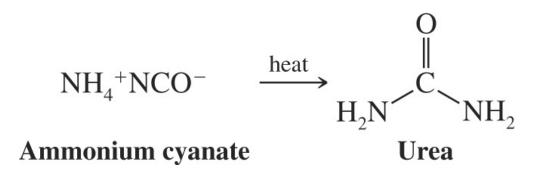
Chapter 1,2 Carbon Compounds, Chemical Bonds, Lewis Structures, Functional Groups

Introduction

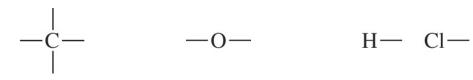
- Organic Chemistry
 - ➡ The chemistry of the compounds of carbon
 - ➡ The human body is largely composed of organic compounds
 - Organic chemistry plays a central role in medicine, bioengineering etc.
- Vitalism
 - It was originally thought organic compounds could be made only by living things by intervention of a "vital force"
 - Fredrich Wöhler disproved vitalism in 1828 by making the organic compound urea from the inorganic salt ammonium cyanate by evaporation:





Structural Theory

- Central Premises
 - Valency: atoms in organic compounds form a fixed number of bonds



Carbon atoms are tetravalent

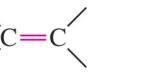
are divalent

Oxygen atoms Hydrogen and halogen atoms are monovalent

Carbon can form one or more bonds to other carbons

Carbon-carbon bonds



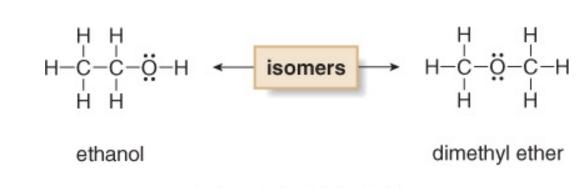


Single bond Double bond Triple bond

Isomers

In drawing a Lewis structure for a molecule with several atoms, sometimes more than one arrangement of atoms is possible for a given molecular formula.

Example:

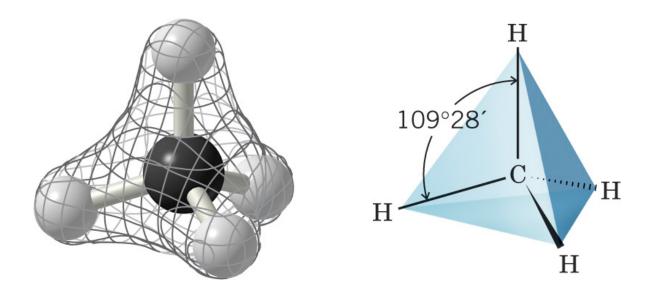


same molecular formula C₂H₆O

Both are valid Lewis structures and both molecules exist. These two compounds are called isomers.

Isomers are different molecules having the same
molecular formula.Chapter 14

- Three Dimensional Shape of Molecules
 - Virtually all molecules possess a 3-dimensional shape which is often not accurately represented by drawings
 - It was proposed in 1874 by van't Hoff and le Bel that the four bonds around carbon are not all in a plane but rather in a tetrahedral arrangement *i.e.* the four C-H bonds point towards the corners of a regular tetrahedron



Review of Bonding

- Bonding is the joining of two atoms in a stable arrangement.
- Through bonding, atoms attain a complete outer shell of valence electrons.
- Through bonding, atoms attain a stable noble gas configuration.
- Ionic bonds result from the transfer of electrons from one element to another.
- Covalent bonds result from the sharing of electrons between two nuclei.

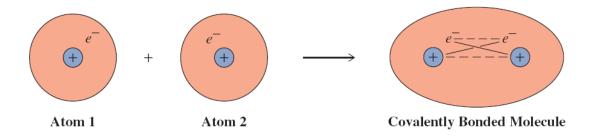
Chapter 1

Ionic and Covalent Bonds: The Octet Rule

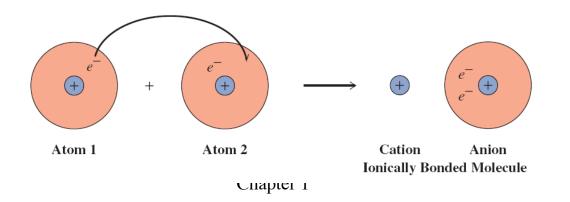
1. Covalent Bonds are based on the sharing of electrons.

1-3

If the electrons are shared equally between the two atoms, a pure covalent bond is formed.



2. Ionic Bonds are based on the transfer of one or more electrons from one atom to another. The resulting cation and anion are electrostatically attracted to each other.



Covalent Bonds

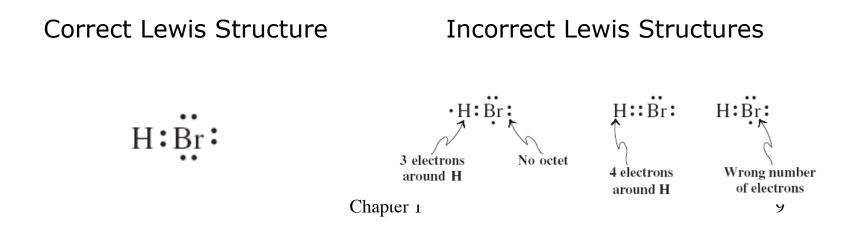
- Covalent bonds occur between atoms of similar electronegativity (close to each other in the periodic table)
- ➡ Atoms achieve octets by *sharing* of valence electrons
- Molecules result from this covalent bonding
- Valence electrons can be indicated by dots (electron-dot formula or Lewis structures) but this is time-consuming
- The usual way to indicate the two electrons in a bond is to use a line (one line = two electrons)

$$\begin{array}{cccc} H_{2} & H \cdot + \cdot H \longrightarrow H \colon H & \text{or} & H \longrightarrow H \\ \hline CI_{2} & : \ddot{C}I \cdot + \cdot \ddot{C}I \colon \longrightarrow : \ddot{C}I \colon \ddot{C}I \colon & \text{or} & : \ddot{C}I \longrightarrow \ddot{C}I \colon \vdots \\ \hline CH_{4} & \cdot \dot{C} \cdot + 4 H \cdot \longrightarrow H \colon \ddot{C} \colon H & \text{or} & H \longrightarrow H & H & H \\ \hline H & H & H & H \end{array}$$

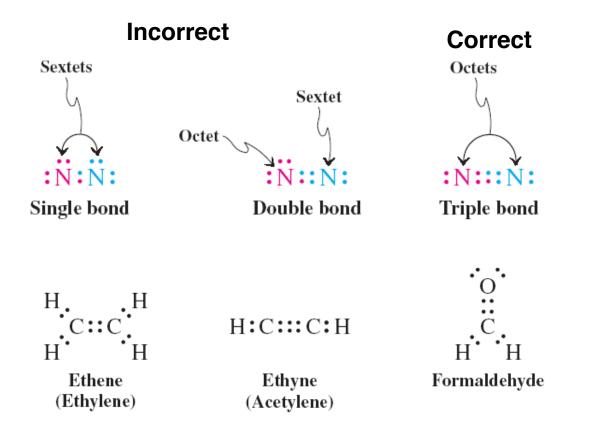
1-4 Electron-Dot Model of Bonding: Lewis Structures

Lewis structures are drawn by following simple rules.

- 1. Draw the molecular skeleton
- 2. Count the number of available valence electrons
 - Add one electron for each negative charge, if an anion.
 - Subtract one electron for each positive charge, if a cation.
- Depict all covalent bonds by two shared electrons, giving as many atoms as possible a surrounding electron octet, except for H, which requires a duet.



It is often necessary to use double or triple bonds to satisfy the octet rule:

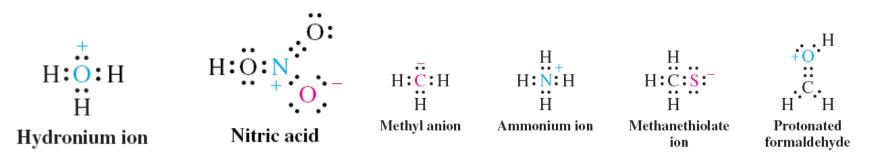




Assign **formal charges** to atoms in the molecule.

Charge = (# valence electrons in free, neutral atom) -

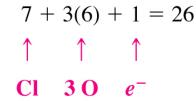
- (# unshared electrons on the atom)
- $-\frac{1}{2}$ (# shared electrons surrounding the atom)



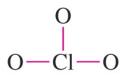
In molecules such as nitric acid, charges occur on individual atoms, even though the molecule itself is neutral.

EXAMPLE: Write the Lewis structure for the chlorate ion (CIO_3)

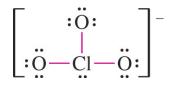
The total number of valence electrons including the electron for the negative charge is calculated

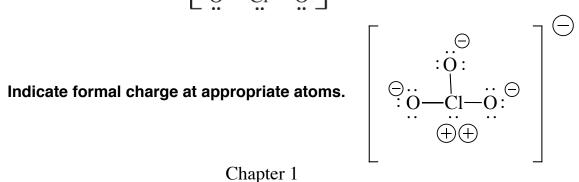


Three pairs of electrons are used to bond the chlorine to the oxygens



The remaining 20 electrons are added to give each atom an octet

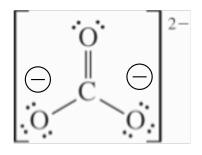




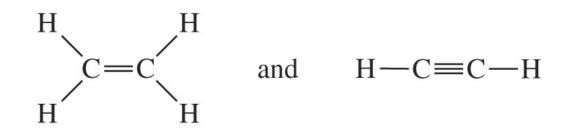
Chapter 1

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The carbonate ion with 24 valence electrons and two negative charges must incorporate a double bond to satisfy the octet rule for every atom



The organic molecules ethene (C₂H₄) and ethyne (C₂H₂) must also use multiple bonds to satisfy the octet rule for each atom



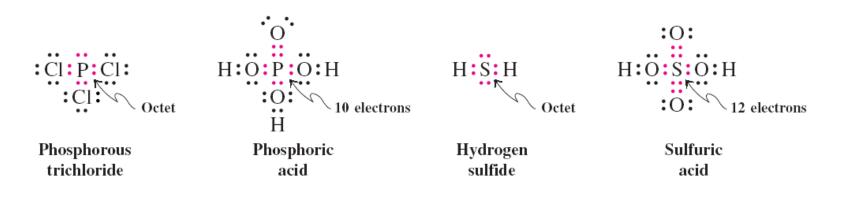
EXCEPTIONS TO THE OCTET RULE

The octet rule does not always hold.

1. If the central atom is from Group III.

BH₃, AICl₃

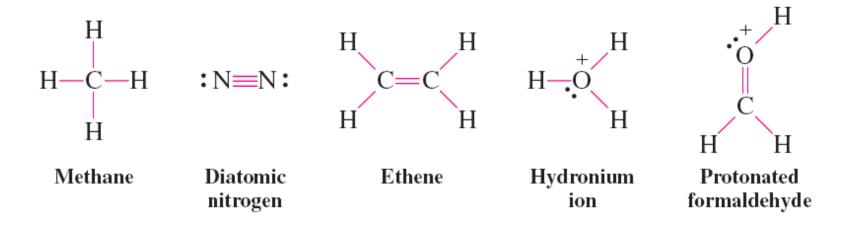
2. Past row 2 of the periodic table, the central atom may be surrounded by more than 8 electrons (expanded octet).



Covalent bonds can be depicted by straight lines.

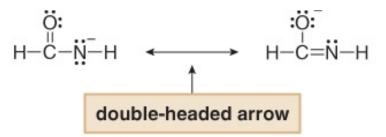
Bonding pairs of electrons are most often represented as straight lines: single bonds as a single line, double bonds as two parallel lines, and triple bonds as three parallel lines.

Lone pairs of electrons are shown as dots.



Resonance

Some molecules cannot be adequately represented by a single Lewis structure. For example, two valid Lewis structures can be drawn for the anion (HCONH)[–]. One structure has a negatively charged N atom and a C-O double bond; the other has a negatively charged O atom and a C-N double bond.

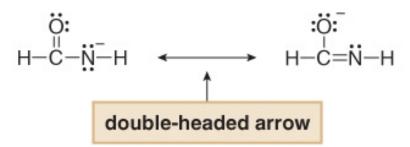


These structures are called resonance structures or resonance forms. A double headed arrow is used to separate the two resonance structures.

 Resonance structures are two Lewis structures having the same placement of atoms but a different arrangement of electrons.

Introduction to Resonance Theory

Regarding the two resonance forms of (HCONH)⁻ shown below, it should be noted that:



- Neither resonance structure is an accurate representation for (HCONH)⁻. The true structure is a composite of both resonance forms and is called a resonance hybrid.
- The hybrid shows characteristics of both structures.
- Resonance allows certain electron pairs to be delocalized over several atoms, and this delocalization adds stability.
- A molecule with two or more resonance forms is said to be resonance stabilized. Chapter 1 17

Introduction to Resonance.

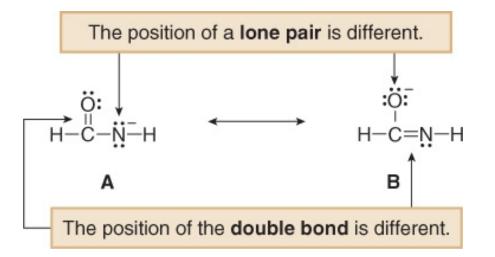
The following basic principles of resonance theory should be kept in mind:

- 1. An individual resonance structure does not accurately represent the structure of a molecule or ion. Only the hybrid does.
- 2. Resonance structures are not in equilibrium with each other. There is no movement of electrons from one form to another.
- 3. Resonance structures are not isomers. Two isomers differ in the arrangement of both atoms and electrons, whereas resonance structures differ only in the arrangement of electrons.

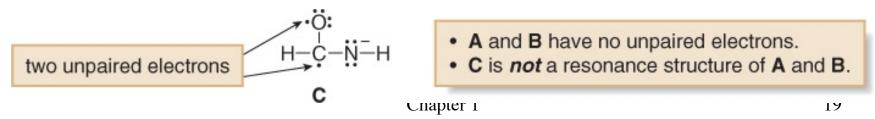
Chapter 1

Drawing Resonance Structures

Rule [1]: Two resonance structures differ in the position of multiple bonds and nonbonded electrons. The placement of atoms and single bonds always stays the same.

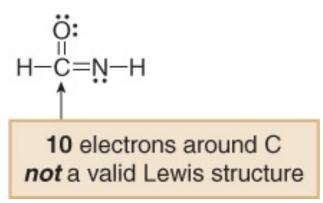


Rule [2]: Two resonance structures must have the same number of unpaired electrons.



Drawing Resonance Structures (continued)

Rule [3]: Resonance structures must be valid Lewis structures. Hydrogen must have two electrons and no second-row element can have more than eight.

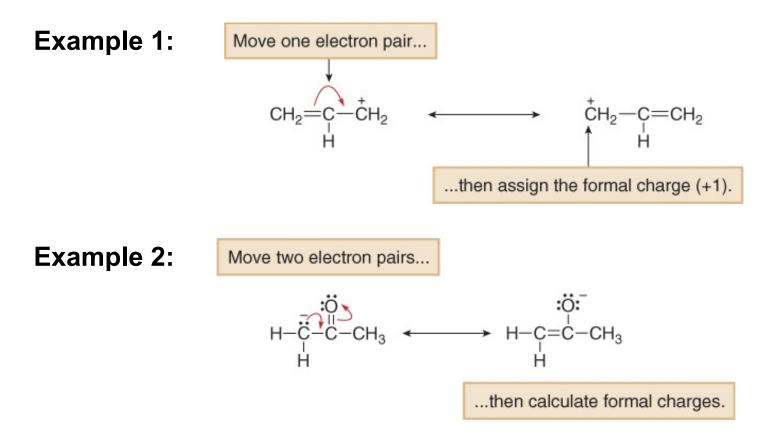


Drawing Resonance Structures

Curved arrow notation is a convention that is used to show how electron position differs between the two resonance forms.

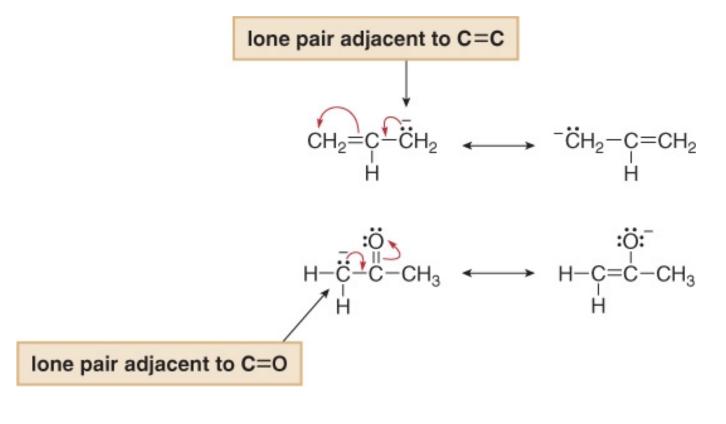
Curved arrow notation shows the movement of an electron pair. The tail of the arrow always begins at the electron pair, either in a bond or lone pair. The head points to where the electron pair "moves."

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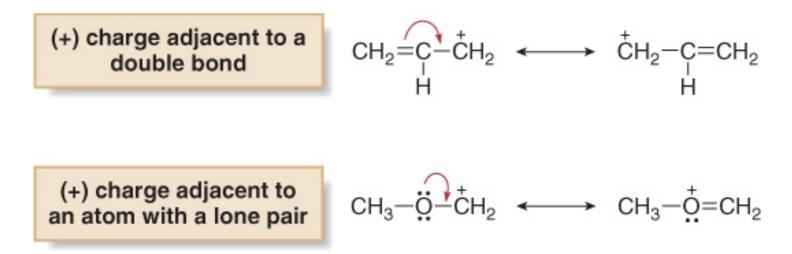
Resonance Structure Examples

In this case, a lone pair is located on an atom right next to a double bond:



Resonance Structure Examples

In this case, an atom bearing a (+) charge is bonded either to a double bond or an atom with a lone pair:

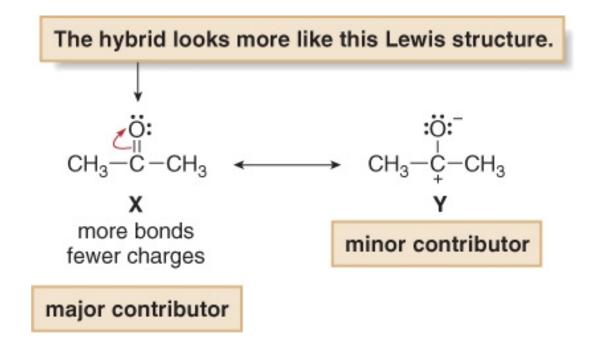


Resonance Hybrids

- The resonance hybrid is a composite of all possible resonance structures. In the resonance hybrid, the electron pairs drawn in different locations in individual resonance forms are delocalized.
- When two resonance structures are different, the hybrid looks more like the "better" resonance structure. The "better resonance structure is called the major contributor to the hybrid, and all others are minor contributors.
- The hybrid (i.e., the true molecule) is a weighted average of the contributing resonance structures.

Resonance Hybrids

A "better" resonance structure is one that has more bonds and fewer charges.



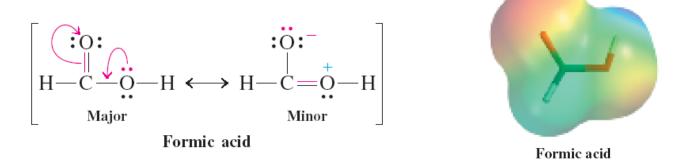
Not all resonance forms are equal; some are "better" than others.

1. Structures with a maximum of octets are most important.

$$:\mathbb{N}\equiv\overset{+}{O}:\longleftrightarrow:\overset{+}{N}=\overset{+}{O}$$

Major Minor resonance resonance contributor contributor Nitrosyl cation

- Charges should be preferentially located on atoms with compatible electronegativity. That is, (-) charges are better on more electronegative atoms; (+) charges are better on less electronegative atoms. However, #1 takes precedence.
- 3. Structures with less separation of opposite charges are more important resonance contributors than those with more charge separation.



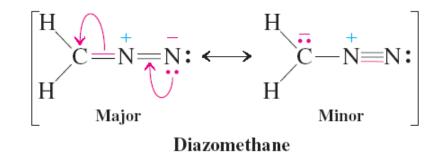
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In some cases charge separation is necessary. That is, guideline 1 takes precedence over guideline 3:



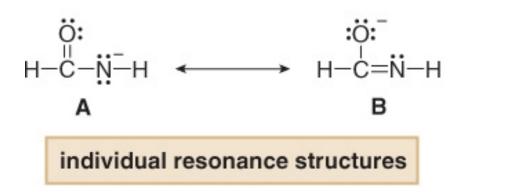


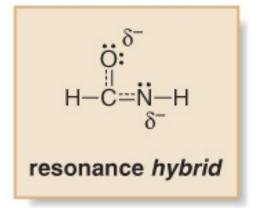
If there are two or more charge-separated resonance structures which comply with the octet rule, the most favorable one places the charges on atoms of compatible electronegativity:



Chapter 1

Drawing Resonance Hybrids





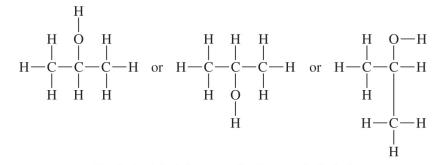
Representations of Structural Formulas

- Dot formulas are more cumbersome to draw than dash formulas and condensed formulas
- Lone-pair electrons are often (but not always) drawn in, especially when they are crucial to the chemistry being discussed

$$\begin{array}{rcl} H & H & H & H \\ H & C & O & C & H \\ H & H & H & H \end{array} = H - \begin{array}{c} H & H & H & H \\ C & O & C & - C & - H \\ H & H & H & H & H \end{array} = CH_3 \overset{\circ}{O}CH_3 \\ Condensed formula \end{array}$$

Dash formulas

- Each dash represents a pair of electrons
- This type of representation is meant to emphasize connectivity and does not represent the 3-dimensional nature of the molecule
 - ★ The dash formulas of propyl alcohol appear to have 90° angles for carbons which actually have tetrahedral bond angles (109.5°)



Equivalent dash formulas for isopropyl alcohol

Constitutional isomers

- ★ Constitutional isomers have the same molecular formula but different connectivity
- ★ Isopropyl alcohol (above) is a constitutional isomer of propyl alcohol (below)

$$\begin{array}{cccccccc} H & H & H & H & H & O-H \\ I & I & I & I \\ H-C-C-C-C-O-H & or & H-C-C-C-H \\ I & I & I & I \\ H & H & H & H & H \end{array}$$

Equivalent dash formulas for propyl alcohol

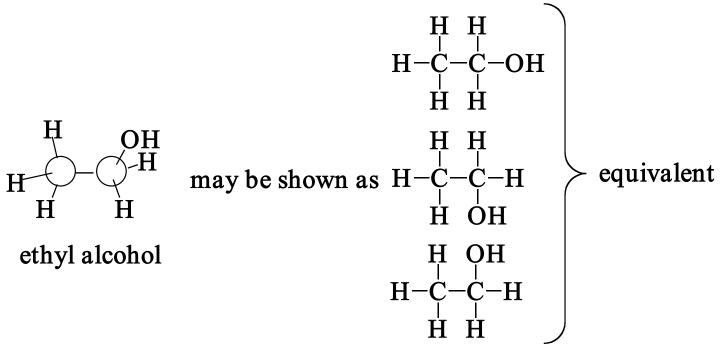
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Equivalency of Dash Structural Formulas

Dash structural formulas may, to the inexperienced eye, appear to be nonequivalent, when, in fact, they represent the same compound.

Because of rotation around single bonds, it is possible to have several perspectives of a structure that are drawn in different dash formulas. They all represent the same structure.



Chapter 1

Condensed Structures

- All atoms are drawn in, but the two-electron bond lines are <u>usually</u> (but not always) omitted.
- Atoms are usually drawn next to the atoms to which they are bonded.
- Parentheses are used around similar groups bonded to the same atom.
- Lone pairs are omitted.

$$\begin{array}{rcl} H & H & H & H \\ H - C - C - C - C - C - H & = & CH_3CH_2CH_2CH_3 & \text{or} & CH_3(CH_2)_2CH_3 \\ H & H & H & H & H \\ \end{array}$$

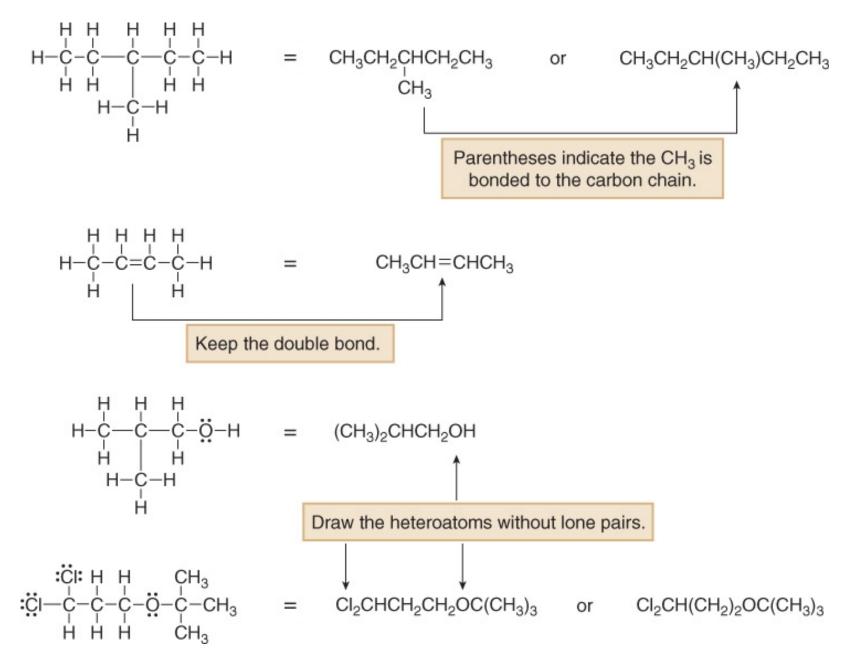
$$\begin{array}{rcl} \bullet & \text{Draw a C with 3 H's as CH_3.} & \text{Draw a C with 2 H's as CH_2.} \\ \end{array}$$

$$\begin{array}{rcl} H & -C - H \\ H - C - H \\ H & -C - H \\ H & -C - C - C - H \\ H & H & H \\ \end{array}$$

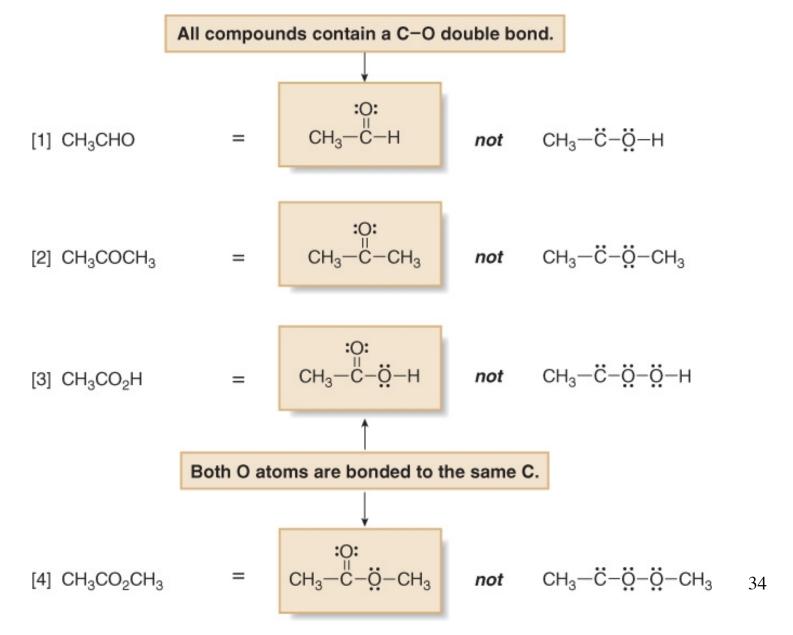
$$\begin{array}{rcl} \bullet & \text{Draw 3 CH_3 groups bonded to 1 C.} \end{array}$$

$$\begin{array}{rcl} \bullet & \text{CH}_3(CH_2)_2CH_3 \\ \bullet & \text{CH}_3(CH_2)_2CH_3 \\ \bullet & \text{Draw a C with 2 H's as CH_3.} \\ \end{array}$$

Examples of Condensed Structures



Examples of Condensed Structures Containing a C-O Double Bond



Examples of Condensed Structures

Sometimes, even in condensed structures, the bonds between horizontal carbons are shown as lines.

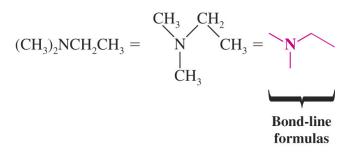
CH₃-CH₂-CH₂-CH₋CH₃ | CH₃

Bond-Line Formulas

- A further simplification of drawing organic molecules is to completely omit all carbons and hydrogens and only show heteroatoms (*e.g.* O, Cl, N) explicitly
- Each intersection or end of line in a zig-zag represents a carbon with the appropriate amount of hydrogens
 - ★ Heteroatoms with attached hydrogens must be drawn in explicitly

$$CH_{3}CHClCH_{2}CH_{3} = \underbrace{CH_{3} \quad CH_{2}}_{CH} CH_{3} = \underbrace{CH_{3} \quad CH_{3}}_{CI} CH_{3} CH_{3} = \underbrace{CH_{3} \quad CH_{3}}_{CI} CH_{3} CH_{$$

$$CH_{3}CH(CH_{3})CH_{2}CH_{3} = \begin{array}{c} CH_{3} & CH_{2} \\ CH & CH_{3} \\ CH_{3} \end{array} = \begin{array}{c} CH_{3} & CH_{2} \\ CH_{3} & CH_{3} \end{array} = \begin{array}{c} CH_{3} & CH_{3} \\ CH_{3} & CH_{3} \end{array}$$

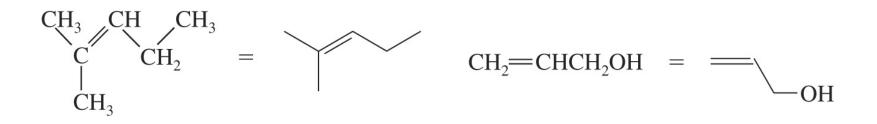


Chapter 1

Cyclic compounds are condensed using a drawing of the corresponding polygon

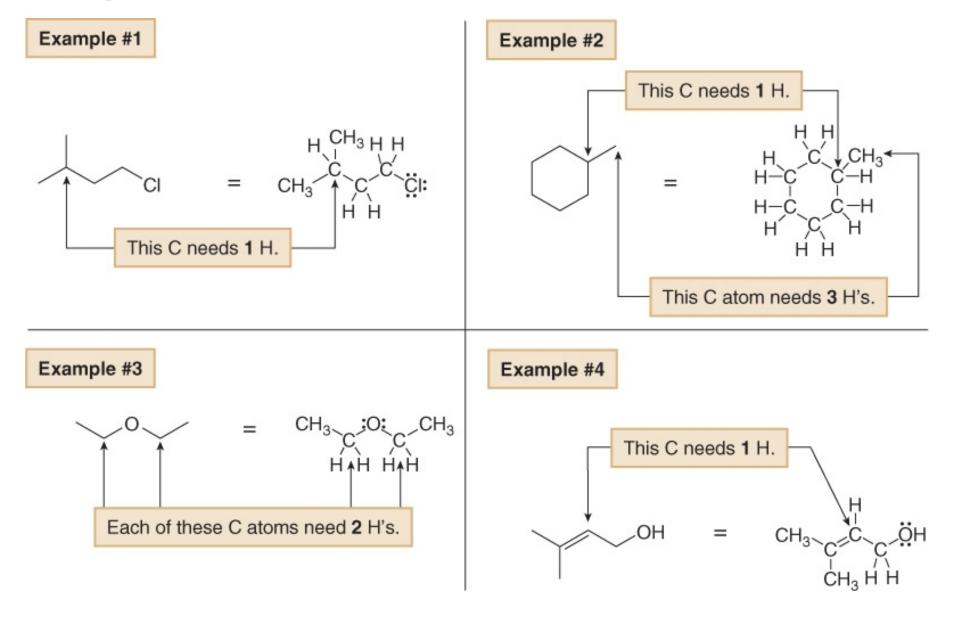
$$\bigwedge_{H_2C-CH_2}^{CH_2} = \bigwedge_{and} \inf_{\substack{H_2C-CH_2\\H_2C-CH_2}}^{H_2C-CH_2} = \bigcap_{H_2C-CH_2}^{H_2C-CH_2}$$

Multiple bonds are indicated by using the appropriate number of lines connecting the atoms



Structure and Bonding

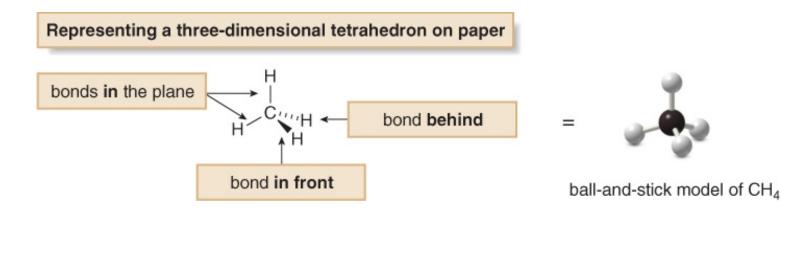
Examples of Bond-Line Structures



Structure and Bonding

Drawing Three Dimensional Structures

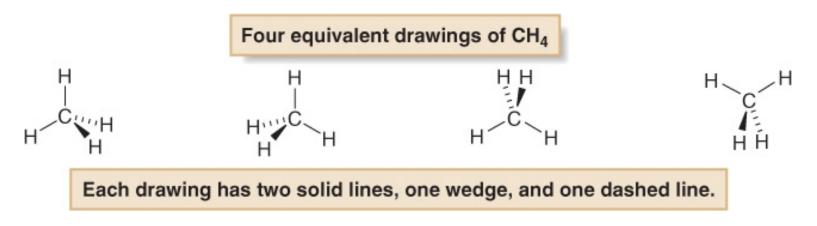
- A solid line is used for a bond in the plane of the paper.
- A wedge is used for a bond in front of the plane.
- A dashed line is used for a bond behind the plane.



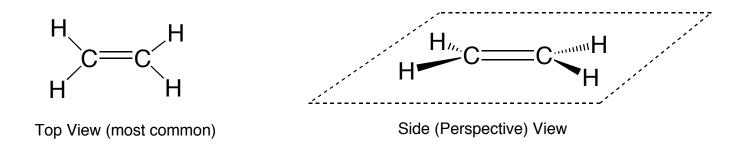
Structure and Bonding

Drawing Three Dimensional Structures

The molecule can be turned in many different ways, generating many equivalent representations. All of the following are acceptable drawings for CH_4 .

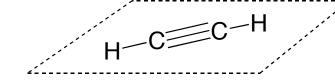


- Trigonal planar arrangements of atoms can be drawn in 3-dimensions in the plane of the paper (top view)
 - ★ Bond angles should be approximately 120°
- These can also be drawn side-on with the central bond in the plane of the paper, one bond forward and one bond back



Linear arrangements of atoms are best drawn in the plane of the paper, but they can also be drawn at an angle to show perspective.





Top View (most common)

Side (Perspective) View

Chapter 1

Chapter 2

Representative Carbon Compounds: Functional Groups

Functional Groups

An atom or groups of atoms that gives a molecule its particular chemical properties is called a *functional group* because this is the site of most chemical reactivity of a molecule.

The functional group is also responsible for many of the physical properties of a molecule

Alkanes are not considered to have a functional group

An alkene has the C=C as its functional group

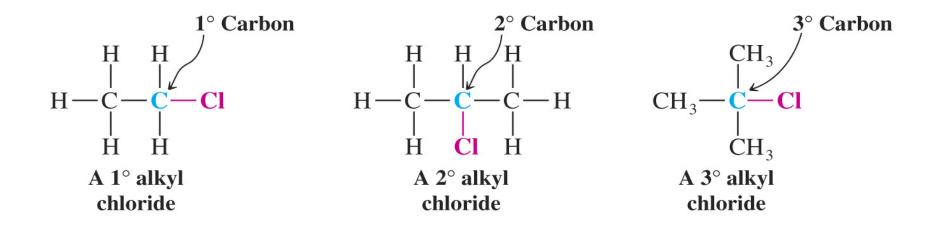
An alkyne has the triple bond as its functional group

Haloalkanes or Alkyl Halides

Compounds that contain one or more halogen atoms

examples CH_3Br CH_3CH_2Cl

Alkyl halides are classified by how many other carbons are attached to the carbon bearing the halogen



Identifying Alkyl groups

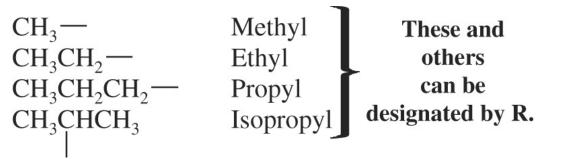
Alkyl groups are identified by removing 1 H from an alkane

| ALKANE | ALKYL GROUP | ABBREVIATION |
|---|---|---------------|
| CH_4 | CH ₃ — | Me— |
| Methane | Methyl group | |
| CH ₃ CH ₃ | CH_3CH_2 — or C_2H_5 — | Et— |
| Ethane | Ethyl group | |
| CH ₃ CH ₂ CH ₃ | CH ₃ CH ₂ CH ₂ — | Pr— |
| Propane | Propyl group | |
| | CH ₃ | |
| CH ₃ CH ₂ CH ₃ | CH_3CHCH_3 or CH_3CH — | <i>i</i> -Pr— |
| Propane | Isopropyl group | |

Note the two groups that can be obtained from propane

Alkyl Groups and the Symbol R

 Since we will refer to alkyl groups so often, we use the letter R to symbolize any alkyl group



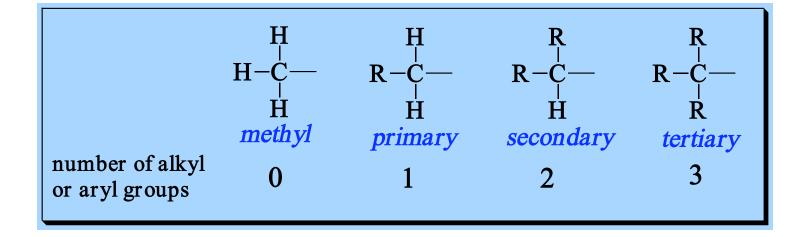
Example of an equation using the general symbol "R"

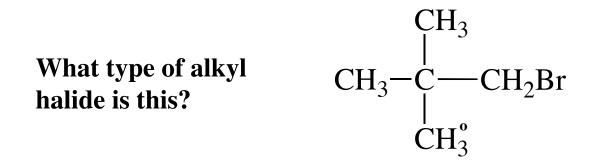
$$\mathbf{R} - \overset{\mathbf{O}}{\overset{\mathbf{O}}}{\overset{\mathbf{O}}}{\overset{\mathbf{O}}{\overset{\mathbf{O}}{\overset{\mathbf{O}}{\overset{\mathbf{O}}{\overset{\mathbf{O}}{\overset{\mathbf{O}}}{\overset{\mathbf{O}}{\overset{\mathbf{O}}}{\overset{\mathbf{O}}{\overset{\mathbf{O}}{\overset{\mathcal{O}}{\overset{\mathcal{O}}{\overset{\mathcal{O}}{\overset{\mathcal{O}}{\overset{\mathcal{O}}{\overset{\mathcal{O}}{\overset{\mathcal{O}}{\overset{\mathcal{O}}{\overset{\mathcal{O}}{\overset{\mathcal{O}}{\overset{\mathcal{O}}}{\overset{\mathcal{O}}{\overset{\mathcal{O}}}{\overset{\mathcal{O}}{\overset{\mathcal{O}}{\overset{\mathcal{O}}}{\overset{\mathcal{O}}}{\overset{\mathcal{O$$

Example of an equation using a specific alkyl group:

$$\mathbf{CH}_{3} - \overset{\circ}{\mathbf{O}} - \overset{\mathbf{H}}{\mathbf{H}} + \mathbf{Na}^{+} : \overset{\circ}{\mathbf{H}}^{-} \longrightarrow \mathbf{CH}_{3} - \overset{\circ}{\mathbf{O}} : \mathbf{Na}^{+} + \overset{\mathbf{H}}{\mathbf{H}} - \mathbf{H}$$

Classification of Alkyl Halides





Aromatic groups are generalized differently from alkyl groups

A benzene ring with a hydrogen removed is called a *phenyl group* and can be represented in various ways

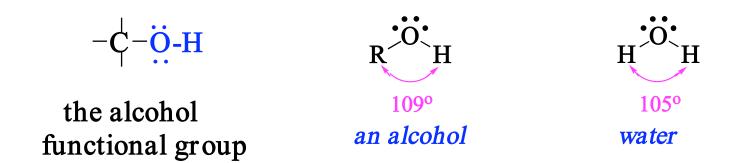
Ways of Representing a Phenyl Group

Another common aromatic group is called a *benzyl group* and can be represented in various way

$$\bigcirc$$
 -CH₂- or \bigcirc -CH₂- or C₆H₅CH₂- or Bn-

Ways of Representing a Benzyl Group

Functional Group: Alcohols: R-OH

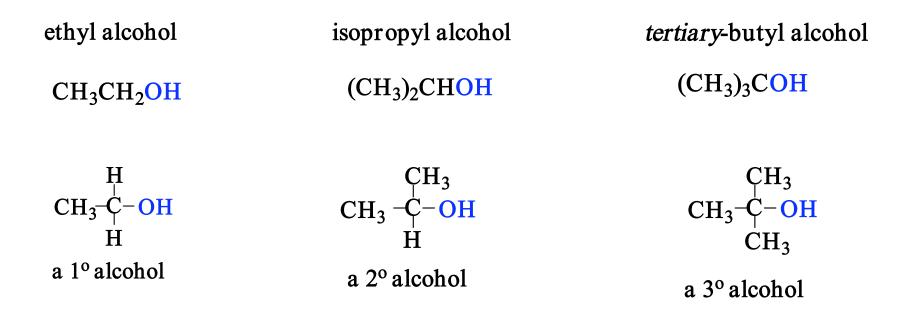


Simple alcohols often are named by using the alkyl group name followed by "alcohol."

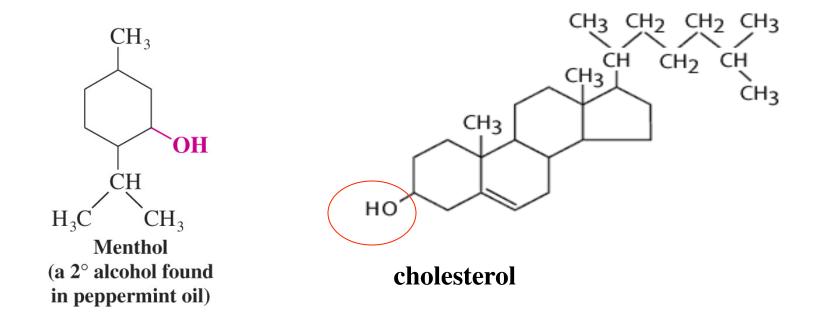
| CH_4 | CH ₃ - | CH ₃ -OH |
|---------------------------------|-----------------------------------|-------------------------------------|
| methane | methyl | methyl alcohol |
| | | |
| CH ₃ CH ₃ | CH ₃ CH ₂ - | CH ₃ CH ₂ -OH |
| ethane | ethyl | ethyl alcohol |

Classification of alcohols

Alcohols are classified as primary, secondary or tertiary according to the structure around the carbon to which the hydroxyl group is attached.



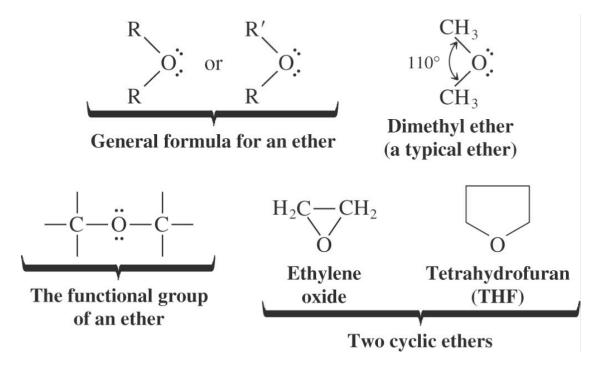
Some typical alcohols



Ethers

Contain oxygen bonded to two alkyl groups

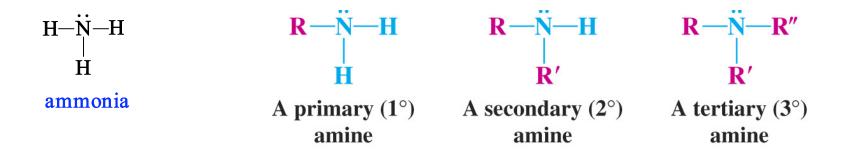
- **R-O-R** (a symmetrical ether)
- R-O-R' (unsymmetrical ether)



Ethers are less polar and less reactive than alcohols

Amines – the Bases of Organic Chemistry

Amines are organic derivatives of ammonia



Classified as 1°, 2°, or 3° depending on number of R groups (not the type of R group)

Some Typical Amines

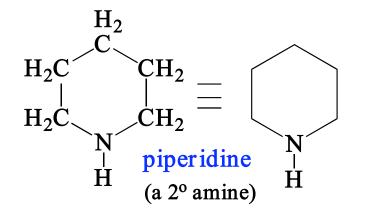
 $CH_3CH_2NH_2$

ethylamine (a 1º amine) NH₂ isopropylamine (a 1° amine)

CH₃CHCH₃

CH₃ CH₃CCH₃ NH₂ tertiary-butylamine (a 1° amine)

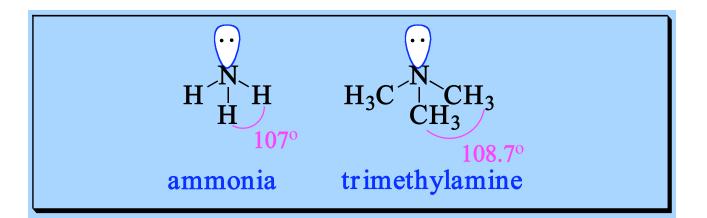
(CH₃)₂CHNHCH(CH₃)₂ diisopropylamine (a 2° amine)



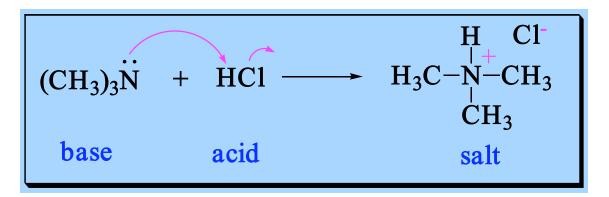
 $\begin{array}{c} CH_2CH_3\\ CH_3CH_2NCH_2CH_3\\ \hline triethylamine\\ (a\ 3^{\circ}\ amine)\end{array}$

 $\begin{array}{c} CH_{2}CH_{3}\\ CH_{3}CH_{2}NCH_{3} \end{array}$

diethylmethylamine (a 3° amine)

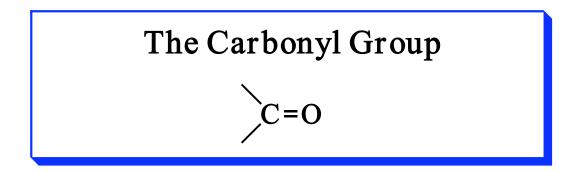


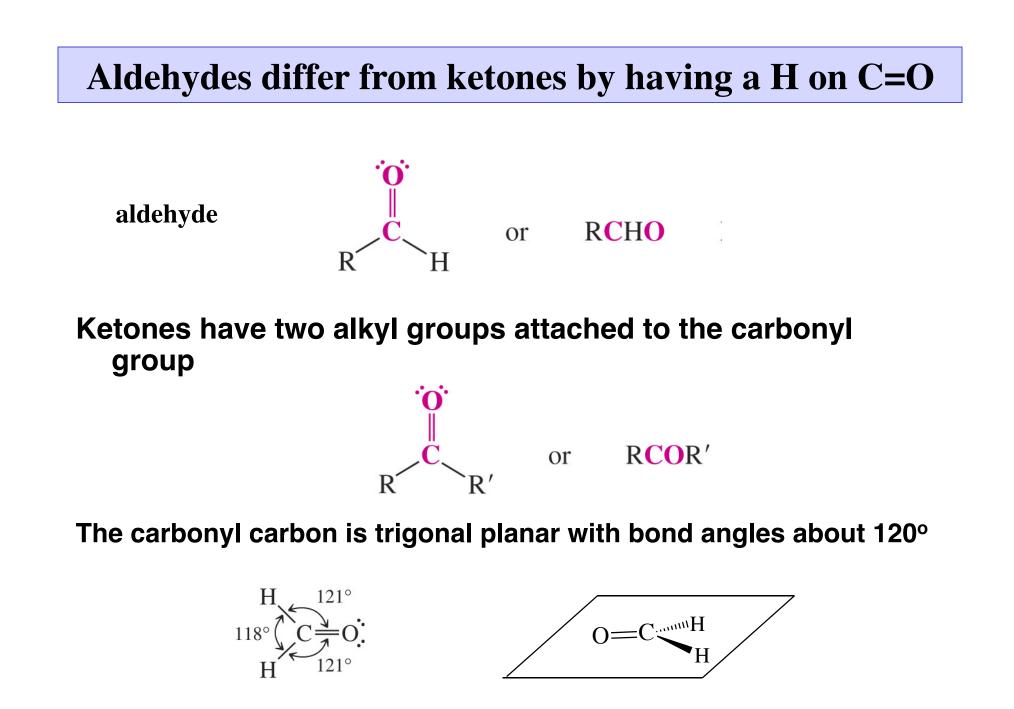
Amines are bases.



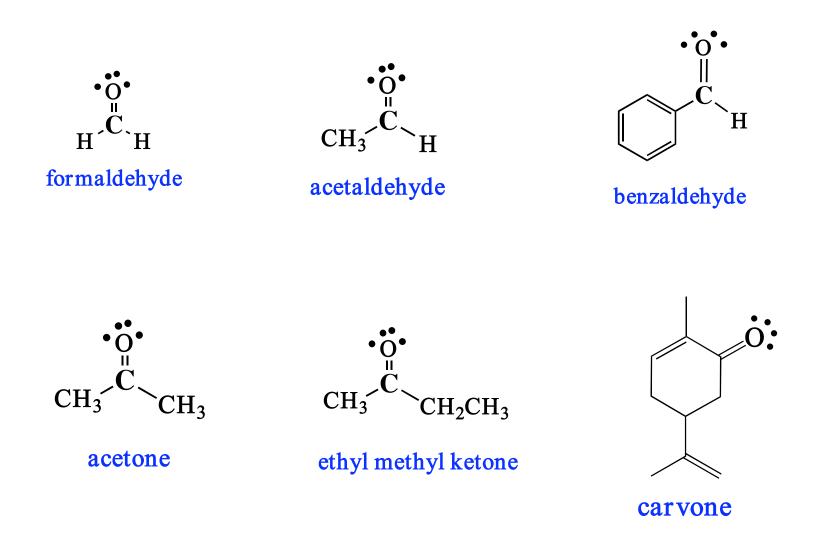
Aldehydes and Ketones

Aldehydes and ketones both contain the very important carbonyl group .



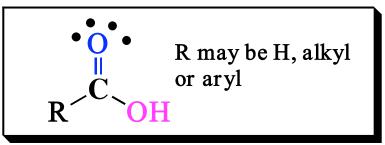


Examples of aldehydes and ketones

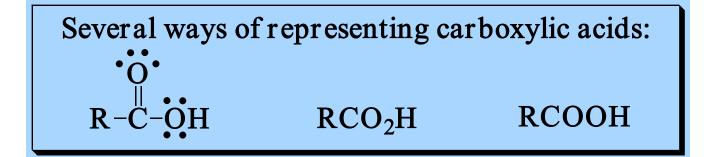


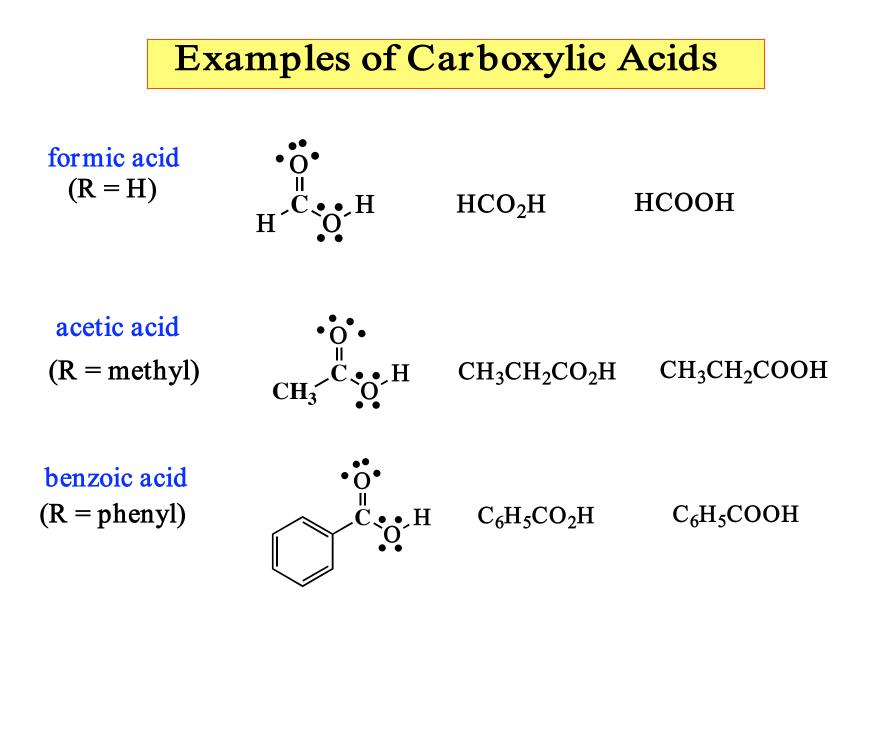
Carboxylic acids: The Acids of Organic Chemistry

Carboxylic acids have a general structure that incorporates the carbonyl and hydroxyl groups:



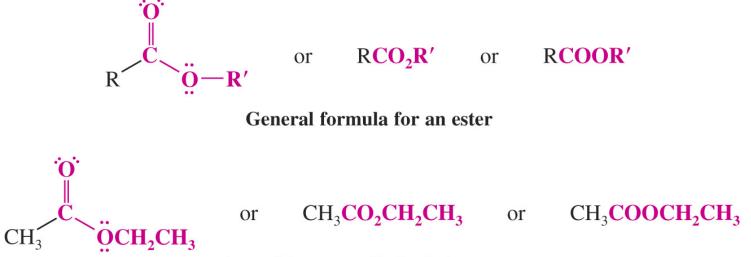
The characteristic functional group of a :O: carboxylic acid is called the carboxyl group. :C-





Esters & Amides: Members of the Carboxylic Acid Family (sometimes referred to as Carboxylic Acid Derivatives)

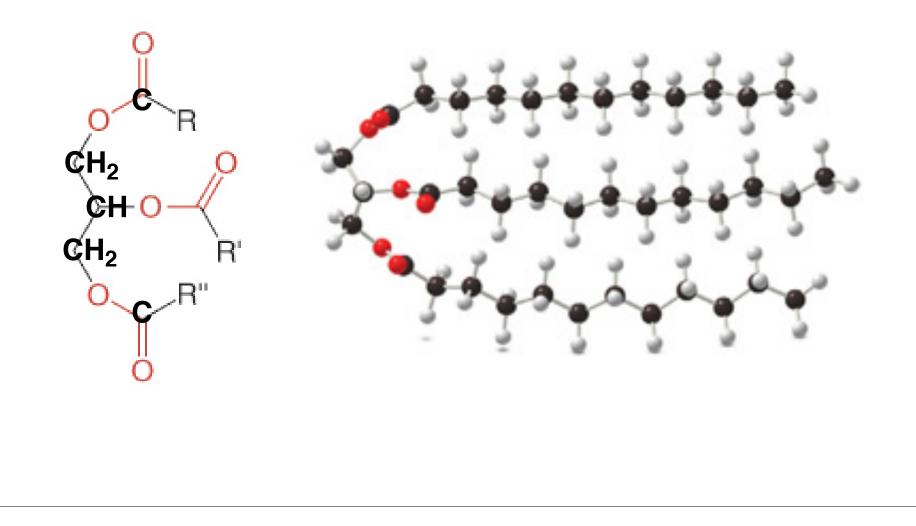
Esters: carbonyl group is bonded to an alkoxyl (OR') group



A specific ester called ethyl acetate

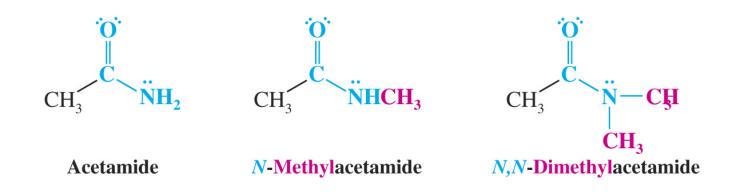
Example of Ester Groups

Most common lipids (fats and oils) are esters of the trihydroxy alcohol, glycerol, plus carboxylic acids of 10 to 20 carbon atoms.



Amides: Another Carboxylic Acid Derivative

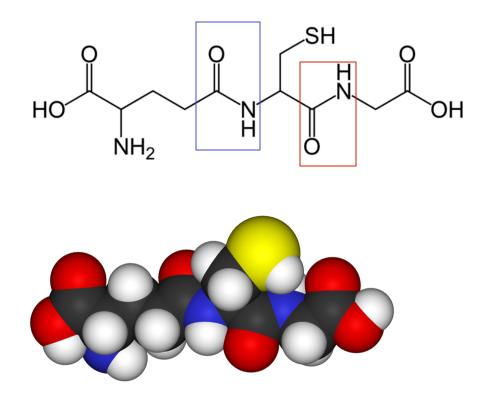
Amides have a nitrogen attached directly to the C=O



Amides are called carboxylic acid derivatives because they are usually made from carboxylic acids.

We'll learn later that amides, unlike amines, are <u>not</u> bases.

Amide bonds are the backbone of peptides and proteins



Glutathione: an antioxidant

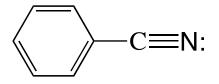
Tripeptide (cysteine, glutamate, and glycine) with two amide links

Nitriles: R-CN

Alkyl group attached to a carbon triply bonded to a nitrogen

• This functional group is called a nitrile.

The $-C \equiv N$: is called a cyano group.



Benzonitrile

The CN triple bond is structurally similar

to the triple bond of an alkyne.

Summary of Major Families of Organic Compounds

| | | | | Family | | | |
|-----------------------------|---------------------------------|---|----------------|------------------|------------------------------------|------------------|----------------------------------|
| | Alkane | Alkene | Alkyne | Aromatic | Haloalkane | Alcohol | Ether |
| Functional group | C—H and C—C bonds | C=C | —C≡C— | Aromatic ring | Ċ;: | —с́—ён | -cöc |
| General formula | RH | $\begin{array}{l} \text{RCH} = \text{CH}_2 \\ \text{RCH} = \text{CHR} \\ \text{R}_2\text{C} = \text{CHR} \\ \text{R}_2\text{C} = \text{CR}_2 \end{array}$ | RC≡CH RC≡CR | ArH | RX | ROH | ROR |
| Specific example | CH ₃ CH ₃ | CH ₂ =CH ₂ | HC≡CH | \bigcirc | CH ₃ CH ₂ Cl | CH₃CH₂OH | CH ₃ OCH ₃ |
| IUPAC name | Ethane | Ethene | Ethyne | Benzene | Chloroethane | Ethanol | Methoxymethane |
| Common name ^a | Ethane | Ethylene | Acetylene | Benzene | Ethyl chloride | Ethyl alcohol | Dimethyl ether |

^aThese names are also accepted by the IUPAC.

Summary (cont.)

