

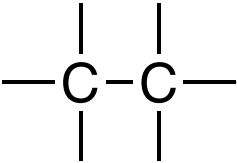
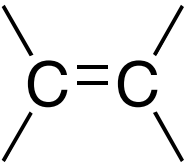
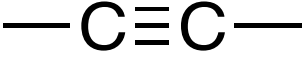

# Functional Groups

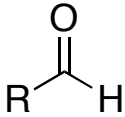
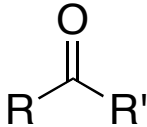
A functional group is a bond or several bonds in an organic molecule that have certain properties and reactions that are consistent in all molecules containing those sets of bonds

- Functional groups often involve heteroatoms or multiple bonds or both.
- Compounds with multiple functional groups will be classified (and react) as all appropriate functional groups.
  - $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{OH}$  is an **alkene** and an **alcohol**
  - $\text{CH}_3\text{CHBrCH}_2\text{CH}_2\text{CHO}$  is an **aldehyde** and an **alkyl halide**
- Single functional groups are not broken apart into sub-groups
  - $-\text{COOH}$  is a **carboxylic acid** *NOT* a ketone and an alcohol
  - $\text{HCOOR}$  is an **ester** *NOT* an aldehyde and an ether.
- Functional groups have a strict hierarchy in IUPAC nomenclature and the ending of the name often depends on the highest priority functional group, but functional groups and substituents are **NOT** the same thing.
  - Functional groups have distinct reactions, bonds, and properties
    - E.g. an alcohol, an alkene, a nitrile.
  - Substituents are a way of simplifying molecules for naming.
    - E.g. a methyl group, an ethyl group, an isopropyl group

## NOTE:

Whether alkane is a functional group often depends on whom you ask. Alkanes are often considered to be the basic organic structure and are thus not included as a functional group, but as a skeleton structure common to all molecules. Sometimes alkanes are considered to be a functional group if there is no other functional group in the molecule (e.g. 2,2,3,3-tetramethylbutane is a branched alkane).

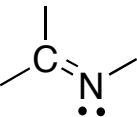
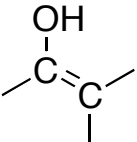
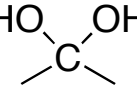
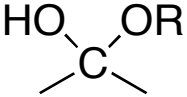
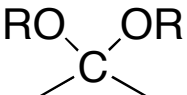
| <b>Hydrocarbons</b><br>Just C and H atoms |   |   |
|---|---|---|
| Alkane                                    |    | All C and H<br>All single bonds<br>Unreactive, except with F <sub>2</sub> , Cl <sub>2</sub> , Br <sub>2</sub> , and O <sub>2</sub><br>Insoluble in water, low boiling points<br>General alkane abbreviated as R |
| Alkene                                    |    | All C and H<br>At least one C=C double bond<br>Undergo electrophilic addition reactions, hydrogenation, and other reactions at the pi bond.<br>Insoluble in water, low boiling points                           |
| Alkyne                                    |    | All C and H<br>At least one C-C triple bond<br>Undergo electrophilic addition reactions, hydrogenation, and other reactions at the pi bond.<br>Insoluble in water, low boiling points                           |
| Aromatic<br>(Arene)                       |  | C and H (possibly N, O, or S)<br>Conjugated, cyclic, planer systems with 4n+2 pi electrons. Undergo electrophilic aromatic substitution reactions.<br>General aromatic abbreviated as Ar                        |

| <b>Carbonyls</b><br>Class II: attached to C/H |   |  |
|---|---|--|
| Aldehydes<br>(Class II)                       |  | C and O double bond with an H on the same carbon.<br>Polar bonds give moderate bp<br>Nucleophilic Acyl Addition Reactions<br>Redox reactions<br>pKa of alpha H 18-20 (enolate reactions) |
| Ketones<br>(Class II)                         |  | C and O double bond with two alkyl groups<br>Polar bonds give moderate bp<br>Nucleophilic Acyl Addition Reactions<br>Reduction reactions<br>pKa of alpha H 19-21 (enolate reactions)     |

| <b>Heteroatoms</b>                |  |  |
|-----------------------------------|--|--|
| Contain atoms other than C and H  |  |  |
| Haloalkanes<br>(Alkyl<br>Halides) | $R-F$<br>$R-Cl$<br>$R-Br$<br>$R-I$   | Contain F, Cl, Br, or I<br>General halogen abbreviated as X<br>Low water solubility<br>Bp increases with size of halogen.<br>$S_N2$ , $S_N1/E_1$ , and $E_2$ reactions<br>Good leaving groups  |
| Alcohols                          | $R-OH$   | Contain O<br>High water solubility and boiling point<br>due to hydrogen bonds<br>$S_N2$ , $S_N1/E_1$ , and $E_2$ reactions<br>Acid/Base reactions<br>Oxidation/Reduction reactions<br>Moderate nucleophiles and poor leaving<br>groups |
| Ethers                            | $R-OR'$  | Contain O<br>Mod. water solubility and boiling point<br>due to polar bonds<br>Can react with strong acids to give $S_N2$ ,<br>$S_N1/E_1$ , and $E_2$ reactions   |
| Amines                            | primary amine $R-NH_2$<br><br>secondary amine $R-NH$<br> <br>$R'$<br><br>tertiary amine $R-N-R'$<br> <br>$R$ | Contain N<br>Moderate to high water solubility and bp<br>due to hydrogen bonds<br>Good bases and nucleophiles poor<br>leaving groups.<br>Protonated at acidic pH, protonated<br>amines are poor nucleophiles                           |
| Thiols                            | $R-S-H$  | Similar to alcohols. S is very<br>nucleophilic   |
| Thioethers                        | $R-S-R'$   | Similar to ethers, S is very nucleophilic<br>and can expand its octet.   |

| <b>Carbonyls</b>   |  |  |
|--|--|--|
| <b>Class I: Attached to a heteroatom (leaving group)</b> |  |  |
| Carboxylic Acids<br>(Class I)                            | $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$  | <p>C and O double bond with an OH on the same carbon.</p> <p>Acidic Hydrogen pKa of OH 4-5</p> <p>Hydrogen bonds give very high bp.</p> <p>Nucleophilic Acyl Substitution Reactions</p> <p>Reduction reactions</p>   |
| Carbonyl Halides<br>(Class I)                            | $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{Cl} \end{array}$  | <p>C and O double bond with a halogen on the same carbon.</p> <p>Very reactive with water</p> <p>Nucleophilic Acyl Substitution Reactions</p> <p>Reduction reactions</p>   |
| Anhydrides<br>(Class I)                                  | $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R}' \end{array}$   | <p>C and O double bond with an acid ester on the same carbon.</p> <p>Moderately reactive with water</p> <p>Nucleophilic Acyl Substitution Reactions</p> <p>Reduction reactions</p>   |
| Esters<br>(Class I)                                      | $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OR}' \end{array}$   | <p>C and O double bond with an ether on the same carbon.</p> <p>Nucleophilic Acyl Substitution Reactions</p> <p>Reduction reactions</p> <p>pKa of alpha hydrogens ~25 so can do enolate reactions</p>  |
| Amides<br>(Class I)                                      | $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{N}-\text{H} \\   \\ \text{H} \end{array}$<br>$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{N}-\text{R} \\   \\ \text{H} \end{array}$<br>$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{N}-\text{R} \\   \\ \text{R} \end{array}$ | <p>C and O double bond with an amine on the same carbon.</p> <p>Lots of double bond character in the C-N bond due to resonance.</p> <p>N-H are moderately acidic and can hydrogen bond.</p> <p>Nucleophilic Acyl Substitution Reactions</p> <p>Reduction reactions</p> |
| Nitriles<br>(Class I)                                    | $\text{R}-\text{C}\equiv\text{N}$  | <p>C and N triple bond. Same oxidation state as Class I carbonyls.</p> <p>Hydrolyzes to a carboxylic acid</p> <p>Reduction reactions</p>   |

## Advanced

|              |   |  |
|--------------|---|--|
| Imines       |  | C/N double bond. Easily converted to carbonyl in the presence of water.  |
| Enols        |  | Formation is unfavored and the diol will usually revert to the carbonyl unless the alkene forms an aromatic ring               |
| Geminal Diol |  | Not isolable. Formation is unfavored except with formaldehyde and electron poor carbonyls. Formation catalyzed by acid or base |
| Hemiacetals  |  | Easily reversed to carbonyl, except with cyclic hemiacetals. Formation catalyzed by acid or base.                              |
| Acetals      |  | Formation catalyzed by acid only. Stable and isolable except in the presence of acid.  |