- Neither aldehydes nor ketones possess the ability to H-bond with other molecules like themselves. Consequently, boiling points for aldehydes and ketones are lower than for alcohols of similar molar mass.
- The C-O double bond in these molecules is polar, so dipole-dipole forces do exist. As a result, their boiling points tend to be higher than for alkanes of similar molar mass.



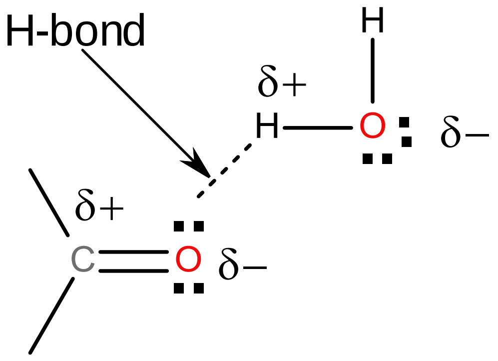
Physical properties of aldehydes and ketones

Type of Compound	Compound	Structure	Molecular Mass	Boiling Point (8°C)
alkane	ethane	$CH_3—CH_3$	30	−89
aldehyde	methanal	$H—CHO$	30	−21
alcohol	methanol	$CH_3—OH$	32	65
alkane	propane	$CH_3—CH_2—CH_3$	44	−42
aldehyde	ethanal	$CH_3—CHO$	44	20
alcohol	ethanol	$CH_3—CH_2—OH$	46	78
alkane	butane	$CH_3—CH_2—CH_2—CH_3$	58	−1
aldehyde	propanal	$CH_3—CH_2—CHO$	58	49
alcohol	1-propanol	$CH_3—CH_3—CH_2—OH$	60	97

Physical properties of aldehydes and ketones

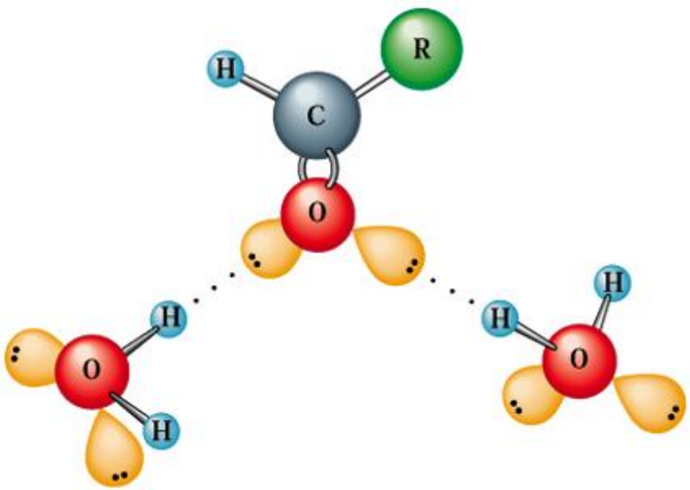
Water-solubility

- Water molecules can interact (H-bond) with the non-bonding pairs of the carbonyl group oxygen atom, enabling aldehydes and ketones that have small carbon chain components to be water-soluble.

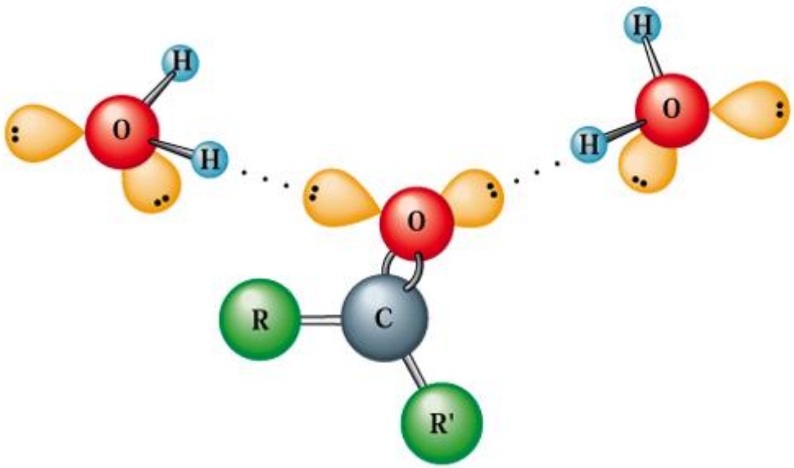


- As we saw for alcohols, the greater the carbon chain length, the lower the water-solubility (makes the molecule less polar)

Physical properties of aldehydes and ketones



(a) Aldehyde–Water Hydrogen Bonding



(b) Ketone–Water Hydrogen Bonding

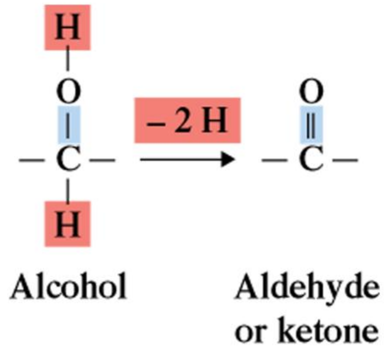
Physical properties of aldehydes and ketones

Number of Carbon Atoms	Aldehyde	Water Solubility of Aldehyde (g/100 g H_2O)	Ketone	Water Solubility of Ketone (g/100 g H_2O)
1	methanal	very soluble		
2	ethanal	infinite		
3	propanal	16	propanone	infinite
4	butanal	7	2-butanone	26
5	pentanal	4	2-pentanone	5
6	hexanal	1	2-hexanone	1.6
7	heptanal	0.1	2-heptanone	0.4
8	octanal	insoluble	2-octanone	insoluble

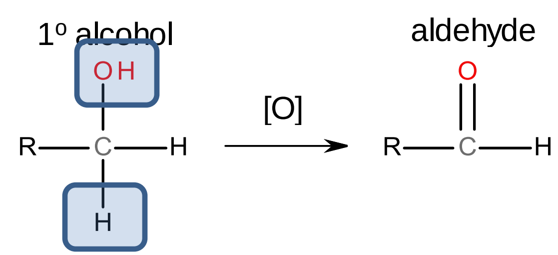
Comparing an aldehyde and a ketone of a given number of C-atoms, the ketone is generally more soluble. Why?

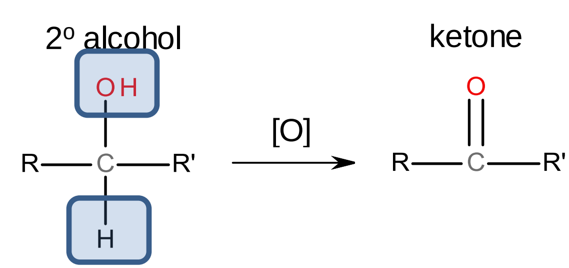
Preparation of aldehydes and ketones

- We saw already (in Ch-14) how alcohols can be oxidized to form aldehydes and ketones.
- Primary (1^o) alcohols are oxidized to aldehydes (and subsequently to carboxylic acids)
- Secondary (2^o) alcohols are oxidized to ketones



(a)



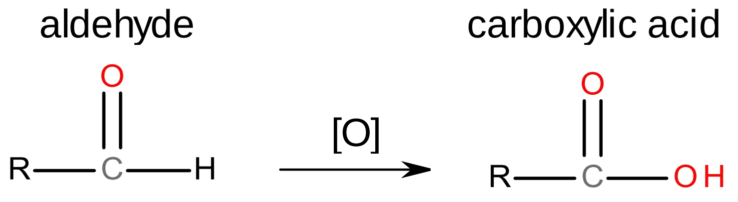


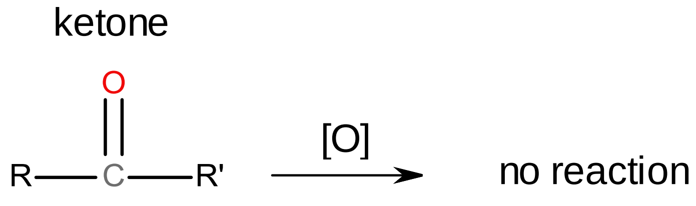
[O] = $KMnO_4$ or $K_2Cr_2O_7$

Oxidation and reduction of aldehydes and ketones

Oxidation reactions

- Aldehydes can be oxidized easily to carboxylic acids
- Ketones are resistant to oxidation.

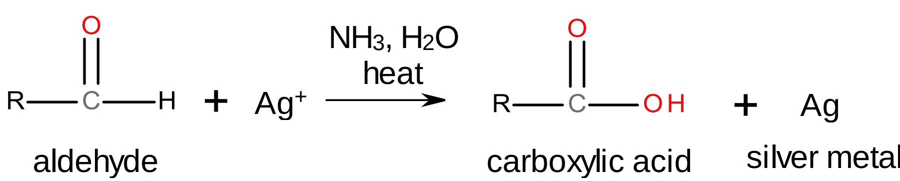




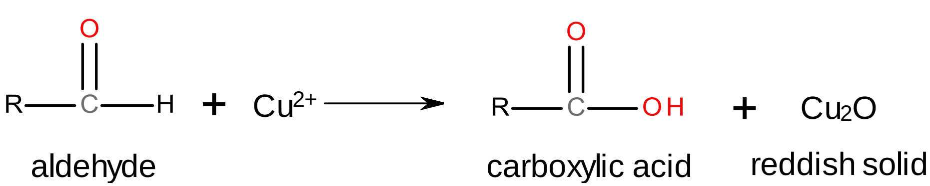
Oxidation and reduction of aldehydes and ketones

Oxidation reactions

- There are several tests that have been developed to determine the presence of aldehydes, based on their oxidation to carboxylic acids:
  - Tollen's test



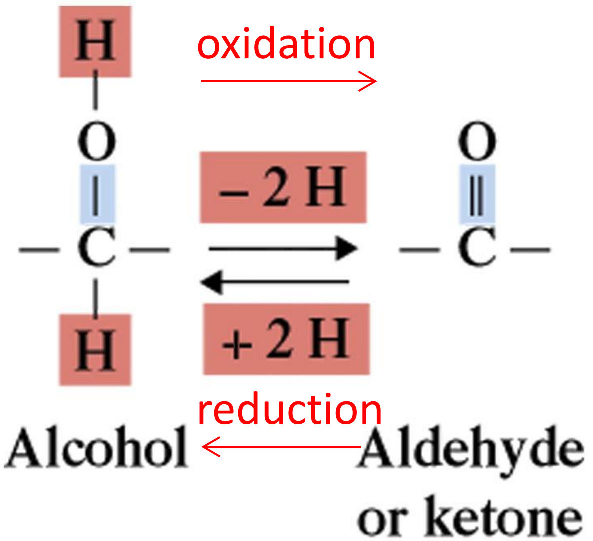
  - Benedict's test



Oxidation and reduction of aldehydes and ketones

Reduction reactions

- Both aldehydes and ketones are easily reduced to alcohols with H_2 in the presence of a catalyst (Ni, Pt, Cu).
- Biologically, this is accomplished with enzymes.



Reduction: make C-H bond, break C-O bond

HSS Fig 15.1 Red'n

Reactions of aldehydes and ketones with alcohols

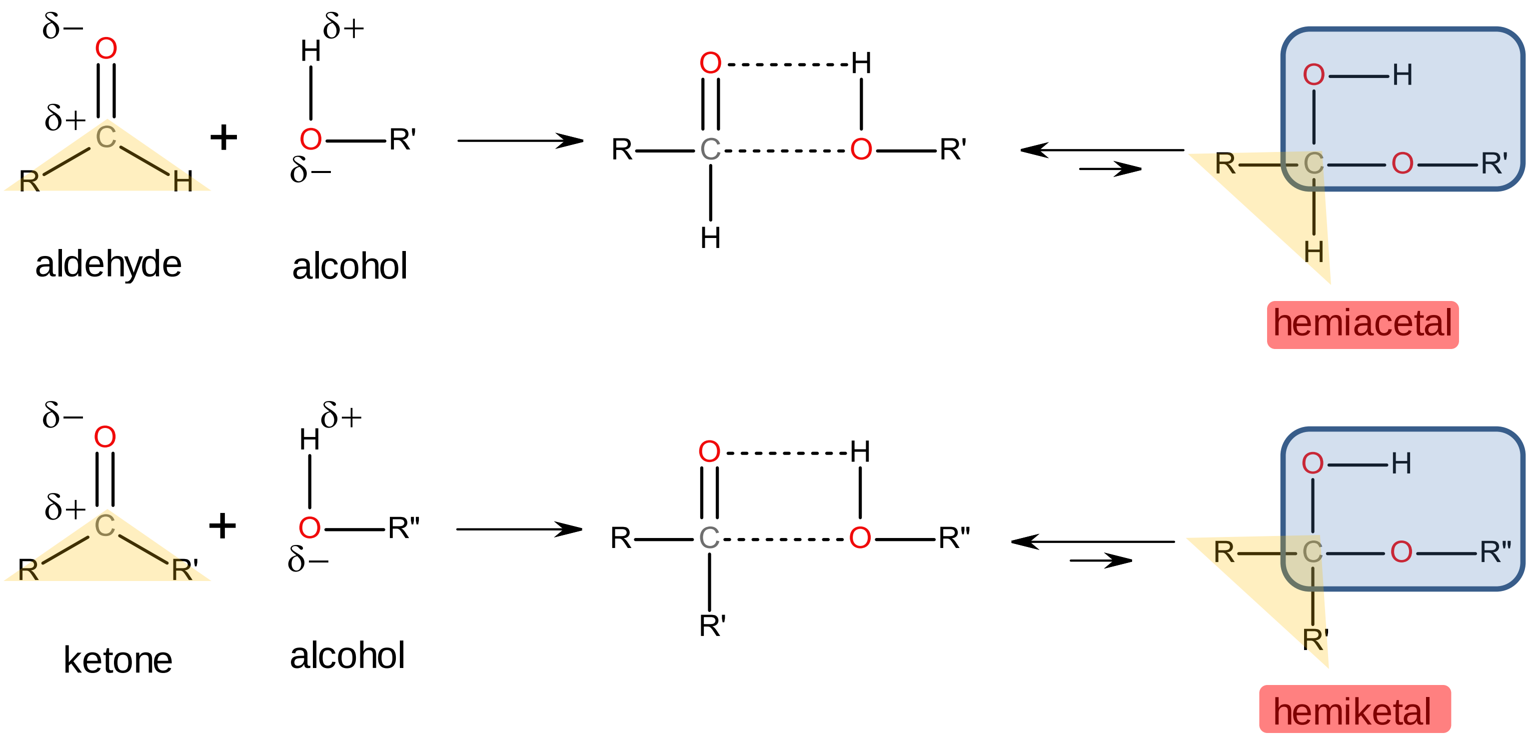
Hemiacetals and hemiketals

- When aldehydes and ketones react with alcohols in the presence of an acid, the resulting product is called a hemiacetal. Hemiacetals can further react with alcohols to form acetals:

$$\text{aldehyde or ketone} + \text{alcohol} \underset{}{\overset{\text{acid catalyst}}{\rightleftharpoons}} \text{hemiacetal}$$

$$\text{hemiacetal} + \text{alcohol} \xrightarrow{\text{acid catalyst}} \text{acetal}$$

Reactions of aldehydes and ketones with alcohols



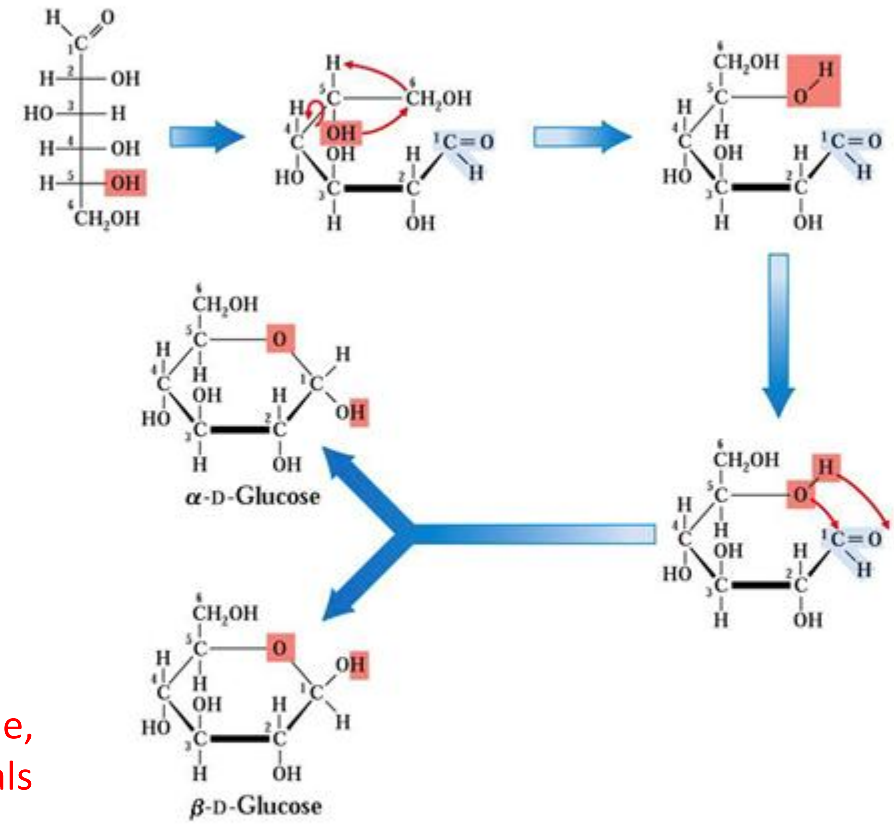
A hemiacetal is an organic compound that derives from an aldehyde and possesses a carbon atom that is bound to an OH (hydroxy) group and an OR (alkoxy) group

Hemiketal: same as above, but it derives from a ketone, not an aldehyde.

Reactions of aldehydes and ketones with alcohols

Hemiacetals

- Hemiacetal/hemiketal formation can also involve a carbonyl group and OH group <u>on the same molecule</u>. Here is an important process which involves this reaction:



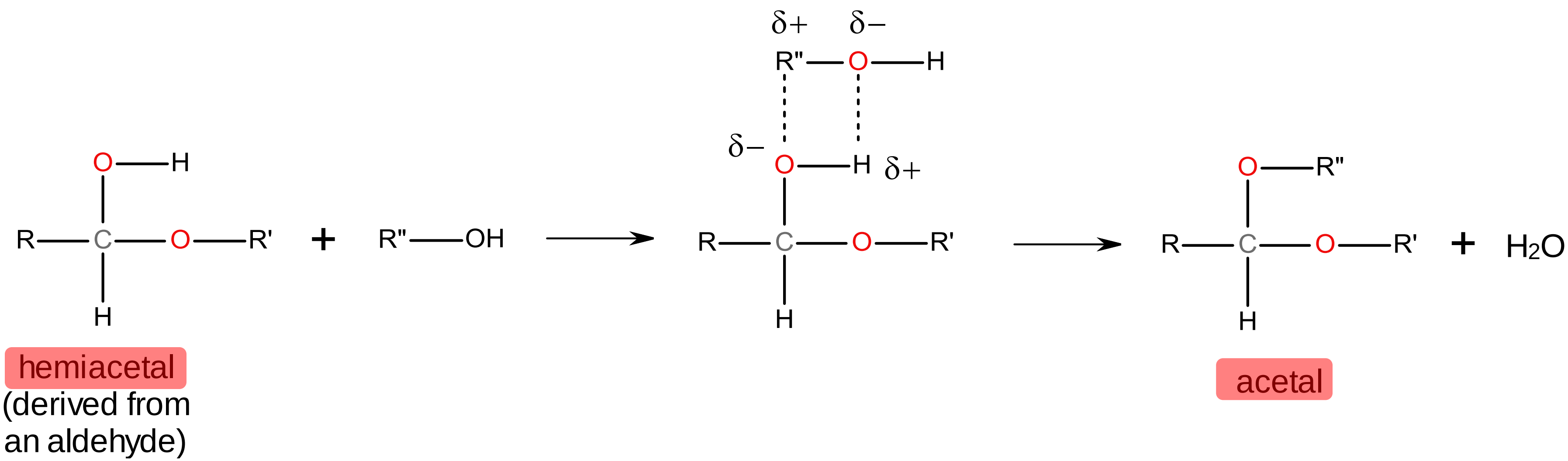
Cyclic hemiacetals are stable, unlike non-cyclic hemiacetals

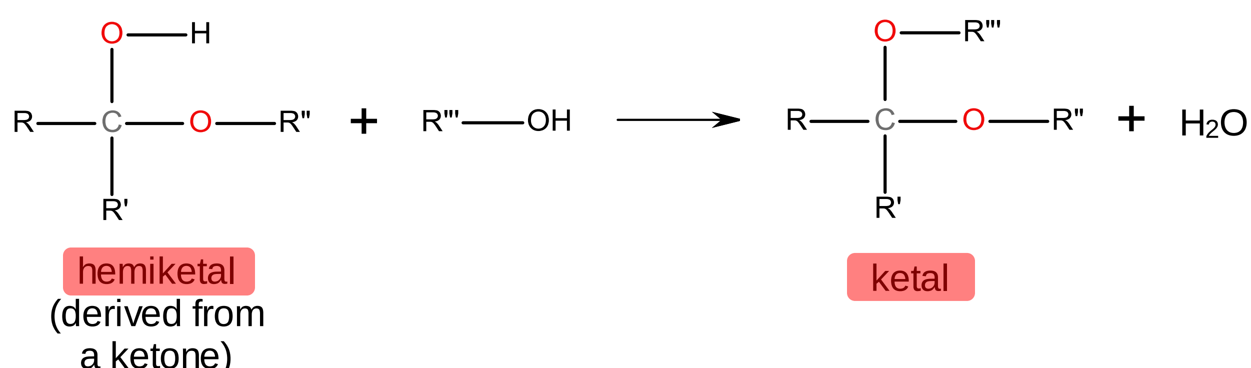
See this again in Ch-18

Reactions of aldehydes and ketones with alcohols

Acetals and ketals

- Hemiacetals can be converted to acetals in the presence of an alcohol and a catalytic amount of acid:





Reactions of aldehydes and ketones with alcohols

- Indicate whether each of the following structures is a hemiacetal, acetal, or neither: