

## FUNCTIONAL GROUPS: A REVISION

### X.6 FUNCTIONAL GROUPS

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**Definition:** A **FUNCTIONAL GROUP** is a specific group of atoms that exists in a molecule and gives a molecule an ability to react in a specific manner or gives it special properties.

Hydrocarbons have a limited range of properties and uses. Functional groups give specific properties to a molecule. By carefully choosing the functional groups present in a molecule, a chemist can:

- make a molecule act as a base, an acid, or both
- make a molecule react with specific chemicals
- give a molecule a particular solubility
- make a molecule explosive
- give a molecule a pleasant or unpleasant smell

The previous sections have already introduced some functional groups: halides, carbon-carbon double bonds (in alkenes) and carbon-carbon triple bonds (in alkynes). This section examines some other important functional groups and how their presence changes the properties of the parent hydrocarbon.

**IMPORTANT:** Recall that when naming hydrocarbons with attached methyl, ethyl, etc. groups, the numbering is started from the end of the parent hydrocarbon giving the lowest set of numbers. As you will see, the lowest possible number is also used to indicate the point of attachment for a functional group. However, a problem arises when a molecule contains more than one type of functional group on opposite ends of a parent hydrocarbon: which functional group is assigned the lowest number? The problem is resolved by using the following Table of Precedence, which was developed by the International Union of Pure and Applied Chemistry (IUPAC). The Table is a more-or-less **arbitrary** assignment of precedence, so there is no easy way to decide which functional group has precedence over others without either memorizing the Table or having the Table available for ready reference. **Note:** as a result of a particular group in a molecule having precedence, the overall set of numbers for the attachments may be higher than if there was no precedence.

#### Functional Group Table of Precedence for Nomenclature

A functional group higher in the Table has precedence over functional groups below it. Refer back to this Table as new functional groups are introduced and discussed in the Sections below.

Highest Priority	Carboxylic acid
	Ester
	Amide
	Aldehyde
	Ketone
	Alcohol
	Amine
	Alkene
	Alkyne
Lowest priority	Alkane, Ether, Halide, Nitro (in equal priority order)

## A. ALCOHOLS

**Definition:** An **alcohol** is an organic compound containing an OH ("hydroxyl") group.

**RULES:** When naming an ALCOHOL:

- Drop the "e" ending of the parent hydrocarbon and add "ol". (The ending **ol** comes from **alcohol**.)
- Number the hydrocarbon chain to give the LOWEST possible number to the OH group.
- Place the number identifying the location of the OH group immediately before the name of the parent hydrocarbon, separated by a dash. Alkyl groups (and their numbers) are placed in front of the number identifying the location of the OH.

**EXAMPLES:**  $\text{CH}_3\text{-OH}$  = methanol (commercial name = methyl hydrate)

$\text{CH}_3\text{-CH}_2\text{-OH}$  = ethanol ("beverage alcohol")

$\text{CH}_3\text{-CH(OH)-CH}_2\text{-CH}_3$  = 2-butanol

$\text{CH}_3\text{-CH(CH}_3\text{)-CH}_2\text{-CH(OH)-CH}_2\text{-CH}_3$  = 5-methyl-3-hexanol

### Properties of Alcohols

- Two opposing solubility tendencies exist in alcohols:
  - The polar OH group tends to make alcohols soluble in water.
  - The non-polar hydrocarbon chain tends to make alcohols insoluble in water.
- Methanol, ethanol and propanol are highly soluble in water ("miscible") because the hydrocarbon chain is small and the hydrogen-bonding of the OH group to water molecules "wins out."
- Butanol is moderately soluble in water as a result of a "tie" between the tendency of the OH group to promote solubility and the tendency of the longer hydrocarbon chain to resist dissolving.
- Pentanol and higher alcohols are effectively insoluble in water as a result of the increasing dominance of the hydrocarbon chain.
- Alcohols are frequently used as solvents for other organic compounds.
- All alcohols are poisonous; ethanol is no exception – it is simply less poisonous than other alcohols.
- Most liquid alcohols have a "sharp" odour.

### EXERCISES:

32. Draw the following compounds.

- |                                    |                               |
|------------------------------------|-------------------------------|
| a) 1-butanol                       | b) 2,5-diethyl-1-cyclohexanol |
| c) 2-methyl-1-cyclopentanol        | d) 3-methyl-1-pentanol        |
| e) 2,2-dichloro-3-methyl-4-nonanol | f) 1,1,1-trifluoro-2-propanol |

33. Name the following compounds.

- |                                                    |                                                           |                                                        |
|----------------------------------------------------|-----------------------------------------------------------|--------------------------------------------------------|
| a) $\text{CH}_3\text{-CH(OH)-CH}_3$                | b) $\text{CF}_3\text{-CH}_2\text{-CH(OH)-CH}_3$           | c) $\text{CH}_2\text{-CH}_2\text{-CH(OH)-CH}_3$        |
| d) $\text{CH}_3\text{-C(CH}_3\text{)}_2\text{-OH}$ | e) $\text{CH}_2\text{-CH(OH)-CH}_2\text{-CH}_2\text{-Cl}$ | f) $\text{CH}_3\text{-HC(CH}_3\text{)-CH}_2\text{-OH}$ |

## B. AMINES AND NITRO COMPOUNDS

**Definitions:** An **amine** is an organic compound containing an  $\text{NH}_2$  group.

A **nitro compound** is an organic compound containing an  $\text{NO}_2$  group.

The group names are:  $-\text{NH}_2$  = amino and  $-\text{NO}_2$  = nitro.

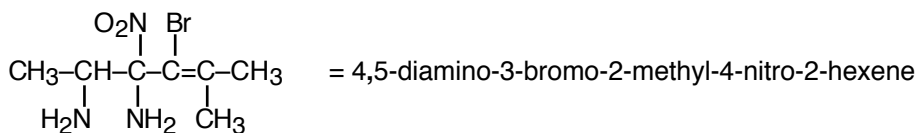
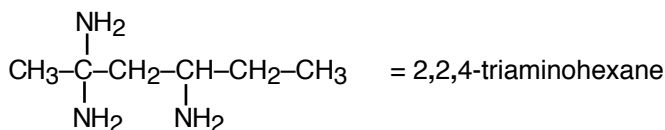
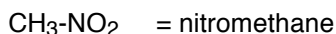
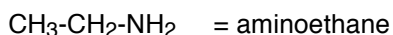
(Note that the “o” endings are the same as those used with the halo compounds.)

The naming rules for amines and nitro compounds are similar to those used for alkyl halides.

**RULES:** a) Use a number to indicate the position of attachment on the hydrocarbon chain.  
 b) If more than one of the same group is present, use the prefixes di, tri, etc.  
 c) Start numbering from the end giving the lowest set of numbers to the amine or nitro group.

**Note:** If a compound contains more than one of an attached group (such as an alkyl, halo, amino, nitro), list the attached groups in alphabetical order, disregarding prefixes such as di, tri, etc. Cyclic groups, such as cyclopropyl, are alphabetized as beginning with “c,” not “p” for “propyl.”

**EXAMPLES:**



(In this last example, note that there is no “cis/trans” terminology required.)

### Properties of Amines and Nitro Compounds

#### 1. Amines:

- a) often have a “fishy” smell or very foul odour
- b) are generally soluble in water. For example:  

$$\text{CH}_3\text{-NH}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{CH}_3\text{-NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$$
- c) are organic BASES and form SALTS when reacted with ACIDS. For example:  

$$\text{CH}_3\text{-NH}_2(\text{g}) + \text{HCl}(\text{aq}) \longrightarrow \text{CH}_3\text{-NH}_3^+(\text{aq}) + \text{Cl}^-(\text{aq})$$

#### 2. Nitro Compounds:

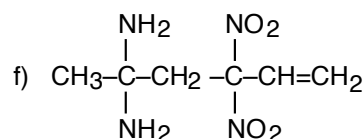
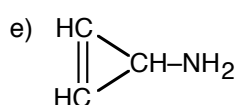
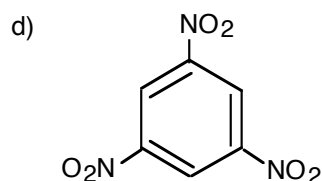
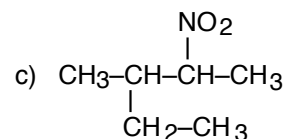
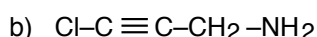
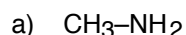
- a) are normally insoluble in water. The nitro group is not polar enough to allow such solubility.
- b) are unreactive to chemical attack, except under drastic conditions.
- c) normally have somewhat pleasant odours.
- d) Many are explosive. For example: “TNT” = trinitrotoluene, nitroglycerine, “guncotton” = nitrocellulose.

**EXERCISES:**

34. Draw the following compounds.

- |                                |                                                       |
|--------------------------------|-------------------------------------------------------|
| a) bromochlorodinitromethane   | b) 1,3-dinitrocyclobutane                             |
| c) trans-2,3-diamino-2-pentene | d) 1,4-diamino-1-cyclohexene                          |
| e) 1,3-dinitrobenzene          | f) 1-amino-3-bromo-5-ethyl-2-methyl-4-nitro-2-heptene |

35. Name the following compounds.

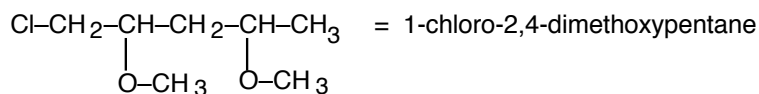
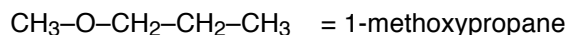

**C. ETHERS**

**Definition:** An **ether** is a compound in which an oxygen joins two hydrocarbon groups.

**RULES:** When naming an ETHER:

- The larger of the two hydrocarbon groups is taken to be the PARENT hydrocarbon.
- The smaller group, *together with the oxygen atom*, is renamed by changing the ANE ending to OXY. For example:  $\text{CH}_3\text{-O-}$  = meth**oxy**,  $\text{CH}_3\text{-CH}_2\text{-O-}$  = eth**oxy**, etc.
- The rest of the naming is similar to that for alkyl groups, halides, amines and nitro compounds.

**EXAMPLES:**


**Properties of Ethers**

- highly flammable
- very weakly polar and hence are insoluble in water
- good solvents for other organic compounds.
- Several ethers have anaesthetic properties. Ethoxyethane was formerly used in hospitals and is still used by biologists to "quiet" or anaesthetize insects.

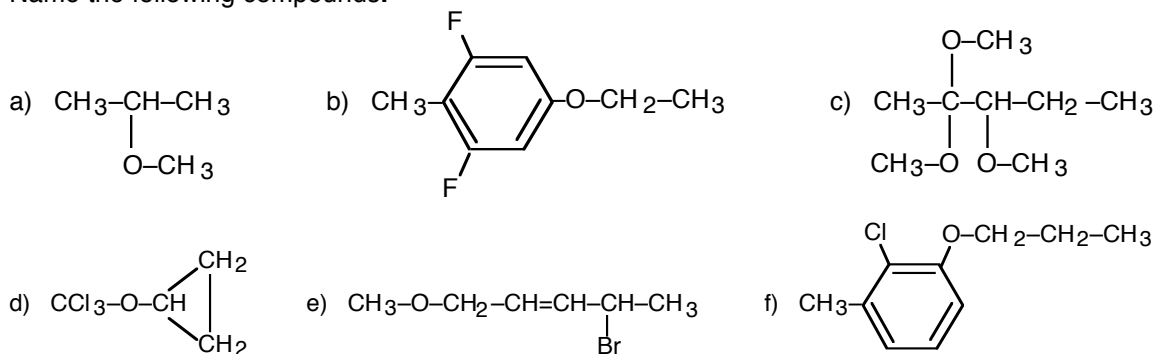


### EXERCISES:

36. Draw the following compounds.

- |                        |                           |
|------------------------|---------------------------|
| a) methoxymethane      | b) 2,3-diethoxybutane     |
| c) 1-propoxypentane    | d) cyclobutoxycyclobutane |
| e) 1,2-dimethoxyethane | f) 1,3,5-triethoxybenzene |

37. Name the following compounds.



## D. ALDEHYDES

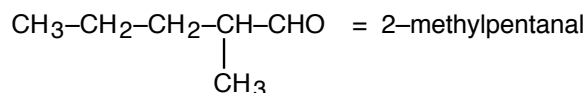
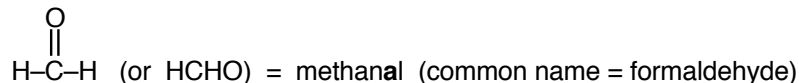
**Definition:** An **aldehyde** is an organic compound containing a C=O group at the **end** of a hydrocarbon chain. The C=O group is called the **CARBONYL GROUP**.

The aldehyde group looks like  $\begin{array}{c} \text{O} \\ \parallel \\ \text{--C} \\ | \\ \text{H} \end{array}$  and can also be written as  $\text{--CHO}$

**RULES:** When naming an ALDEHYDE:

- Drop the “e” ending from the name of the parent hydrocarbon and add “al”. (The ending **al** comes from **aldehyde**.)
- The numbering of the carbon atoms starts at the C in the aldehyde group.

**EXAMPLES:**



## Properties of Aldehydes

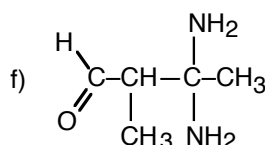
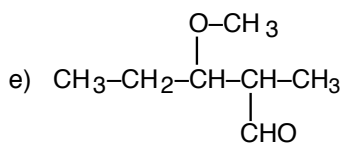
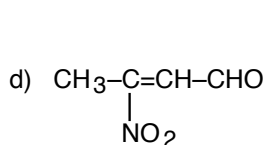
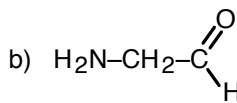
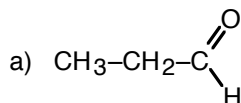
- Because the carbonyl group is polar, aldehydes are soluble to at least a limited extent in polar solvents such as water.
  - Methanal is a gas and is very soluble in water.
  - Ethanal is a liquid that boils at  $21^\circ\text{C}$  and is also miscible with water.
  - Propanal boils at  $49^\circ\text{C}$  and is soluble in water.
- The polar carbonyl group creates dipole-dipole forces that cause aldehydes to have higher melting and boiling temperatures than alkanes and ethers of similar molar masses.
- Lower molar mass aldehydes have strong odours but some with higher molar masses have pleasant odours and are used in perfumes.
- Aldehydes are very reactive and are easily converted to carboxylic acids (see Section G).

**EXERCISES:**

38. Draw the following compounds.

- |                    |                                |
|--------------------|--------------------------------|
| a) butanal         | b) 3-pentynal                  |
| c) 3-ethylhexanal  | d) 3-nitropropenal             |
| e) 2-aminopropanal | f) 2-amino-4-methyl-3-pentenal |

39. Name the following compounds.



## E. KETONES

**Definition:** A **ketone** is an organic compound containing a C=O (carbonyl) group at a position OTHER THAN AT THE END OF A HYDROCARBON CHAIN.

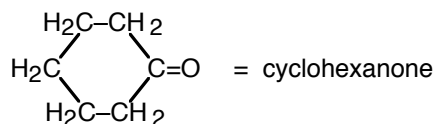
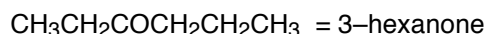
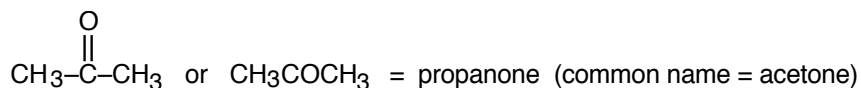
**RULES:** When naming a KETONE:

- Drop the “e” ending from the name of the parent hydrocarbon and add “one”. (The ending **one** comes from **ketone**.)
- The position of the C=O group along the hydrocarbon chain is indicated by a number.
- Numbering of the parent hydrocarbon chain starts from the end that give the carbonyl carbon the lowest possible number.

The carbonyl group is sometimes shown as CO. For example:  $\text{CH}_3\text{COCH}_3$ .

**SPECIAL NOTE:** There is no need to add position numbers to functional groups if there is only one possible place for the group. As examples, propanone (1<sup>st</sup> example, below) does not require a “2” in front of its name. Similarly, in the third example, cyclohexanone does not require a number because all positions on the ring are equivalent and a lone functional group (or branch) on a ring is automatically assumed to be at position “1-.”

**EXAMPLES:**



## Properties of Ketones

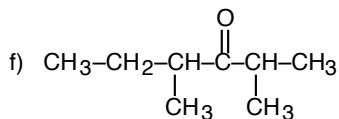
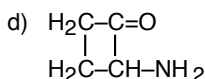
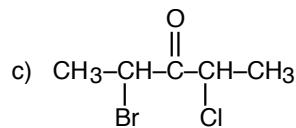
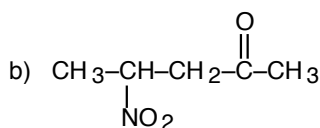
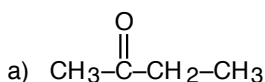
- Similar to aldehydes, ketones are strongly polar. Propanone is miscible in water, while butanone is moderately soluble in water and miscible with several organic solvents.
- Similar to aldehydes, the polar carbonyl group in ketones gives them higher melting and boiling temperatures than alkanes and ethers having similar molar masses.
- Ketones are relatively unreactive.

**EXERCISES:**

40. Draw the following compounds.

- |                                     |                                    |
|-------------------------------------|------------------------------------|
| a) 1-bromo-2-pentanone              | b) 1,3-diethoxypropanone           |
| c) cyclopropanone                   | d) 3,5-dinitrocyclohexanone        |
| e) 4-chloro-2,2-dimethyl-3-hexanone | f) 5-amino-2,4-dimethyl-3-octanone |

41. Name the following compounds.



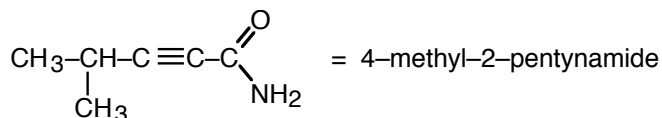
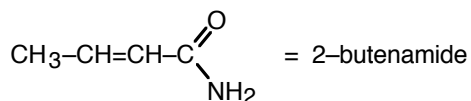
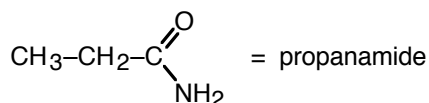
## F. AMIDES

**Definition:** An **amide** is an organic compound containing a  $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C} \\ | \\ \text{NH}_2 \end{array}$  ( $\text{CONH}_2$ ) group.

**RULES:** When naming an AMIDE:

- Drop the 'e' ending from the name of the parent hydrocarbon and add "amide".
- Numbering is started with the C atom in the amide group.

**EXAMPLES:**



### Properties of Amides

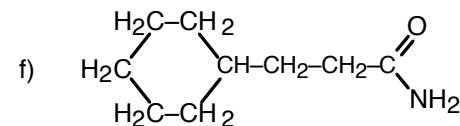
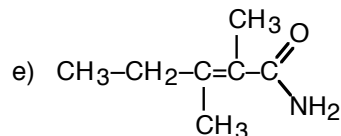
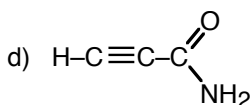
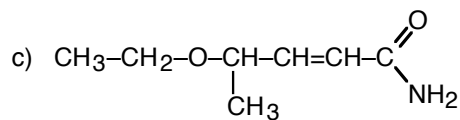
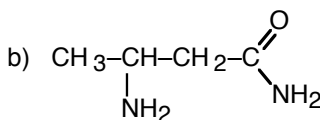
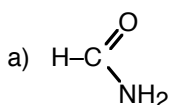
- Amides are very weakly basic.
- Most amides are insoluble in water.

**EXERCISES:**

42. Draw the following compounds.

- |                          |                          |                                  |
|--------------------------|--------------------------|----------------------------------|
| a) pentanamide           | b) cyclopropylethanamide | c) 2-methylbutanamide            |
| d) 3-chloro-2-butenamide | e) chloromethanamide     | f) 2-bromo-3-chloro-4-hexynamide |

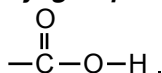
43. Name the following compounds.





## G. CARBOXYLIC ACIDS

**Definition:** A **carboxylic acid** is an organic compound containing a COOH group. The COOH group is known as a **carboxyl group** and is sometimes shown as:



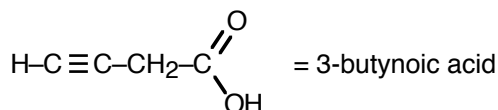
**RULES:** When naming a CARBOXYLIC ACID:

- Drop the "e" ending from the name of the parent hydrocarbon and add "oic acid".
- Numbering is started with the C atom in the carboxyl group.

**EXAMPLES:** CH<sub>3</sub>COOH = ethanoic acid (common name = acetic acid; vinegar is 5% acetic acid)

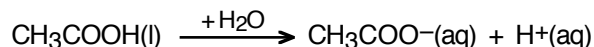
HCOOH = methanoic acid (common name = formic acid; the acid injected by red ants)

Br-CH<sub>2</sub>-CH<sub>2</sub>-COOH = 3-bromopropanoic acid



## Properties of Carboxylic Acids

- As would be expected from the name, carboxylic acids are commonly referred to as "organic acids".
- Carboxylic acids tend to be soluble in water and form ions. For example:



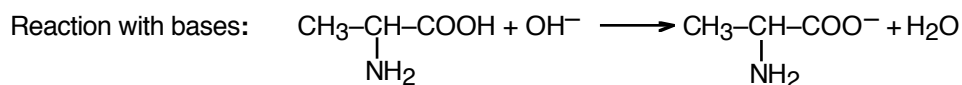
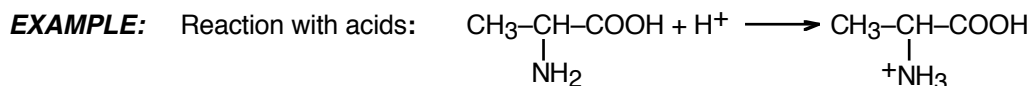
- Most liquid carboxylic acids have a sharp, pungent and biting odour which is often quite unpleasant. For example, butanoic acid has the odour of "rancid sneakers," only FAR MORE CONCENTRATED!

## A Digression on Amino Acids

An **amino acid** is a carboxylic acid with an amine group at the 2-position. Although there are numerous amino acids, only 20 different amino acids are essential biological "building blocks."

**EXAMPLE:**  $\text{CH}_3-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}$  = 2-aminopropanoic acid (common name = alanine)

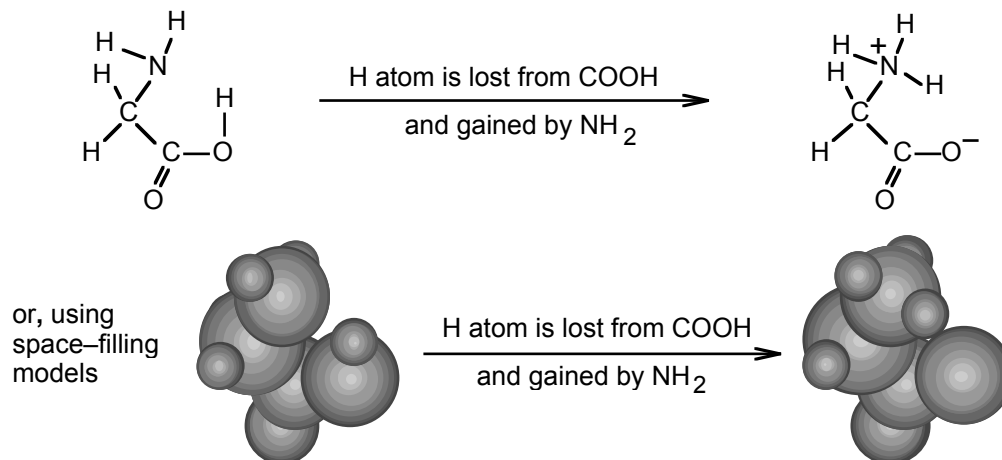
Amino acids can react with both acids and bases.



After reacting with either an acid or base the amino acid is ionic and remains soluble in water.

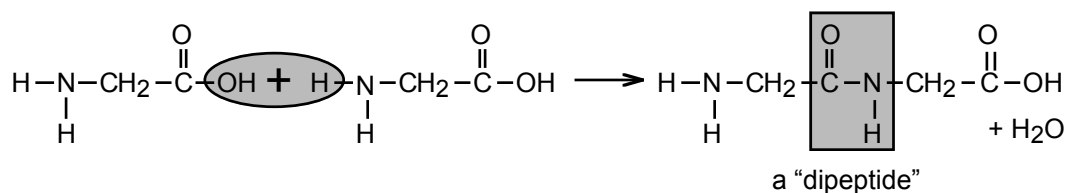
There are two properties of amino acids which are especially important.

- a) **Amino acids are highly soluble in water** because amino acids have both acid and base groups arranged such that the acid and base groups can "neutralize" each other.

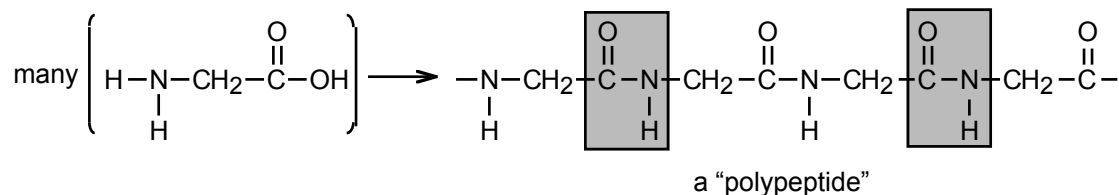


The resulting ionic compound is highly soluble in water.

- b) **Amino acids link with each other to form "dipeptides" and "polypeptides."**



The shaded oval, above, shows how water is removed from two molecules and allows the molecules to link together. The box indicates that the molecules are now joined together by an "amide linkage" (or "peptide bond" or "peptide linkage").



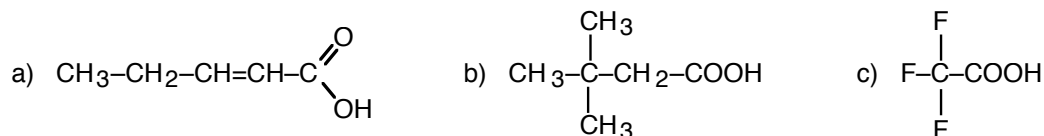
As seen above, a series of amino acid molecules can be joined by a series of linkages to form a polypeptide.

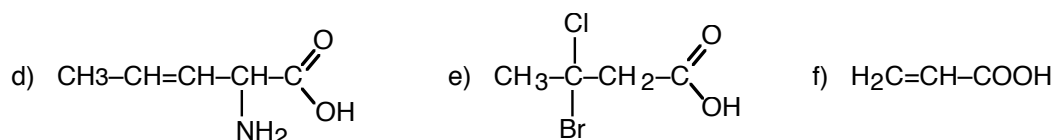
### EXERCISES:

44. Draw the following compounds.

- |                           |                                  |
|---------------------------|----------------------------------|
| a) butanoic acid          | b) 2-chloro-3-heptynoic acid     |
| c) 2-aminopropanoic acid  | d) 3-cyclopropoxybutanoic acid   |
| e) trichloroethanoic acid | f) 3,4-dimethyl-2-pentenoic acid |

45. Name the following compounds.





## H. ESTERS

**Definition:** An **ester** is an organic compound in which the hydrogen of a COOH group is replaced by a hydrocarbon group.

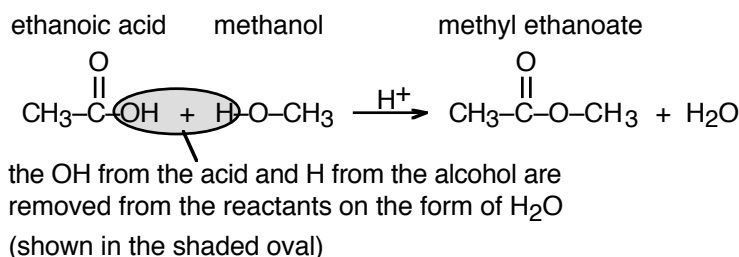
**RULES:** When naming an ESTER:

- The hydrocarbon chain attached directly to the carbon side of the COO group has its "e" ending changed to "oate". The C in the COO group is considered to be part of the parent hydrocarbon chain.
- The hydrocarbon chain attached to the oxygen side of the COO group is named as an alkyl group; the name of the alkyl group is used as a separate, initial word.

**EXAMPLES:**  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-COO-CH}_3$  = methyl butanoate  
 $\text{HCOO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$  = butyl methanoate  
 $\text{CH}_3\text{-CH}_2\text{-COO-CH}_2\text{-CH}_3$  = ethyl propanoate  
 $\text{CH}_3\text{-COO-CH}_2\text{-CH}_2\text{-CH}_3$  = propyl ethanoate

## Preparation and Properties of Esters

Esters are prepared by reacting an organic acid and an alcohol in the presence of an inorganic acid such as HCl or  $\text{H}_2\text{SO}_4$ . In the example below, ethanoic acid reacts with methanol (written backwards); the " $\text{H}^+$ " over the reaction arrow indicates that  $\text{H}^+$  is used as a catalyst.



The actual experimental procedure for producing small amounts of impure esters is quite simple.

Mix a few millilitres of the desired carboxylic acid and a few millilitres of the desired alcohol. Add a few drops of a catalyst and heat for a minute or so. Be sure not to overheat the liquid. (The distinctive presence of the ester is detected by cautiously smelling the resulting mixture.)

Recall that carboxylic acids have a sharp, pungent and biting odour. Alcohols also have a "sharp" odour, although generally less so than that of acids having a similar number of carbon atoms. Methanol and ethanol have very little odour but their smell tends to "catch" in the nasal passage. Propanol and higher alcohols have more intense and often unpleasant odours which also tend to "catch" in the nasal passage.

The odour of esters, on the other hand, is generally very pleasant. In small amounts, esters form the basis of many fragrant fruit and flower smells.

**EXAMPLE:**

Ester	Odour	Ester	Odour
methyl butanoate	pineapple	nonyl octanoate	orange
pentyl ethanoate	banana	propyl ethanoate	pear
ethyl pentanoate	apple	2-methylpropyl methanoate	raspberry



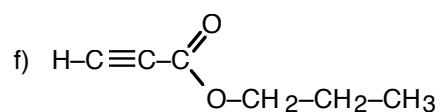
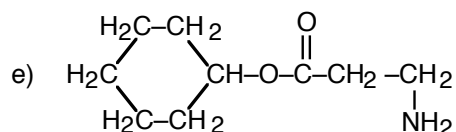
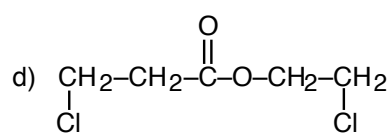
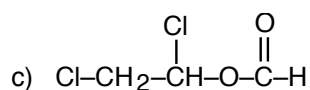
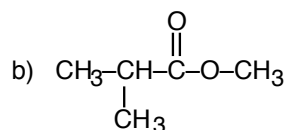
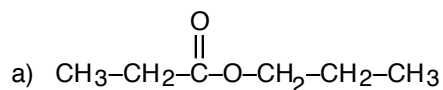
**The new Chemistry 11 teacher is about to find that not all esters have a pleasant smell.**

**EXERCISES:**

46. Draw the following compounds.

- |                              |                                            |
|------------------------------|--------------------------------------------|
| a) methyl methanoate         | b) methyl 2-butynoate                      |
| c) ethyl butanoate           | d) cyclopentyl 2-amino-3-methoxypropanoate |
| e) 2-methylpropyl propanoate | f) propyl 2,3-dimethoxyhexanoate           |

47. Name the following compounds.



## I. PHENOLS

**Definition:** A **phenol** is an organic compound containing a hydroxyl group (OH) attached to an aromatic ring.

Although phenols appear to be just another type of alcohol, their chemical and physical properties are actually very different. As a result, a hydroxyl group attached to a carbon in an aromatic compound can be considered to be a separate functional group.

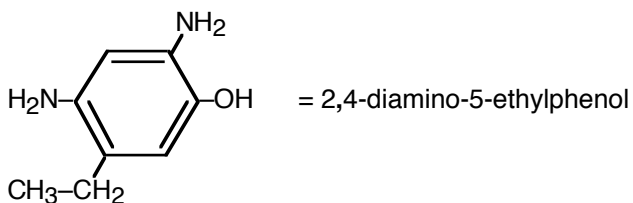
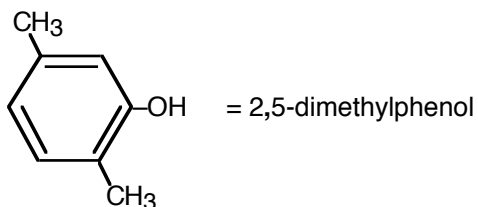
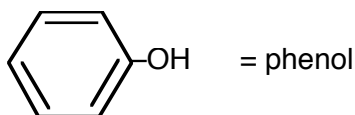
The IUPAC naming scheme used for phenols is more complicated than that used for other functional groups. We must examine 2 cases:

### a) A single OH group attached to a benzene ring

**RULES:** To name a PHENOL having a single OH group attached to a benzene ring:

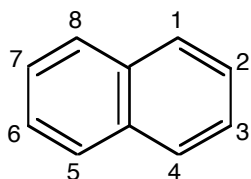
- The “parent” name is “phenol” and attached groups are named in the same manner as when groups are attached to an alkane.
- The hydroxyl group is assumed to be at ring position “1”.
- Continue the numbering towards the carbon having the substituent closest to the hydroxyl group.

#### EXAMPLES:



### b) Two or more OH groups attached to aromatic ring systems

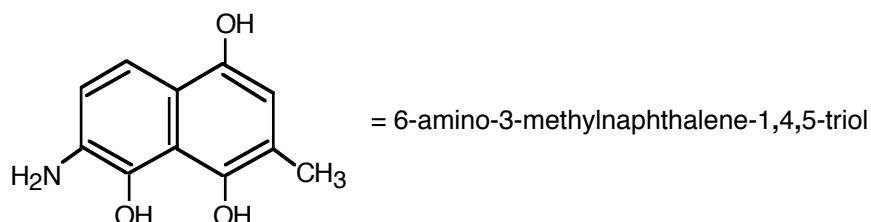
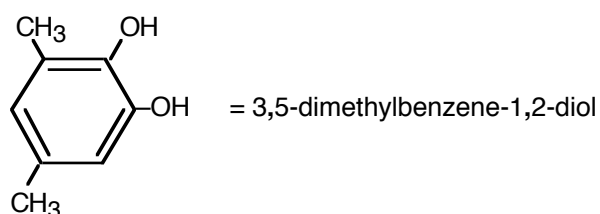
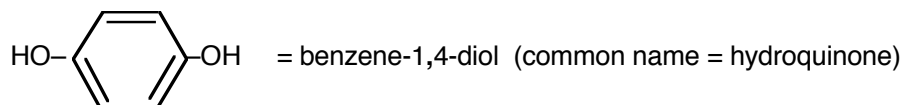
We will use benzene and naphthalene as examples of aromatic rings. The aromatic compound **naphthalene** has the numbering system shown below. These numbers are always used, regardless of the priority of attached functional groups.



**RULES:** To name a PHENOL having two or more OH groups attached to an aromatic ring:

- The “parent” name is the name of the aromatic ring (eg. benzene, naphthalene) and attached groups are named in the same way as when groups are attached to an alkane.
- The position of each hydroxyl group is indicated by adding a position-numbering suffix such as diol, triol, tetrol. (See examples below to make this clear.)

**EXAMPLES:**



## Properties of Phenols

- The OH group on phenols is more polar than the OH group in alcohols. As a result, phenols are less acidic than carboxylic acids, but more acidic than alcohols.
- Phenols tend to be soluble in water, as a result of the polar hydroxyl group.
- Phenol molecules tend to form hydrogen bonds amongst themselves, leading to higher melting and boiling temperatures relative to similar molecules lacking the hydroxyl group.
- The reactivity of the hydroxyl group gives many phenols important biological functions and effects. For example, phenol itself is toxic and can burn the skin on contact, although dilute solutions have antiseptic properties.

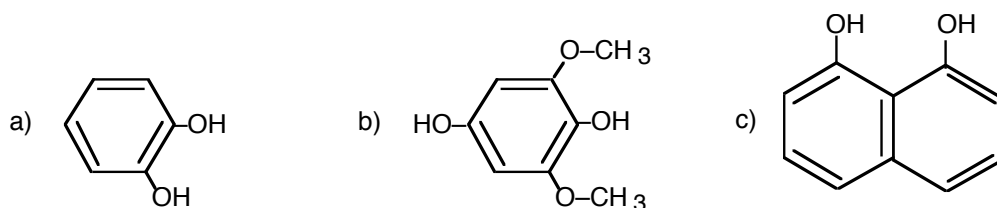
**Note:** Many of the biologically important phenols have structures that are too complicated to name and draw using the simple naming conventions introduced in Chemistry 11.

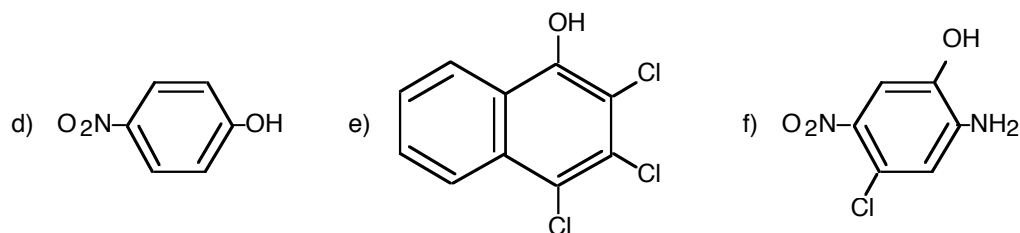
**EXERCISES:**

48. Draw the following compounds.

- |                                    |                                              |
|------------------------------------|----------------------------------------------|
| a) 1,3-dihydroxybenzene            | b) 4-bromo-2-hydroxy-1-methylnaphthalene     |
| c) 7-amino-2-hydroxynaphthalene    | d) 1-hydroxy-3-methoxy-5-nitrobenzene        |
| e) 1-hydroxy-2,4,6-trinitrobenzene | f) 2,3,5-trichloro-1-hydroxy-4-methylbenzene |

49. Name the following compounds.





## X.7 A SUMMARY OF THE FUNCTIONAL GROUPS

The functional groups that have been introduced in this unit are shown below (except for phenols which are special cases).

### A. GROUPS ADDING A PREFIX TO THE HYDROCARBON NAME

Group name	Group	Prefix
Halogen	F, Cl, Br, I	fluoro, chloro, bromo, iodo
Amine	NH <sub>2</sub>	amino
Nitro	NO <sub>2</sub>	nitro
Ether	R-O (*)	<b>Alkoxy</b> (“ <i>alkoxy</i> ” derived from parent <i>alkane</i> )

(\*) “R” is a general term used to indicate a hydrocarbon chain.

### B. GROUPS MODIFYING THE ENDING OF THE HYDROCARBON NAME

Group Name	Functional Group	Ending Dropped	Ending Added
Alkene	C = C	ane	ene
Alkyne	C ≡ C	ane	yne
Alcohol	R-OH	e	ol
Aldehyde	R-CHO	e	al
Ketone	R <sub>1</sub> -CO-R <sub>2</sub>	e	one
Amide	R-CONH <sub>2</sub>	e	amide
Carboxylic Acid	R-COOH	e	oic acid
Ester	R <sub>1</sub> -COO-R <sub>2</sub>	e	oate

### ADDITIONAL MIXED EXERCISES:

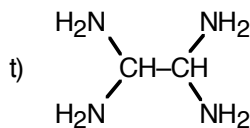
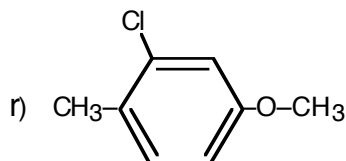
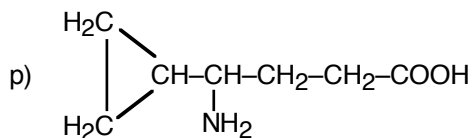
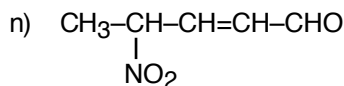
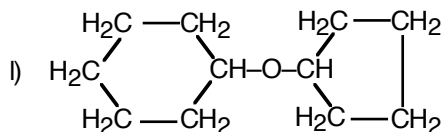
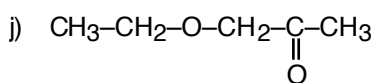
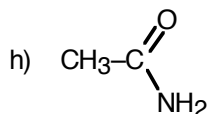
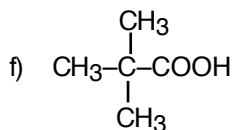
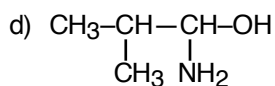
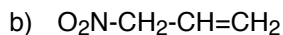
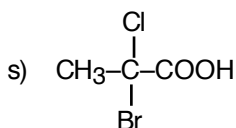
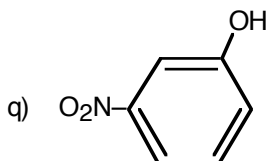
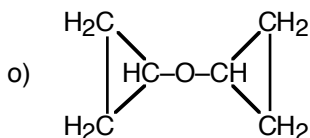
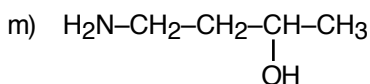
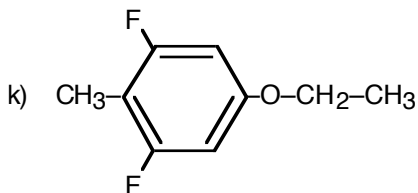
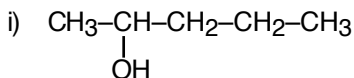
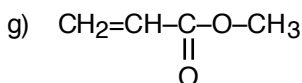
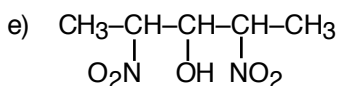
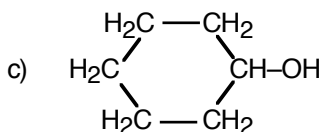
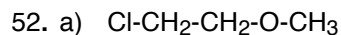
50. Which group of organic compounds:

- can neutralize bases?
- are easily converted to carboxylic acids?
- often smell fishy?
- are very weakly basic
- can be prepared by reacting a carboxylic acid with an alcohol?
- are fairly strong bases?
- have fruity odours?
- are often explosive?
- are especially flammable and are good solvents?

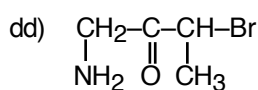
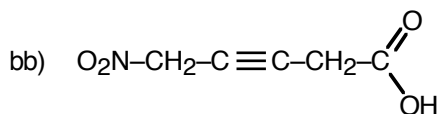
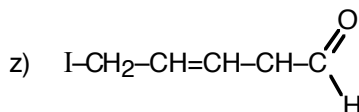
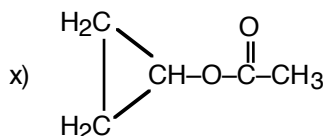
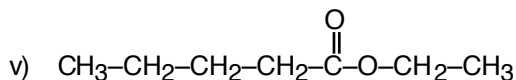
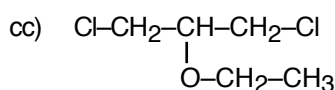
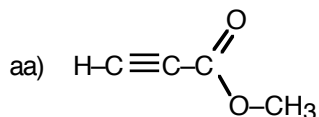
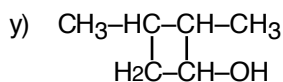
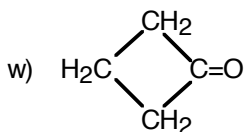
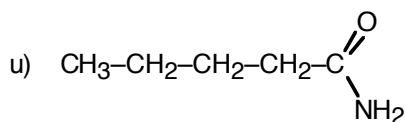
51. Draw the following compounds.

- 2-chloroethyl ethanoate
- 3-cyclopentenone
- 3-pentanol
- chloromethanoic acid
- 2-nitrobutane
- 1-amino-4,4-difluoro-2-pentanol
- dichloroethanoic acid
- propyl 2-methylbutanoate

- |                                       |                                     |
|---------------------------------------|-------------------------------------|
| i) 2-bromo-3-chloro-2-butenamide      | j) 4-nitro-3-butenal                |
| k) 1,2,4-triaminobenzene              | l) 3-bromo-2,3-dimethyl-2-butanol   |
| m) hexyl pentanoate                   | n) 1,3-diaminohexane                |
| o) ethenol                            | p) methoxybenzene                   |
| q) 3-cyclopropyl-4-methyl-2-pentanone | r) cyclopentanone                   |
| s) 2-chloro-3-pentenoic acid          | t) 1-bromo-3-chlorobenzene          |
| u) ethyl ethanoate                    | v) dinitromethane                   |
| w) methanamide                        | x) hexyl pentanoate                 |
| y) cycloheptanol                      | z) benzene-1,2,3-triol              |
| aa) 1,4-diaminobenzene                | bb) 2-bromo-3-chloro-2-butenamide   |
| cc) methyl 2,3-dimethoxypropanoate    | dd) 3,7-dinitronaphthalene-2,6-diol |







## X.8 ORGANIC SYNTHESIS

We shall look at four types of organic reactions:

- reactions in which a group is **displaced** by another group
- reactions in which a group is **altered**, but not replaced
- reactions which **add** across double and triple bonds, and
- reactions in which a hydrogen on a benzene ring is **substituted** by functional groups

There are hundreds of different types of organic reactions. So as not to overwhelm you, we will consider just a few reactions to let you see how some organic compounds react and can be transformed into other compounds. Each reaction is demonstrated by a typical example. In two cases, the reactions are very similar to inorganic reactions, which are shown in square brackets after the organic reaction.

To avoid being confused by the presence of non-reacting carbon chains, sometimes we shall use the symbols R, R<sub>1</sub>, R<sub>2</sub> to mean “a non-reacting part of a hydrocarbon chain.” For example, CH<sub>3</sub>CH<sub>2</sub>–OH becomes R–OH, CH<sub>3</sub>–NH<sub>2</sub> becomes R–NH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>–COOH becomes R–COOH, etc.

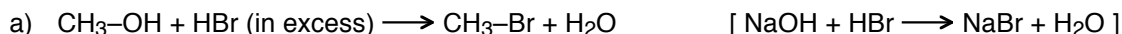
Some of the reactions to be shown have symbols above the reactions' arrows:

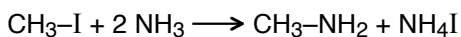
$\xrightarrow{[\text{O}]}$  : [O] above the arrow means “oxidizing conditions,” which means “conditions that remove two H atoms OR add an oxygen atom.”

$\xrightarrow{\text{H}^+}$  : H<sup>+</sup> above the arrow means “acidic conditions.”

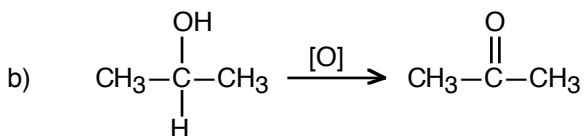
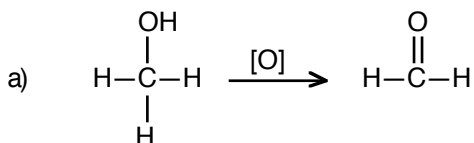
### A. DISPLACEMENT REACTIONS

Halides and OH groups can displace each other



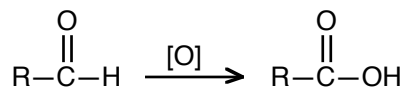
**Synthesis of amines from iodo compounds** (does *not* work with the other halogens)

**B. GROUP-ALTERING REACTIONS**


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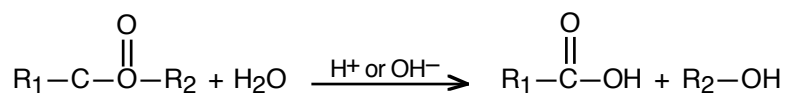
**Conversion of alcohols to aldehydes and ketones**


**Note:** In both reactions,  $\begin{array}{c} | \\ \text{H}-\text{C}-\text{OH} \\ | \end{array}$  is converted to  $\begin{array}{c} | \\ \text{C}=\text{O} \\ | \end{array}$ , that is, two H atoms are removed.

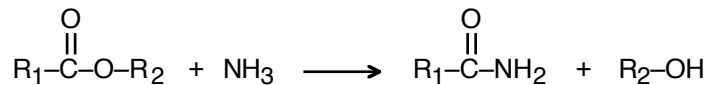
If the OH group is at the end of a chain, an aldehyde is produced; if the OH group is in the middle of a chain, a ketone is formed.

**Conversion of aldehydes to carboxylic acids**


Aldehydes are unstable and decompose slowly to form carboxylic acids as a result of the presence of oxygen in the air.

**Decomposition of esters to carboxylic acids and alcohols**


This is the opposite of the reaction that forms an ester.

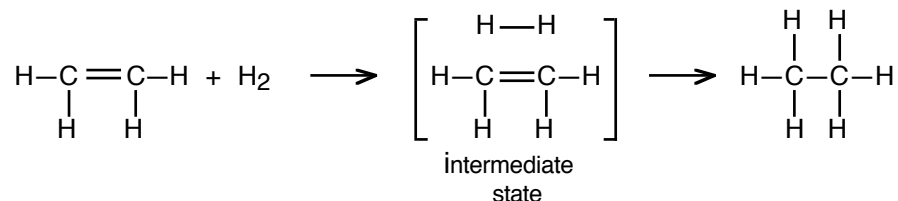
**Conversion of esters to amides**


## C. ADDITION ACROSS DOUBLE AND TRIPLE BONDS

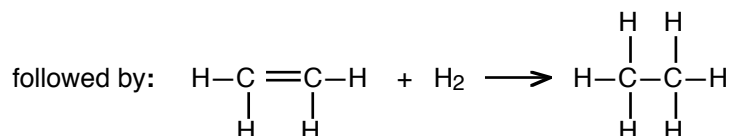
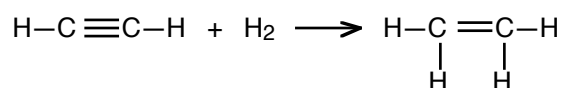
Compounds having double and triple bonds are said to be **unsaturated** because the carbon atoms involved have not used up their capacity to bond to more atoms.

### Reaction with hydrogen

Addition to a double bond:

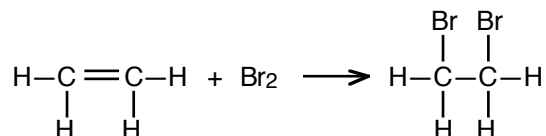


Addition to a triple bond:

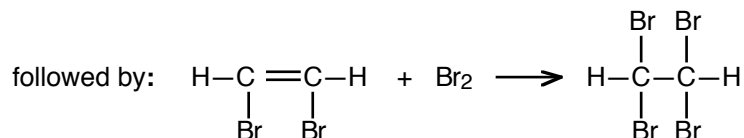
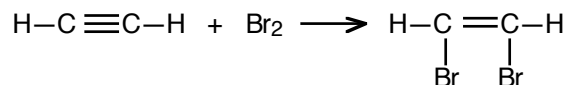


### Reaction with halogens

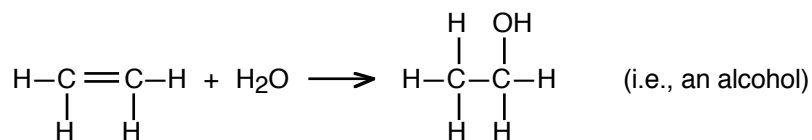
Addition to a double bond:



Addition to a triple bond:



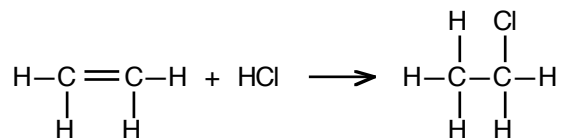
### Reaction with water (i.e. H-OH)



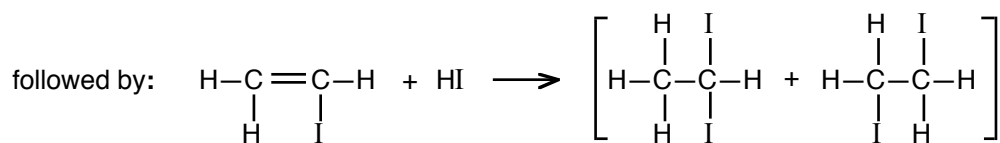
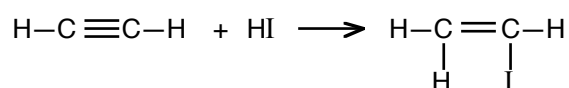
The reaction of water with triple bonds is too complicated for us to consider here. (The results are not what you might expect!)

**Reaction with halogen acids** (eg. HCl, HBr, HI)

Addition to a double bond:



Addition to a triple bond:

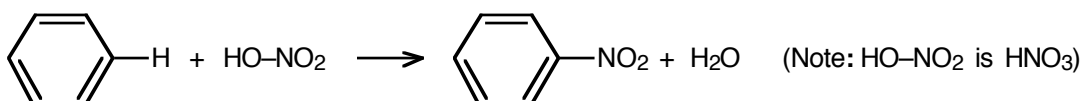
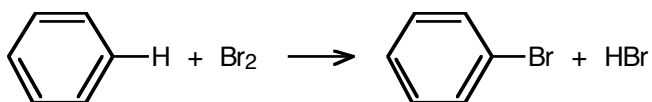


Note that the final result is a mixture of two different isomers since the iodine atom can add to either end of  $\text{CH}_2=\text{CH}-\text{I}$ .

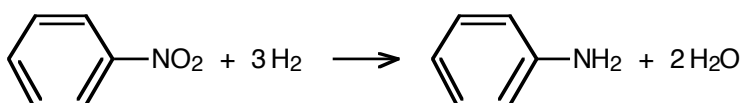
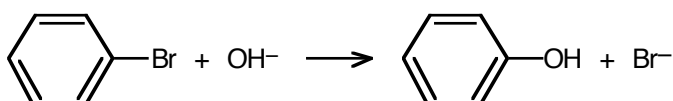
**D. SUBSTITUTION REACTIONS ON A BENZENE RING**


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Because the double bonds in benzene are VERY unreactive, addition to the double bonds does **not** occur. The only reaction that occurs is the *substitution* of a functional group for a ring hydrogen.



Once a substituent is on the ring, the substituent can react further.

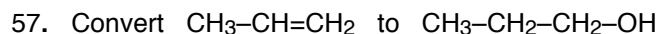
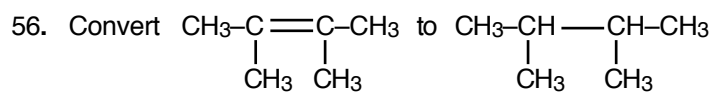

**EXERCISES:**

Write the reactions for the following.

53. Convert  $\text{CH}_3\text{CH}_2\text{I}$  to  $\text{CH}_3\text{CH}_2\text{OH}$

54. Convert  $\text{CH}_3\text{CH}_2\text{I}$  to  $\text{CH}_3\text{CH}_2\text{NH}_2$

55. Convert  $\text{CH}_3\text{CH}_2\text{OH}$  to  $\text{CH}_3\text{C}(=\text{O})\text{H}$

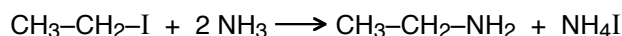
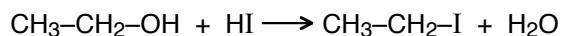


### MULTI-STEP SYNTHESIS REACTIONS

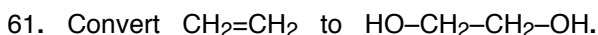
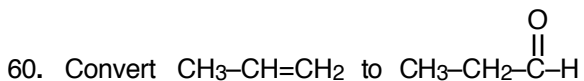
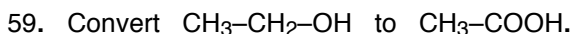
The next set of exercises require you to start with a compound, react it to convert it to another compound and repeat the process one or more times. A good way to think your way through the sequence of reactions is to look at the final product and decide what compound (or compounds) must have existed that could react to create the final product. Then, decide what compounds must have existed to create this next-to-last compound. In this way, you can work your way back to the original compound. (Note: this “working backwards” process is similar to the highly-recommended procedure used when proving geometry theorems.)

**EXAMPLE:** Convert  $\text{CH}_3-\text{CH}_2-\text{OH}$  to  $\text{CH}_3-\text{CH}_2-\text{NH}_2$ .

You have not been shown any reaction that converts an  $-\text{OH}$  group directly to an  $-\text{NH}_2$  group, so this must require at least 2 steps. Looking at the desired product, an  $-\text{NH}_2$  group is created by reacting ammonia,  $\text{NH}_3$ , with an iodo compound. But an iodo group is created by reacting  $\text{HI}$  with an alcohol. Aha! We are starting with an alcohol. So ...



### EXERCISES:



- a) aminoethane?      b) ethyl ethanoate?      c) ethanamide?

