Bio-Organic Chemistry

Objectives for Bio-Organic Chemistry

Properly prepared students, in random order, will

1) Be able to define and apply the concepts of Boiling, Freezing, Melting and Flash points;

2) Be able to list the color of light that solutions will absorb by virtue of the solution's color, itself;

3) Be able to explain how UV spectroscopy works in a very simplistic manner;

4) Be able to explain how IR energy interacts with organic molecules in a very simplistic manner;

5) Be able to sketch examples of bond stretching and bending in organic molecules subjected to IR energy;

- 6) Be able to identify an IR spectrum;
- 7) Be able to identify an NMR spectrum;
- 8) Be able to list the nuclei that spin under NMR conditions;

9) Be able to explain, fundamentally, how proton-generated magnetic fields line up with external magnetic fields;

10) Be able to explain, illustrate and differentiate between parallel and anti-parallel alignment of protons with external magnetic fields;

11) Be able to identify "identical" and "non-identical" protons ("H's") on organic molecules;

12) Be able to identify primary, secondary and tertiary carbon and hydrogen atoms;

13) Be able to explain the NMR spectrum for ethyl alcohol within the scope of the course;

- 14) Be able to determine the ratio of protons ("H's") on different functional groups from NMR spectra;
- 15) Be able to explain roughly how MRI works on human diagnostics;
- 16) Be able to list 5 characteristics that differ between inorganic and organic compounds;
- 17) Be able to list 5 uses of organic molecules and examples of each use;
- 18) Be able to define organic chemistry;
- 19) Be able to define biochemistry;
- 20) Be able to define what an alkane is and match alkanes with the appropriate formula definition;

21) Be able to name alkanes and alkyl groups using both common names and IUPAC rules for nomenclature;

- 22) Be able to identify reactions of alkanes that generate carbon monoxide;
- 23) Be able to write halogenation reactions for alkanes;
- 24) Be able to write combustion reactions for alkanes;
- 25) Be able to identify the hybridization and geometry of carbon atoms in alkanes;
- 26) Be able to name alkenes using both common names and IUPAC rules for nomenclature;
- 27) Be able to define what an alkene is and match alkenes with the appropriate formula definition;
- 28) Be able to identify the hybridization and geometry of carbon atoms in alkenes;
- 29) Be able to write hydrogenation reactions with alkenes;
- 30) Be able to write hydrohalogenation of alkenes with and without peroxides;
- 31) Be able to write hydration reactions of alkenes;
- 32) Be able to draw the structures of alkanes and alkenes given the IPUC names;
- 33) Be able to recognize and draw the structures for alkanols (alcohols of alkanes);
- 34) Be able to write dehydration reactions of alkanols;
- 35) Be able to write oxidation reactions of alkanols;
- 36) Be able to identify, name and draw simple diols and triols;

37) Be able to identify, name and draw the furanoses and pyranoses;

38) Be able to identify, name, give functions of and draw the disaccharides lactose, maltose and sucrose;

39) Be able to draw, name and identify the glycoside bonds that form disaccharides and polysaccharides;

- 40) Be able to give at least 2 locations of glycogen storages in humans;
- 41) Be able to explain what a reducing sugar is and give at least 3 examples;
- 42) Be able to explain what an anomeric carbon is and how it effects metabolism in humans;

43) Be able to identify tests for reducing sugars and explain the fundamental concept behind each test (Benedict's, Fehling's, Tollen's, Barfoed's and bromine water);

44) Be able to explain what a hexose is and a pentose is; what an aldose is and what a ketose is;

45) Be able to explain why humans metabolize lactose but not cellulose;

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46) Be able to identify, name and draw aldehydes, ketones and carboxylic acids by common name and by IUPAC rules;

47) Be able to identify, name and draw four (4) saturated fatty acids using common names, IPUAC rules and delta nomenclature;

48) Be able to identify, name and draw one (1) mono-unsaturated fatty acid (MUFA) using common name, IPUAC nomenclature rules and delta nomenclature;

49) Be able to identify, name and draw four (4) poly-unsaturated fatty acids (PUFA) using common name, IPUAC nomenclature rules and delta nomenclature;

50) Be able to to identify, name and draw two (2) poly-unsaturated fatty acids (PUFA) of the ω -3 class of PUFA's using common name, IPUAC nomenclature rules and delta nomenclature;

51) Be able to explain the importance of arachidonic acid;

52) Be able to identify, name and draw prostanoic acid;

53) Be able to identify and name at least 3 important prostaglandins and give at least one function of each PG;

54) Be able to identify and name three leukotrienes and give at least one function of each LT;

55) Be able to recognize and name two lipoxins and give one function of each;

56) Be able to explain the effect of ASA on COX-2 activity;

57) Be able to write reactions for the synthesis of triglycerides, placing fatty acid on the glycerol backbone properly;

58) Be able to identify phospholipids and fatty acid proper location in PL's;

59) Be able to identify a steroid backbone and identify each ring as well as label each carbon on the backbone;

60) Be able to identify the moieties of digestive detergents and give the function of digestive detergents;

61) Be able to identify at least 3 steroid hormones including cholesterol, itself;

62) Be able to give the names for the lipoproteins and roughly qualitate their protein levels and their cholesterol levels;

- 63) Be able to explain verbally, writing and/or illustratively electrophoresis;
- 64) Be able to explain why electrophoresis of lipoproteins is useful diagnostically;
- 65) Be able to explain the difference between ethers and esters;
- 66) Be able to discuss MTBE and its putative effects on humans and the environment;
- 67) Be able to write esterification reactions and name esters by IUPAC rules;
- 68) Be able to name, draw and identify thiols and thio-acids;
- 69) Be able to identify nitro compounds;
- 70) Be able to name, identify, write synthetic reactions for and name amides;

71) Be able to name, identify and draw at least 10 of the amino/imino acids in any of the 4 possible formats;

- 72) Be able to provide at least one function of at least 10 amino/imino acids;
- 73) Be able to explain what makes an amino/imino acid an amino/imino acid;
- 74) Be able to explain the concept of zwitterions;
- 75) Be able to identify a peptide bond and give at least one characteristic of it;
- 76) Be able to identify the N-terminal and C-terminal end of a peptide;
- 77) Be able to name a pentapeptide properly;
- 78) Be able to explain the function in general terms of an enzyme;
- 79) Be able to list and explain the 6 IUB EC classes of enzymes;
- 80) Be able to explain the three models of enzyme activity;
- 81) Be able to explain, identify and/or draw the 3 kinds of enzyme inhibition;
- 82) Be able to identify, draw and name cyclo-compounds;

83) Be able to identify aromatic compounds qualitatively (benzene-based) and quantitatively (Huckel's Rule);

84) Be able to explain ortho, meta and para directors and to identify those positions on a benzene ring;

85) Be able to identify and name at least 4 significant aromatic compounds;

86) Be able to identify catechol-based compounds;

87) Be able to identify catecholamines;

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88) Be able to identify, and give at last one function of, catecholamines, naturally occurring and artificially synthesized;

89) Be able to identify and draw phenol;

90) Be able to identify phenolic compounds and explain the difference between phenol and aliphatic alcohols' impacts on solutions' pH;

91) Be able to explain what DNA and RNA are and give at least one function of each;

92) Be able to explain (and identify) the difference between purine and pyrimidine;

93) Be able to explain (and identify) the difference between purines and pyrimidines;

94) Be able to identify and name G,C,A,T, U;

95) Be able to identify and name nucleosides and de-oxy nucleosides and explain which occur in nature and which are lab-generated;

96) Be able to identify and name nucleotides and de-oxy nucleotides and explain which occur in nature and which are lab-generated;

97) Be able to write out and explain (with proper structural illustrations) the formation of nucleosides and de-oxynucleosides;

98) Be able to identify and name three nucleotides by acronyms;

99) Be able write out and explain the reaction of carbon dioxide with water;

100) Be able to write out and explain the reactions of carbonic acid per each deprotonation step;

101) Be able to explain the biological function of buffers, in general, and of carbonic acid/bicarbonate ion, specifically;

102) Be able to match chemical entity (pH, bicarbonate ion) with anatomical arena (lungs, kidneys);

103) Be able to explain graphically alkalosis, acidosis and normal acid-base balance;

104) Be able to explain the chloride shift;

105) Be able to draw out and explain the Haldane effect;

106) Be able to walk through and explain the process of acidosis, both respiratory and metabolic, and the process of compensation;

107) Be able to walk through and explain the process of alkalosis, both respiratory and metabolic, and the process of compensation;

and demonstrate that comprehension and applications thereof per assessment tool at no less than a score of 75%.

Bio-Organic Chemistry: Applications of Light, Atoms and Energy in Organic Chemistry

Colors are complimentary: 1 color plus its complement equals BLACK. For example, if one wore a green shirt into a photographic dark room that uses red light, the shirt would appear black

Yellow solutions absorb violet light (short wavelength); green solutions absorb red light (long wavelength); red/orange solutions absorb blue/green light (intermediate wavelengths). All of this is useful in the clinical lab, where colored species are studied

electronically to determine how much of a particular substance is present in a person's plasma, serum, or urine, for example.

Ultraviolet-Visible (UV-Vis) Spectroscopy

In general, UV-Vis spectroscopy works by "boosting" a "target" light acceptor up to another energy level. The UV portion, like the visible region mentioned in the earlier lecture, is also used to study substances in biological fluids. There will be more applications of UV-Vis spectroscopy in CHEM 122 and 220.

Infra-Red (IR) Spectroscopy

IR energy is long wavelength (hence low energy) light below visible red in the spectrum. It is the same as what you feel in your toaster and what you [don't] see in your toaster. IR spectroscopy is interested in studying the twist, stretch, bend, rotation, rock, scissoring and vibrations of atoms in an organic molecule (carbon-based molecules). Specifically, IR spectroscopy is interested in studying functional groups, i.e., organic radicals that substitute for hydrogen on a hydrocarbon chain or ring (more on all of this at a later date/lecture).

"Stretching" between bonds after IR electromagnetic energy (EME) stimulates the bonds

An Example of Bond Bending



The next two images illustrate the IR spectra (fingerprints, if you will) of two different compounds -- with and without peak labeling. Note that "peaks" on these IR spectra go down, not up -- they are pointed, blunt, rounded or dips. Each functional group interacts with IR EME differently than other groups and allows IR EME to help us determine what functional groups are present. Note also that sometimes peaks cover a range of wave numbers. Each spectrum has the structure of the whole organic molecule drawn in





its boundaries. The spectrum labeling has been purposely distorted to accommodate the labeling and to emphasize peaks. Specific functional groups absorb specific IR EME to give a characteristic IR spectrum.

Nuclear Magnetic Resonance Spectroscopy

Remember from our earlier discussion that electricity is defined as the flow of electrons through a wire.

As the current flows through the wire, a magnetic field is induced perpendicular to the flow of electrons.

To find this induced

electromagnetic field (EMF), use the right hand rule: put your right thumb in the direction of the electron flow and curl your hand around the wire. The direction your hand curls is in the region of the generated magnetic field about the whole wire.

Some nuclei spin, ¹H, ¹³C, ¹⁹F, ³¹P -these are the biggees. Remember that the nucleus contains neutrons and protons. Protons, specifically those in Protium (¹H), spin about the axis of the atom's rotation, Figure, top right, (the "B" with the vector sign is the induced magnetic field). This spin induces a very tiny magnetic field along the spin axis (like the electrons and wire). For our discussion, Figure, bottom right, represents equivalent ways in which to illustrate the spin axis of the proton.

The effect of external magnetic fields on nuclear "magnetic fields" is this: quantum mechanics says that $S = \pm \frac{1}{2}$. In the presence, then, of an external magnetic field (represented by an arrow pointing from left to right with a "cross"





through the left end), the proton-generated magnetic field will either line up with the external field (called parallel alignment) or line up against the magnetic field (called anti-parallel alignment).

The table, below, summarizes this:



The way in which these alignments are caused is to spin the sample inside a magnet.

Radiofrequency radiation effects alignment, as well. Remember that $\upsilon = c/\lambda$ and that $E = h\upsilon$. To detect the proton in Protium, it needs to be "tweaked" into the ANTI-PARALLEL alignment. It is the radiofrequency radiation (radiofrequency energy is less than IR energy) that makes the "tweak". At a fixed radiofrequency, all protons absorb at a constant radiofrequency energy. BUT when an external magnetic field strength is altered, protons absorb at different, specific, magnetic field energies

The table, below, illustrates, as well, the idea that all protons (in this case H) are not identical and will give different "signals" under the right stimulation:

"Identical Protons" Each carbon atom has	"Non-Identical Protons" each carbon has
hydrogens bonded to them in an identical	different numbers of protons (H) bonded to it
manner and will, then, give 1 signal.	and will, then, give two different signals.

Specific functional groups have specific magnetic field energy attractions (like what we saw with IR) and give a characteristic NMR spectrum as a function of altered radiofrequency absorption (R_f).

Figure illustrates a generic representation of an NMR spectrum with the axes labeled. The basic organization of the NMR spectrometer follows.









In general a sample is placed in the appropriate solvent and "dropped" inside the spinner in the magnet with variable energy. The sample is also surrounded by an R_f generator and a detector. The latter leads to some sort of display visualizer (screen, printer).

Magnetic Resonance Imaging

Figure, below, illustrates a crude NMR spectrum for ethyl alcohol (EtOH; H_3CCH_2OH). Note that the CH_3 peak is the more electropositive and appears on the low end of the magnetic energy/field axis; the CH_2 is neutral and is roughly mid-way; the OH is more electronegative and is at the high electromagnetic field strength end. Note, too, the ratios of the peak areas to each other. The first is roughly 3 times as large as the last and the second is roughly twice that of the last. The ratio, then, is 3:2:1 -- note that that is the arrangement of the three parts of the EtOH as it was deconstructed.



For Next Two Images



Peaks are labeled. While I don't expect you to become expert spectroscopists over night, I do expect you to recognize the ratios of the peak areas compared to each other.

Illustrative NMR Spectra for Two Different Organic Compounds



Note the "s" shaped lines that go through the peaks on the spectrum. This is an integration line that is measured to obtain the height for each peak. These heights are then compared with each other. Note that the ratio of 60:45:14 is approximately 4:3:1. Note that there are three different kinds of protons on this molecule: 3 methyl protons (the "3"), 4 methelenyl protons (the "4") and 1 methynl protons (the "1"). The integrator signals tell you information about the numbers of H's in proton NMR (pNMR). The Page | 12 same idea using the bottom ppm scale instead of the top Hz scale.

The next logical step, then, is to examine how this might be used on a daily basis in health care. That is by MRI. MRI came about because when it first was used, the public felt frightened about the word "nuclear". So a PR firm was hired to put a positive spin on it. They decided to leave off the "N" and add the "I" for Imaging. Still the same thing -- it's all in the presentation.

MRI: Human Applications

Had to decide what to look for in the body. There are lots of organic compounds in the body that contain protons. Water, of which we are made up the most is HOH -- has a proton. The next problem was how to spin the patient in the magnet. The conditions necessary to make MRI work are to hold the R_f at a constant and the magnetic field energy at the energy for water (i.e., also a constant).

MRI: Drawbacks

The patient can NOT have any magnetic items on or in their body. VERY dangerous! The patient must hold still and in less recent models the patient slot was small. That's getting better. It is also expensive. The plus is that the images are better and MRI gives better diagnostic capabilities than CT.

Organic Chemistry: Carbon-Based Chemistry

Compare and Contrast Inorganic and Organic Compounds

Inorganic Compounds	Organic Compounds
Composed of various combinations of more than 100 elements	Organic compounds are composed of only a few elements. Carbon always organic chemistry is the chemistry of carbon compounds. Hydrogen, oxygen and nitrogen are usually involved and sulfur, phosphorus, chlorine, bromine and iodine, occasionally, are present, as well.
Very few inorganic compounds will burn. They have high melting points, above 350° C; some vaporize at high temperatures.	Nearly all-organic compounds burn. They tend to have low melting points, much less then 350° C. Some char and decompose rather than melt.
Inorganic compounds (excluding compounds of the transition metals) are usually odorless and colorless and are soluble in water to varying degrees.	Organic compounds tend to possess color and odor; e.g., benzaldehyde is artificial oil of almond.

Inorganic compounds are "held together" by ionic bonding and ionize in aqueous solutions.	Organic compounds are soluble in organic compounds and are typically insoluble in water. Notable exceptions include acetone and ethanol.	
Compared to organic compounds, there are only a few isomers of inorganic compounds. Remember that "isomers" means equal units, e.g., same chemical formula, but a different geometrical arrangement.	Organic compounds are generally held together by covalent bonds. A few, e.g., carboxylic acids and phenols, ionize and effect the pH of solutions. There are many isomers of organic compounds you'll be introduced to a few of them as we go along.	F

Definitions

Freezing Point: is the temperature at which a liquid becomes a solid at normal atmospheric pressure. **Boiling Point**: is the temperature at which a liquid changes to a gas (vapor) at normal atmospheric pressure. A more specific definition of boiling point is the temperature at which the vapor pressure of a liquid is equal to the external pressure. **Melting Point**: is the temperature at which a solid becomes a liquid at normal atmospheric pressure. **Flash Point**: is the lowest temperature at which a liquid can form an ignitable mixture in air near the surface of the liquid. The lower the flash point, the easier it is to ignite the material.

We Use Carbon-Based Compounds Every Day			
Health	food, digestion, metabolism, drugs, vitamins, hormones		
Daily Use and Survival	heat, electricity, flavorings, colorants, sweeteners, containers		
Transportation	gas, diesel, oil, grease, plastics, tires		
Clothing	nylon, rayon, dacron, Kevlar		
Personal Use	soap, detergents, perfumes, paints, ink, explosives, photography, PVC pipe		

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Number of Carbons	Organic Prefix	Number of Carbons	Organic Prefix
1	Meth	11	Undeca
2	Eth	12	Dodeca
3	Prop	13	Trideca
4	But	14	Tetradeca
5	Pent	15	Pentadeca
6	Hex	16	Hexadeca
7	Hept	17	Heptadeca
8	Oct	18	Octadeca
9	Non or nona	19	Nonadeca
10	Dec or deca	20	Eicosa

Organic Prefixes in "Organic-ese"

IUPAC Conundrum: Eicosa vs Icosa -- An ICOSAHEDRON is composed of 20 equilateral triangles and 12 vertices, and because of the axes of rotational symmetry is said to have 5:3:2 symmetry (between 5 triangles joined at 1 vertex,3 triangles joined across a fourth triangle's three sides, and 2 triangles butted up against each other on one side).

Nomenclature with Fundamental Reactions in Organic Chemistry

Alkanes

The general formula of an alkane is C_nH_{2n+2} . All of the carbons in an alkane are in sp³ hybridization and possess tetrahedral geometry. There is one sigma bond between the carbon atoms that permits freedom of rotation about the carbon-carbon single bond. They also consist only of carbon and hydrogen, hence the name "hydrocarbon". The simplest of the alkanes is CH₄ or methane -- "meth" for one carbon and "ane" for the alkane.



Ethane has the formula $\mathsf{C_2H_6}$ -- "eth" for two carbons and "ane" for the alkane.



Propane is C₃H₈:





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Butane and Isobutane are C_4H_{10} :











Pentane is C₅H₁₂







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English and O. Chem.

Note also, that one does NOT have to draw on each hydrogen atom in the structures. Each carbon can take 4 bonds. If there appears to be only one bond between the first and second carbon, then there must be 3 hydrogen's UNDERSTOOD to be present on the end



carbons. If there appears to be one bond between carbons in the middle of the chain, i.e., one to the

left and one to the right for 2 single bonds, then it follows that there must be 2 hydrogen atoms UNDERSTOOD to be present. If you think back to when you diagrammed sentences in high school, recall how you had to diagram the following sentence: Do it! What is the subject? An UNDERSTOOD "You"!

$$C_{3}H_{8} = H - \frac{H}{c} - \frac{H}{c}$$

Alkyl groups

While alkanes can be and are exciting in and of themselves, there is more to organic chemistry than just looking at alkanes. We must have a way in which to name them when they become reactive or when an organic functional group substitutes onto a hydrocarbon chain for a hydrogen atom. When an alkane loses a hydrogen atom, the left over hydrocarbon becomes an "alkyl" group -- "alk" for the parent hydrocarbon and "yl" to indicate that it is a reactive radical. If methane (CH_4) were to lose a hydrogen atom, it becomes the methyl radical ($CH_3 \bullet$), where the dot represents the leftbehind electron after the hydrogen atom was removed from methane. The same applies to ethane (C_2H_6) when it loses an electron to become the ethyl radical: ($CH_3CH_2 \bullet$). These are the two simplest alkyl radicals. The following radicals have isomers and require memorization. In most cases, their common names make NO sense -- that's why we have a systematic manner in which to name them coming up.







Propyl Radicals – Detail

When propane loses an electron, it may lose it from either one of the end carbons or from the middle carbon. The end carbons, notice, are directly bonded to only one other carbon atom. These carbons are called primary or first degree carbons. Hydrogen atoms or other substituting groups carry the same nomenclature when they are bound to first degree or primary carbons. The middle carbon, though, is bonded directly to two carbons. This carbon is a secondary or second-degree carbon. Hydrogen atoms or substituting groups onto a secondary carbon carry the same name, i.e., the hydrogen would be called a secondary hydrogen because it was bound to a secondary carbon. When the hydrogen atom is lost from one of the end carbons in propane, the radical is called the n-propyl radical and is a primary or first degree radical. When the hydrogen atom is lost from the middle carbon, this is called the isopropyl radical by common name. This radical is a secondary or second-degree radical. For propane, then, there are 2 isomers.

Butyl Radicals – Detail

With butane, it gets a bit hairier. There are 4 isomers of the butyl radical. If the hydrogen atom is removed from the end carbon, the n-butyl radical is obtained. If the hydrogen atom is removed from the second carbon while all 4 carbons are in a 4-carbon chain, the secondary-butyl radical is obtained. These are the easy isomers. The more complicated isomers involve taking one carbon atom from the 4-carbon chain and attaching it to the middle carbon of the leftover 3-carbon chain. The center carbon, now, is directly bonded to 3 carbon atoms. This carbon is, then, a tertiary or third degree carbon and the hydrogen atom on it is a tertiary or third degree hydrogen atom. When the tertiary hydrogen is removed, the t-, tert-, or tertiary butyl radical is obtained. But, wait! What if you leave that one and remove a











mean about the common names not making sense? Do NOT try to make the common names or nicknames make sense -- won't work, e.g., the pentyl radical isomers.

Another Way to View Radicals

IUPAC -- the International Union for Pure and Applied Chemistry

So now that we know that we can't make sense out of common names, what do we do? We fall back onto the IUPAC -- the International Union for Pure and Applied Chemistry. The IUPAC met to determine a systematic manner in which to name compounds so that EVERYONE would know exactly



which compound EVERYONE was talking about. The rules are pretty straight-forward and we'll walk through a few of them as we delve deeper into this fascinating field of chemistry!

When naming alkanes

Example

- name the longest continuous "straight" chain (remember, the carbon atoms are in sp³ hybridization so the chain is not "straight", rather it is "bent" continuously),
- 2. enumerate the substituting groups with the lowest numbers possible and
- if there is more than one group, alphabetize the substituting groups regardless of enumeration.





Note that there are two ways in which count the numbers of carbon atoms: from the left or from the right. It is only after you assign numbers to the carbons in the longest chain that you can see that you number this one from the right going left. To do

otherwise puts substituting groups at carbons 3, 5 and 6; when done, in this case, from the right, the substituting groups are now on carbons 2, 3 and 5.











The longest continuous chain is 7 carbons: it's a heptane. The substituting groups are all methyl groups (CH3·), and they are on carbons 2, 3 and 5. Since they are identical groups, we'll group them as "trimethyl" for "three methyl groups"; the "di" or "tri" type of prefixes are not used to alphabetize, BTW. To name the compound, it is 2,3,5-trimethylheptane. Note that this is ALL one word. Numerals are kept separated from each other by commas. Numbers and letters are separated by dashes. The name tells everyone that the longest chain is 7 carbons long, it's an alkane and there are methyl groups on carbons Page | 19 2, 3 and 5.

Example

In this case, the longest chain is 6 carbons long. While it really doesn't matter how we enumerate the carbons in this example, for "neatness" we'll number from the top to the bottom (this makes the alphabetization easier).

The longest chain is 6 carbons long and there are only single bonds between the carbons. The longest chain, then, is hexane.

There are 2 substituting groups on the hexane: an ethyl group on #3 and a methyl group on #4.

By alphabetizing the substituting groups, the name is 3-ethyl-4-methylhexane.



Example





The longest chain is 10 carbons long: decane. We enumerate the carbons from right to left (in right image and vice versa in left image; can you figure out why?). There are 2 methyl groups on carbons 2 and 8; an ethyl group on carbon 4 and an isopropyl group on carbon 6. The name, then, is **4-ethyl-6-isopropyl-2,8-dimethyldecane**. Do you see how the name makes it easy to draw the structures?



Example

This is a symmetrical molecule, with the longest chain being 5 carbons long. The substituting groups are on carbons 2, 3 and 4 -- regardless how you count them. This molecule is 2,3,4-trimethylpentane.

A Couple of Reactions Characteristic of Alkanes: Halogenation and Combustion Reactions.

Halogenation reactions do just what the name says: they put halogens on compounds. Chlorine is more reactive than bromine and tertiary hydrogens are more easily extracted than secondary hydrogens, which are more easily extracted than primary hydrogens. As a general rule, an "X" represents a halogen. Page | 20

The Simplest Halogenation Reaction: The Halogenation of Methane



The reaction is driven by either light (hv) and room temperature (RT) or by temps between 250 and 400° C. Note that the products are halomethane (chloromethane if we had used chlorine; bromomethane had we used bromine) and the hydrohalic acid (HCl or HBr, respectively, with our earlier example).

Halogenation Reaction Example

The reaction with ethane is very straight-forward: chloroethane and hydrochloric acid are obtained. The reaction with propane, though, is not as clear. Remember those primary and secondary hydrogens? That's what makes it so murky. There will be two halohydrocarbon products: chloropropane and 2chloropropane -- did I need to put a "1" in front of the chloropropane? No. If there is no number, it is understood to be the "1" substitution. In the latter reaction note that the HCl is not included. For my

classes, it's not necessary to be as anal retentive with organic chemistry as it is in inorganic chemistry, i.e., I'm interested in the organic products, not the trivia.

Note in the figure (ON SCREEN!) that there are arrows pointing to the two products of the halogenation of propane. Given the higher reactivity of secondary hydrogens, in the olden days, the 2-halopropane was considered the MAJOR product and the halopropane was considered the MINOR product. We now know that that is not necessarily the case. Remember Elementary Reaction Rates?



Combustion Reactions

Go on around us every day: driving a car powered by gasoline or diesel, using natural gas water heaters or dryers or by burning coal for electricity. As a general rule, when an alkane is burned in the presence of excessive oxygen, carbon dioxide and water are formed:

 $C_{n}H_{2n+2} \xrightarrow{XSO_{2}} nCO_{2} + (n+1)H_{2}O$ n = n = n = n

Note that you always get 1 more mole of water vapor than the number of carbons in the original alkane, e.g., if you were to combust eicosane, you would obtain 20 moles of carbon dioxide and 21 moles of water vapor.

Combustion Examples



The first is the combustion of hexane to 6 moles of carbon dioxide and 7 moles of water vapor and the second is the combustion of octane to 8 moles of carbon dioxide and 9 moles of water vapor.

Incomplete, Abnormal, Combustion of Hydrocarbons

Major Health Concern

ethene

"Old", Inefficient Propane Burners: $2 C_3H_8 + 7 O_2 \rightarrow 6 CO + 8 H_2O + heat$

Deadly!

From Gasoline (using octane as the gas form), as well. $2C_8H_{18} + 17O_2 \rightarrow 16CO + 18H_2O + heat$

Alkenes

AlkENES are hydrocarbons that contain one double bond between two carbon atoms. The general formula for an alkene is C_nH_{2n} . The two carbons are in sp² hybridization and have a planar triangular (trigonal planar) geometry. There is 1

sigma bond and 1 pi bond between the two carbon atoms. There is NO freedom of rotation about the double bond as there is in the single bonds in

The simplest alkene is ethene -- "eth" for 2 carbons and "ene" for the double bond -- C_2H_4

Propene, C_3H_6 , has only one conformation.

The Butene family has 4 isomers. Butene has the double bond between the first two carbons in the 4-carbon chain. 2-butene has 2 isomers, both of which have the double bond between the 2d and 3d carbons. If you look at the first 2-butene, you'll note that the 2 hydrogen atoms on the carbons involved in the double bonds are across from each other and on opposite sides of the double bond plane. This is the trans isomer. Thus, this molecule is called trans-2-butene. The bottom 2-butene isomer you'll note has the hydrogen atoms on the same side of the plane of the double bond. This is the cis isomer. Thus, this molecule is called cis-2-butene. The last isomer in the butene family is a 3-carbon chain

with a methyl group off the 2d carbon. It is called 2-methylpropene.

Naming alkenes is about as simple as naming alkanes.

2-methylpropene

Another rule, though, is to give the location of the double bond numerically and give it the lowest number possible.

Example

The longest chain is 5 carbons long. The double bond is between carbons 2 and 3 -- thus it is a 2-ene. You only give the lowest number of the carbon in the double bond, not both numbers. There is a methyl group on carbon #2. The name of this compound is 2-methyl-2-pentene.











еес с=с еес Example

cis-4-octene and trans-4-octene. Both have 8 carbon chains with a double bond between carbons 4 and 5. The former has both hydrogen atoms on the same side of the plane of the double bond and the latter has the hydrogens on opposite side of the plane of the double bond.

Example

There are 7 carbons in its longest continuous chain. There is a methyl group on carbon #3 and an ethyl group on carbon #4. There is a double bond between carbons 3 and 4. The name of this compound is 4-ethyl-3-methyl-3-heptene.





Di-enes

A four carbon chain with double bonds between carbons 1 and 2 and carbons 3 and 4 is called 1,3-butadiene.

A seven carbon chain with double bonds between carbons 1 and 2 and carbons 5 and 6 is called 1,5-heptadiene.

A four carbon chain with double bonds between carbons 1 and 2 and carbons 2 and 3 is called 1,2-butadiene.

The last example in this graphic has 10 carbons in its longest chain, double bonds between carbons #1 and 2 and carbons #6 and 7. Off carbon #6 is an ethyl group as there is off carbon #7. The name of this compound is 6,7-diethyl-1,6-decadiene.

There are 3 reactions about which you need to be aware regarding alkenes; hydrogenation, hydrohalogenation and hydration.

Hydrogenat ion

Molecular hydrogen requires a catalyst such as Rainey nickel, Pt or Pd to add across a double bond. The reason for this is that the molecular hydrogen spreads out across the powdered catalyst and "separates" into atomic hydrogen, making it more reactive. In the course of the reaction regarding 2-butene, the bond



polarizes and the two electrons in one of the bonds are repelled forming a reactive radical on carbons 2 and 3. The atomic hydrogen reacts with these reactive moieties forming (reducing the alkene to) the alkane, butane.

Hydrohalogenation -- #1

The use of a hydrohalic acid to add across the double bond, reducing the alkene to a haloalkane, may be performed under two conditions where HBr is concerned. The first is without the presence of peroxides. In this case, the H in the HBr adds to the carbon in the double bond with the most hydrogen atoms on it and the Br adds to the carbon in the double bond with the least number of hydrogen atoms. This is called Markovnikov



addition. In short: them that has, gets! Or, the rich get richer. This means that the carbon in the double bond that is richer in hydrogen atoms gains the hydrogen atom from the HBr. The short version is that the bond polarizes and the Br separates (dissociates) from the H so that they may react with the reactive portions of the radical. The product of this reaction with propene is 2-bromopropane.

Hydrohalogenation -- #2

The second is an interesting phenomenon that seems to occurs <u>only with HBr</u>: in the presence of peroxides, the H and the Br react in an anti-Markovnikov fashion, i.e., the rich don't get richer. Or, them what don't have, gets. Using propene, again, when peroxides are present, the product is 1bromopropane.



Hydration

Is the addition of water (HOH) across the double bond. This reaction occurs in a Markovnikov manner and requires a mineral acid as the catalyst. The OH reacts with the 2d carbon in the double bond and the

H reacts with the first carbon in the double bond. The product is, by common name, isopropyl alcohol or, by IUPAC, 2-propanol. Organic compounds that contain the OH group are called alcohols.





Alcohols

Although they are a bit out of sequence, since they have been mentioned, above, we'll discuss alcohols at this time. Alcohols consist of carbon, hydrogen and oxygen. They are named by the Page | 25 same rules we've already discussed with one addition: by IUPAC, the name of an alcohol ends in "ol". The simplest alcohol is methanol (CH₃OH). Methanol (methyl alcohol by common name) is named as follows: "meth" for one carbon, "an" for the alkane and "ol" for the OH Ethanol (ethyl alcohol by common group.

name), C_2H_5OH , has two carbons, all single carbon-carbon bonds and the OH group.

"Prop" alcohols



2-methyl-1-butanol

Like the alkyl radicals, the alcohols have isomers that follow the radicals. In the propyl alcohol family, there are two isomers: 1-propanol (n-propyl alcohol by common name) and 2-propanol (isopropyl alcohol by common name). The numbers tell you where the OH group is on each isomer. Image, right, is of isopropyl alcohol or 2-propanol

In the butyl alcohol family (at left), there are 4 isomers: 1-butanol (n-butyl alcohol by common name), 2butanol (sec-butyl alcohol by common name), 2-methyl-1-propanol (iso-butyl alcohol by common name) and 2-methyl-2-propanol (t-, tert- or tertiary butyl alcohol).



The reactions of alcohols with which you need to be well versed are two: Dehydration and Oxidation.

Dehydration Reactions 2° Alcohol

When dehydrating alcohols, the bottom line is two-fold: 1) tertiary alcohols are more reactive than secondary and secondary alcohols are more reactive then primary alcohols and 2) water is always removed in dehydration reactions.

The dehydration of primary, secondary and tertiary alcohols follows the same general principles. The reaction requires heat and



sulfuric acid. The OH is always lost as the hydroxide ion and the H is always removed as the proton -note that $H^+ + OH^- \rightarrow HOH$. In general, the hydroxide ion and proton "lasso" each other leaving a negatively charged carbon ion behind (**carbanion**) where the proton was removed and a positively charged carbon ion behind (**carbocation**) where the hydroxide ion was removed.

Since opposite charges attract, the two electrons on the carbanion "flip" down onto the carbocation, "sealing" the bond and leaving us with the alkene product, e.g., propene, propene and 2-methylpropene per the graphic in order.

Dehydration Reactions – Tertiary Alcohol

When dehydrating alcohols, the bottom line is two-fold: 1) tertiary alcohols are more reactive than secondary and secondary alcohols are more reactive then primary alcohols and 2) water is always removed in dehydration reactions.

The dehydration of primary, secondary and tertiary alcohols follows the same general principles. The reaction requires heat and sulfuric acid. The OH is always lost as the hydroxide ion and the H is always removed as the proton -- note that $H^+ + OH^- \rightarrow HOH$. In



general, the hydroxide ion and proton "lasso" each other leaving a negatively charged carbon ion behind (carbanion) where the proton was removed and a positively charged carbon ion behind (carbocation) where the hydroxide ion was removed.

Since opposite charges attract, the two electrons on the carbanion "flip" down onto the carbocation, "sealing" the bond and leaving us with the alkene product, e.g., propene, propene and 2-methylpropene per the graphic in order.

Oxidation of Alcohols

There are 3 general rules about which you need to know: 1) primary alcohols are oxidized to aldehydes which may be oxidized to acids, 2) secondary alcohols are oxidized to ketones and 3) tertiary alcohols either do not react or explode violently.



Oxidizing agents include potassium dichromate, potassium permanganate or chromium (VI) oxide.

As you can see in the graphic, ethanol may be oxidized in a step- Page | 27 wise manner ethanal to (acetaldehyde by common name) which may then be oxidized to ethanoic acid ("eth" for 2 carbons, "an" for the alkane and "oic" as it's an organic acid; common name is acetic acid).

2-butanol is directly oxidized to 2butanone ("but" for 4 carbons, "an" for the alkane and "one" for the ketone; the "2" tells us that the

double bonded oxygen atom is bonded on carbon number 2; the common name for this compound is methyl ethyl ketone or MEK). T-butyl alcohol, of course, doesn't react.

Diols and Triols

without proper PPE.



Poly-ols: Carbohydrates ("Sugars")

The last group of alcohols for discussion are the "polyols" or the carbohydrates. There are, for all intents and purposes, 2 classes of carbohydrates: pyranoses and furanoses. These two classes are so called because their carbon skeletons are based off of pyran and furan. Note that both pyran and furan each have an oxygen atom in the closed ring. At each corner is a carbon atom.



Pyran

Alcohols don't just come as a single OH group on a hydrocarbon. Sometimes there are 2 OH's (diols) or 3 OH's

(triols). Ethylene glycol is known as 1,2-ethanediol and is used as an antifreeze. Efforts are being made to reduce its use as it's not environmentally friendly. Propylene glycol is

known as 1,2-propanediol and is used as a preservative. Glycerin is also known as 1,2,3-propanetriol. It is used as a lubricant and a precursor in the synthesis of nitroglycerine.

One way that cardiac patients can tell if their nitro is going bad is if the headache they get while using it doesn't hurt as

bad. Explosives people who work in the nitro shack often go home with headaches from working around nitro all day

Furan

Carbohydrates are generally seen as sources of quick energy. They consist of carbon, hydrogen and oxygen. In the old days, they were named carboHYDRATES as the ratio of hydrogen to oxygen was thought to be 2:1. We now know differently, although the name has stuck throughout time. There are three categories of carbohydrates in which we have interest: monosaccharides, disaccharides and polysaccharides.

Two of the simplest carbohydrates are glucose and fructose, the sugar in our blood and fruit sugar.



As you can see, both have unique geometric shapes in their

base structures and each has a unique orientation of the -OH groups upon the base structure. Remember that at each corner, there is a carbon atom and that carbon takes 4 bonds. The hydrogen atoms that are by themselves are not shown but are understood to be present.

Biochemists developed a short-hand for quickly sketching carbohydrates called the Hayworth projections. The graphics of each of the above sugars show the Hayworth projections, where the -OH's are replaced with lines going in the correspondingly correct directions. Each of the above carbohydrates has a base structure that contains one oxygen atom in its ring. Glucose and fructose are both hexoses (6-carbon sugars); glucose is a pyranose and fructose is a furanose. The sugars are so called because their base ring structures are based upon furan and pyran.

Monosaccharides – Furanoses

These two compounds (furan and pyran) provide the framework for numerous monosaccharides (single sugars). Ribose is found in ribonucleic acid (RNA); xylose is wood sugar and is non-fermentable; arabinose is gum sugar -- it may sometimes



be found in urine. A form of ribose is found in deoxyribonucleic acid (DNA): deoxy-ribose. Ribose must lose the -OH on the 2' carbon to become deoxy-ribose. Note that ribose, xylose and arabinose are pentoses (5 carbon sugars). In addition, the proper names of the above furanoses are: D-ribofuranose, D-xylofuranose and D-arabinofuranose.

Pyranoses

Glucose, we've briefly discussed. Galactose is of significance in that it forms half of the disaccharide



(double sugar) lactose (milk sugar). Mannose is a plant sugar. Note that these sugars differ in their geometric structure simply by the orientation of the -OH groups. Indeed, the orientation of the -OH groups -- only differing by the position of $\underline{1}$ -OH group -- changes the sweetness of the sugar. To remember these sugars, I've got three mnemonics for you. They are based off the first 4 carbons (1,2,3,4) and #5 carbon has no -OH group on it and #6 carbon is always up and to the left for our purposes. To remember glucose, the mnemonic is DDUD: down, down, up, down. This describes the orientation of the -OH groups on the first four carbons. Galactose is DDUU, while mannose is DUUD. The proper names for the above pyranoses are: D-glucopyranose, D-galactopyranose and D-mannopyranose.



Anomeric Carbon

We can go another step in naming monosaccharides based upon the position of the -OH on carbon #1. This carbon is called the anomeric carbon. When the -OH group is down on carbon #1, that is said to be in the α -configuration. When the -OH group is

up on carbon #1, it is said to be in the β -configuration. Humans metabolize monosaccharides in the α -configuration. The graphic illustrates glucose in both configurations.





The Disaccharides

We are interested in only three of them:

Maltose is also known as malt sugar; Maltose consists of two glucose molecules bonded together;

Lactose as milk sugar; Lactose consists of one molecule of galactose and one molecule of glucose -- pretty clever considering that young animals living on mother's milk use the glucose for quick energy and send the galactose to their livers where it will stored for future energy needs as glycogen -- bonded together;

Sucrose as table sugar. Sucrose consists of one molecule of glucose and one molecule of fructose bonded together.

Glycoside Bonds

The bonds that hold these sugars together are called glycoside bonds. An oxygen atom between the first and 4th carbons of each respective glucose molecule (see above) connects the two glucose molecules linked together in maltose. Since the linkage is from an -OH group on the left glucose molecule that

is in the α -configuration, this is called an $\alpha 1$ to 4 link, or $\alpha 1 \rightarrow 4$ link. Since the linkage between the galactose molecule and the glucose molecule starts in the β -configuration and is also between the 1st and 4th carbons via an oxygen atom, this is called a $\beta 1 \rightarrow 4$ link, or $\beta 1 \rightarrow 4$ link. The linkage between the glucose and fructose molecules in sucrose occurs through the 1st and 2nd carbons of glucose and

fructose, respectively. This is an α 1 to 2 link, or α 1 \rightarrow 2 link. Refer to the above graphics for clarification of the shapes of these bonds. Remember, also, that there are NO carbons in the actual glycoside bond: ONLY an oxygen atom links the monosaccharides together.

The Polysaccharides

We are interested in three polysaccharides: starch, glycogen and cellulose.

Starch consists of two forms of complex carbohydrates: amylose and amylopectin

Amylose	Amylopectin
Is the less abundant form and forms $\boldsymbol{\alpha}$ helix	The more abundant form in starch
Iodine "crawls" into the helix and forms inclusion compounds which turns a dark blue	Forms BOTH α 1 \rightarrow 4 and α 1 \rightarrow 6 links (shown in glycogen below)
Starch is found in PLANTS	Similar to glycogen due to the branching caused by the α 1 $\!$
Amylose is hydrolyzed by amylase in our mouths	Has lesser helix amount, hence less iodine binding; the color obtained is a red-violet color
	Found in PLANTS

Glycogen

Glycogen is found in ANIMALS, specifically in the skeletal muscle and liver of animals. It is also found in fetal hearts and fetal lungs. Fetal hearts run off glycogen while adult hearts run off lipids. The glycogen in fetal lungs is necessary to form surfactant to make oxygen passage into the body from the lungs easier when the fetus is in room air rather than the womb. Glycogen branches due to the same sort of linkages found in amylopectin ($\alpha 1 \rightarrow 6$ links).



Having both 1 to 4 and 1 to 6 links lets the glycogen molecule become very dense and be very efficient for storage. Approximately 1/3 of the weight of the human liver is glycogen. The branches that are formed are then "de-formed" by an enzyme called the "debranching enzyme" when glycogen is needed for energy. Although glycogen has some helix, it is more like amylopectin: it forms less inclusion compounds with iodine. The color obtained is amber red and may be stabilized with the addition of the dihydrate of calcium chloride. Each glycogen molecule contains approximately 100,000 molecules of glucose per molecule of glycogen.

Cellulose

Cellulose, our last carbohydrate, is a bit different. In order to hold the glucose molecules together, they are linked by $\beta 1 \rightarrow 4$ linkages. Humans can not metabolize these β links, while ruminants can.

Ruminants digest cellulose because they have bacteria in their stomachs that contain the enzyme cellulase that hydrolyzes these links. Cellulose is the most abundant carbohydrate on earth; humans utilize it as dietary fiber.



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Reducing Sugars

ANY CHO which can reduce an alkaline solution of Cu(II). ALL monosaccharides; Lactose and Maltose; NOT sucrose!!!!!! IN GENERAL: if a free –OH is on the **ANOMERIC CARBON**, the CHO is a reducing sugar.



Benedict's Test

Benedict's test is basis for Clinitest: urine test for urinary sugar excretion in diabetes: Green: NO glucose in urine; Brick Red: > 2 g glucose/100 mL urine





Tollen's Test

Ammoniacal silver (I) is reduced to elemental silver $(Ag^{0}) - aka$ silver mirror test.

Barfoed's Test

In acid solution, Cu(II) is a WEAKER oxidizing agent. Barfoed's Test is used to differentiate BETWEEN monoand di-saccharides. If the solutions are heated for > 10 minutes, false positive results will be obtained.



Bromine Water

Bromine water oxidizes aldoses but NOT ketoses.

Alkynes

Getting back into sequence with the hydrocarbons, our next functional group for discussion is the alKYNES. The general formula for the alkynes is C_nH_{2n-2} . An alkyne is a hydrocarbon that has a triple bond between two carbons: one a sigma bond and the other 2 are pi bonds. The geometry is linear and the hybridization is sp. There is no freedom of rotation about the triple bond.





Ethyne

The simplest alkyne is ethyne -- "eth" for 2 carbons and "yne" for the triple bond. The common name for ethyne is acetylene.

The next simplest alkyne is propyne. Once we get past propyne, we move into the alkynes that have isomers.

In the butyl alkyne family, there are 2 isomers: 1- and 2-butyne where the triple bond is between carbons 1 and 2 and carbons 2 and 3, respectively.

Likewise, the pentyl family has two continuous chain isomers: 1- and 2-pentyne.

The hexyl family of alkynes is more complex and only a few isomers are shown for examples.

There are two general kinds of reactions that you need to be aware of with alkynes: hydrogenation (reduction of the triple bond) and hydration.



Hydrogenation - 1

The first is the hydrogenation of an alkyne with molecular hydrogen and Rainey Ni to reduce the alkyne to the cis alkene isomer, top. Again, simple mechanistics are used so that you can see the, more or less, elementary movement of electrons and bonds.



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CIS



The second hydrogenation reaction: the utilization of either sodium or lithium with aqueous ammonia to form the trans alkene isomer. Remember, too, that Li is easily substituted for the Na in this reaction mechanism.

Hydrogenation -- 2

TRANS

Hydration Reactions -- #1

The production of an aldehyde from an alkyne is illustrated below.



Butyne reacts with water, sulfuric acid and mercuric sulfate to form butanal ("but" from 2 carbons, "an" for the alkane and "al" for the aldehyde functional group). In a nut-shell, two electrons in one of the pi bonds polarize and repel each other forming a reactive alkenyl group. Water reacts at each radical to form an alcohol-like intermediate. Simultaneously, the proton on the OH leaves. The 2 electrons left behind by the proton loss "flip" down to bond with the carbon atom. Since carbon can only take 4 bonds, one bond has to give somehow. The remaining pi bond then "flips" down much like how Page | 34 dominoes push each other over. The two electrons that just flipped down bind the proton, completing the reaction.

Hydration Reactions -- #2

In the case of an intra chain (i.e., mid-chain) triple bond, the mechanism is pretty much the same, albeit inside the carbon chain rather than on the end of the carbon chain.



The products, though, are 1) different and 2) may be more than one. The products are ketones. The product from the reaction of 2-butyne is 2-butanone. "But" from 4 carbons, "an" for the alkane and "one" for the ketone; the numbers tell you that the double-bonded oxygen is on carbon #2.

Aldehydes, Ketones and Acids

Aldehydes

The functional group of an aldehyde is an end carbon that is double bonded to an oxygen and single bonded to a hydrogen atom. The remaining fourth bond may be bound to either another hydrogen atom (to make formaldehyde -- methanal by IUPAC) or to a hydrocarbon "tail". The names that end in "al" are the IUPAC names. Image, right, is of ethanal or acetaldehyde



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Aldehydes



Ketones

The functional group of a ketone is a double bonded oxygen atom to a carbon atom. That carbon atom MUST be bonded to two other hydrocarbons to make the ketone. The simplest ketone is acetone for this very reason. The IUPAC name for acetone is propanone -- "prop" for 3 carbons, "an" for the alkane and "one" for the ketone. It's not necessary to enumerate the ketone in either propanone or butanone. Once one moves into the pentanone family and beyond, it is necessary to enumerate where the ketone is on the chain. Ketones are generally used as solvents. Acetone (right) is used as finger nail polish remover; MEK is finding some use in that area, as well.





Carboxylic Acids

The functional group of the organic acids is the end carbon double bonded to an oxygen and single bonded to an OH group. The COOH group, or carboxyl, or CO_2H group ionizes and causes changes in the pH of solutions. The fourth remaining bond may be bound to a hydrogen atom (making formic acid or methanoic acid by IUPAC) or to a hydrocarbon tail.


IUPAC Name of Acid	Common Name
Methanoic Acid	Formic acid
Ethanoic Acid	Acetic acid
Propanoic Acid (at right)	Propionic acid
Butanoic Acid	Butyric acid# # from butyrium for butter
Pentanoic Acid	Valeric acid



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Hexanoic Acid	Caproic acid*
Heptanoic Acid	Enanthic acid
Octanoic Acid	Caprylic acid*
Nonanoic Acid	Pelargonic acid
Decanoic Acid	Capric acid* *from Capricorn, the goat first isolated in goat urine or blood, depending on the author



Lipids: An introduction

Fatty Acids

The simplest lipids are the fatty acids. These are long chain hydrocarbons with carboxyl groups (COOH groups). We are interested in two groups of fatty acids: saturated and unsaturated fatty acids.



Saturated fatty acids are so called because each carbon atom in the chain

holds all the possible hydrogen atoms it can. These lipids tend to be solids at room temperature. These are also the sorts of lipids found around organs in the

human body, acting a cushions. The only bonds present between the carbon atoms are single bonds.



Unsaturated fatty acids do not have all the hydrogens they can hold, for there are occasional carbon-carbon double bonds in addition to the single

bonds between carbon atoms. These fatty acids tend to be liquids at room temperature and are the primary type of lipid found in skin deposits. Naturally occurring unsaturated fatty acids contain double bonds that are in the "cis" form and artificial unsaturated fatty acids



contain double bonds that are in the "trans" form. The trans-fatty acids are found in oleo and margarine and have a high link with heart disease. Below is a graphic of the two types of double bonds. The squiggly lines represent the rest of the molecule. The top graphic shows the hydrogens across from each other in the double bond. This is the "trans" form. The bottom graphic shows the hydrogens on the same side of the double bond. This is the "cis" form.

Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid
$C_{12}H_{24}O_2$	$C_{14}H_{28}O_2$	$C_{16}H_{32}O_2$	$C_{18}H_{36}O_2$
Dodecanoic acid 12:0	Tetradecanoic acid 14:0	Hexadecanoic acid 16:0	Octadecanoic acid 18:0
found in coconut oil	found in coconut oil	found in lard	found in lard

Fatty Acids – Special Carboxylic Acids – Saturated



There are 4 unsaturated fatty acids that are important to remember, as well. NOTE: EFA = essential fatty acid. There are three items that need discussion, here, before examining the fatty acids: 1) the "n-" nomenclature, 2) the "w" (omega) system of nomenclature and 3) the "delta" system of nomenclature.

The "n-" system of nomenclature comes from going to the CH_3 end of the molecule and counting in from the end (end - [e + d] = n) to the carbon with the first double bond. The omega system is the same system, just another name.

The delta (Δ) system of nomenclature of fatty acids, specifically unsaturated fatty acids, is equally as simple: the first number is the number of carbon atoms in the hydrocarbon chain. The number after the colon is the number of double bonds in the whole molecule between carbon atoms. The numbers superscripted above the delta (Δ) sign tell you the location of the double bonds, e.g., $^{\Delta 9, 12, 15}$: the double bonds are between carbons 9 and 10, 12 and 13, and 15 and 16, where we only identify the carbons by the lowest number in the double bonds.



18:1, n-9 or 18:1 ω 9 or 18:1 Δ^9 ; Oleic Acid = Cis-9-octadecenoic acid (trans isomer is elaidic acid and causes a great deal of cardiovascular troubles). Sources: Olive oil (best), Canola oil, grapeseed oil, vocado oil, avocado, almond oil, pecan oil, peanut oil, HOSO's (high oleic sun/safflower oil) pretty good, too. Slows development of heart disease; seems to lower blood pressure in hypertensives and lowers total cholesterol levels; Raises HDLs; Lowers LDLs; See also: http://www.spectracell.com/media/supplement-oleic-acid.pdf

Linoleic Acid	α -Linolenic Acid	γ-Linolenic Acid	Arachidonic Acid
9,12-octadecadienoic acid	9,12,15-octadecatrienoic acid	6,9,12-octadecatrienoic acid	5,8,11,14-eicosatetraenoic acid
ESSENTIAL for life			
18:2 Δ ^{9, 12}	18:3 Δ ^{9, 12, 15}	18:3 $\Delta^{6, 9, 12}$	20:4 $\Delta^{5, 8, 11, 14}$
n-6 or w 6 18:2, n-6	n-3 or w 3 18:3, w 3	n-6 or w 6 18:3, n-6	n-6 or w 6 20:4, w 6
found in corn oil, soybean oil, cottonseed oil	found in leafy vegetables and vegetable oils, flaxseed/meal (ALA), walnuts	found in leafy vegetables and vegetable oils	found in peanut oil, brain/nervous tissue

Poly-Un-Saturated Fatty Acid (PUFA) Nomenclature

PUFA Structures, below

Fatty Acid Anomalies

"hydrogenated" margarines contain 15-40% trans fatty acids; \uparrow trans-fatty acids \rightarrow hypercholesterolemia \rightarrow \uparrow CAD, ASHD, CHD.

C=C cis-fattyacid (UFA) in vegets ble oil | Partial deby drogenation c= c trans- fatty acid isomerization

Arachidonic Acid

Why is Arachidonic acid important? It is important because it is the precursor fatty acid for prostaglandin and leukotriene biosynthesis. These compounds are known as <u>eicosanoids</u>, i.e., compounds based off 20 carbons.

PG's and LT's

Prostaglandins are based off prostanoic acid; representative PG's and leukotrienes (LT's) are shown, as well. There are nomenclature rules that follow prostaglandins, too. PG is short for prostaglandin. The **letter** tells us about the ring constituents and the **subscripted number** tells us how many double bonds there are on the side chains. PG's may be inhibited at the level of synthesis with aspirin; anti-leukotriene agents are now available for treating airway diseases, e.g., Accolate, Singulair, Zyflo.





LTA₄ Its biological actions are determined primarily by its metabolites.

LTB_4

chemotactic agent for PMN's (segmented neutrophils); has been proposed to play a role in a variety of acute and chronic inflammatory diseases such as arthritis, dermatoses, inflammatorybowel disease (IBD), and chronic obstructive pulmonary disease (COPD). In particular, LTB₄ seems to play a role in the recruitment of inflammatory cells to the site of tissue injury. (http://sircem.atsionrels.org/.eg/(content/htl/161/2/51/522)





LTC_4

involved in allergy and anaphylaxis; more potent than HISTAMINE in shutting down airways and increasing swelling; component of SRS-A; bronchoconstrictor and vasodilator ω 3 PUFA's

Note that arachidonic acid gives rise to the PG_{"2"} series of prostaglandins – most of these are proinflammatory and can lead to serious consequences, e.g. myocardial infarction.



Recently, two significant PUFA's (EPA and DHA) in fish oils have found more and more use for the treatment of various hyperlipidemias because they are n-3 fatty acids which produce the $PG_{"3"}$ family which are primarily anti-inflammatory and, hence, heart healthy (EPA and DHA are illustrated above). There is some preliminary research (2010) that suggests that mammalian cells can elongate ALA (18:1, n-3) to 20:5, n-3 (EPA) – the conversion is not very efficient: 11 g of ALA (10 Tbsp of flaxseed meal a day!) are needed to biosynthesize 1 g EPA. It also seems that 20:5, n-3 is elongated to 22:6, n-3.

Lipoxin's

"LX's": derived from ω 3 fatty acids (EPA) as well as ω 6 fatty acids such as 20:4^{Δ 5,8,11,14}. ASA CHANGES COX-2 activity to produce anti-inflammatory lipoxins



Lipoxins anti-inflammatory Triglycerides (TG's or TAG's)

TG is fairly self explanatory; TAG's are triacyl glycerols - the same thing, just a slightly different name. AG's are made by condensing one molecule of glycerol with three molecules of fatty acids. The products are the triglyceride (in this case, tristearin) and 3 moles of water.



FA's in TG's

PL's

As a general rule, fatty acids align themselves on a glycerol molecule in such a manner that the #1 carbon has a saturated fatty acid bound to it, #2 carbon has an unsaturated fatty acid bound to it and #3 is fair game.



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A lipid related to the TAG is the

phospholipid (PL). Instead of a third fatty acid bound, proper, to the #3 carbon on glycerol, a phosphate is bound there. Other groups will bind with the phosphate. Figure is representative of phosphatidic acid. A representation/illustration of phosphatidyl choline (PC) or lecithin is below. You may know the latter name as it is in non-dairy creamers as an emulsifying agent.

PC is also important in cell membranes by assisting in membrane rigidity. A related PL, cardiolipin, is a sort of "dimer" of PC. Cardiolipin is found in the inner mitochondrial membrane. This PL causes the inner mitochondrial membrane to be more fluid so that



the protein complexes on electron transport will be brought closer together during active cellular respiration.

The Steroids

The steroids are ALL based off of a 4-fused ring system. The

rings are labeled A thru D. Each carbon is numbered as shown in the graphic.



Cholesterol

ĊН

The primary steroid, i.e., that one compound from which all steroids are derived is cholesterol. As you can see, the enumeration of cholesterol (once you are beyond the basic 4 ring system) is different than what one might expect. Carbons 18 and 19 are called bridging carbons. On carbon #3 is an -OH group and between carbons 5 and 6 is a double bond. The hydrocarbon tail off carbon 17 is enumerated for you, above. In addition, the hydrocarbon chain will be modified by the body as necessary for the synthesis of specific steroids.

Digestive Detergents

Cholesterol also plays an important role in digestion. The manner in which this occurs is that a derivative of cholesterol (cholic acid) reacts with one of two amino acids or derivatives to form detergents. Detergents emulsify fat in the small bowel as small particles so that the enzymes in our small bowels may begin digesting the lipid. The two big bile salts, as these detergents are called, are glycocholic acid and taurocholic acid. Glycocholic acid is formed by the reaction of gly with cholic acid. Taurocholic acid is formed by reacting the oxidized product of cys, taurine, with cholic acid. Note that there is a polar, charged end and a nonpolar, uncharged, lipid-like end. It is due to these features

that detergents work, i.e., the lipid-like end binds the lipid-like molecules and the polar end interacts with the water, in effect lifting the grease into the water.



D

В

1



Important Steroid Hormones

The first is Vitamin D₃. This steroid is necessary for proper bone uptake of calcium and for adequate calcium metabolism in the body. The synthesis of this steroid begins in the skin with the photolysis of a cholesterol metabolite called 7-dehydrocholesterol. The synthesis of this "vitamin" is completed in Page | 45 the liver and kidney, respectively.

Sex Hormones

Cholesterol is also the precursor for the steroid sex hormones. Note that each estrogen (estriol, estradiol and estrone) has an aromatic ring A. This is due to an enzyme found in the biological fat layer in females called aromatase. Aromatase aromaticizes testosterone to the estrogens.



Other Steroid Hormones of Importance:

Cortisol is known as the muscle wasting hormone. This hormone kicks in as a stress hormone during starvation and causes muscle protein to be catabolized in such a manner that the carbon back bone of the individual amino acids is used to synthesize glucose. Cortisone we're familiar with as an anti-inflammatory agent. Aldosterone is a mineralocorticoid that is responsible for directly regulating sodium/potassium ion regulation and indirectly with water balance and chloride ion regulation. Progesterone is the last female sex steroid hormone and is also the precursor for the synthesis of testosterone in the male.

The Most Complex Lipids: The Lipoproteins of The Blood -- Lipid Complexed with Water-Soluble Proteins

We are interested in 4 categories of lipoproteins: Chylomicrons, VLDL's, LDL's and HDL's (very low density lipoproteins, low density lipoproteins and high density lipoproteins). The table below describes the characteristics of the lipoproteins:



Classes of Lipoproteins				
	% Protein % TAG % PL % Cholesterol est			
Chylomicrons	1-2	85-95	3-6	2-4
VLDL	6-10	50-65	15-20	16-22
LDL	18-22	4-8	18-24	45-50
HDL	45-55	2-7	26-32	15-20

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Chylomicrons, by and large, are artifactual in the sense that they appear after we've eaten or if we have some sort of lipid metabolizing disease, e.g. diabetes mellitus, and are usually rapidly cleared from the blood stream under normal circumstances.

The LDL's are the cholesterol forms we hear about as the "bad" cholesterol. This portion is true as when we get too many LDL's, the cholesterol plates out in our arteries and forms atherosclerotic plaques.

While the HDL's are touted as the "good" cholesterol, it is important to remember that it is ONE form of the HDL that is the good cholesterol.

Not all cholesterol is "bad" cholesterol. Remember, we need some cholesterol in our diets to synthesize steroid hormones. While our bodies WILL synthesize steroids from smaller molecules, they prefer cholesterol as the starting molecule.

Note that LDL-cholesterol runs about half cholesterol.

LDL-Cholesterol

In many instances, it is difficult to obtain an actual lab analysis of the LDL-cholesterol. In that case, it may be calculated in one of two ways:

Method 1:

LDL = Cholesterol_(total) - (VLDL + HDL)

Method 2:

 $LDL = Cholesterol_{(total)} - [(0.2*TAG) + HDL]$

where TAG are the triglycerides in your blood

These lipoproteins may be separated in a polyacrylamide gel or on paper that is in an appropriate buffer by applying an electrical current. This is called electrophoresis. As the molecules migrate into the gel under the influence of the current, they "are looking" for the region of the gel at that particular pH and charge where the medium is most "like themselves". Once these molecules reach that region, they stop migrating and may be analyzed. Below is a representative graphic that demonstrates the separation of these lipoproteins at pH 8.6

Note that with the exception of the Chylomicrons, the other lipoproteins are attracted to the positive side of the gel (or paper), indicating that their charges are more negative. The origin is the place where the samples are place in tiny wells in



the gel. The Chylomicrons did not move from the origin. Information like this is very useful, clinically.



Patterns of lipoproteins may be detected by utilizing a gel scanner that uses light to detect how much of

a particular lipoprotein is present. Some sample scans and their associated disease states are presented to the right. Note that diabetics have elevated Chylomicrons and VLDL's with lowered LDL-cholesterol; those eating a high cholesterol diet have elevated LDL's and VLDL's; those with gout have elevated LDL's and VLDL's, as do pregnant women; those with pancreatitis or alcoholism have elevated Chylomicrons, LDL's and VLDL's.

Esters

When an organic acid and an alcohol react in the presence of a mineral acid catalyst, an ester is obtained. Image, right, is methylethanoate.

To name the ester formed between propanoic acid and propanol, name the



alcohol root first ("propyl"), then name the acid root ("propano") and add "ate" to the name, hence, propyl propanoate.



Aspirin is another example of an ester (an ester has a hydrogen or a hydrocarbon on the acid side and a hydrocarbon on the alcohol side of the carboxyl group): acetylsalicylic acid.



A Few Notable Esters

Esters	
Amyl acetate	Banana oil
Ethyl butyrate	Pineapple
Amyl butyrate	Apricots
Octyl acetate	Oranges
Isoamyl valerate	Apples

Esters are also used in perfumes, drugs and finger nail polish remover.

Ethers

NOT to be confused with esters, ethers are hydrocarbons linked to each other through an oxygen atom. The most commonly known ether is diethyl ether $(CH_3CH_2OCH_2CH_3)$. R-O-R'. It was used as an anesthetic until it became very obvious that it caused more problems than it solved. It is currently used as a starter fluid with diesel tractors. Image, right, is of ethylisopropyl ether



MTBE

An ether that has been in the news in the past is MTBE (methyl-t-butyl ether). MTBE was originally used for a gasoline additive to reduce emissions and smog in winter-time in areas like Reno, NV. While it worked, it seems that since it was discovered to be leaking from underground gas tanks at filling stations at Lake Tahoe that a huge flurry about the potential for it to be disease causing or carcinogenic has erupted.



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MTBE: methyl-t-butyl ether

MTBE was also used experimentally -- and may still be -- to dissolve gallstones that were made up primarily of cholesterol. The gall bladder would be visualized by ultrasound, then a needle would be introduced across the abdominal wall into the gall bladder and the MTBE would be injected into the gall bladder. The stone would dissolve within a couple of hours and be excreted in the bile through the small bowel. At the time, there were no known side effects of this treatment.

It remains to reputable scientists to demonstrate whether or not MTBE causes disease or cancer without any external biasing pressures.

Sulfur Derivatives

Thiols

A thiol sounds just like what you might think --it's a sulfur alcohol, i.e., the functional group of a thiol is the SH group. 4 examples of thiol compounds are below. The old way of naming these compounds was

H3CSHmethylmercaptanthiomethaneC-C-SHethylmercaptanthioethaneC-C-C-SHisopropylmercaptan2-thiopropane

to add "mercaptan" at the end of the phrase; IUPAC says you name it by thio followed by its alkane name, e.g., methyl mercaptan is thiomethane, ethyl mercaptan is thioethane, ad nauseum. The significant reaction between thiols is the formation of disulfide bonds -more on this in the amino acid section. Image, right, is of thioethane.

Thioacids

Thioacids, instead of having a COOH group, have a COSH group. 5 examples of thioacids are below:

Nitrogen Containing Compounds: Nitro Compounds, Amines, Amides

Nitro Compounds

The functional group of this group of compounds for this course is R-O-NO₂ where R is a hydrocarbon. The illustrative nitro compound is nitrogylcerin. Its synthesis is driven by reacting glycerine, nitric acid and a catalyst to form the nitroglycerin and water. Besides being



used as an explosive, it is also used as a vasodilator for people with heart problems.



Amines

The functional group of an amine is the NH₂ group. Primary, secondary and tertiary amine illustrations follow this page. Note that the degree of an amine depends upon the number of hydrogen atoms that are replaced by a hydrocarbon group, e.g., primary amines have had one hydrogen replaced with one hydrocarbon; secondary amines have had 2 hydrogens replaced with hydrocarbons; tertiary amines have had 3 hydrogens replaced by hydrocarbons. The simplest primary amine is methylamine. Other examples, ethyl, n-propyl and isopropyl amine are shown in the figure. The simplest secondary amine is dimethylamine, i.e., there are two methyl groups on the nitrogen. Diethyl, di-n-propylamine and di-isopropylamine are illustrated, as well. The simplest tertiary amine is trimethylamine, i.e., there are 3 methyl groups on the nitrogen. Triethyl, tri-n-propyl and tri-isopropylamine are illustrated, as well. Note

needs to be made that these amines are insoluble in water. The simplest way in which to render these amines water-soluble is to add a bit of acid, protonating the nitrogen, making the ion polar -- remember, like dissolves like.

$$\begin{array}{ccccc} H & CH_3 \\ H_3C--NH_2 & H_3C--N--CH_3 & H_3C--N--CH_3 \\ H_3C--NH_2 & C-C-N-C-C & C-C-N--C-C \\ C-C--NH_2 & C-C-N-C-C & C-C-N-C-C \\ C-C-C-NH_2 & C-C-C-N-C-C & C-C-C-N-C-C-C \\ C-C-C-NH_2 & C-C-C-N-C-C-C & C-C-C-N-C-C-C \\ C-C-C & C-C-C & C-C-C-N-C-C-C \\ NH_2 & N-H & N--C \\ NH_2 & C-C-C & C-C-C \\ C-C-C & C-C-C \\ N-H & N--C \\ C-C-C & C-C-C \\ C-C-C & C-C-C \\ C-C-C \\ N-H & N--C \\ C-C-C \\ C-C \\$$



Image, far right, is of the quaternary ethylisopropylmethylammonium ion.

Amino Acids

These compounds contain a carboxyl group (acid) and an amine (NH_2) . Image is of Cysteine, a sulfur containing (thio) amino acid found in hair and nails and hooves and horns.

Any time one deals with anything in Biology, one must also contend with proteins: the products of gene activation. To understand proteins, it is necessary to understand amino acids, to learn their structures and to learn a few of the functions and essentiality of the amino acids. There are 20 amino acids and 1



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imino acid we will study:

glycine (gly) alanine (ala) valine (val) leucine (leu) isoleucine (ile or ileu) proline (pro) ← imino acid phenylalanine (phe) tyrosine (tyr) tryptophan (trp) serine (ser)

cysteine (cys) cystine (cys-cys) threonine (thr) methionine (met) aspartic acid (aspartate; asp) asparagine (asn) glutamic acid (glutamate; glu) glutamine (gln) histidine (his) lysine (lys) arginine (arg)



The simplest amino acid is glycine (gly). It consists of two carbon atoms covalently bonded to each other. To one carbon atom, two oxygen atoms are bonded; to the other carbon atom, an amino group (NH_3^+) and 2 hydrogen atoms are bonded. The carbon that is directly attached to the CO_2^- is called the

 α -carbon. It is this carbon that makes all amino acids used by man the α -amino acids. Gly is typically found in proteins where there are turns in the amino acid sequence, as it is very small and has a small "R" group



(a hydrogen). R groups are radical groups, representative groups or reactive groups. In this case, and for the case of all the amino acids, we will use the second definition of R group to mean the rest of the

amino acid molecule beyond the 2d carbon in the back bone of the amino acid. Gly is an amino acid with an uncharged polar R group.

Another way to look at Glycine. The same manner may be used with the other 19 amino acids.

Amino Acids with Hydrophobic R Groups



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The next simplest amino acid is alanine. The difference between ala and gly is that the H in gly has been replaced by a CH_3 in ala. Ala is a small amino acid, especially suited for diffusing from muscle cells into the blood to be transported by the blood to the liver for utilization in gluconeogenesis.











Val







lle

Valine (val), leucine (leu) and isoleucine (ile or ileu) are the next three simplest amino acids (bottom previous page). These three amino acids are called branched chain amino acids (BCAA's) and are utilized for the synthesis of substrates for gluconeogenesis and for ketogenesis. Leu is the only purely ketogenic amino acid. Ketones are <u>usually</u> associated with someone who has diabetes mellitus and who is in diabetic coma. It is the ketones, or ketone bodies, that give the patient the sweet, fruity smelling breath Page | 53 of diabetic coma.

 $^{+}H_2N \xrightarrow{C} C \xrightarrow{H} H_2C \xrightarrow{C} CH_2$

Proline is actually an *imino* acid. Note that it is a closed ring amino acid. Pro, like gly, is usually found in proteins where turns are required. A derivative of proline, hydroxyproline is found in connective tissue and helps make the tissue stronger.

Phenylalanine is alanine with a benzene ring attached to it (C_6H_6) . Phenylalanine



is necessary for the synthesis of the catecholamines dopa, dopamine, norepinephrine and epinephrine.



Some people are born lacking an enzyme that regulates the catabolism of phe. When this happens, a metabolite of phe, phenylpyruvic acid, builds up in nervous tissue and causes severe mental retardation.

This condition is known as phenylketonuria, or PKU. The people who have PKU are generally blonde, blue-eyed and fair complected. The reason for this is that phe is also necessary for the synthesis of a pigment called melanin that contributes to eye, hair and skin color. People who have PKU must eat a diet low in phe the rest of their life. Since phe is required by the body to initiate

the synthesis of the catecholamines for neurotransmitter and hormonal functions, people who have PKU must add tyrosine to their diet -- the product of the hydroxylation of phe that doesn't occur in PKU.

Methionine is a sulfur containing amino acid. Its necessity is to provide the methyl group (CH_3) to acceptor molecules in one-carbon metabolism. One-carbon metabolism is important in the production of red blood cells, white blood cells and platelets.

200

CH

+H3N

Met





Tryptophan (trp) is the last of the amino acids with hydrophobic R groups. Trp is the precursor for the synthesis of serotonin (aka nature's downer). Serotonin from the health food store will NOT cross the blood brain barrier; trp is required for this to occur. Turkey and milk have high levels of trp. There seems to be some controversy as to whether or not there is enough trp in milk (especially warm milk) to render a person drowsy so



that they will fall asleep when it is difficult for them to do so without assistance. In recent times, *selective serotonin reuptake inhibitors* have seen use in depression, eating disorders, obsessive compulsive disorder, to name a few, e.g. prozac, celexa

Amino Acids with Uncharged Polar R Groups

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At physiologic pH, the R groups are not ionized as are the amino and carboxyl groups of the amino acids.

⁺H₃N

COO

ser

OH

Glycine has already been mentioned. Serine (ser) is alanine with an -OH group replacing a -H. As a rule, ser has a function similar to that of threonine (thr), another hydroxylated amino acid: it serves as an activation site in enzymes, i.e., when it is phosphorylated or dephosphorylated, the enzyme is turned on or off. The last hydroxylated amino acid is tyrosine (tyr – with phe discussion). It is, simply, hydroxy phenylalanine, with the -OH group straight across the benzene ring from the alanine moiety. Tyr has been discussed, previously, as well.

Cysteine (cys) is a sulfur containing amino acid. It is found in most connective tissues. The most often thought about site of cys, though, is the hair. Hair maintains its shape by the presence of disulfide bonds (-S-S-). The disulfide bonds come from the loss of -H from the -SH group of two cys molecules in the hair which then bond to hold the hair in its appropriate shape to form cystlne (cys-cys). Cosmetologists, beauticians utilize this property every day when they give perms. They first reduce the



natural disulfide bonds in hair, then place the hair in the shape the customer asks, then finish the job with an oxidizing agent that forces the formation of the disulfide bonds and, voila!, a new style comes out from under the curlers, drier, *etc*.





Asparagine (asn) and glutamine (gln) are 4 and 5 carbons in length, respectively. They are derivatives of the dicarboxylic



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amino acids aspartate and glutamate (coming up below). Note that each has an extra NH₂ group on the carbon double bonded

to an oxygen <u>farthest</u> from the α -carbon. These two molecules serve as ammonia transporters to the liver and kidney for urea synthesis. Urea is a small, non-toxic compound (compared to ammonia's effects on the cell) that is excreted via the urine.

Amino Acids with Negatively Charged R Groups at Physiological pH



The next two amino acids under study are the acids aspartate (asp) and glutamate (glu)-- the precursor amino acids of asn and gln, respectively.



Both are dicarboxylic amino acids, i.e., there is a COOH group on each end of the molecules.

Amino Acids with Positively Charged R Groups at Physiological pH



Arginine (arg) and lysine (lys) have positively charged R groups at physiological pH. Lysine is heavily involved in connective tissue biosynthesis. Children with low levels of



arginine tend to be mentally retarded (hypoargininemia). Arginine is the last product of the urea cycle from which urea is clipped for excretion.

Histidine (his) is positively charged at a pH of approximately 6 or below. His is the precursor molecule to



histamine, the compound that causes many allergic reactions and which may be blocked by the use of anti-histamines. Histamine synthesis may be stimulated by the influence of norepinephrine or psychological stress. Because of this, many people who have itching-related health problems may be prescribed a drug like doxepin which has both histamine antagonistic properties and anxiolytic properties: both of which combat the health problem by reducing the anxiety felt by the patient which reduces the itching, which reduces the anxiety which reduces the itching, *ad nauseum*.

⁺H₂N

lvs

Of these 20 amino acids, 8 are essential (humans require them in their diets as humans lack the enzymes to synthesize them from scratch) and 2 are semi-essential (required for growth by the young human). The essential amino acids are phe, val, trp, thr, ile, met, lys, leu. The semi-essential amino acids are his and arg. A helpful mnemonic to remember these is: PVT TIM HALL, where the first letter of each amino acid makes up this mnemonic.

Peptides and Peptide Bond

Amino acids are the building blocks of proteins. In order for the amino acids to link together to form the numerous proteins necessary to keep a human functioning, they form a special bond between each other: the peptide bond. The peptide bond is formed between the carboxyl group of the first amino acid and the amino group of the second amino acid to form a dipeptide. The peptide bond is unique in that it appears to be a single bond, but has the characteristic of a double bond, i.e., it is a rigid bond. This kind of bond only occurs between amino acids. As the amino acid chain increases, the next amino acid adds onto the previous carboxyl group by its amino group.

Peptide Bond and Peptides



By convention, the left amino acid is always #1; is the free amino end or the N-terminus. The farthest amino acid residue to the right is the amino acid in the protein that has the highest number and, as a general rule, is the free carboxyl end or the C-terminus. In some cases, the -OH may be replaced with an NH₂, making it an amide. When dealing with peptides, there is always one LESS peptide bond than there are amino acid residues in the protein, i.e., a tripeptide has 2 peptide bonds and three amino acids; a hexapeptide has five peptide bonds and six amino acids, *ad nauseum*. The sequence[s] of the amino acids held together by peptide bonds ONLY is called the primary structure of a protein.

Enzymes: Biological Catalysts

Enzymes Have Specific Functions

Enzymes are categorized into one of 6 biological activities according to the Enzyme Commission: E.C. #.#.#.#; Oxidoreductases: catalyze redox reactions -- involve NAD and FAD – E.C. 1; Transferases: catalyze group transfers -- E.C. 2; Hydrolases: use water to lyse bonds – E.C. 3; Lyase: nonhydrolytic and non-oxidative group removal – E.C. 4; Isomerases: catalyse isomerization reactions – E.C. 5; Ligase: catalyzes reactions requiring ATP hydrolysis – E.C. 6.

Enzyme Models

Of significance, of course, is the fact that the shape of the enzyme gives it its function (the shape of a protein gives it its function). Enzymes speed up the reaction rate in biological systems 100,000 - 1,000,000 fold! Enzymes have specific substrates (chemical group upon which the enzyme works), but can work on limited kinds of substrates. There are two generally accepted models for the functioning of enzymes: the lock and key model and the induced fit model. A third model, the Three Point Attachment Theory is making a "come-back" of sorts in enzymology We will address the lock and key model first.

Model #1: Lock-n-Key



In this model, see graphic, above, the substrate (S) is complimentary to the binding/active site in the enzyme (E). This is likened to the lock and key, where the lock is complimentary to the key. As the E and S bind, they form the Enzyme-Substrate complex (ES). This is an intermediate in the reaction that will cause S to be changed into a product (P). The enzyme acts as a sort of scaffold, holding the substrate so that one specific reaction may occur. In this case, a bond (or bonds) is (are) broken as the enzyme changes its shape ever so slightly, causing the substrate to break exactly where it's supposed to, releasing the new products and the enzyme for use, again. Remember that the active sites (a, b, c) of the enzyme are complimentary to the SHAPE of the substrate.

Model #2: Induced Fit

The second model is called the induced fit model. This means that as the S gets closer to the E, the E actually undergoes a conformational change (shape change) to fit the S, i.e., its shape is INDUCED to

change by the presence of the substrate. Note that as S gets closer to E, the active site "a" changes shape to match the complimentary site on S. As S continues to get even closer, site "b" shifts its shape, as does site "c" when S is all but bound to the enzyme. Once ES is formed, this model conforms to the remainder of the lock and key theory of enzyme-substrate binding.

E E

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Enzyme Inhibition: Descriptive Introduction







The left graphic represents the normal ES complex.

Competitive Inhibition

The right graphic represents competitive inhibition of an enzyme, i.e., an inhibitor specific to this enzyme COMPETES with the substrate for the active site of this enzyme. It is reversible; will block S from binding. One example of this sort of inhibition is carbamoyl choline that competitively inhibits acetylcholinesterase.



Uncompetitive Inhibition

The right graphic represents uncompetitive inhibition. This sort of inhibition involves covalently bound inhibitor and inactivates the enzyme irreversibly. Two examples of this sort of inhibitor are nerve gas and organophosphates that inhibit acetylcholinesterase. Organophosphate poisoning may be reversed by injecting a drug called 2-PAM. Valium and atropine are useful to treat muscle spasms and breathing difficulties, as well.



Non-Competitive Inhibition

The right graphic represents noncompetitive inhibition. Note that the inhibitor does NOT bind to the active site of the enzyme, rather it has its own unique binding site. When a noncompetitive inhibitor

binds to an enzyme, it causes the enzyme to change shape and shuts off its activity reversibly by not allowing S to bind completely. This sort of inhibition is also referred to as allosteric inhibition and plays major roles in metabolic regulation. An example of a noncompetitive inhibitor is aspirin. Aspirin inhibits cyclo-oxygenase which is the main enzyme in prostaglandin



biosynthesis. Prostaglandins mediate pain, inflammation, blood pressure, gastric mucous secretion, blood clotting, labor and delivery, to name a few.

Enzyme Inhibition: A Second and Third Look



Amides

The functional group of the amide is a carbon atom double bonded to an oxygen atom, single bonded to the NH₂ group and either a single bonded hydrogen (to make formamide or methanamide by IUPAC) or a hydrocarbon tail.

The preparation of amides is a two step process. The first step is to react a carboxylic acid with thionyl chloride (SOCl₂). This forms an acid chloride (R-COCl in the graphic), SO₂ and HCl. The general mechanism is that one chlorine atom reacts with the hydrogen in the COOH group as the oxygen atom in the OH part of the COOH reacts with the sulfur and the other chlorine atom reacts with the CO.



The second step is to react the acid chloride (R-COCI) with ammonia to form the amide and ammonium chloride. The elementary mechanism is that as the chlorine atom in the acid chloride reacts with one mol of ammonia and a hydrogen atom, the remaining NH₂



urea

sulfanilamide

reacts with the R-CO to form the amide.

3 Examples of Amides -- Some Obvious, Some Hidden

The last group of aliphatic hydrocarbons, but the introductory group dealing with "ringed" structures of hydrocarbon compounds, to be discussed is shown in the graphic. These are compounds that form "ringed" compounds, i.e., a carbon chain that closes up onto itself resembling a "ring". These compounds are named, first, with "cyclo" in front and the alkane name after the prefix.



Aromatic Hydrocarbons

Benzene

For the purposes of this introduction, the aromatic hydrocarbons are based off of benzene, C₆H₆. Note that there are several ways in which to draw the structure of benzene. These different forms are called resonant structures, i.e., the atoms are arranged in a constant manner, but the electrons in the second of the bonds are distributed slightly differently. The middle structure is the more correct form. This structure was determined in the 1800's by Kekule'. The story has it that he was working on the structure of benzene without the benefit of the technology we have, now, and he dreamed one night of a snake biting its tail. That gave him the idea for the circle in the middle of the benzene ring. The circle represents a floating half bond between carbons. Remember, that for the second bond in a double bond (the pi bond), one needs overlap of both the upper and lower lobes of the p

succinoyl sulfathiazole

orbitals. In benzene, though, there is only half an overlap, i.e., either top halves overlap or the bottom halves overlap, alternately, creating a bond and a half between the carbon atoms in the ring. Turns out that Kekule' was correct.





Substituted Benzene Compounds



There are a number of substituted benzene compounds that are important to have in your handbag of chemical knowledge. The top figure illustrates a generic way of drawing a xylene if the actual name is not given. What, though, happens if one of the three xylenes is drawn as in the bottom of the figure? How is it named?

Before we answer that question, let's look at the anatomy of a monosubstituted benzene compound like toluene (top) and aniline (bottom). We'll put the methyl (amino) group that substitutes for the hydrogen on the top of the graphic. There are three positions on the ring that are un-substituted relative to the methyl (amino) group: 2 carbons next to the carbon with the substituting methyl (amino)

group, 2 carbons that are located 2 carbons away from the carbon with the substituting methyl (amino) group and 1 carbon directly across the ring from the carbon with the substituting methyl (amino) group. In order, these other carbons in the benzene ring are called, ortho, meta and para -- "next to", "in between" and "across from".



Toluene

When hydrogen atoms are substituted for on the ring by other groups, the substitutions occur following a very specific set of rules. These rules hinge on what substituting group makes it onto the benzene ring first. If groups like the -OH, -X add first, these will direct the next substituting groups into either the ortho OR the para positions. These groups are very small and take up



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a very small amount of space, i.e., have small steric hindrance. If groups like the nitro, carboxyl or trimethylammonium groups add first, these will direct

the next substituting groups onto the meta position. The former group is called "ortho/para directors" and the latter group is called the "meta directors".



So, now let's go back to the xylenes (bottom left, previous page) -- the dimethyl-substituted benzene compounds. The names, now, are fairly simple: ortho-xylene (o-xylene), meta-xylene (m-xylene) and para-xylene

(p-xylene). Notice that the mxylene doesn't make much sense as it's drawn. During the synthesis, though, it becomes easily seen how it's made -- that's for another course, though.



Terephthalic Acid

synthesized (not discussed at this juncture). Note that phthalic, isophthalic and terephthalic acids are as drawn in this graphic.

they are named, either, without knowing how they were

Generic Benzene Derivatives



Benzyl alcohol, benzaldehyde and benzoic acid, are shown below. Note that the $C_6H_5CH_2\bullet$ is the benzyl radical, NOT the $C_6H_5\bullet$ radical, which is the phenyl radical. Benzaldehyde is artificial almond extract. Benzoic acid is used as a food preservative.

Aniline, styrene, benzoin, cinnamaldehyde and trans-

cinnamic acid, are benzene derivatives. Cinnamaldehyde is oil DDT, or dichloro-diphenyl-trichloro-ethane, is of cinnamon. also illustrated below. Controversies still surround DDT to this day, e.g., did it really cause eagles' egg shells to get weak and decimate the eagle populations?, could it have been the codumped mercury instead?, does DDT cause cancer in locations



where there are still high levels of DDT in the soil?, what role did politics (before social media) play in taking DDT off the market for use only with a special permit, now?

Phenols

ОН

o-cresol



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CH2

Hydroxylated benzene compounds are based off of phenol (fuh NOLE),

 C_6H_5OH . Phenol is a bit different than the aliphatic alcohols in that its proton DOES dissociate, effecting the pH of solutions unlike the proton on aliphatic alcohols.

There are a number of important hydroxylated benzene compounds. The first are the methyl-substituted phenols, or cresols (o-, m- and p-cresol). These are produced from the purification of coal tar.

> The second group of important phenolic compounds is the catechols (KAY tuh koals). Catechol has the structure in the

figure. Note that catechol is an ortho-substituted benzene "dialcohol", or ortho-hydroxyphenol.

The hormone epinephrine, neurotransmitter norepinephrine and the vasoactive dopamine are all biologically important catecholamines

Isoproterenol is a synthetic catecholamine (drug) that mimics the effects of epinephrine.



Catechol The third group of important phenolic compounds, or derivatives of phenol, are the essential oils.



Ω

m-cresol

CH₂

ĊНз

D

p-cresol













Eugenol (oil of cloves)	Isoeugenol (oil of nutmeg)
Anethole (oil of aniseed)	Vanillin (oil of vanilla bean)
Thymol (oil of thyme and mint)	Safrole (oil of sassafras)

Aromatic Ketones

Two aromatic ketones jump out: chloroacetophenone and acetophenone. The former is a lacrimator (what is that?) and the latter is a hypnotic -- simply by removing the chlorine atom from the lacrimator!



Antimetabolites

For folic acid to be fully activated for use by bacteria for growth and reproduction, it requires PABA (para-aminobenzoic acid). Scientists figured out that if they modified a compound to LOOK like PABA, it might confuse the micro-organism and it would die. The parent/generic compound they came up with is sulfanilamide -- both shown below -- that came from sulfanilic acid.



Heterocyclic Compounds of Nitrogen

Heterocyclic means that there is more than one kind of atom in the closed ring of an organic ringed compound. These compounds have been saved for this point of the lecture as many of them are aromatic, as well.

By definition, an aromatic compound (nowadays; in the "olden days" all a compound had to be was a derivative of benzene to be considered aromatic) is a compound that "contains cyclic clouds of delocalized p electrons above and below the plane of the molecule ... furthermore, the p clouds must contain a total of (4n+2) p electrons" to be aromatic.

This is the Hückel rule. This means that if n=1, there must be 6 p electrons for the compound to be aromatic; if n=2, there must be 10 p electrons for the compound to be aromatic; if n=3, then there must be 14 p electrons for the compound to be aromatic, ad nauseum. The numbers 6, 10 and 14 are called Hückel numbers.

Hence, benzene is aromatic as it has 6 p electrons, i.e., the Hückel hextet.

Heterocyclic compounds also may follow the Hückel rule to be classified as aromatic. Pyrrole <u>does not</u> conform to Hückel's rule, but is, nevertheless, a cyclic compound that contains a nitrogen atom in the ring, below. It only has 4 p electrons, and does not

C - C = N

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conform to Hückel's rule for aromaticity. 4 pyrrole rings are found in each hemoglobin molecule in our red blood cells and 4 are also found in each chlorophyll molecule in plants. Hemoglobin binds iron(II) and chlorophyll binds magnesium through these pyrrole rings.

The next two heterocyclic compounds are purine and pyrimidine. Both are aromatic as each has 6 p electrons. Note the short hand notation in the graphic as to the drawn structures of each compound. Each compound gives rise to special groups of heterocyclic nitrogenous compounds found in DNA and/or RNA, images follow. G, C, A, and T are found in DNA; G, C, A, and U are found in RNA.

The last group of aromatic heterocyclic compounds is the nucleotides. These consist of three parts: a **purine or pyrimidine, ribose** and **phosphate (a "P" with a circle around it is biochemist's short hand for phosphate)**. Three representative molecules are shown below. All three are involved in energy production in the body. ATP, NAD⁺ and FAD.

H₃C



Introduction to Nucleic Acids

Definitions

By definition, nucleic acids are biomolecules that store genetic information in cells or that transfer this information from old cells to new cells. There are two groups of nucleic acids:

DeoxyRiboNucleic Acid (DNA) -- DNA codes for the functioning of the cell; DNA is located mainly in the nucleus of the cell (with a small amount in the mitochondrion of eukaryotic cells -- to be discussed at a later date); DNA is double stranded.

RiboNucleic Acid (RNA) -- RNA is the "worker" that helps get the DNA message out to the rest of the cell. RNA is primarily in the cytosol of the cell. RNA is single stranded – with one "exception. BOTH are "codes" for the cell and, hence, the body's activities at the cellular level.

Nucleic acids consist of nitrogenous compounds called purines or pyrimidines, a carbohydrate and phosphate. The figure shows what the structures of purine and pyrimidine look like in the lower right-

hand corner. Purine is a 2-fused ring system that consists of one 6-membered ring fused to a 5membered ring. In each ring, there are 2 nitrogens. Pyrimidine has only the 6-membered ring with the 2 nitrogens.

Purines

The two purines of significance are adenine and guanine. Note that they differ very simply: adenine has an amino group on the top of the 6-membered ring, while guanine has an amino group between the 2 nitrogens on the 6-membered ring, a double bonded oxygen in place of adenine's amino group (called a ketone) and has lost a double bond to accommodate the ketone.

Pyrimidines

There are three pyrimidines of interest in Biological Chemistry: Cytosine, Uracil and Thymine. Cytosine has a ketone between its two nitrogens, an amino group atop its ring and has lost a double bond to accommodate the ketone. Uracil is a modified form of cytosine, where the amino group is replaced by a

ketone and a double bond in the ring is lost to accomodate the new ketone. Thymine is uracil with a CH_3 (methyl) group attached adjacent to the ketone at the top of the ring.





Generally, the 5 nitrogenous compounds with their carbohydrate moiety are abbreviated as one letter abbreviations: A, G, C, U, T. It is important to keep in mind that when referring to RNA, these shortcuts are o.k. When referring to them in DNA, it is important to remember that we're discussing dA, dG, dC, dU, dT. The reason for this is shown in the d-R. The carbohydrate that binds with the nitrogenous compounds in RNA is ribose. The carbohydrate that binds with the nitrogenous compounds in DNA is deoxyribose. Deoxyribose is ribose that has had the 2' -OH group removed. The last portion of nucleic acids is the phosphate group. This group is of immense importance, as it is through this group that DNA and RNA are "held together".



NucleoSides

In the hierarchy of nucleic acid structure, there are two more levels of nomenclature: nucleoSides and nucleoTides. We'll address the nucleoSides first. Nucleosides consist of a purine or pyrimidine and a Page | 69 carbohydrate. When a purine or a pyrimidine reacts with ribose or deoxy-ribose, water is always one of the products.

When the purine is adenine and it reacts with ribose, the other product is adenosine (A). When adenine reacts with deoxy-ribose, the other nucleoside is deoxy-adenosine (dadenosine or dA).

When the purine is guanine and it reacts with ribose, the other product is guanosine (G). When guanine reacts with deoxy-ribose, the other nucleoside is deoxy-guanosine (dguanosine or dG).

When the purine is cytosine and it reacts with ribose, the other product is cytidine (C). When cytosine reacts with deoxy-ribose, the other nucleoside is deoxy-cytidine (dcytidine or dC).

When the purine is uracil and it reacts with ribose, the other product is uridine (U). When uracil reacts with deoxy-ribose, the other nucleoside is deoxy-uridine (d-uridine or dU).

When the purine is thymine and it reacts with ribose, the other product is thymidine (T). When thymine reacts with deoxy-ribose, the other nucleoside is deoxy-thymidine (d-thymidine or dT).

Likewise with the remainder purines and pyrimidines. One point to keep in mind is that d-uridine and thymidine are produced only in the lab, not in DNA or RNA, respectively.

Adenine + ribose γ	Adenine + deoxyribose ~	
water loss	water loss 🔻	
NH2 NH2 NH2	NH2 NIN IN NN NN NN NN NN NN NN NN NN NN NN NN N	
Adenosine	d-Adenosine	

Guanine + ribose γ	. Guanine + deoxyribose 7	
water loss 🖌	water loss 😽	
NON LAN LAND	HUN TON	
Guanosine	d-Guanosine	







NucleoTides



The last simple level of nucleic acid nomenclature hierarchy is the nucleoTide. Nucleotides are nucleosides that have added a phosphate group to the 5' carbon of ribose or deoxy-ribose. Biochemist's short-hand the PO_4^{-3} as a "P" with a circle around it (O). Note that if there were three (3) phosphates instead of one, the names would end as "triphosphate", hence, ATP is adenosine triphosphate and dATP is deoxy-adenosine triphosphate.

With three (3) phosphates instead of one, the names of the previous nucleotides would end as

"triphosphate", hence, ATP is adenosine triphosphate and dATP is deoxy-adenosine triphosphate. ATP below.





Special Topic

Carbonic Acid-Bicarbonate Ion: Physiological Interactions

 CO_2 is fairly soluble in water (more soluble in cold water like in cold soda; less soluble in warm water like in "flat" soda). A saturated solution at 1 atm and 25° C is approximately 0.033M. At equilibrium only 0.17% of dissolved CO_2 is in the form of carbonic acid (H_2CO_3). An aqueous solution of CO_2 is typically acidic:

$$CO_2(g) + H_2O(I) \rightarrow H^+ + HCO_3^-$$

(Remember the trick with phenolphthalein and blowing into it during titrations in CHEM 121 Lab?)

 CO_2 plays a major role in maintaining the pH of blood (and sea water). CO_2 is not normally transported as such, rather as HCO_3^- . This occurs via an enzymatic reaction catalyzed by carbonic anhydrase:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow HCO_3^- + H^+$$

IMPORTANT in acid/base balance!

Buffers

Consist of a weak acid and its conjugate base. In this case: H_2CO_3 and HCO_3^- . The acid-base pair serves to maintain an essentially constant pH. The acid-base pair can NOT regulate excessive amounts of acid/alkaline substances secondary to a pathology of respiration or of metabolism.

Buffers work to: Neutralize excess acid to elevate the pH and neutralize excess base to reduce the pH. End result: keep pH within normal (7.35-7.45 in human arterial blood) limits under normal circumstances. This is simply a physiological TITRATION!! It just doesn't use phenolphthalein.

Under normal conditions, the bicarbonate to proton ratio is about 20 to 1 and the hydrogen ion concentration may be calculated by multiplying 24 times the ratio of pCO_2 to the bicarbonate ion concentration:

$$[H^+] = 24 * \frac{pCO_2}{[HCO_3^-]}$$

That means, then, that the pH is proportional to the ratio of the pCO_2 (the respiratory contributor to pH balance) to bicarbonate (the metabolic contributor to pH balance) ion concentration.

Bicarbonate, Protons and Their Relationship
Condition:	Alkaline	Normal	Acidic
Bicarbonate to proton ratio:	44 to 1	20 to 1	8 to 21
Shifts to:	Right making the blood alkaline	7.35-7.45 or normal balance	Left making the blood acidic

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Red Cells and Acid-Base Balance



Cl^{-} and CO_2 are Intertwined



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Haldane Effect

With \uparrow Hb(O₂)₄, at some pCO₂ $\rightarrow \downarrow$ CO₂ content of blood; With \downarrow Hb(O₂)₄ at some pCO₂ $\rightarrow \uparrow$ CO₂ content of blood.



pCO₂ Levels Above 70 mm Hg

May decrease respirations; May cause stupor, coma (CO_2 narcosis); May cause hypoxemia. SLOWLY decrease the p CO_2 so as to not cause posthypercapnic metabolic alkalosis.







Problem Sets

Problem Set 27

1.	Name the	following	organic	compounds	:
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А	CH_4	К	C_2H_4	U	C_2H_2
В	C_2H_6	L	C_3H_6	V	C_3H_4
С	C_3H_8	М	C_4H_8	W	C_4H_6
D	C_4H_{10}	Ν	C_5H_{10}	Х	C_5H_8
E	C_5H_{12}	0	C_6H_{12}	Y	C_6H_{10}
F	C_6H_{14}	Р	C_7H_{14}	Z	C ₇ H ₁₂
G	C_7H_{16}	Q	C_8H_{16}	AA	C_8H_{14}
Н	C_8H_{18}	R	C_9H_{18}	AB	C_9H_{16}
I	C_9H_{20}	S	C ₁₀ H ₂₀	AC	$C_{10}H_{18}$
J	C ₁₀ H ₂₂	Т	$C_{11}H_{22}$	AD	$C_{11}H_{20}$

2. Name the following radicals, including all the isomers of the radicals:

А	CH ₃ •
В	C₂H₅•
С	C₃H ₇ •
D	C₄H₃•
E	C ₅ H ₁₁ •
F	C ₆ H ₁₃ •

3. Draw the following compounds based on their IUPAC names:

А	2,3,5,7-tetramethylnonane	к	Cis-2-butene
В	2,3-dimethylbutane	L	1,3-butadiene
С	3,4-dimethylhexane	М	2-methyl-2-butene
D	5-ethyl-2,4,6-trimethylheptane	Ν	4-methyl-1,3,6-octatriene
E	4-isopropyl-2-methylhexane	0	1,3,5-hexatriene

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F	2,2-dimethylpropane	Р	3-isopropyl-2,4-dimethyl-1-pentene
G	7-ethyl-4-isobutyl-2- methylnonane	Q	1,2,4,5-hexatetraene
н	2,2,3,3-tetramethylpentane	R	2-butene
I	Ethane	S	1-trans-4-hexadiene
J	4-ethyl-3,7-dimethyldecane	Т	3-ethyl-4-propyl-3-heptene

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- 4. Write out and complete the following reactions:
- A. ethane plus chlorine in light
- C. isobutane plus chlorine in light
- E. 2,3-dimethylpropane plus Br2 in light
- G. C_5H_{12} plus XS O_2
- H. C_2H_6 plus XS O_2
- J. $C_{20}H_{42}$ plus XS O_2

- B. propane plus chlorine in light
- D. butane plus bromine in light
- $F. \ C_6H_{14} \ plus \ XS \ O_2$
- I. C₈H₁₈ plus XS O₂
 K. CH₄ plus XS O₂
- 5. What kinds of bonds are between carbon atoms in alkanes? What is the hybridization of these carbon atoms?
- 6. What kinds of bonds are between carbon atoms double-bonded to each other? What is the hybridization of these carbon atoms?

Problem Set 28

1. Draw the structures for the following organic molecules:

A. Ethyne	B. Propyne	C. 1-Butyne	D. 2-Butyne
E. 1-Pentyne	F. 2-Pentyne	G. 1-Hexyne	H. 2-Hexyne
I. 3-Hexyne	J. 2-Heptyne	K. 3-Heptyne	L. 4-Octyne

2. Write out and complete the following reactions:

A. 1-butene + HCl	B. 1-butene + HF
C. 1-butene + $H_2O + H^+$	D. 2-butyne + H_2 + Ni
E. 2-butyne + Na + NH ₃ (aq)	F. 3-hexyne + H_2 + Ni
G. 3-hexyne + Na + NH₃(aq)	H. propyne + water + H ₂ SO ₄ + HgSO ₄
I. 1-butyne + H_2O + H_2SO_4 + $HgSO_4$	J. 2-butyne + H_2O + H_2SO_4 + $HgSO_4$
K. isopropyl alcohol + H_2SO_4 + heat	L. 1-propanol + KMnO₄
M. 2-butanol + CrO_3	N. formic acid + methanol + H^+
O. toluene + Br_2	P. Benzoic acid + trimethylammonium ion
Q. glycerine + nitric acid	R. Make any acid chloride, then use your product to make any amide and name it correctly

3. Draw the structures for the following organic molecules:

- A. Hexanal B. Propanal C. Ethanal
- D. Octanal

Ε.	Butana	F.	Ethanoic acid	

H. Pentanoic acid I. Heptanoic acid J. Formamide

G. Nonanoic acid

L. Propanamide

4. Draw the following amino acids:

A. Ala	B. Gly	C. Leu	D. Ile
E. Phe	F. Trp		
G. Pro	H. Ser	I. Thr	J. Pro
K. Tyr	L. Asp		
M. Asn	N. Glu	O. Gln	P. Lys
Q. Arg	R. His		
S. Cys	T. Cys-Cys	U. Met	

K. Decanamide

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