**Chapter 14 – Single-bond Derivatives**

Alcohols & Phenols: R-OH

IUPAC (one-word) names: change alkane name by dropping "-e" and adding "-ol.": ethanol, methanol

Common names for common solvents: ethyl alcohol, methyl alcohol, isopropyl alcohol. (pg312)

Ethanol concentrations are often expressed using the "proof" scale, where 100% = "200 Proof"

Polyhydroxy alcohols: 1,2-ethanediol (ethylene glycol): HO-C-C-OH, propylene glycol, glycerin (p313)

Phenols names: IUPAC: phenol, 4-methylphenol; common name: phenyl alcohol

Properties of alcohols: boiling points go up with number of carbons and alcohol groups (p316-7)

Alcohols form strong hydrogen bonds to themselves and water

Reactions of alcohols:

combustion: R-OH + $O_2 \rightarrow$ $CO_2 + H_2O$

dehydration yields alkenes (reversal of hydration)

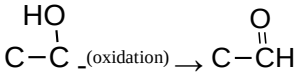
C-C-OH $\xrightarrow{(H+)}$ C=C + $H_2O$

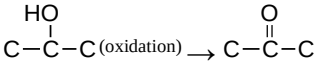
condensation yields ethers

C-C-OH + HO-C-C $\rightarrow$ C-C-O-C-C ($H_2SO_4$, 140°C)

halogenation C-C-OH + $PX_3 \rightarrow$ C-C-X (substitution)

oxidation: primary alcohols yield aldehydes, secondary alcohols yield ketones





Ethers: R-O-R

Names: ethyl methyl ether: C-O-C-C, dimethyl ether: C-O-C (p322)

*o,m,p*- cresol, catechol, resorcinol, hydroquinone, ortho-phenylphenol (Lysol), 4-hexylresorcinol(mouthwash), BHT (antioxidant in foods)

Properties: flammable, anesthetic activities

Thiols: R-SH *(sulfhydryl group)*

Recognize thiol functional group(s)

Thiols have strong, disagreeable odors; e.g., skunk odor, added to natural gas for safety

Oxidation of thiols yields disulfide bonds: C-C-SH + HS-C-C $\rightarrow$ C-C-S-S-C-C decreases odor; (dilute $H_2O_2$ is an excellent oxidizing agent)

**Chapter 15 – Carbon-oxygen Double Bonds**

Carbonyl group: C=O

Aldehydes: -CHO; names end in "-al": 

methanal (formaldehyde), ethanol (acetaldehyde), propanal, benzaldehyde, etc.

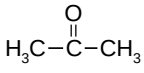
usually have peculiar odors (almonds, cinnamon, vanilla)

reactions: reduction to alcohols: C=O + $H_2$ -> CH-OH

oxidation to acids: C=O -> -COOH

during oxidation, aldehydes can reduce metal ions: $Cu^{2+}$ to $Cu^{1+}$ (Benedict's test)

or $Ag^{1+}$ to $Ag^{o}$ (Tollen's test - mirror forms)

Ketones:  names end in "-one":

2-propanone (acetone), 2-butanone (ethylmethylketone), 3-pentanone (diethylketone), etc.

Reactions: reduction to alcohols C=O + $H_2$ -> CH-OH

oxidation does not occur!

Excellent solvents used industrially e.g., finger-nail polish remover, varnish remover, etc.

**Chapter 16 – Carboxylic acids, esters**

Carboxylic acids: -COOH, names end in "-ic acid":

All carboxylic acids are WEAK acids.

Formic acid (from ants), acetic acid (vinegar), propanoic acid, butanoic acid, benzoic acid, etc.

Acids release protons in aqueous solutions: -COOH -> $-COO^- + H^+$

Some acids have more than one –COOH group: oxalic acid(2), succinic acid(2), glutaric acid(2), citric acid(3)

Three common OTC pain relievers are carboxylic acids: Ibuprofen and Naproxen and aspirin

Carboxylate salts form when acids are neutralized with base: -COOH + NaOH -> $-COO^- Na^+ + H_2O$

Carboxylate salts are principle ingredient in soaps

Oxalic acid (2-carbon diacid) is toxic, precipitating $Ca^{2+}$ ions.

Small molecular weight carboxylic acids are preservatives: benzoic acid, sorbic acid, propionic acid

Carboxylic acid reactions (condensations):

with alcohols to form esters: R-COOH + HO-R' -> R-COO-R' + $H_2O$

with amines to form amides: R-COOH + $H_2H$-R' -> R-CONH-R' + $H_2O$

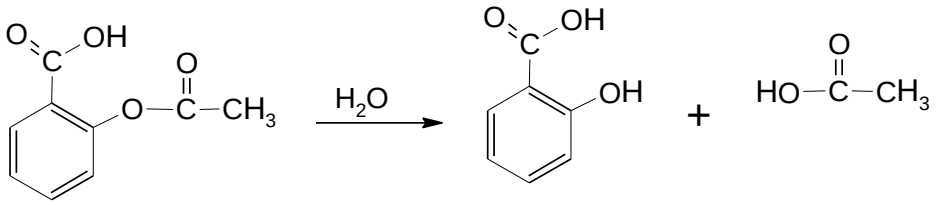
Esters: -COOR, names end in "-ate."

Methylformate, methylacetate, propylbutanonate, ethylbenzoate, etc.

Recognize the acid and alcohol building blocks for esters

Esters have characteristic flavors and odors ("fruit-like" smells)

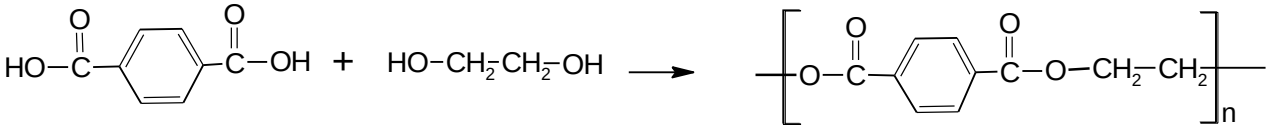
Aspirin is an ester of acetic acid and the alcohol group on salilcylic acid, "acetylsalicylic acid"



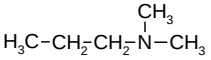

Esters are easily hydrolyzed, yielding the original acids and alcohols.

Condensation Polymers: polyesters

Polyesters are synthesized from diacids and dialcohols: PET: Dacron, Mylar, soft-drink bottles, etc.




**Chapter 17: Amines: R-$NH_2$ (R-NH-R, or R-N-$R_2$)**

Names: ethyl amine: C-C-$NH_2$, ethylmethylamine: C-C-NH-C, *N,N*-dimethylpropanamine: 


Dopamine, epinephrine, and ephedrine are all biologically active amines

Low molecular weight amines have a "fishy" smell

Amines can be protonated with acid to form amine salts, making them much more soluble in water:

R-$NH_2$ + $H^+ \rightarrow$ R-$NH_4^+$ (non-volatile; increases solubility of amines: e.g, "hydrochloride"salts)

Heterocyclic amines have ring systems where N has been substituted for at least one C in the ring.

Caffeine, nicotine morphine, codeine, heroin are all examples of heterocyclic amines

Codeine and heroin are derivatives of morphine; heroin is a diacetyl ester of codeine.

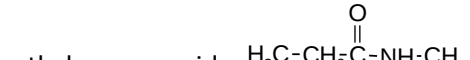
Hydrocodone and oxycodone are also derivatives of morphine

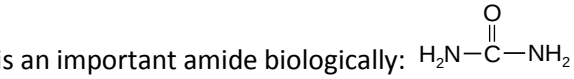
Review key reactions and equations:

Alkylation: alkyl halides add to amines, linking carbon to the amine nitrogen

Amides: - CONH-R, names end in "-amide."

Formamide, acetamide, benzamide, etc.

IUPAC names include "*N*-": N-methylpropanamide: 

Urea is an important amide biologically: 

The pain reliever, acetaminophen, is an amide of acetic acid

Amides are synthesized from carboxylic acids and amines through condensation reactions

Reactions of amides: hydrolysis yields carboxylic acids and amines

Condensation Polymers: polyesters and polyamides

Polyesters are synthesized from diacids and dialcohols: PET: Dacron, Mylar, soft-drink bottles, etc.

Polyamides are synthesized from diacids and diamines: nylons, Kevlar, etc.

**Chapter 18 - Carbohydrates**

General: $C_n(H_2O)_n$; Subclasses: pentoses($C_5$), hexoses($C_6$); aldoses (aldehydes) and ketoses (ketones)

Handedness ("D" & "L") forms of monosaccharides; rotation of plane-polarized light right or left

Important monosaccharides:

Glucose (dextrose, blood sugar) is a hexose ($C_6$) and an aldose, (an aldohexose), is a reducing sugar, and rotates light to the *right* in aqueous solution; it is an important nutrient in the blood stream.

Fructose (levulose) is a ketohexose ($C_6$, hexose and ketose); it is the sweetest tasting sugar; it rotates light to the left, and is an important sweetener for soft drinks and other foods;

Ribose is an aldopentose (aldose and pentose); this 5-carbon sugar is an important building block in nucleic acids (DNA and RNA).

Monosaccharides exist primarily as cyclic forms in solution; ring closure gives rise to α- and β- configurations.

Most monosaccharides are reducing sugars; that is, they are aldehydes that oxidize easily to acids and concomitantly reduce other chemicals such as $Cu^{2+}$ ions (Benedict's test).

Disaccharides:

| | |
|---|---|
| Maltose: glucose-glucose | reducing sugar; common in foods (malt flavoring, beer) |
| Lactose: galactose-glucose | reducing sugar; "milk sugar" |
| Sucrose: glucose-fructose | non-reducing sugar; "table sugar," "cane and beet sugar" |
| | Sucrose has a head-to-head β(1→2) glycosidic linkage |

Polysaccharides:

Cellulose: polyglucose, linked with β(1→4) bonds, not digestible, structural component of plants

Starch: polyglucose, linked with α(1→4) bonds, complex carbohydrate, good glucose source

Glycogen: branched polyglucose, linked with α(1→4) bonds; very soluble, "animal starch"

**Chapter 19 – Lipids**

Lipids are fats and oils that are extractable into non-polar organic solvents such as hexane

Fatty acids are the principle components of fats and oils; fatty acids have 12-20 carbon reduced atoms (contain mostly hydrogen atoms);

Saturated and unsaturated fatty acids: (*cis*- double bonds in fatty acid chains)

Essential fatty acids: linoleic and linolenic acid, omega-3 family of fatty acids,

Triacylglycerols are tri-esters of 3 fatty acids and glycerol

Unsaturated nature of fatty acids lowers the melting point and as such, "oils" are liquids at room temp.

| | |
|---|---|
| Reactions: | hydrolysis / saponification: yields free fatty acids and glycerol; components of soaps |
| | Hydrogenation: adding hydrogen across C=C double bonds to create more saturated FAs |
| | Oxidation: oxygen reacts with C=C double bonds to create small aldehydes and acids. |
| Phospholipids: | Tri-esters of glycerol with 2 fatty acids and one phosphoric acid group. ("lecithin") |
| | Principle components of biological membranes |
| Sphingolipids: | fatty-acid liked to sphingosine via an amide linkage; present in nerve tissues. |
| Steroids: | Lipids that contain a characteristic fused 4-ring system |
| | Cholesterol – the most abundant human steroid; alcohol; building block for hormones |
| | Bile salts: emulsifying agents to help solubilize dietary lipids; stored in the gall bladder |
| | Steroid hormones: estrogens (estradiol), androgens (testosterone), progestins |

Cell Membranes are composed of lipids; phospholipids are most common lipids; membranes also contain significant amounts of protein and some carbohydrates and cholesterol.

**Chapter 20 – Proteins**

Amino acids are the building blocks for proteins
AA properties are determined by their side-chains: e.g., polar, non-polar, aromatic, acids, bases, etc.
Two AAs contain sulfur; cysteine, forms disulfide linkages that are easily oxidized and reduced.
The reduction and subsequent oxidation of these –S-S- bonds is the chemical basis for hair "permanents."
AAs are classified as either "essential" or "non-essential"
Phenylalanine can cause developmental problems for PKU babies, leading to mental retardation
Tryptophan is a precursor for serotonin
AAs are linked together with amide (peptide) bonds to form long polymers called proteins
Peptide bonds may be hydrolyzed in acid, yielding free amino acids and smaller peptide chains
There are four levels of protein structure:
Primary: linear sequence of AAs
Secondary: α-helix and β-sheet
Tertiary: Overall 3-D shape of protein
Quaternary: Interactions between separate subunits of proteins
Proteins are easily denatured by chemicals, mechanical treatment, or heat.
Food preservation and cooking utilize heat to kill bacteria and make foods taste better by denaturing their respective proteins.
Important proteins: Collagen, hemoglobin, myoglobin, immunoglobins

**Chapter 21: Enzymes & Vitamins**

Biological catalysts; apoenzymes, coenzymes, cofactors
Lock-and-Key theory of enzyme-substrate interaction; Induced-fit model of binding
Turnover number: Number of substrate molecules converted to product by an enzyme per second or minute
Plots of enzyme activity vs substrate concentration and enzyme activity vs enzyme concentration
Inhibition: Irreversible: heavy metals, covalent bonding, etc.
Inhibition: competitive and non-competitive; Infinite substrate concentration overcomes competitive inhibition.
Feedback inhibition
Penicillin: contains β-lactam ring; inhibitor of transpeptidase enzyme.
Other "-cillins" also function in similar fashion, some with enhanced acid resistance.
Sulfa drugs are competitive inhibitors of enzymatic conversion of PABA in bacteria.
Vitamins: Water-soluble vs lipid-soluble
Lipid-soluble: Vitamins A, D, E, K; general activities/roles of each one in living systems
Water-soluble: All B-types, including B12 (contains Cobalt ion), ascorbic acid (C).
What diseases or conditions are prevented by specific vitamins? (thiamine, ascorbic acid, etc.)

**Chapter 22: Nucleic Acids**

Nucleic acids are long, copolymers of adenine, guanine, cytosine, and thymine (uracil in RNA)
Purine (double-ring bases): A, G
Pyrimidine (single-ring bases): C, T, U
Backbone of nucleic acids are alternating sequences of sugar and phosphates, linked by phosphodiester bonds.
Complementary hydrogen bonds between strands: A=T, G≡C (A=U in RNA)
Replication of DNA: unwinding, 5'→3' direction, Okasaki fragments, ligase enzyme
Bacterial plasmids are small, circular DNA strands
Transcription and Protein synthesis: Codons vs anticodons, ribosomes, genetic code.
Redundancy in the code allows minor errors to exert only minimal effects, depending on its position in a codon.

**Chapter 23: Biochemical Energy Production**

Know the general (block) structures (components) of CoA, FAD, ATP, NADH, NADPH

Glycolysis

General pathway: glucose → pyruvate → lactic acid; glucose in phosphorylated in first step;

Phosphofructokinase (PFK) enzyme is the control point

Net number of ATPs produced in aerobic glycolysis

What are the metabolic fates of pyruvate?

Fermentation: ethanol formation by microorganisms under anaerobic conditions, proof scale

TCA Cycle

Krebs Cycle or Citric Acid Cycle; 8 cyclic reactions in mitochondria that produce ATP (GTP), NADH, $FADH_2$, $CO_2$.

NADH carry high-energy electrons to electron-transport pathway.

This is where the majority of $CO_2$ is formed in living cells.

Oxidative Phosphorylation

Mitochondrial structure (matrix, inner-membrane space); electron transport chain, sites (1,2,3,4), $e^-$ carriers

Protons are pumped across the inner membrane from the matrix to the intermembrane space at Sites I, III, IV (not II).

The flow of protons through the ATP-synthetase complex drives the synthesis of ATP

**Chapter 24 Carbohydrate Metabolism**

Glycolysis

General pathway: glucose → pyruvate → lactic acid; glucose in phosphorylated in first step;

Phosphofructokinase (PFK) enzyme is the control point

What are the metabolic fates of pyruvate?

Net number of ATPs produced in aerobic glycolysis

ATP accounting: 30 ATP from glucose → $CO_2$+$H_2O$ (glycolysis, TCA cycle, electron transport)

Fermentation: ethanol formation by microorganisms under anaerobic conditions, proof scale

Pentose Phosphate "Shunt" - Pathway provides for the metabolism of, $C_3$, $C_4$, $C_5$, $C_6$, $C_7$ sugars

Gluconeogenesis: Many reactions of glycolysis are reversible, allowing the conversion of pyruvate back to glucose

Glycogen Metabolism: Glycogen is a highly-efficient storage form of glucose;

Glycogenesis: process of synthesizing glycogen; glucogenolysis is the opposite process of breaking down glycogen

Glucose-phosphate is released from glycogen during glucogenolysis, yielding one more net ATP (31) compared to glucose (30) when completely oxidized through to $CO_2$ and $H_2O$.

Epinephirine (muscle) & glucagon (liver) both trigger glycogenolysis, increasing the concentration of blood glucose.

Insulin causes the opposite effect: glucose is absorbed into cells and stored as glycogen.

**Chapter 25: Lipid Metabolism**

Carntine required for fatty acyl CoA transport into mitochondria; Identify biotin's role in fatty acid synthesis

β-oxidation process; activation of fatty acids requires two ATP's to form acyl CoA

Know general chemical structures of β-oxidation "cycle;" oxidation steps where $FADH_2$ & NADH are formed

Number of cycles for $C_{12}$, $C_{l4}$, $C_{l6}$, $C_{l8}$- fatty acids.

ATP accounting for $C_{18}$ fatty acids, stearic acid (saturated $C_{18}$) yields 120 ATP; Unsaturated fatty acids yield less.

Ketone bodies: reason for their formation and their identity; caused by fasting; clinical use in diagnosis of diabetes

**Chapter 26: Protein and Amino Acid Metabolism**

Protein hydrolysis yields amino acids that can be absorbed into the body; primary source of nitrogen.

Amino groups are removed, leaving carbon skeletons that then enter into the Krebs cycle.

Ammonium ions and $CO_2$ combine, forming carbamoyl phosphate which enters the Urea Cycle, eventually yielding urea.

Amino acid carbon skeletons that are degraded to pyruvate are "glucogenic" those going to acetyl CoA are "ketogenic."

Hemoglobin is broken down into bilirubin and excreted, causing yellow color of urine and brown color of feces.

Excess bilirubin in neonates is responsible for the yellow skin color of some new babies.