

Organic Chemistry—An Introduction

I am not the best person to be giving a lecture on organic chemistry—the world is filled with two kinds of people, the ones who despise organic, and the ones who love it. During the year I took organic in college, I was also plastering the words from sad songs all over my dorm room walls—looking back I realize there was a cause and effect relationship between organic and typing up those songs. Honestly, I always thought the lunch each Tuesday afternoon before my organic lab felt pretty much like a person going before a firing squad, only it happened over and over and over for an entire year.

With that off my chest, here is a nice lecture that surveys the important foundational concepts for the vocabulary that describes organic chemistry. Mostly you will get a feel for the fact that organic is a lot of nomenclature and a lot of systematic rules. For those who likes languages and lists, and for those who can close their eyes and imagine a three-dimensional world of molecular structures, organic is quite easy. For those, like me, who would rather reduce the subject to a couple of simple mathematical formulas, it is quite difficult. I mean, what kind of science course doesn't need a calculator.

But enough rant.

Things you already know about organic just because you took my course.

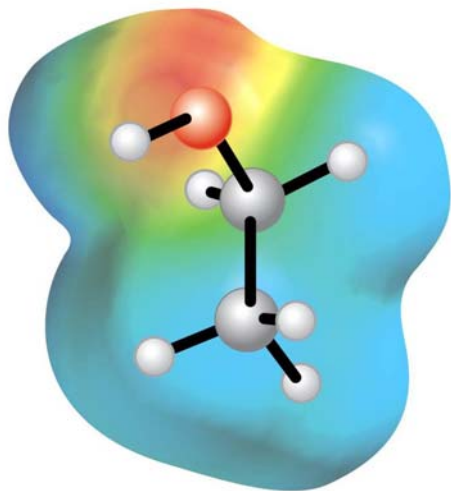
As much as I don't like organic, the physical basis for pretty much everything you would learn in organic is developed in freshman chemistry—some things you need to remember throughout your organic course are:

- Bonding theory like VSEPR, VB and MO that allow you to draw the structures, even in three dimensions.
- Your friend, ΔEN , which allows you to assign local and molecular polarities of the electron clouds and armed with where δ^+ and δ^- assignments across an organic compound, let you intelligently discuss physical properties and chemical reactivities with the best of them.

After all, you have worked a huge number of organic chemistry problems throughout the year. For example:

Tell me everything you know about the compound $\text{CH}_3\text{CH}_2\text{OH}$ (ethanol):

To start, you are actually capable of drawing this 3-dimensional image of ethanol yourself using simple bonding ideas. The large grey balls are the carbon, the small grey balls are the hydrogen and the red ball is oxygen.



So what can you already say about this molecule from being a student in general chemistry? Plenty.

- All the atoms achieve a Noble gas structure, either $1s^2$ for H or $2s^22p^6$ for the C and O.
- The C and O have four electron rich regions which means they have tetrahedral electronic geometry, are approximately 109.5° bond angles, and have sp^3 hybridization.
- The carbons have four bonding regions and are either tetrahedral or distorted tetrahedral molecular geometries, AB_4 . The oxygen has two non-bonding electron pairs and is AB_2U_2 , or angular, electronic geometry.
- There are only sigma bonds in the molecule—in other words, all the bonds lie between the atoms. Specifically there are 8 sigma bonds, 5 formed from sp^3-1s overlap in C-H bonds, one formed from sp^3-sp^3 overlap in the C-C bond, one formed from the sp^3-sp^3 overlap in a C-O bond and one formed from the sp^3-1s overlap in an O-H bond.
- If we were to assign electronegativities (H = 2.1, O = 3.5 and C = 2.5) we would find that all eight bonds are polar covalent ($\Delta EN < 1.5$).
- If we tried to sum all the ΔEN in the molecule, we would find that the CH_3 (methyl) region is fairly non-polar (small total ΔEN in the region), but the region around the oxygen is fairly polar, as is the overall molecule, because of the big electronegativity of oxygen relative to H.
- This polar molecule also happens to possess both instantaneous dipoles associated with the hydrocarbons, but more importantly, hydrogen bonding because of the H attached to an electronegative atom, O. This means that ethanol is going to have very strong intermolecular forces.

- Having very strong electronegative forces means that ethanol has a low vapor pressure, a high viscosity, a large capillary action, and high melting and boiling points among other physical properties related to a large IMF.
- Having hydrogen bonds means that ethanol will be miscible in water, which is good because it means liquor can be diluted. It is also immiscible in most non-polar materials.
- Those carbon-hydrogen bonds love to react with O₂ and halogen gases for that matter, and a nice combustion reaction, with CO₂ and H₂O as products can be drawn. Among other things we know that this combustion reaction will be spontaneous, exothermic, increase the entropy of the surroundings and do work on the surroundings.
- Oh, and of course, there is an activation barrier to this combustion reaction which is why we have to toss a match on the ethanol for the combustion reaction to happen (with a large pre-exponential factor in an Ozarka bottle and a small A value on a surface like my hand.)
- And that O in the 3-dimensional picture is red for a reason. It screams: I have all the electron density. This means this is where the action is in a chemical reaction. And for those of you who take organic, you would do well to draw a δ^- near the oxygen and remember that is where the δ^+ in other molecules is likely to go if given the chance in a reaction.

Well I could go on and on and on with other stuff we have learned and can apply to ethanol. But I will stop and reemphasize two important points:

- You aren't really going to be taught any new chemistry next year in organic
- Instead, you will spend the year doing what I have done above for ethanol, for a million other compounds. So all I really need to do now is to teach you some nomenclature and you can just go ahead and test out of organic by saying, yeah, yeah, Laude already taught us all that bonding, reactivity, thermo and kinetics stuff.

Organic Chemistry Nomenclature.

Why does it take a year to do organic—the study of a single atom, carbon? The reason is that pesky carbon atom is remarkably adept at forming different kinds of molecules. For example, if I were to draw all the legal ways to put together 12 C atoms and 26 H atoms (to satisfy the Nobel gas configuration) there are 355 correct structures, each with its own unique properties. And then if we let the C react with all the compounds that form covalent bonds, like N, O, Cl, P, S, etc., the possibilities explode exponentially. And organic chemists want you to be able to draw and name everyone of those compounds and then explain why one of them evaporates just a little faster, or reacts just a little slower, than another.

So I guess they can have their year. But it is still just stuff you learned in my class.

Alkanes: The basic organic compound is an alkane—it has only C and H bonds, and every one of those bonds is a sigma bond. Alkanes are not very exciting because they don't do much reacting. But they are a great place to start learning nomenclature.

To begin, every organic molecule has three parts defined by a VERY systematic set of rules:

a prefix

a parent

a suffix

- The parent is the length of the longest carbon chain—like **methane** for one carbon, **ethane** for two carbons, **heptane** for seven carbons
- The prefix contains any substituents on the molecule besides the parent C chain—like an extra methyl or hydroxyl group
- The suffix is the family in which the compound falls based upon the functional group attached to the parent chain—for example, the suffix **-ol** indicates that ethan**ol** is an **alcohol**.

For the first molecules we are studying, the **alkane** family has a suffix **-ane** to indicate that nothing more exciting than a bunch of hydrocarbon sigma bonds are found in the molecule.

So whether you have

Pentane or decane or 2-methylpropane or 2,4 dimethylheptane

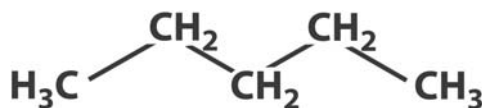
The **ane** suffix indicates you have an alkane.

So what are all the possible parent names? Not surprisingly, they kind of make sense if you know your Greek, and are so consistent that you pick them up quickly even if you don't speak the language.

TABLE 18.1 Alkane Nomenclature

Number of carbon atoms	Formula	Name of alkane	Name of alkyl group	Formula
1	CH ₄	methane	methyl	CH ₃ —
2	CH ₃ CH ₃	ethane	ethyl	CH ₃ CH ₂ —
3	CH ₃ CH ₂ CH ₃	propane	propyl	CH ₃ CH ₂ CH ₂ —
4	CH ₃ (CH ₂) ₂ CH ₃	butane	butyl	CH ₃ (CH ₂) ₂ CH ₂ —
5	CH ₃ (CH ₂) ₃ CH ₃	pentane	pentyl	CH ₃ (CH ₂) ₃ CH ₂ —
6	CH ₃ (CH ₂) ₄ CH ₃	hexane	hexyl	CH ₃ (CH ₂) ₄ CH ₂ —
7	CH ₃ (CH ₂) ₅ CH ₃	heptane	heptyl	CH ₃ (CH ₂) ₅ CH ₂ —
8	CH ₃ (CH ₂) ₆ CH ₃	octane	octyl	CH ₃ (CH ₂) ₆ CH ₂ —
9	CH ₃ (CH ₂) ₇ CH ₃	nonane	nonyl	CH ₃ (CH ₂) ₇ CH ₂ —
10	CH ₃ (CH ₂) ₈ CH ₃	decane	decyl	CH ₃ (CH ₂) ₈ CH ₂ —
11	CH ₃ (CH ₂) ₉ CH ₃	undecane	undecyl	CH ₃ (CH ₂) ₉ CH ₂ —
12	CH ₃ (CH ₂) ₁₀ CH ₃	dodecane	dodecyl	CH ₃ (CH ₂) ₁₀ CH ₂ —

Drawing an organic molecule in two-dimensions. So a simple five carbon alkane is called pentane and has the following structure:



2 Pentane, C₅H₁₂

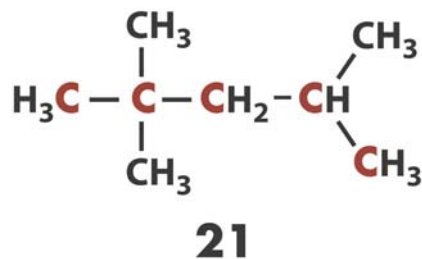
Note that in trying to tell people about the molecule, you can give the compound a formal name, like pentane, or you can draw a simple structure in which the bonds between the carbons are shown adjacent to the CH₂ and CH₃ groups, or, if you are a real organic chemist, you don't waste your time ever drawing C and H, since that is 99% of what you have in your molecules anyway, and instead you just draw the bonds (so zig-zag sticks above), and let everyone else make a mental note that at the vertices are carbons and that every carbon is fitted out with enough hydrogens to satisfy the octet rule.

By the way, if you wanted, you could turn pentane into a nice three dimensional picture just like the ethanol above, that is, if you wanted to, and after awhile, you just automatically imagine that 3-dimensional picture in your head and don't bother with any more than squiggly lines.

Adding Substituents to the Parent Chain.

Organic would be very boring if everything was a great big long straight chain. How about hanging stuff off of the various carbons.

Like this:



To name this more complicated compound, you still need to find out what your longest carbon chain is. The red carbons point out that this is a compound with five carbons at its longest length. So the parent name root is **pentane**. But notice that a bunch of alkane units are hanging off the red carbon chain. These are substituents, and the table above describes them as various alkyl groups depending on the length. This particular compound has three different single carbon alkyl groups, or methyl groups. So we need to name this compound something like: methyl, methyl, methyl pentane. Except that the carbon unit to which they are attached, matters, so we probably need to number the pentane carbons.

Without going into too much detail, we try to keep the numbers as small as possible, and this means labeling the carbons from left to right, in order from 1 to 5.

We then end up with the follow compound name—see if it makes sense to you:

2, 2, 4-trimethylpentane

I am not going to teach you the 3,000,000 technical rules about how compounds are names, you get that in organic. But I will tell you that those rules are very strict, and are referred to as IUPAC nomenclature. (By the way, Dr. Bard in this department was the head of IUPAC for a long time, he is an important guy.)

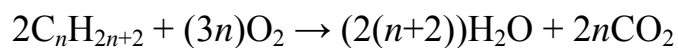
Also know that long before there was IUPAC, organic chemists were assigning common names to compounds that exist to this day. So for example, what IUPAC refers to as 2-propanol you know as isopropanol or better yet, rubbing alcohol.

Structural Isomers. Recall that I told you that there were 355 ways you could write forms of $C_{12}H_{26}$? Well now you see how this can be done. A structural isomer is a compound which has the same molecular formula, but a different structure. And while smaller chain hydrocarbons don't have many structural isomers (for example, butane with four carbons has just two structural isomers), by the time you reach the C_{32} alkanes, there are about 3×10^7 structural isomers (trust me on this.)

As we near the end of the section on alkanes, a question, can you state a general formula for hydrocarbons of length n ? This is as close as we get to math:

Answer: C_nH_{2n+2} --take a look at the table and you will see it is so.

Now some chemistry of alkanes. Basically, alkanes burn, and cleanly, I might add, following the combustion equation below:



In the table below is a who's who of fuels which are basically hydrocarbons, mostly alkanes, all of them fractional cuts of petroleum, separated by boiling point range as the number of carbons increases. And as you can see, even though alkanes are the most boring of organic molecules, they are the only ones over which people fight wars.

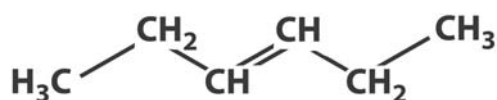
TABLE 18.2 Hydrocarbon Constituents of Petroleum

Hydrocarbons	Boiling range ($^{\circ}C$)	Fraction
C_1 to C_4	-160 to 0	natural gas and propane
C_5 to C_{11}	30 to 200	gasoline
C_{10} to C_{16}	180 to 400	kerosene, fuel oil
C_{17} to C_{22}	350 and above	lubricants
C_{23} to C_{34}	low-melting-point solids	paraffin wax
C_{35} upward	soft solids	asphalt

Alkenes and alkynes-- π -bonds—some of you are jumping up and down to ask about the organic molecules we learned about in CH301 that have π bonds, specifically the carbon-carbon double and triple bonds. These structures were introduced when we learned about π -bonding, the overlap of electron density above and below and in front and behind the central atoms. Organic nomenclature easily accommodated these compounds which are given the designations alkene and alkyne with corresponding -ene and -yne suffixes.

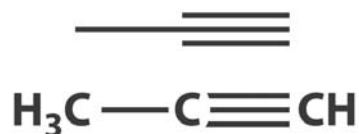
In the two examples below, identify the number of σ and π bonds for old time's sake. And note that the same attention to numbering and root names is in place as for other organic molecules.

17 σ and 1 π bond



5 3-Hexene, C_6H_{12}

6 σ and 2 π bonds

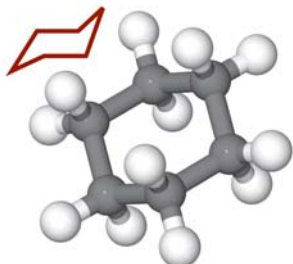


8 Propyne, $CH_3C\equiv CH$

Let's get cyclic.

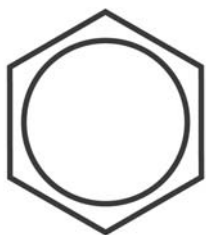
A bit more nomenclature involving hydrocarbons. It is possible for a molecule to form a loop on itself. These are two kinds of cyclic compounds.

Cyclic hydrocarbons are known as cyclic compounds, and we designate them with the prefix, cyclo--



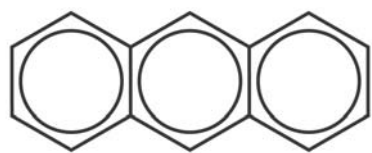
16 Cyclohexane, C_6H_{12}

Benzene and its aromatic friends. The really important cyclic species are aromatic compounds—those based on the ring structure shown below:

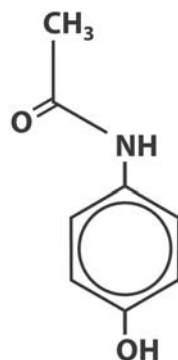


31 Benzene, C_6H_6

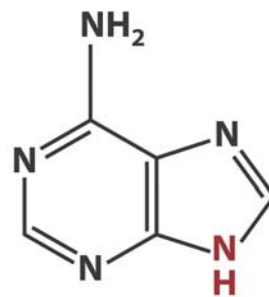
As we learned while discussing molecular orbital theory in CH301, aromatic compounds are hexagonal ring structures formed from the overlap of C_{sp^2} - C_{sp^2} that form σ bonds. What makes aromatic compounds is the leftover 6 electrons that form a sea of delocalized π electrons positioned above and below the ring. It is this p-bonding structure that creates a unique stability and reactivity for aromatic species. While we won't spend any more time on these structures, it is enough to know that aromatic species are ubiquitous in nature, whether in petrochemicals like anthracene or drugs like Tylenol or biological-active molecules like adenine.



33 Anthracene, $C_{14}H_{10}$



14 Tylenol **22** Adenine



Other functional groups in organic molecules.

Rather than methodically work my way through all the suffixes for organic molecules besides, -ane, I think I will simply provide you with a nice table listing them. Note that if you want to have each suffix explained in mind-numbing detail, take an organic course (oops, my bitterness about that time of my life is oozing through.)

Now don't panic—I list them all here, straight from Wikipedia (because your book doesn't think a table of functional groups is useful) so that those of you salivating over starting organic can have at it over the summer. For the rest of us, the ten or so highlighted in red are the ones I will test on.



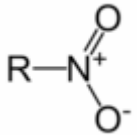
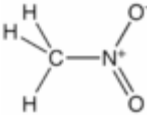

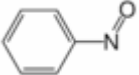
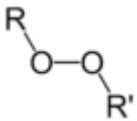

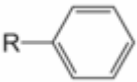
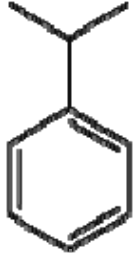
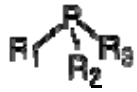

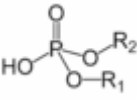
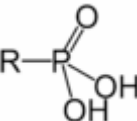

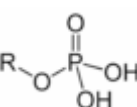

What is most important to note, are the prefixes and suffixes that will surround the family name (largest carbon root). Also, note that there are often two names for the compounds, the result of common name usage dying only very slowly in the traditional world of organic chemistry.

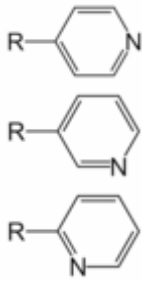
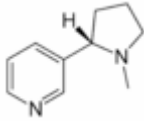
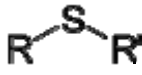
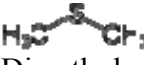
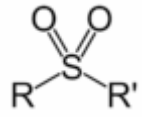
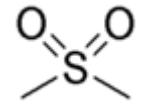
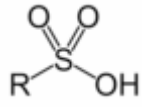
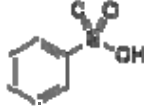
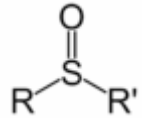
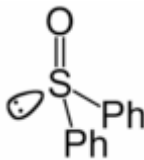
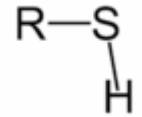
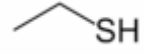
<u>Chemical class</u>	Group	Formula	Structural Formula	Prefix	Suffix	Example
<u>Acyl halide</u>	Haloformyl	RCOX		haloformyl-	-oyl halide	 <u>Acetyl</u> chloride (<i>Ethanoyl chloride</i>)
<u>Alcohol</u>	<u>Hydroxyl</u>	ROH		<u>hydroxy-</u>	<u>-ol</u>	 <u>Methanol</u>
<u>Aldehyde</u>	<u>Aldehyde</u>	RCHO		<u>oxo-</u>	<u>-al</u>	 <u>Acetaldehyde</u> (<i>Ethanal</i>)

<u>Alkane</u>	<u>Alkyl</u>	RH		alkyl-	-ane	 <u>Methane</u>
<u>Alkene</u>	<u>Alkenyl</u>	R ₂ C=CR ₂		alkenyl-	-ene	 <u>Ethylene</u> (Ethene)
<u>Alkyne</u>	<u>Alkynyl</u>	RC≡CR'		alkynyl-	-yne	 <u>Acetylene</u> (Ethyne)
<u>Amide</u>	<u>Carboxamide</u>	RC(=O)NR ₂		carboxamido-	-amide	 <u>Acetamide</u> (Ethanamide)
<u>Amines</u>	<u>Primary amine</u>	RNH ₂		amino-	-amine	 <u>Methylamine</u> (Methanamine)
	<u>Secondary amine</u>	R ₂ NH		amino-	-amine	 <u>Dimethylamine</u>
	<u>Tertiary amine</u>	R ₃ N		amino-	-amine	 <u>Trimethylamine</u>
	<u>4° ammonium ion</u>	R ₄ N ⁺		ammonio-	-ammonium	 <u>Choline</u>
<u>Azide</u>	<u>Azide</u>	RN ₃		azido-	alkyl azide	 <u>Phenyl azide</u> (Azidobenzene)

<u>Azo compound</u>	<u>Azo (Diimide)</u>	RN_2R'		azo-	-diazene	 <u>Methyl orange</u> (p-dimethylamino-azobenzenesulfonic acid)
<u>Toluene derivative</u>	<u>Benzyl</u>	$RCH_2C_6H_5$ RBn		benzyl-	1-(<i>substituent</i>)toluene	 <u>Benzyl bromide</u> (1-Bromotoluene)
<u>Carbonate</u>	<u>Carbonate ester</u>	$ROCOOR$			alkyl carbonate	
<u>Carboxylate</u>	<u>Carboxylate</u>	$RCOO^-$		carboxy-	-oate	 <u>Sodium acetate</u> (Sodium ethanoate)
<u>Carboxylic acid</u>	<u>Carboxyl</u>	$RCOOH$		carboxy-	-oic acid	 <u>Acetic acid</u> (Ethanoic acid)
<u>Cyanates</u>	<u>Cyanate</u>	$ROC\equiv N$		cyanato-	alkyl cyanate	
	<u>Thiocyanate</u>	$RSC\equiv N$		thiocyanato-	alkyl thiocyanate	
<u>Disulfide</u>	<u>Disulfide</u>	$RSSR'$			alkyl disulfide alkyl	 <u>Cystamine</u> (2,2'-Dithiobis(ethylamine))
<u>Ether</u>	<u>Ether</u>	ROR'		alkoxy-	alkyl alkyl ether	 <u>Diethyl ether</u> (Ethoxyethane)
<u>Ester</u>	<u>Ester</u>	$RCOOR'$			alkyl alkanoate	 <u>Ethyl butyrate</u> (Ethyl butanoate)
<u>Haloalkane</u>	<u>Halo</u>	RX	$R-X$	halo-	alkyl halide	 <u>Chloroethane</u> (Ethyl chloride)

<u>Hydroperoxide</u>	<u>Hydroperoxy</u>	ROOH		hydroperoxy-	alkyl hydroperoxide	 <u>Methyl ethyl ketone peroxide</u>
<u>Imine</u>	<u>Primary ketimine</u>	RC(=NH)R'		imino-	-imine	
	<u>Secondary ketimine</u>	RC(=NR)R'		imino-	-imine	
	<u>Primary aldimine</u>	RC(=NH)H		imino-	-imine	
	<u>Secondary aldimine</u>	RC(=NR')H		imino-	-imine	
<u>Imide</u>	<u>Imide</u>	RC(=O)NC(=O)R'		imido-	-imide	
<u>Isocyanide</u>	<u>Isocyanide</u>	RNC	$R-\overset{+}{N}=\overset{-}{C}$	isocyano-	alkyl isocyanide	
<u>Isocyanates</u>	<u>Isocyanate</u>	RNCO		isocyanato-	alkyl isocyanate	 <u>Methyl isocyanate</u>
	<u>Isothiocyanate</u>	RNCS		isothiocyanato-	alkyl isothiocyanate	 <u>Allyl isothiocyanate</u>
<u>Ketone</u>	<u>Carbonyl</u>	RCOR'		keto-, oxo-	-one	 <u>Methyl ethyl ketone (Butanone)</u>
<u>Nitrate</u>	<u>Nitrate</u>	RONO ₂		nitrooxy-, nitroxy-	alkyl nitrate	 <u>Amyl nitrate (1-nitrooxypentane)</u>
<u>Nitrile</u>	<u>Nitrile</u>	RCN	$R-C\equiv N$	cyano-	alkanenitrile alkyl cyanide	 <u>Benzonitrile</u>

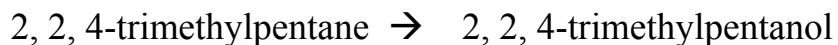
						(Phenyl cyanide)
<u>Nitrite</u>	<u>Nitrosooxy</u>	RONO		nitrosooxy-	alkyl nitrite	 Amyl nitrite (3-methyl-1-nitrosooxybutane)
<u>Nitro compound</u>	<u>Nitro</u>	RNO ₂		nitro-		 Nitromethane
<u>Nitroso compound</u>	<u>Nitroso</u>	RNO		nitroso-		 Nitrosobenzene
<u>Peroxide</u>	<u>Peroxy</u>	ROOR		peroxy-	alkyl peroxide	 Di-tert-butyl peroxide
<u>Benzene derivative</u>	<u>Phenyl</u>	RC ₆ H ₅		phenyl-	-benzene	 Cumene (2-phenylpropane)
<u>Phosphine</u>	Phosphino	R ₃ P		phosphino-	-phosphane	 Methylpropylphosphane
<u>Phosphodiesters</u>	<u>Phosphate</u>	HOPO(OR) ₂		phosphoric acid di(substituent) ester	di(substituent) hydrogenphosphate	DNA
<u>Phosphonic acid</u>	Phosphono	RP(=O)(OH) ₂		phosphono-	substituent phosphonic acid	 Benzylphosphonic acid
<u>Phosphate</u>	Phosphate	ROP(=O)(OH) ₂		phospho-		 Glyceraldehyde 3-phosphate

<u>Pyridine derivative</u>	<u>Pyridyl</u>	RC_5H_4N		4-pyridyl (pyridin-4-yl) 3-pyridyl (pyridin-3-yl) 2-pyridyl (pyridin-2-yl)	-pyridine	 <u>Nicotine</u>
<u>Sulfide</u>		RSR'			di(<i>substituent</i>) sulfide	 <u>Dimethyl sulfide</u>
<u>Sulfone</u>	<u>Sulfonyl</u>	RSO_2R'		sulfonyl-	di(<i>substituent</i>) sulfone	 Dimethyl sulfone <i>(Methylsulfonylmethane)</i>
<u>Sulfonic acid</u>	Sulfo	RSO_3H		sulfo-	<i>substituent sulfonic acid</i>	 Benzenesulfonic acid
<u>Sulfoxide</u>	<u>Sulfinyl</u>	$RSOR'$		sulfinyl-	di(<i>substituent</i>) sulfoxide	 Diphenyl sulfoxide
<u>Thiol</u>	<u>Sulfhydryl</u>	RSH		mercapto-, sulfanyl-	-thiol	 <u>Ethanethiol</u> <i>(Ethyl mercaptan)</i>

Some here are some examples of how we name compounds with functional groups:

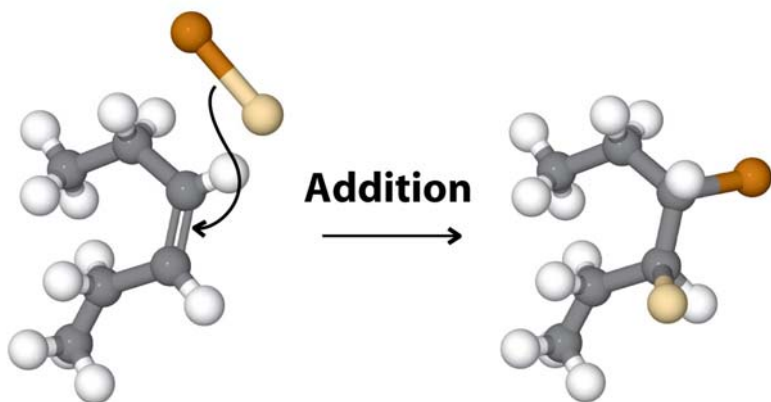
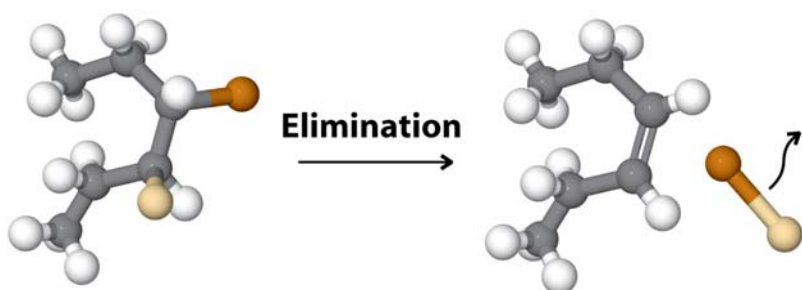
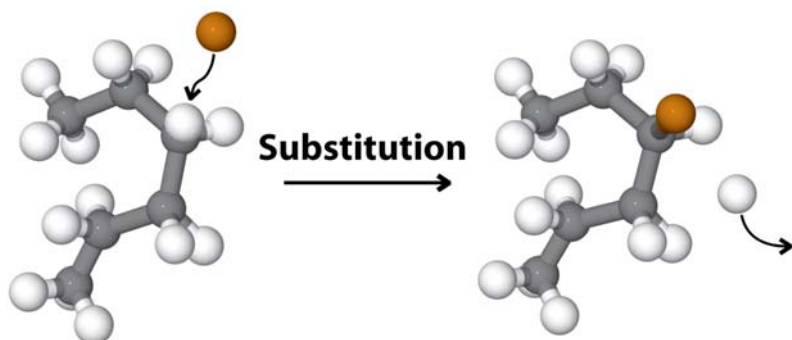
- Alcohols: Ethane plus **-ol** (an alcohol) make ethanol, a 2 carbon alcohol
- Aldehydes: Pentane plus **-al** (a ketone) make pentanal, a 5 carbon ketone
- Carboxylic acids: Dodecane plus **-oic acid** (a carboxylic acid) makes dodecanoic acid, a 12 carbon acid

And if we added an alcohol to the end of our trimethylpentane compounds, we'd have



Organic Chemistry Reactivity. What makes organic such a challenge isn't simply being able to assign names to compounds, it is being able to predict the reactions that this incredibly broad array of compounds undergo. To say an understanding of organic reactivity is beyond the scope of this course, is about as understated a comment as one can make. To understand organic reactivity is to understand the chemistry of not just these relatively small molecules, but also the fields of polymer chemistry and biochemistry—you know, pretty much everything.

But we can create three classes of general reaction mechanisms. They are listed below in some nice pictures from the text that suggest why the names are given to these reactions.



And that is more than enough to know about organic—except that we can make a lot of large polymers and biopolymers with them as we will discuss in the next lecture.