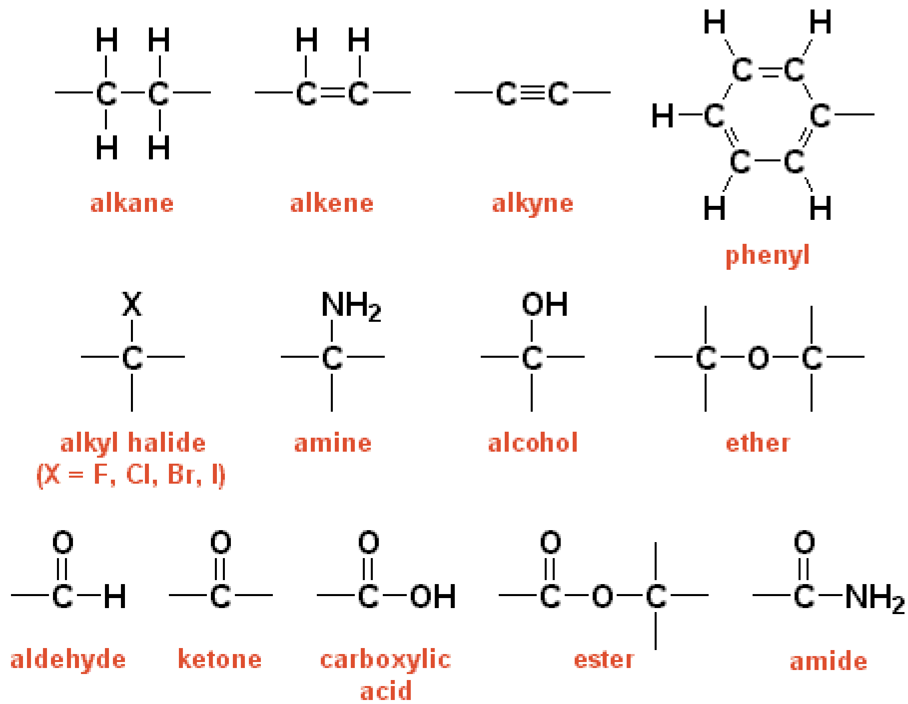
Hydrocarbons and their Functional Groups

- Organic chemistry is the study of compounds in which carbon is the principal element.
    - carbon atoms form four bonds
    - long chains, rings, spheres, sheets, and tubes
    - single, double, triple covalent bonds

- Chemists have produced a wide variety of carbon-based, or **organic compounds**.
    - Organic compounds fall into groups according to particular combinations of atoms in each molecule → the groups are called **organic families.**



An **organic family** is a group of organic compounds with common structural features that impart characteristic physical and chemical properties.

- The particular combinations of atoms in the molecules are called **functional groups**.

Functional group is a structural arrangement of atoms that imparts particular characteristics to the molecule.

- multiple bonds between carbon atoms
- single bond between carbon and a more electronegative atom
- a double bond between carbon and oxygen

Hydrocarbons

These organic compounds contain only hydrogen and carbon atoms.

Aliphatic hydrocarbons consist of molecules with carbon-carbon backbones, which form straight chains with one or more branched chains, or cyclic structures.

Alkanes are hydrocarbons with only single bonds between the carbon atoms → general formula C_nH_{2n+2}

- **saturated** hydrocarbons

Alkenes are hydrocarbons that contain at least one carbon-carbon double bond → C_nH_{2n}

- **unsaturated** hydrocarbons
- alkenes are also called olefins

Alkynes are hydrocarbons that contain at least one carbon-carbon triple bond → C_nH_{2n-2}

- **unsaturated** hydrocarbons

When introducing multiple bonds into an aliphatic hydrocarbon, hydrogen atoms are removed from the compound.

In **cyclic hydrocarbons**, the carbon-carbon backbone forms a closed ring structure → C_nH_{2n}

Isomers

- Compounds with the same chemical formula but different molecular arrangements and properties are called isomers.

Structural isomers

- same chemical formula, but different connectivity of the carbon-carbon backbone

Geometric isomers

- same chemical formula, but different arrangement about the double bond
  - *cis*- and *trans*- isomers

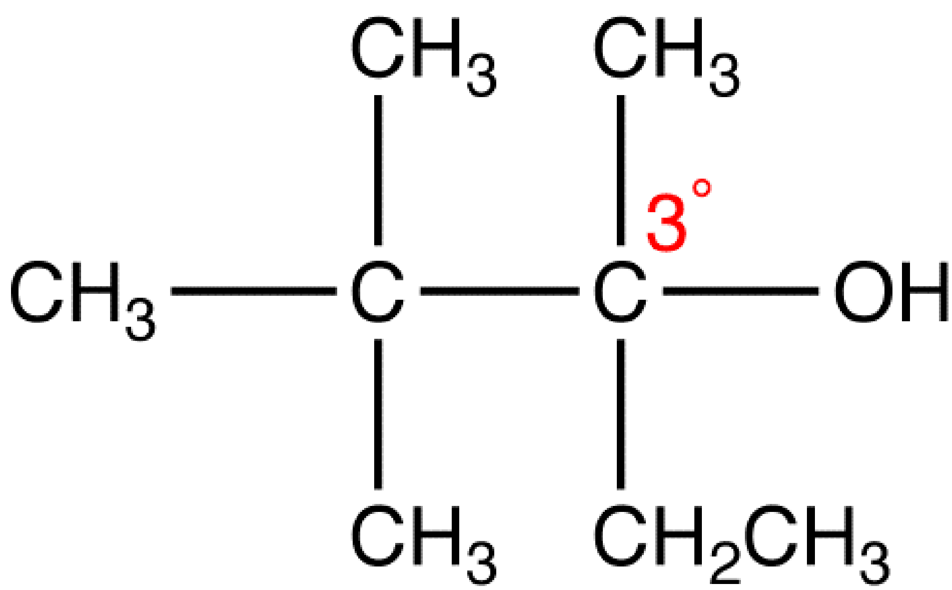
Stereoisomers

- same chemical formula, but different arrangement around a carbon atom
  - a chiral carbon has four bonds with different groups attached on each
    - *D*- and *L*-
    - (+) and (-)

Types of Carbon Atoms in Molecules

- The reactivity of carbon in a molecule depends on the atoms it is already bonded to.

Carbon Type	Definition
primary (**1**^{o}) carbon	A carbon atom that is attached to only **one** other carbon atom.
secondary (**2**^{o}) carbon	A carbon atom that is attached to **two** other carbon atoms.
tertiary (**3**^{o}) carbon	A carbon atom that is attached to **three** other carbon atoms.
quaternary (**4**^{o}) carbon	A carbon atom that is attached to **four** other carbon atoms.



Physical Properties: Hydrocarbons

- H and C have similar electronegativities, so the C-H bond is relatively nonpolar; additionally, the symmetrical nature of the bonding for carbon leads to nonpolar molecules
  - low solubility in polar solvents

- weak intermolecular forces hold the molecules of a hydrocarbon together → London dispersion
  - low boiling points and melting points (see Table 1)

Table 1. Boiling points of the first 10 alkanes

Chemical Formula	Chemical Name	b.p. (^oC)
$CH_{4(g)}$	methane	-161
$C_2H_{6(g)}$	ethane	-89
$C_3H_{8(g)}$	propane	-44
$C_4H_{10(g)}$	butane	-0.5
$C_5H_{12(l)}$	pentane	36
$C_6H_{14(l)}$	hexane	68
$C_7H_{16(l)}$	heptane	98
$C_8H_{18(l)}$	octane	125
$C_9H_{20(l)}$	nonane	151
$C_{10}H_{22(l)}$	decane	174

- as the molecules of the hydrocarbons get larger, they have more electrons/bonds
  - this creates more opportunities for intermolecular interactions to hold the molecules together

- branched hydrocarbons reduce surface area for intermolecular interaction and have lower boiling points
  - butane (-0.5^{o}C) and 2-methylpropane (-10.2^{o}C) are C_4H_{10} isomers with different boiling points

Nomenclature of Hydrocarbons

IUPAC system of nomenclature for organic compounds is based on the names of the alkane hydrocarbons.

- All alkanes end with the suffix “ane”.
- The prefix represents the number of carbon atoms in the longest continuous chain of the compound.

Prefix	IUPAC name	Formula
meth-	methane	CH_4
eth-	ethane	C_2H_6
prop-	propane	C_3H_8
but-	butane	C_4H_{10}
pent-	pentane	C_5H_{12}
hex-	hexane	C_6H_{14}
hept-	heptane	C_7H_{16}
oct-	octane	C_8H_{18}
non-	nonane	C_9H_{20}
dec-	decane	$C_{10}H_{22}$

Branched Alkanes

Hydrocarbons often form branches where smaller hydrocarbon chains stem from the parent chain.

- **alkyl** groups

With the loss of a hydrogen atom, the "ane" ending of the alkane is converted to "yl".

Alkane	Formula	Alkyl Formula	Alkyl Name
methane	CH_4	$-CH_3$	methyl-
ethane	C_2H_6	$-C_2H_5$	ethyl-
propane	C_3H_8	$-C_3H_7$	propyl-
butane	C_4H_{10}	$-C_4H_9$	butyl-
pentane	C_5H_{12}	$-C_5H_{11}$	pentyl-
hexane	C_6H_{14}	$-C_6H_{13}$	hexyl-
heptane	C_7H_{16}	$-C_7H_{15}$	heptyl-
octane	C_8H_{18}	$-C_8H_{17}$	octyl-
nonane	C_9H_{20}	$-C_9H_{19}$	nonyl-
decane	$C_{10}H_{22}$	$-C_{10}H_{21}$	decyl-

Two alkyl groups have **structural isomers**:

Alkyl	Formula	Isomers
propyl-	$-C_3H_7$	*n*-propyl, isopropyl
butyl-	$-C_4H_9$	*n*-butyl, isobutyl, *s*-butyl, *t*-butyl

Naming Branched Alkanes

Step 1 Identify the longest carbon chain; it may travel through one or more "branches".

Step 2 Number the carbon atoms, starting with the end closest to the branches.

Step 3 Name each branch and identify its location on the parent chain by the number of the carbon at the point of attachment.

Step 4 Write the complete IUPAC name, following this format: (number of location)-(branch name)(parent chain).

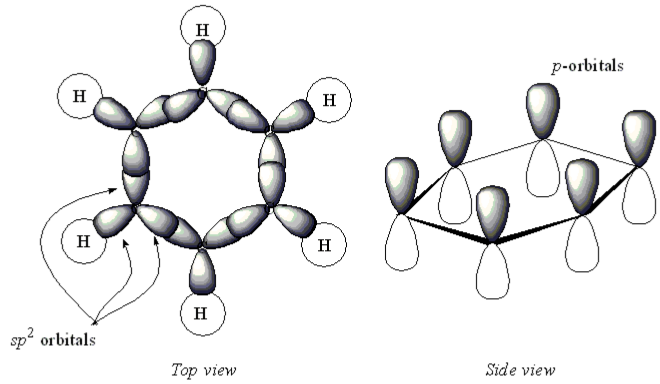
Step 5 When more than one branch is present, the branches are listed in alphabetical order.

Step 6 If more than one type of alkyl branch is present, the number of the carbon for each attachment point is listed and the number of alkyl chains is indicated with the appropriate prefix (di, tri, tetra, etc.).

Aromatic Hydrocarbons

- hydrocarbons with a planar ring structure due to the unique bonds between carbon atoms
- all aromatics are based on the benzene ring

- **Resonance** is a stabilizing effect that involves the movement of covalent bonds within a molecule.
  - gives rise to resonance structures
  - the 18 electrons are delocalized within the ring, shared equally by all six carbon atoms



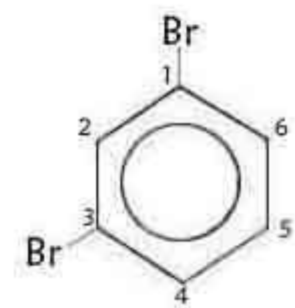
Nomenclature: Aromatics Hydrocarbons

- consider the benzene ring as the parent molecule
  - with a single alkyl group attached, no numbering system is required

    (alkyl name)(benzene)

  - with two or more alkyl groups attached, the groups are numbered such that the lowest numbers possible arise in the compound name

    (number)-(alkyl name)-(number)(alkyl name)(benzene)



Classical System: Di-substituted Benzene

- with two groups attached, a prefix system is used

IUPAC Name	Classical Name
1, 2-diethylbenzene	***ortho***-diethylbenzene
1, 3-diethylbenzene	***meta***-diethylbenzene
1, 4-diethylbenzene	***para***-diethylbenzene

- for complex alkyl groups attached to the benzene ring, it would be easier to treat it as the branch for naming purposes

Some other common functional groups that form compounds with benzene:

Functional group	Prefix
-F	fluoro-
-Cl	chloro-
-Br	bromo-
-I	iodo-
-OH	hydroxy-
$-NO_2$	nitro-
$-NH_2$	amino-

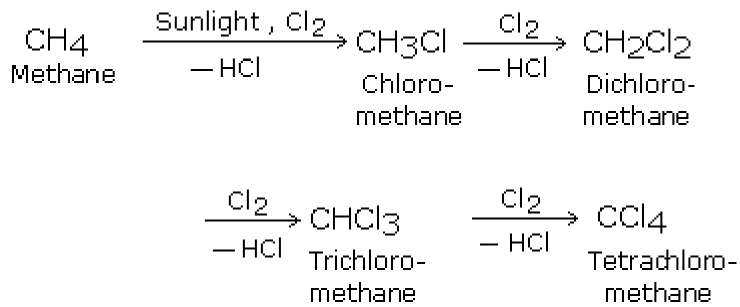
Reactions of Hydrocarbons

- Alkanes, Alkenes, and Alkynes

Combustion reactions: the reaction of a compound with oxygen to form oxides and energy

$$C_xH_{y(g)} + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(g)} + \text{energy}$$

Substitutions reactions: a hydrogen atom in the alkane is replaced by another atom or group of atoms
A mixture of alkyl halides is often generated.



Addition reactions: alkenes and alkynes undergo a reaction with a molecule, such as hydrogen or a halogen, is added to the multiple bond

The following are examples of addition reactions:

Halogenation (with Br_2 or Cl_2)

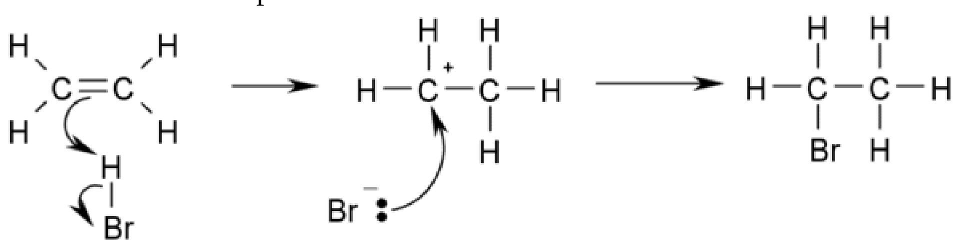
- bromine test for presence of multiple bonds

Hydrogenation (with H_2)

- hydrogen adds to a multiple bond

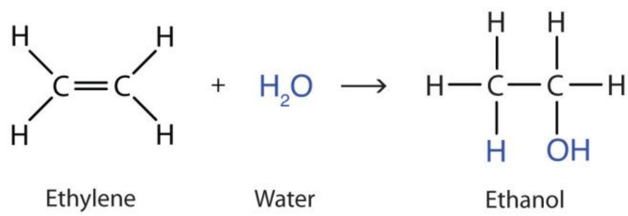
Hydrohalogenation (with hydrogen halides)

- hydrogen and halogen add across a multiple bond



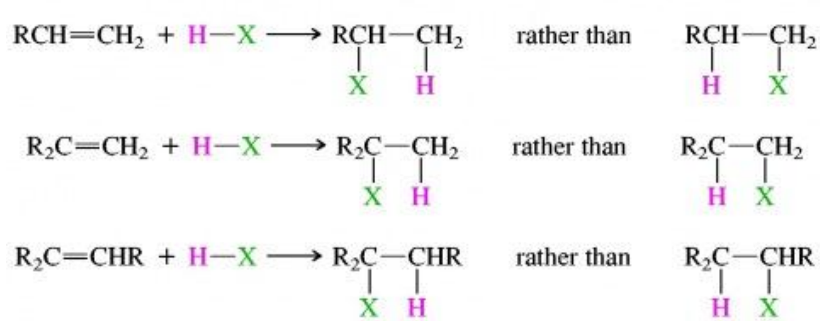
Hydration (with water)

- hydrogen and hydroxyl add across a multiple bond



When two products are possible, we will use Markovnikov's rule for addition.

Markovnikov's Rule states that when water or a hydrogen halide is added to an alkene or alkyne, the hydrogen atom bonds to the carbon atom that has already has more hydrogen atoms.

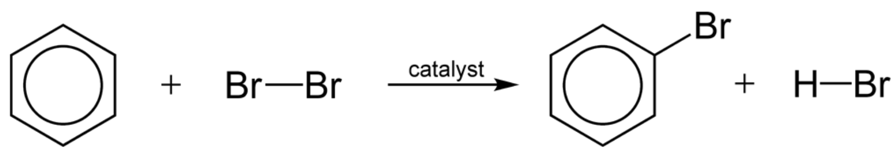


Reactions of Aromatic Hydrocarbons

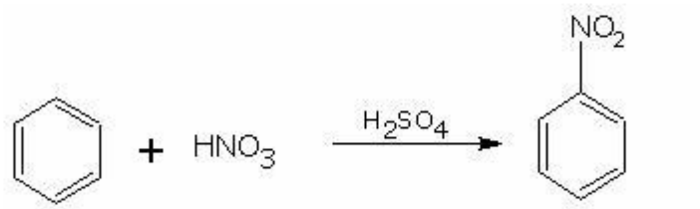
- the reactivity of aromatics is intermediate between alkanes and alkenes/alkynes
  - (most) aklynes > alkenes >> > aromatics > alkanes (least)

Substitution reactions (require a catalyst)

- substitute halogen for hydrogen (catalyst = FeX_3, where X is the halogen)



- substitute nitro group for hydrogen (catalyst = conc. sulfuric acid)



(H of benzene ring replaced by NO_2 group)

- substitute alkyl group for hydrogen (catalyst = AlX_3, where X is a halogen)

(referred to as Friedel-Craft alkylation)

Reactions of Hydrocarbons

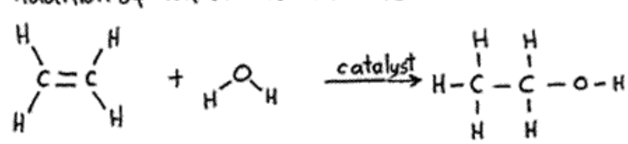
- Production of Alkenes

Elimination reaction is a type of organic reaction that results in the removal of part of a molecule.

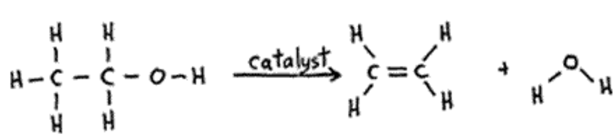
- Elimination with alkyl halides using OH^- (base)
- Elimination with alcohols using H^+ (acid)

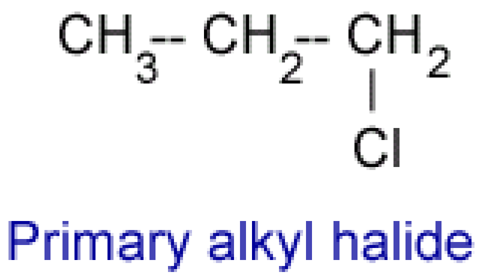
Dehydration reactions are elimination reactions that result in the removal of water.

Addition of water to ethene:



Dehydration of ethanol:





Organic Halides

- hydrocarbons in which one or more hydrogen atoms have been replaced by halogen atoms (functional group)
  - alkyl halide

Functional group	Prefix
-F	fluoro-
-Cl	chloro-
-Br	bromo-
-I	iodo-

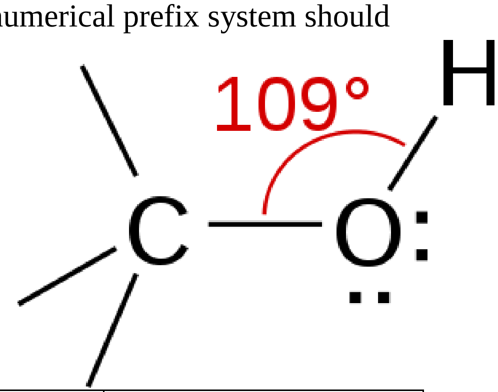
Nomenclature: Organic Halides

Step 1 Find the longest continuous parent alkane chain and number it as before.

Step 2 Treat the halogen as an alkyl branch in the name of the organic halide by indicating the number of the carbon to which it is attached.

Step 3 Write the name of the compound as (number)-(halogen prefix)(parent alkane).

Step 4 If more than one halogen is present, each point of attachment must be indicated by the number of the carbon. If the halogens are the same, the numerical prefix system should be used to indicate how many are present.



Organic Alcohols

- the functional group that characterises alcohols is the hydroxyl group; -OH

R - OH where **R** is an alkyl group

Chemical Formula	Alcohol
CH_3**OH**	methanol
CH_3CH_2**OH**	ethanol
$CH_3CH_2CH_2$**OH**	1-propanol
$CH_3CH_2CH_2CH_2$**OH**	1-butanol
$CH_3CH_2CH_2CH_2CH_2$**OH**	1-pentanol
$CH_3CH_2CH_2CH_2CH_2CH_2$**OH**	1-hexanol
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2$**OH**	1-decanol

- when naming basic alcohols, the name of the parent alkane is used where "ol" replaces the "e" at the end

Polyalcohols are functionalized hydrocarbons that contain more than one hydroxyl group.

- The number of the carbons at each point of attachment must be indicated for every hydroxyl group in a polyalcohol.
- The corresponding numerical prefix is used to indicate how many hydroxyl groups are present; -diol, -triol, etc.

Properties of Alcohols

Alcohol	**Chemical Formula**	**Boiling Point (^oC)**
methanol	CH_3OH	65
ethanol	CH_3CH_2OH	78
1,2-ethanediol	$HOCH_2CH_2OH$	197
propanol	$CH_3CH_2CH_2OH$	97
butanol	$CH_3CH_2CH_2CH_2OH$	117

- The hydroxyl group is highly polarized and allows the compound to hydrogen bond.
  - strong intermolecular forces cause the molecules to hold together better increasing the boiling point

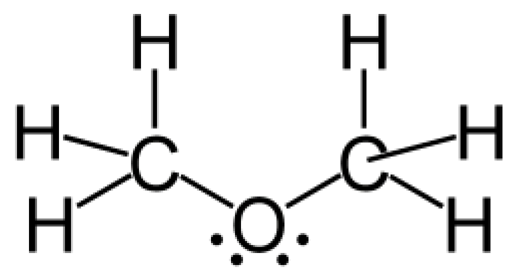
- alcohols are more soluble in polar solvents (water)
  - as the length of the alkyl chain increases, the –OH group becomes less important and the alcohol is less soluble

Ethers

- an organic compound with two alkyl groups attached to an oxygen atom

  R-O-R where the alkyl groups are identical

  R’-O-R” where the alkyl groups are different



- C-O-C bonds are more polar than the bonds of a hydrocarbon
  - stronger intermolecular forces increases the boiling point and solubility of ethers
  - polar and nonpolar portions make ethers good solvents for organic reactions

Nomenclature: Ethers

Step 1 The smaller alkyl group in the ether loses the “ane” ending and adds “oxy”.
Step 2 The larger alkyl group is the parent alkane and is named appropriately.

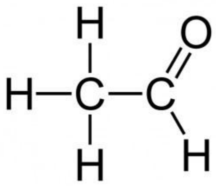
Williamson Synthesis: Making Ethers from Alcohols

$$\mathbf{CH_3OH}_{(l)} + \mathbf{CH_3}OH_{(l)} \rightarrow \mathbf{CH_3OCH_3}_{(l)} + HOH_{(l)}$$

A **condensation reaction** occurs when two molecules combine to form a larger product with the elimination of a smaller molecule.

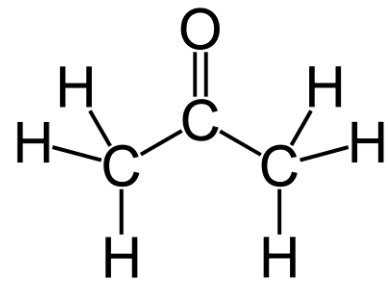
Aldehydes and Ketones

- organic compounds that contain an identical functional group called the **carbonyl group**
  - the carbonyl group contains a carbon atom joined by a double covalent bond to oxygen



aldehydes have terminal carbonyl groups (last carbon in chain)
- bonded to atleast one hydrogen

ketones have internal carbonyl groups
- bonded to two carbon atoms



Nomenclature

- for aldehydes, the ending of the alkane is changed from "e" to "al"
- for ketones, the ending of the alkane is changed to "one" and, if necessary, the number of the carbon in the carbonyl group is indicated

Oxidation Reactions: Carbonyls from Alcohols

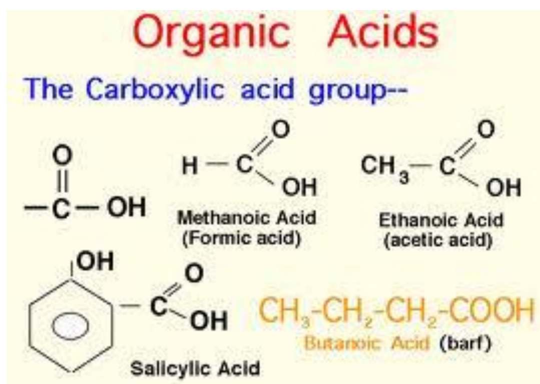
- oxidation reactions have historically described any reactions involving the addition of oxygen or loss of hydrogen in an organic compound
  - making a carbonyl group from an alcohol in a controlled oxidation reaction
- aldehydes are made when primary alcohols are oxidized
- ketones are made when secondary alcohols are oxidized
- tertiary alcohols cannot be oxidized

Hydrogenation Reactions: Alcohols from Carbonyls

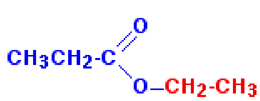
- like alkenes, the double bond of the carbonyl group can undergo addition of H_2, but only hydrogen
  - making an alcohol from a carbonyl group in a reduction reaction
  - basically, a reversal of the controlled oxidation
- primary alcohols are produced when aldehydes are hydrogenated
- secondary alcohols are produded when ketones are hydrogenated
- tertiary alcohols cannot be produced by this method

Carboxylic Acids and Esters

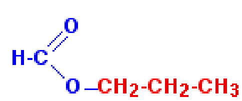
- characterized by the presence of the carboxyl functional group, -COOH, which consists of a hydroxyl group attached to the C atom of a carbonyl group



By replacing the H atom of the carboxyl group with an alkyl group, the carboxylic acid becomes an ester.

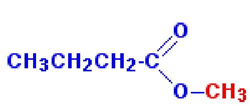


ethyl propanoate

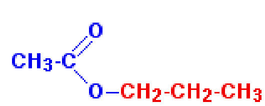


propyl methanoate

Esters are found naturally and artificially prepared as odours and flavours (see Table 2, pp. 64-65).



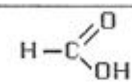
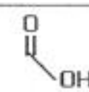
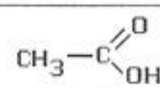
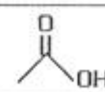
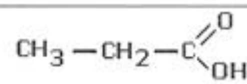
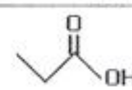
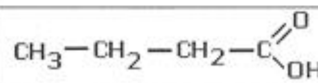
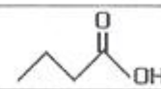
methyl butanoate



propyl ethanoate

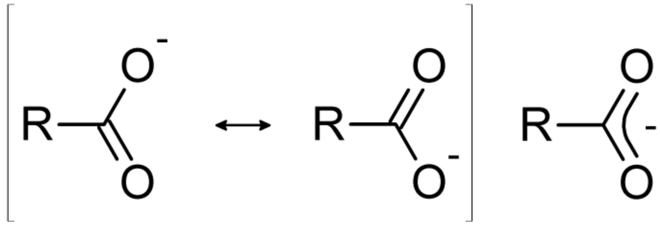
Nomenclature: Carboxylic Acids

Step 1 Find the longest continuous chain of carbons that contains the carboxyl group.
Step 2 Count the carbon atoms, including the carbon of the carboxyl group, that make up this chain.
Step 3 The name of the parent alkane is used by dropping the “e”ending and replacing it with the suffix “oic”, followed by the word “acid”.
Step 4 If there are branches on the hydrocarbon chain, the carbons should be numbered from the carboxyl group. The branches are indicated accordingly.
Step 5 If the hydrocarbon chain has a multiple bond, the name of the parent alkene or alkyne is used instead of the alkane and follow step 3.

Name	Molecular Formulas		Skeletal Formulas
methanoic Acid (formic acid)	$HCOOH$		
ethanoic acid (acetic acid)	CH_3COOH		
propanoic acid (propionic acid)	CH_3CH_2COOH		
butanoic acid (butyric acid)	$CH_3CH_2CH_2COOH$		

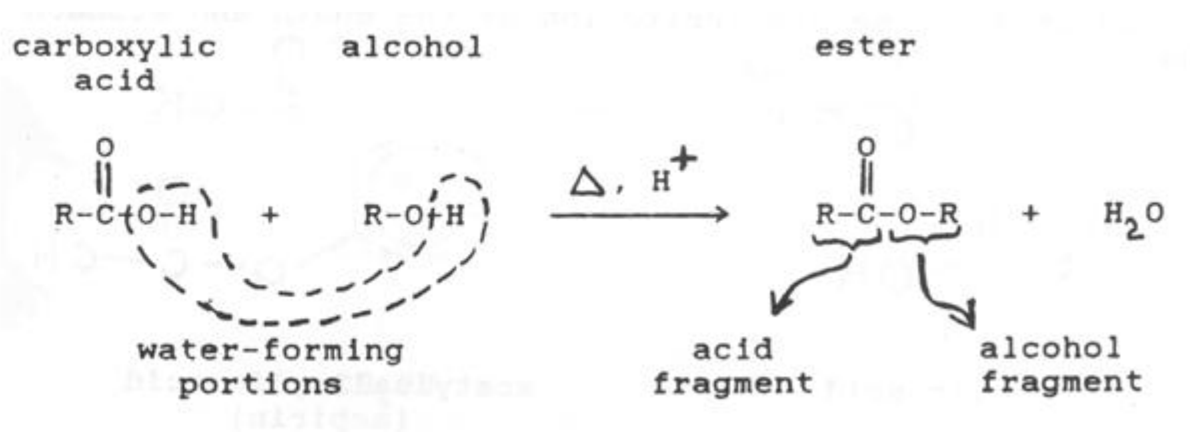
Physical Properties

- The melting and boiling points of carboxylic acids is much higher due to the strong intermolecular forces created by the carboxyl group.
- As the length of chain increases, the melting and boiling points will increase, but the solubility in polar solvents such as water will decrease.
- In the case of dioic acids (carboxyl groups at each end of the chain), the strength of intermolecular forces is maximized.
- The acidity of carboxylic acids is due to the ability of the resulting carboxylate to stabilize its negative charge through resonance (oxygen atoms share the formation of double bonds with carbon).

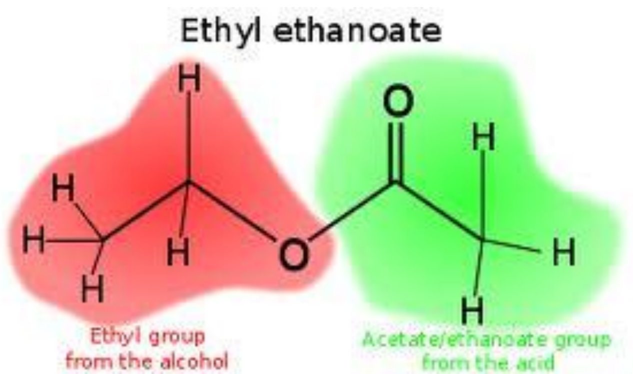


Condensation Reaction: Esterification

- water forms when an alcohol and a carboxylic acid react to produce an ester



Nomenclature: Esters



Step 1 Find the longest continuous chain of carbons that contains the carbonyl group.

Step 2 Count the carbon atoms, including the carbon of the carbonyl group, that make up this chain.

Step 3 The name of the parent alkane is used by dropping the "e"ending and replacing it with the suffix "oate".

Step 4 The name of the alkyl group bonded to the oxygen atom is written in front of the parent alkane.

(alkyl) (alkanoate)

Step 5 If there are branches on the hydrocarbon chain, the carbons should be numbered from the carbonyl group. The branches are indicated accordingly.

Step 6 If the hydrocarbon chain has a multiple bond, the name of the parent alkene or alkyne is used instead of the alkane and follow step 3.

Esters are named by joining the name of the alcohol with the name of the acid. Here are some examples:

Ethanol + Ethanoic acid → Ethyl Ethanoate

Propanol + Ethanoic acid → Propyl Ethanoate

Butanol + Ethanoic acid → Butyl Ethanoate

Ethanol + Propanoic acid → Ethyl Propanoate

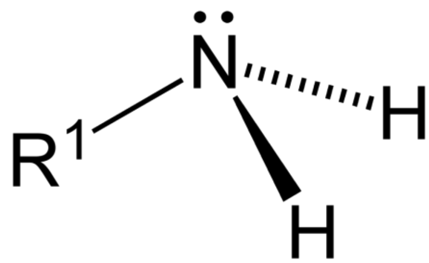
Ethanol + Benzoic acid → Ethyl Benzoate

Amines and Amides

- organic compounds based on the ammonia molecule

$$NH_{3(g)}$$

An **amine** is the ammonia molecule in which one or more H atoms are substituted by alkyls or aromatics.



Nomenclature: Amines

Step 1 Select the largest alkyl chain attached to nitrogen as the parent alkane.

Step 2 Indicate the point of attachment to nitrogen by the number of the carbon atom and use the suffix "amine" replacing the "e" of the parent name.

(number of carbon)-(alkanamine)

OR

Indicate the point of attachment to nitrogen by the number of the carbon atom and use the prefix "amino".

(number of carbon)-(amino)(parent alkane)

Step 3 For multiple amines within the same compound, indicate both points of attachment and use the corresponding prefix (di, tri, etc.)

Step 4 For other alkyl chains attached to the N atom, write the name of the alkyl group first with "N-" before it to indicate that it is bonded to N.

Properties: Amines

- amines are highly polar functional groups due to the higher electronegativity of nitrogen
  - polar N-C bonds and N-H bonds (hydrogen bonding)
  - generally tertiary amines have lower bps

methylamine bp –6^{o}C   dimethylamine bp 8^{o}C   trimethylamine bp 3^{o}C

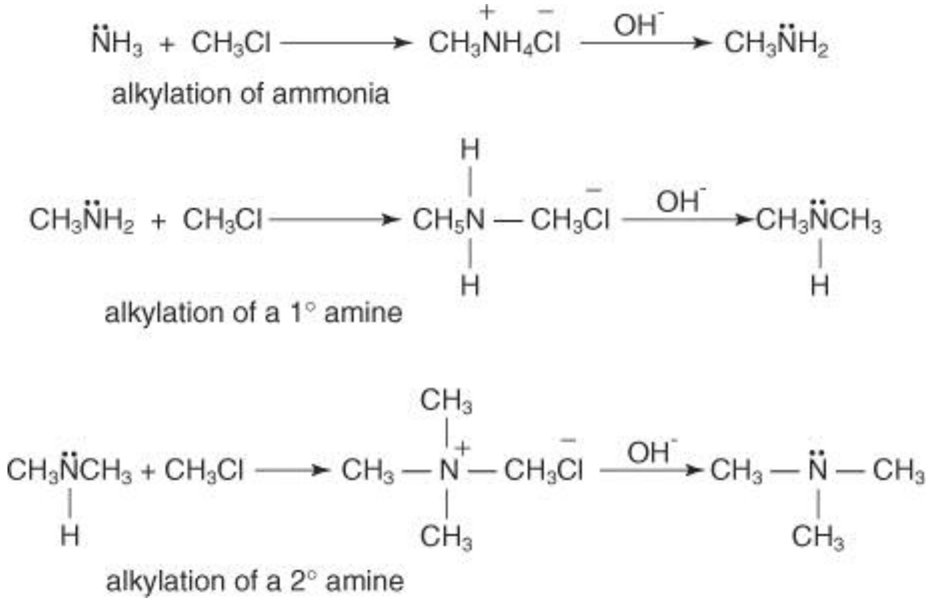
alkane	bp (^{o}C)	alcohol	bp (^{o}C)	amine	bp (^{o}C)
CH_3CH_3	-89	CH_3OH	65	CH_3NH_2	-6
$C_2H_5CH_3$	-42	C_2H_5OH	78	$C_2H_5NH_2$	16
$C_3H_7CH_3$	-0.5	C_3H_7OH	97	$C_3H_7NH_2$	48
$C_4H_9CH_3$	36	C_4H_9OH	117	$C_4H_9NH_2$	78

- O-H bonds are more polar, stronger intermolecular forces than N-H bonds

- amines are soluble; not as soluble as alcohols
  - like alcohols, the larger the alkyl groups in the molecule, the less polar and less soluble in polar solvents

Substitution Reactions

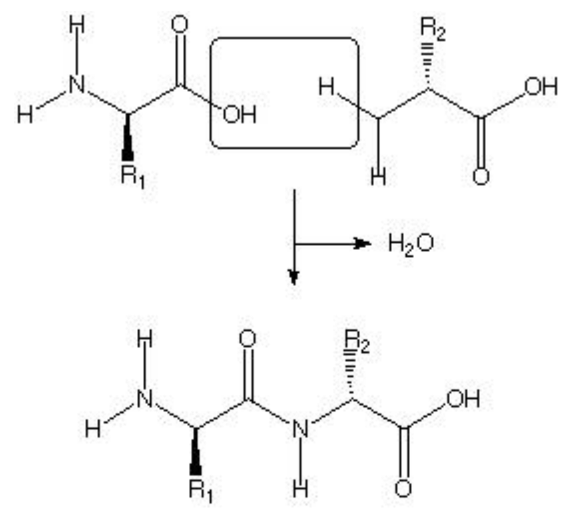
- ammonia is alkylated through simple substitution with organic halides



- the product is treated with base to remove the hydrogen from the nitrogen atom (can be considered the neutralization of acid)

Condensation Reactions: Producing Amides

- amines react with carboxylic acids, in the presence of an acid catalyst to produce **amides**
- example of a condensation reaction
- amides have a carbonyl group bonded to a N atom



Nomenclature: Amides

Step 1 Find the longest continuous chain of carbons that contains the carbonyl group. Count the carbon atoms, including the carbon of the carbonyl group, that make up this chain.

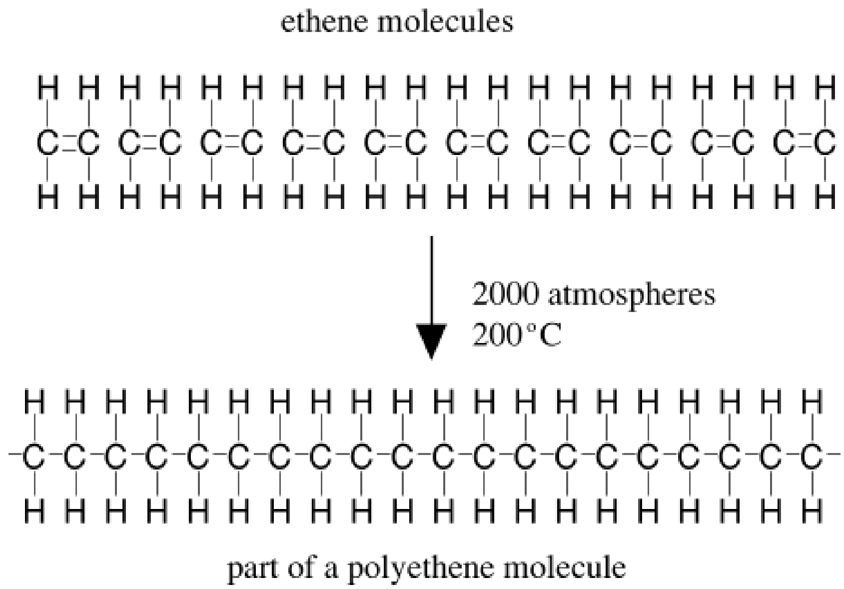
Step 2 The name of the parent alkane is used by dropping the “e”ending and replacing it with the suffix “-amide”.

Step 3 For any alkyl groups bonded to the N atom, the name of the alkyl group is written at the start with “N-“ in front.

N-(alkyl) (alkanamide)

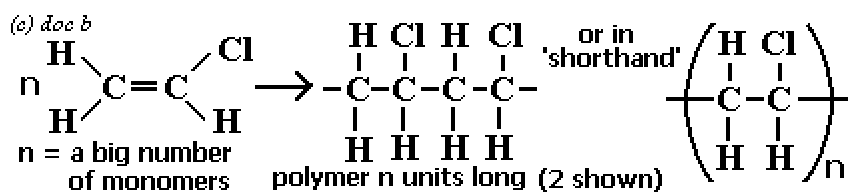
Polymers

- long chains composed of repeating patterns of subunits called **monomers**
- the chemical process by which monomers are joined to form polymers is called **polymerization**

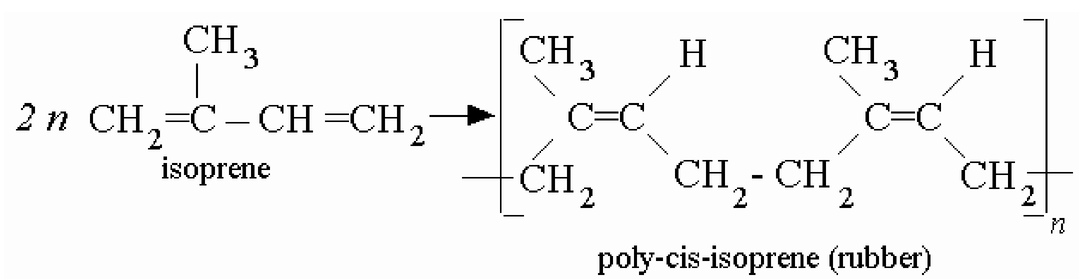


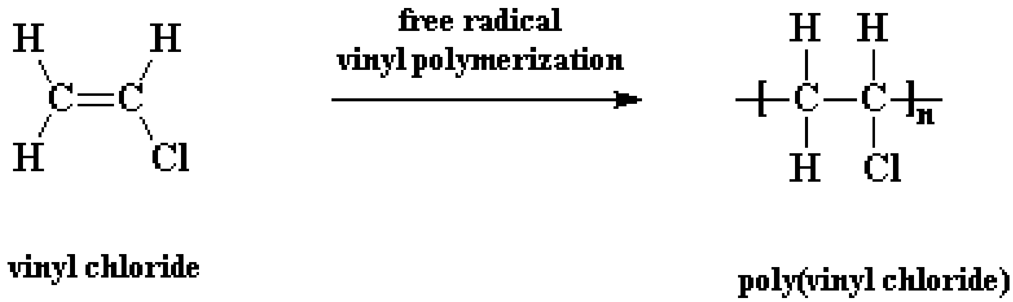
Addition polymers

- result from the additions of monomers containing unsaturated carbon-carbon bonds

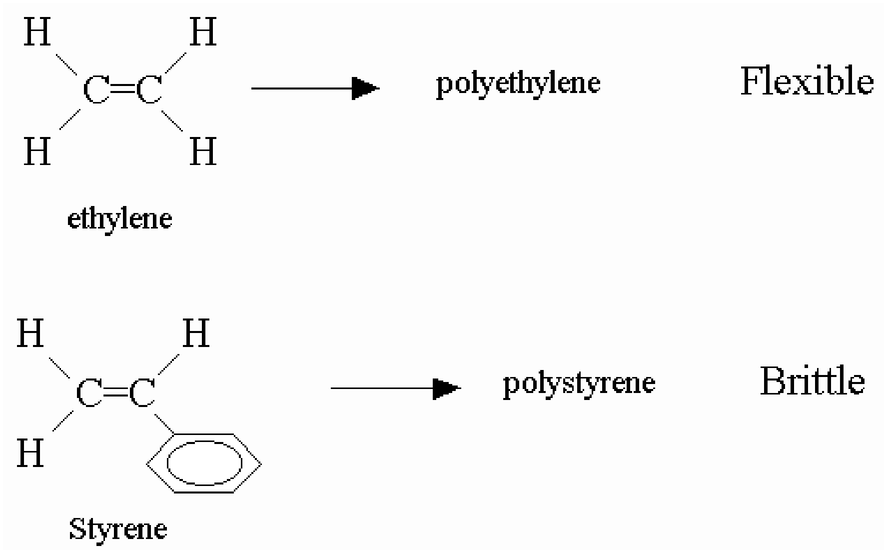


Other addition polymers:





Properties of addition polymers (based on intermolecular forces):

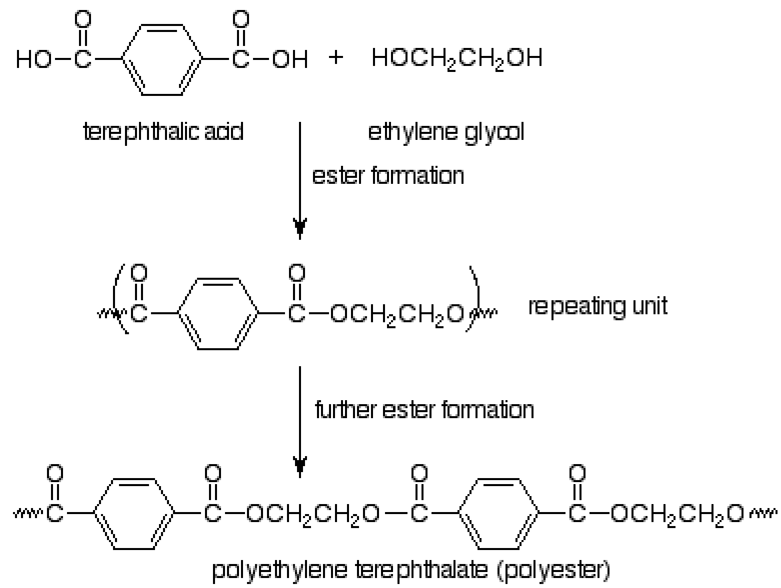


Plastics are synthetic substances that can be moulded (often under heat and pressure) and that then retain the given shape.

- crosslinking polymers can further strengthen them and alter the properties

Synthetic Condensation Polymers

- A polymer formed when the monomer units are linked through condensation reactions; a small molecule is released as a byproduct.



Types of condensation polymers:

- **Polyesters** are prepared from **diols** and **dicarboxylic acids**
- **Polyamides** are prepared from **diamines** and **dicarboxylic acids**
- **Polyethers** are prepared from **diols**