Chem 1B Objective 2:
Understand organic hydrogenation reactions, oxidation-reduction reactions, and reactions that produce esters and amides.

Key Ideas:
Organic reactions are involved in biology.
Organic functional groups have specific physical and chemical properties, e.g., reactivity.
Hydrogenation: alkene + H_2 --> alkane
Oxidation: gain of O or loss of H or both at same carbon. ROH types (1^o, 2^o or, 3^o) and oxidation. Reverse is reduction.
E.g., hangover: ethanol --> acetaldehyde --> acetic acid

Acid + alcohol ---> ester + water. ID bonds that break and form. Like a double replacement reaction.
Acid + amine ---> amide + water

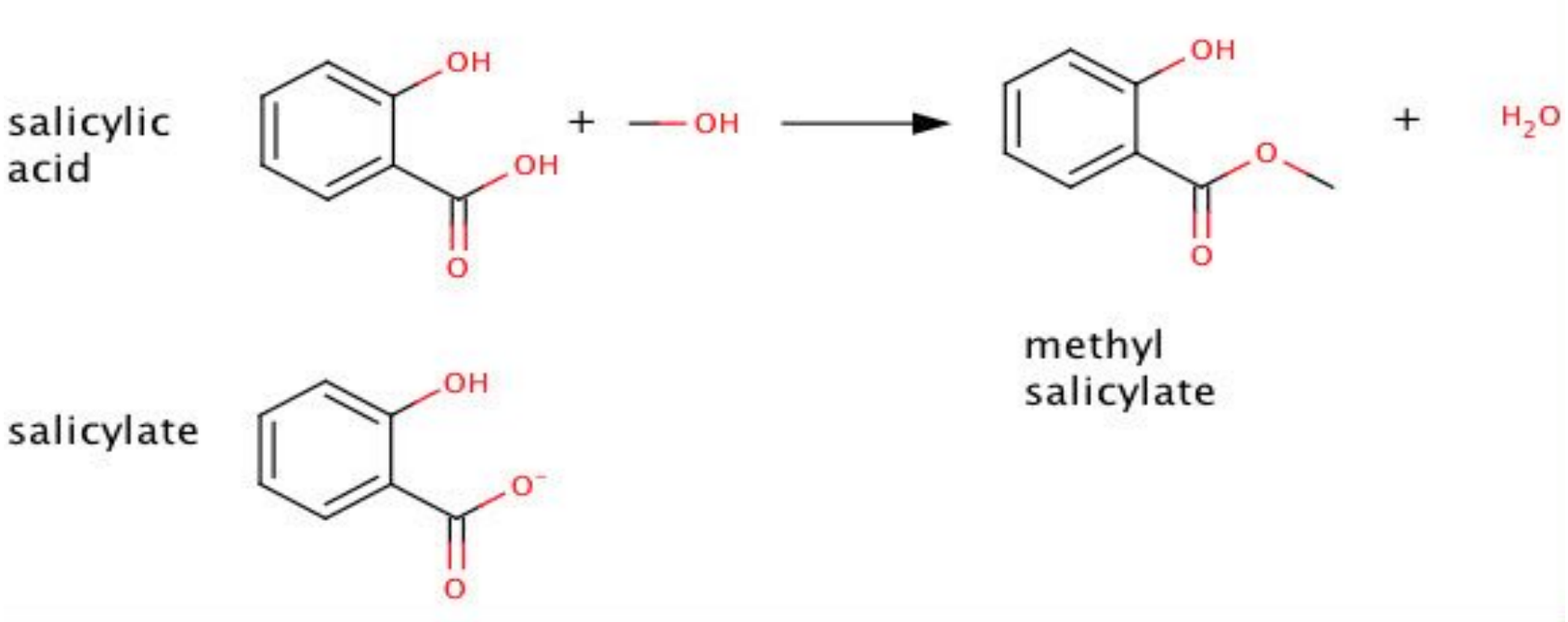
Lab 1 Stinks! Acid + Alcohol --> Ester + water

Salicylic acid + methanol --> methyl salicylate + water.

a. Identify the functional group(s) in each reactant and product.
b. Based on the structure of salicylic acid, name one physical property and one chemical property.

Acid loses a H^+ to form its conjugate base:
Salicylic acid --> H^+ + salicylate

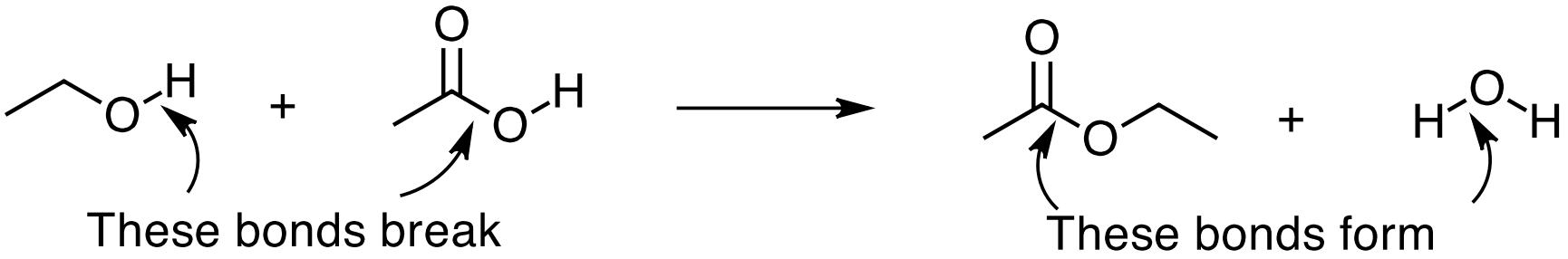
Methyl salicylate (ester) has a methyl group bonded to salicylate.



Objective: Predict product(s) by identifying the bond(s) that break and form

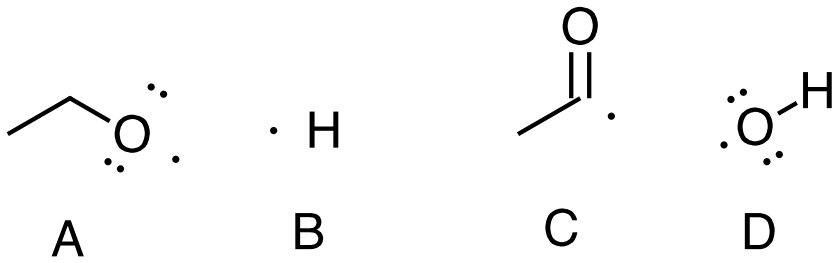
Lab 1: Acid + Alcohol --> Ester + water

Ethanol + acetic acid -----> ethyl acetate + water



This is a Double Replacement reaction (see CHM 1A):

For this reaction: AB + CD → AC + BD



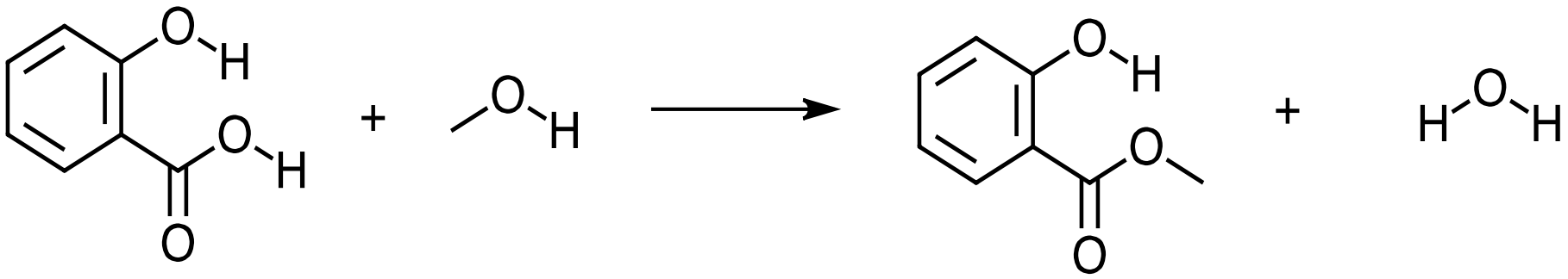
A combines with C to form the ester.

B combines with D to form water.

Objective: Predict product(s) by identifying the bond(s) that break and form

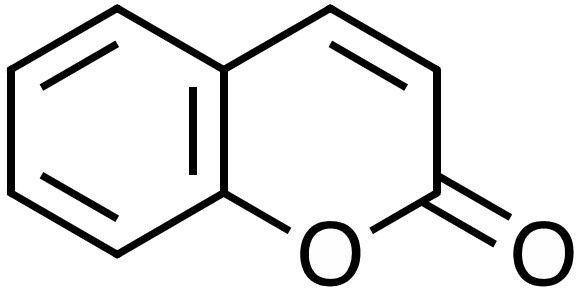
Lab 1: Acid + Alcohol --> Ester + water

Salicylic acid + methanol --> methyl salicylate + water

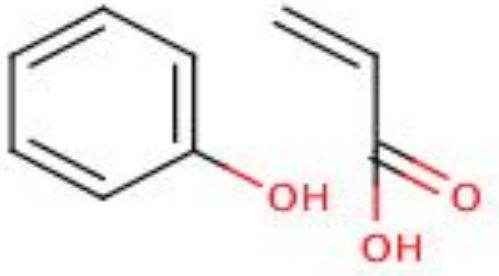


In each reactant, one bond breaks.
In each product, one bond forms.
Circle the bonds that break. Box the bonds that form.

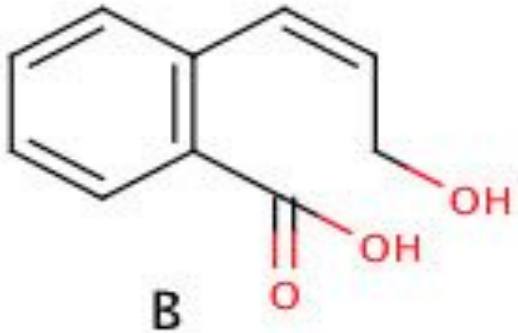
Lab 1: Acid + Alcohol --> Ester + water
Coumarin is an ester with a flowery smell.



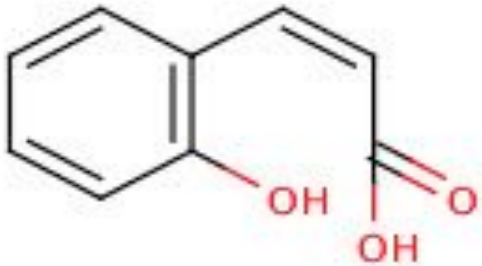
What acid and alcohol is used to make this cpd?



A



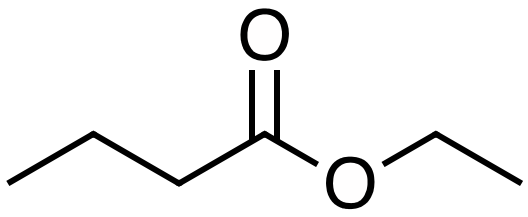
B



C

Lab 1: Acid + Alcohol --> Ester + water

Ethyl butanoate smells like pineapple.
Draw the reactants that make pineapple.



Ethyl butanoate
pineapple

Application: Aging Spirits in 6 days instead of 20 years

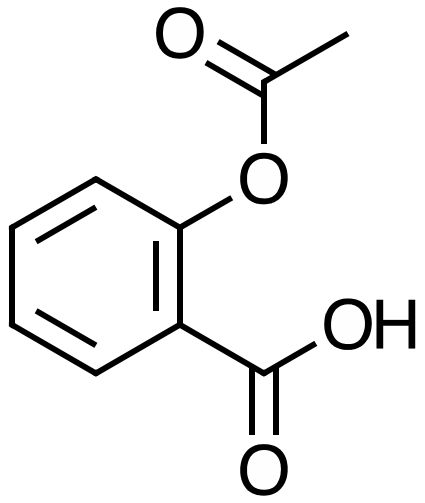
http://www.wired.com/2015/04/lost-spirits/

http://www.lostspirits.net/

"*… the more complex part of the barrel aging process is esterification, which is when alcohol and phenol or weak acids bond together. The result of this reaction is the creation of medium- and long-chain esters, which are responsible for the flavors and aromas of honey, floral elements, and nutty notes—the classic character of a nicely aged spirit.*"

E.g., pineapple (ethyl butanoate)takes years to form depending on barrel storage climate.

(from Sp 12 Exam 1) Aspirin undergoes a hydrolysis reaction to form salicylic acid. Draw the structure of salicylic acid and the other product of aspirin hydrolysis.

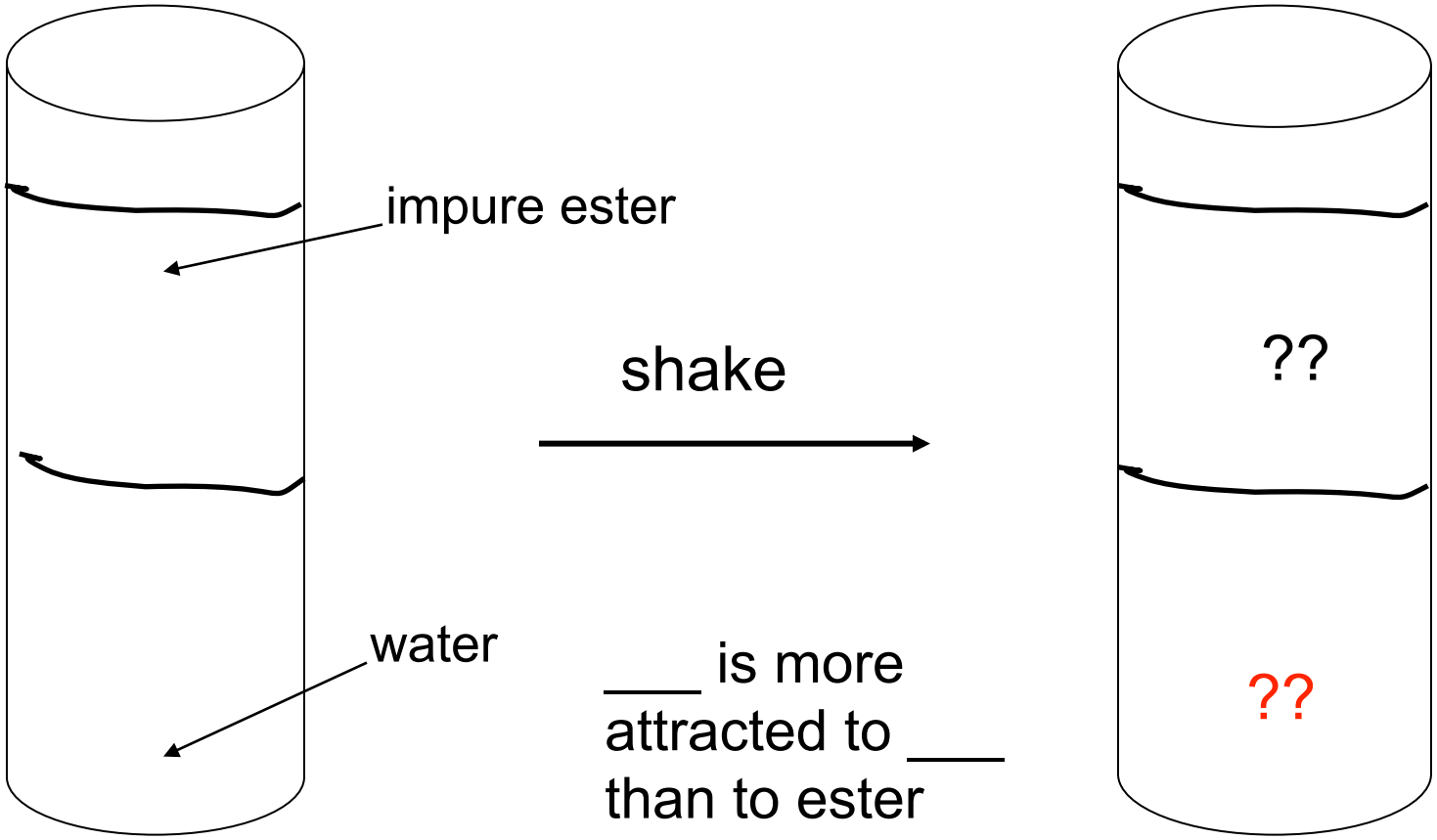


aspirin

Lab 1: Acid + Alcohol --> Ester + water

Synthesis: reactants --- reflux ---> impure (crude) product

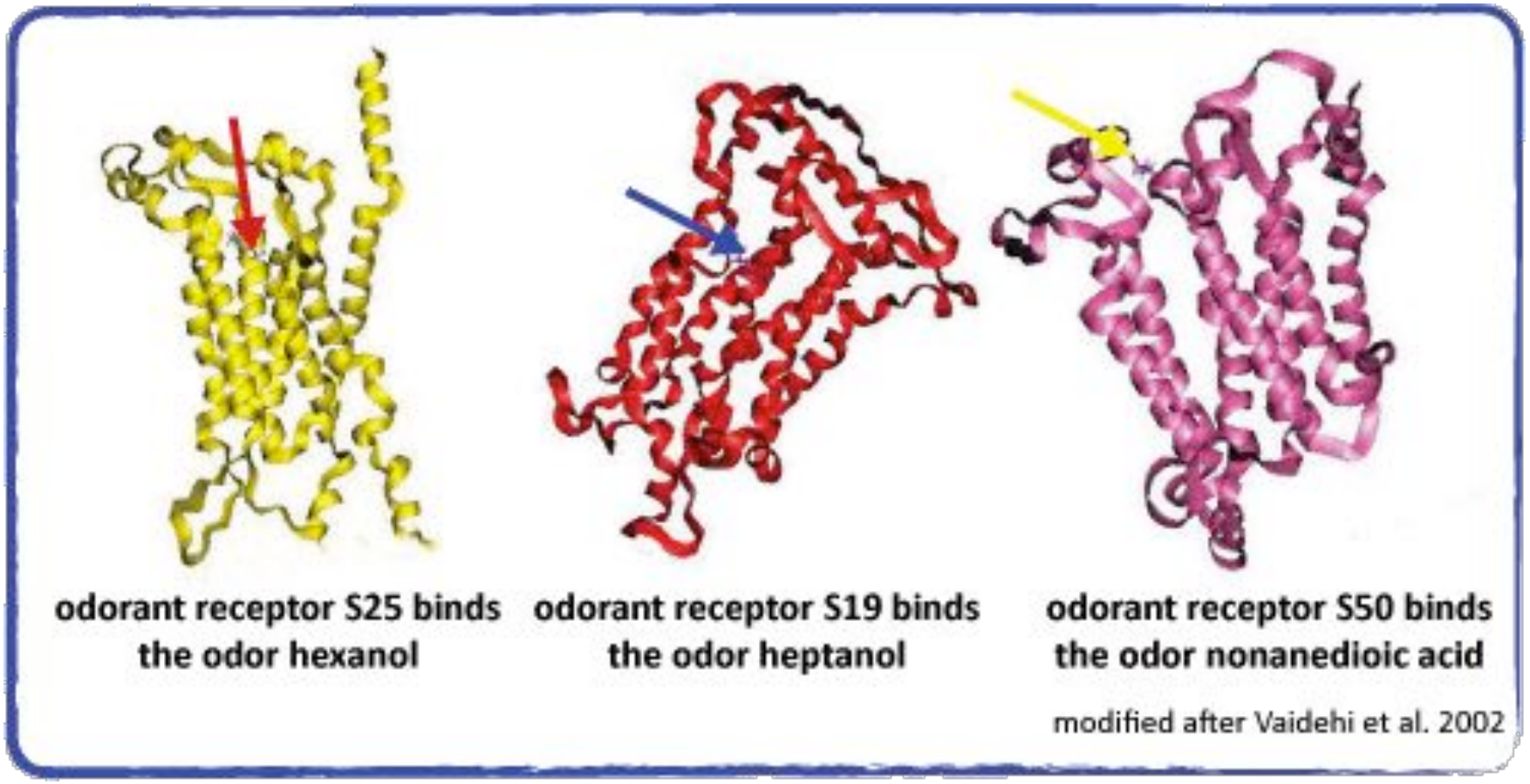
Separate, isolate, purify: liquid-liquid extraction



Characterize: IR and _____

IT STINKS!! Lab 1

"One of the most direct assaults on the senses arising from environmental pollution comes from the ***stinks*** *of civilization."* (Ref: Sienko and Plane, "Chemistry", 1977, p. 685-687)



Objective: Apply structure and shape of ester to determine size of smell receptor site. (http://andreaskeller.squarespace.com/or-genes/)

Objective: Identify chemical features in a molecule

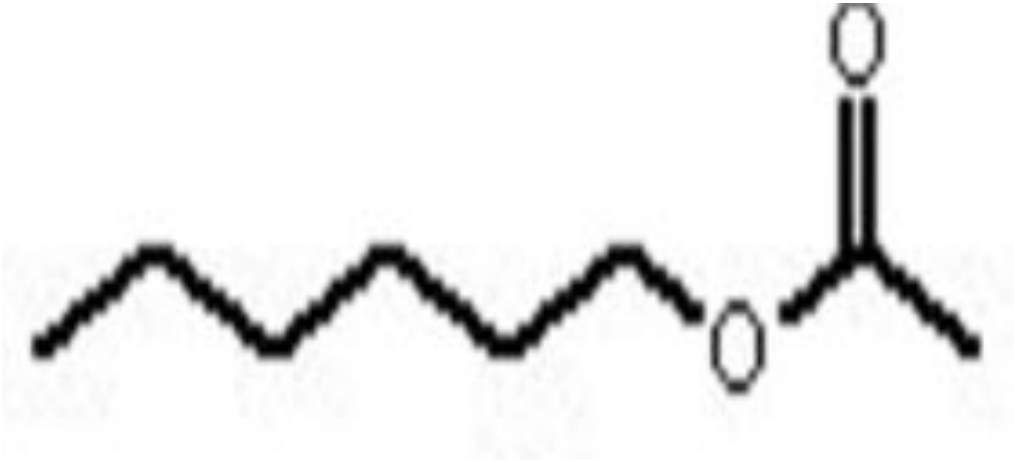
Olfactophore Models for Structure–Odour Correlations in Fragrance Research (2001). See Lab 1, Part D.

Similar smells do *not* always correlate with similarity in chemical structure.

Model: *five chemical features* essential for pear odour

two hydrogen-bond acceptors (HBA)

three hydrophobic features (HYD)



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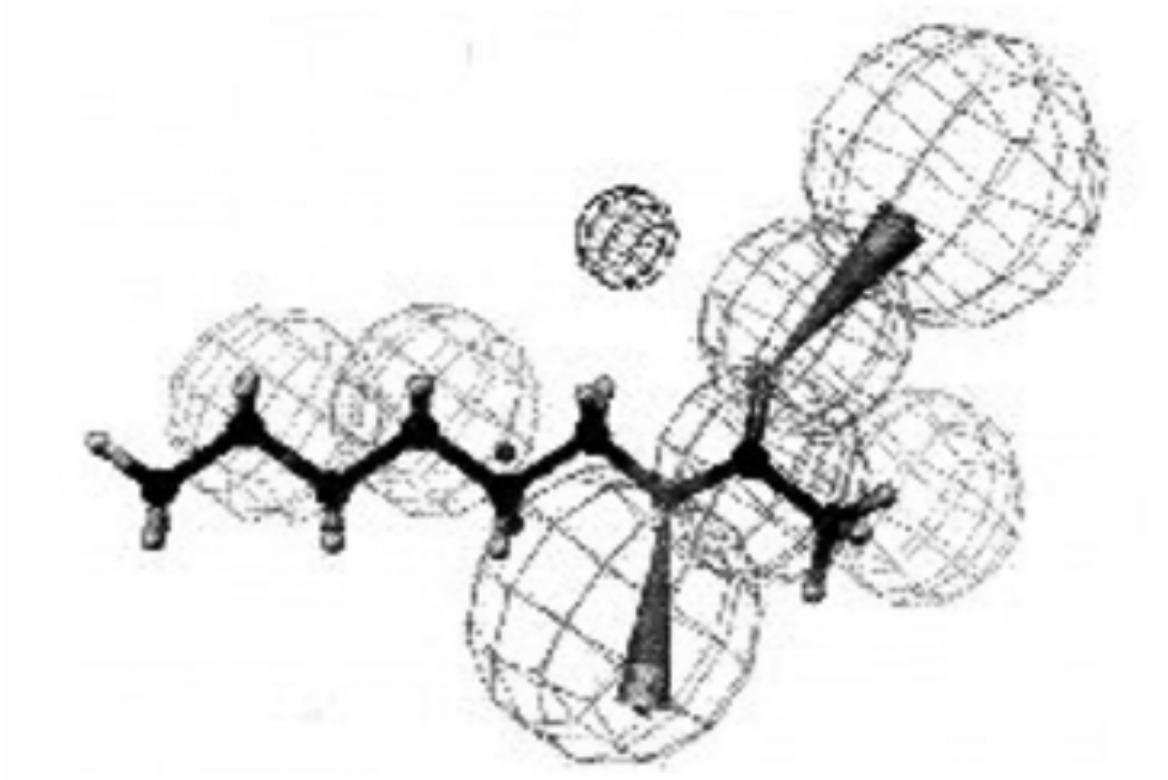
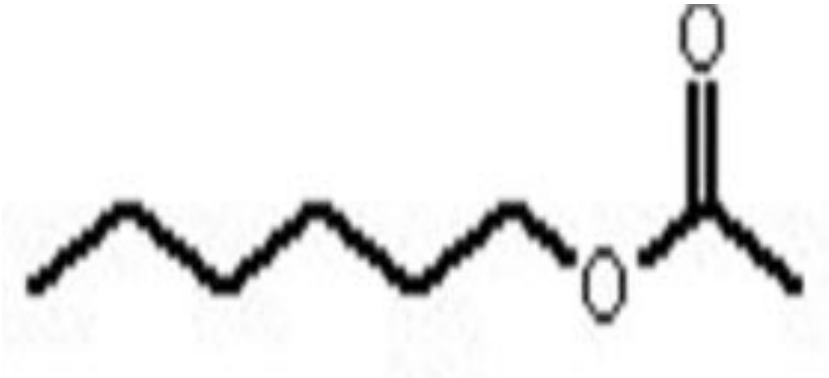
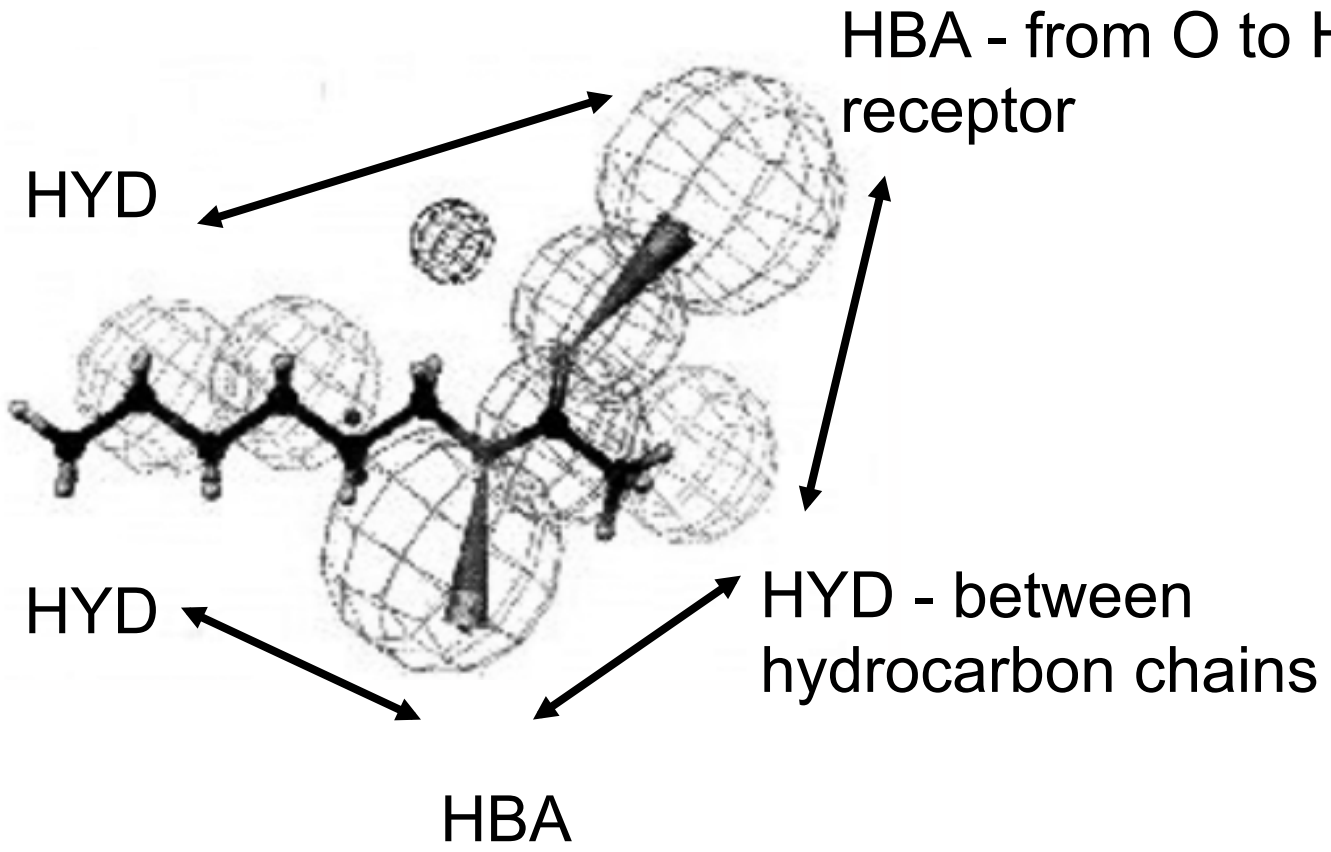
On the model, identify the 2 HBA and 3 HYD



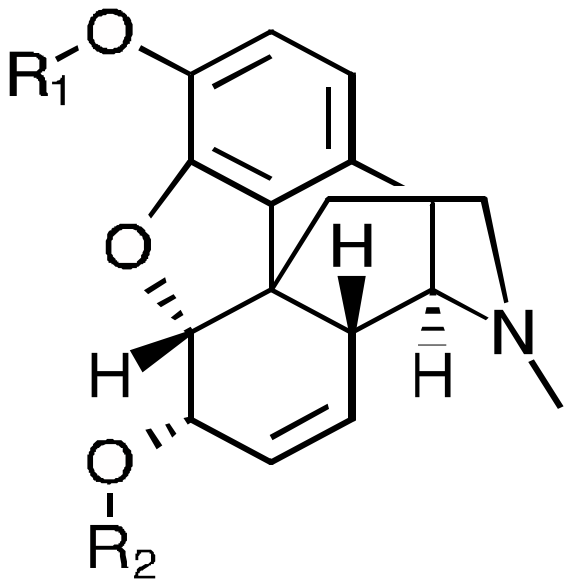


Use Virtual Molecular Model kit (chemagic.com) to measure distances between atoms
Molecule's dimensions ==> receptor site size



Structure, Shape, and IM Forces Determine Drug Interaction
Drug Receptor and Pharmacophore

Morphine - narcotic (analgesic, hypnotic euphoriant)

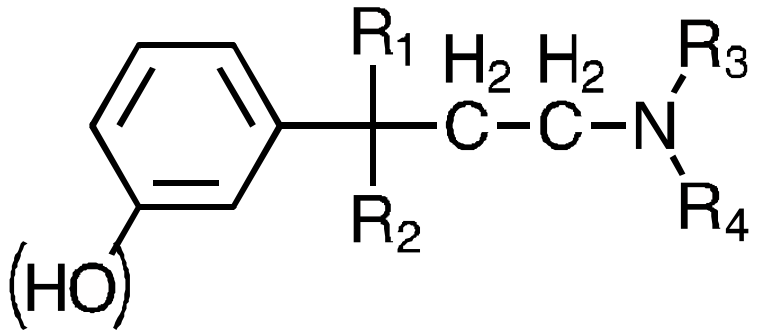


Morphine	$R_1 = H = R_2$
Codeine	$R_1 = CH_3$
	$R_2 = H$
Heroin	$R_1 = CH_3CO-$
	$R_2 = CH_3CO-$

Is this molecule flat (planar)?

"Morphine Rule" - 4 structural features of strong narcotic analgesics

1. Ring
2. Quaternary C
3. Ethylene bridge
4. 3° amine

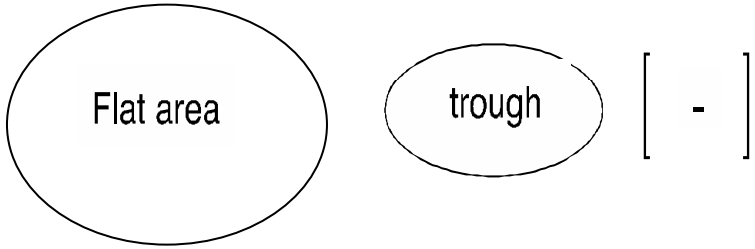


3 essential receptor features:

1. Flat area that binds to ring, probably by van der Waals interaction.
2. an anionic site that attracts the 3° amine. Amine is usually protonated and (+) charged. See pH and pK of amine.

$$NR_3 + H^+ \rightarrow NR_3H^+$$

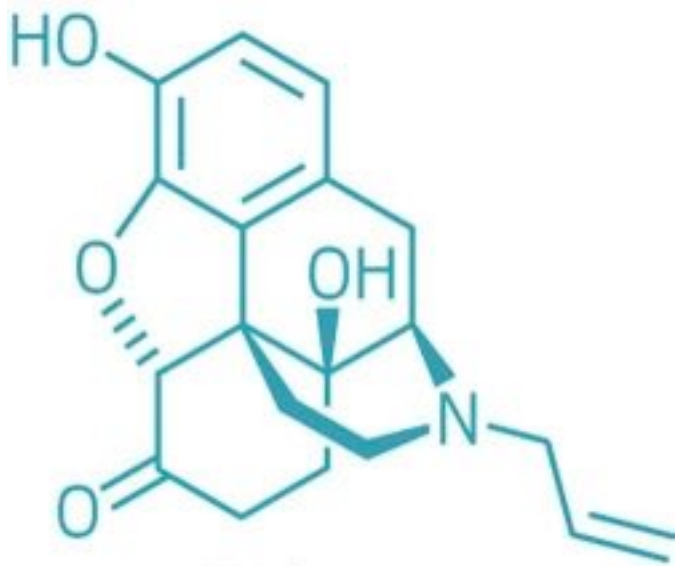
3. a suitably oriented trough between ring and amine to accommodate $-CH_2-CH_2-$ bridge.



Opioid overdose treatment

http://cen.acs.org/articles/94/i20/Improving-old-tool-treat-opioid.html

Heroin, oxycodone (Oxycontin), hydrocodone (Vicodin)



Naloxone

How does Naloxone work?

Hint: Does Naloxone fit the “Morphine Rule”?

Objective: Predict the Product(s) of Organic Chemical Reaction from Functional Groups

What do ***ALCOHOL***s react with?

1. Alcohols react with _____ to form _____.

2. Alcohols react with *oxidizing agents* to form:
aldehydes or ketones or acids

Common Oxidizing Agents: H_2O_2, bleach, $KMnO_4$, $K_2Cr_2O_7$

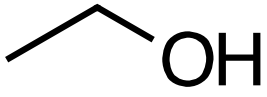
Objective: Predict the Product(s) of Organic Chemical Reaction from Functional Groups

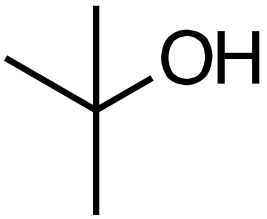
Alcohols react with *oxidizing agents* to form:

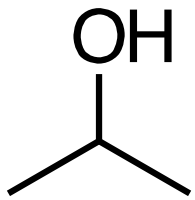
aldehydes or ketones or acids

The **product depends on the type of alcohol**.

How are the three alcohols different?





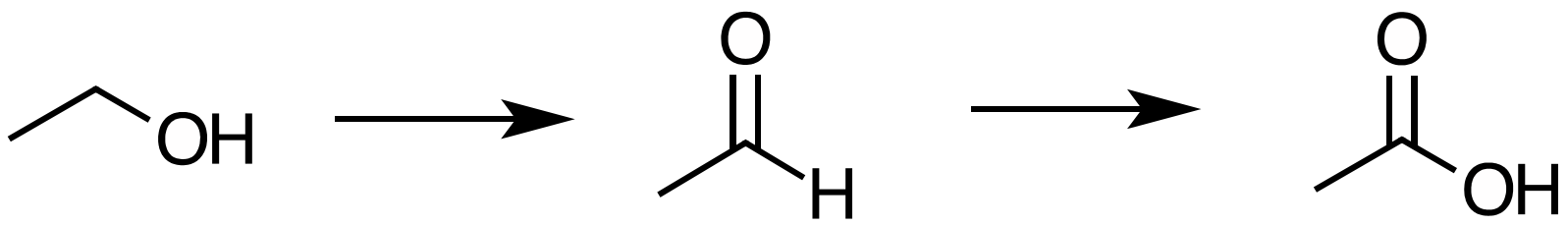


Objective: Predict the Product(s) of Organic Chemical Reaction from Functional Groups

Alcohol oxidation:

1° ROH is oxidized to RCHO is oxidized to RCOOH

1° (primary) ROH = 0 or 1 C bonded to C-OH, e.g., ethanol



1° alcohol aldehyde acid

Chem 1A: oxidation = loss of electrons

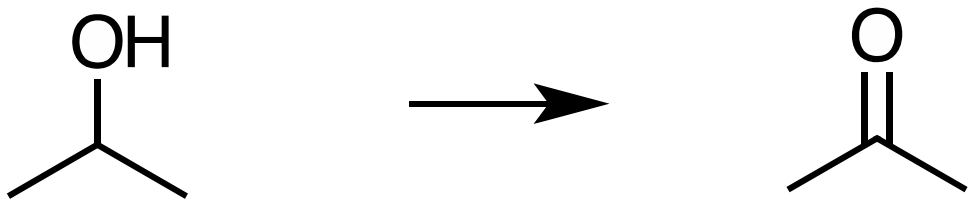
Organic chem: oxidation = gain of O or loss of H

Objective: Predict the Product(s) of Organic Chemical Reaction from Functional Groups

Alcohol oxidation:

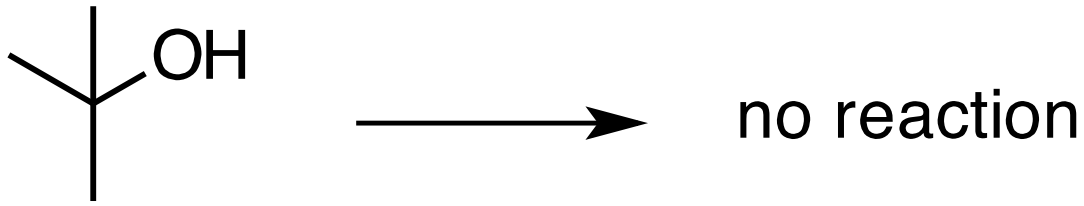
2^o ROH --> RCOR

2^o (secondary) ROH = 2 C bonded to C-OH, e.g., isopropanol

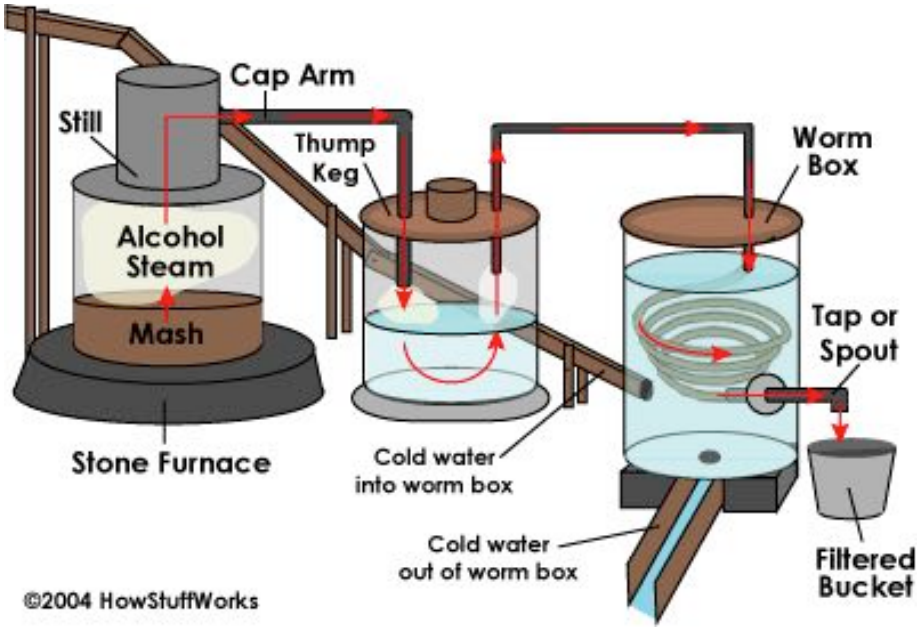


3^o ROH --> no reaction

3^o (tertiary) ROH = 3 C bonded to C-OH



Fermentation: Sugar → Ethanol



http://science.howstuffworks.com/innovation/edible-innovations/moonshine2.htm

What happens to the C_2H_5OH when it gets in our body?

http://www.cafepress.com/+moonshine_cowsbeer_label,654653133

Alcohol metabolism uses dehydrogenases (in liver):

$$C_2H_5OH \xrightarrow{ADH} CH_3CHO \xrightarrow{ALDH} CH_3COOH$$

hangover

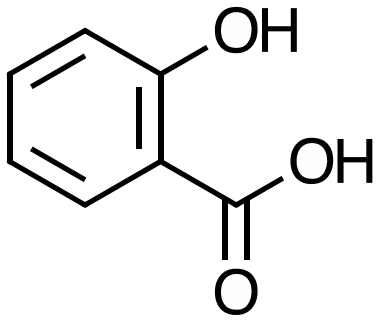
Is ethanol being oxidized or reduced?

Note: acetaldehyde is toxic in our body.
Limited amount of dehydrogenase enzyme present.
When it runs out, what happens?

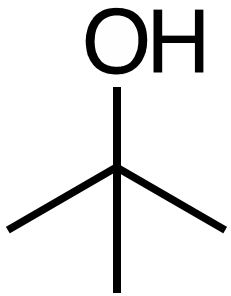
Vasopressin hormone – diuretic
Sleep – GABA and glutamate

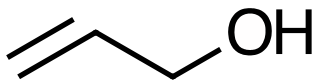
See ACS Reactions (YouTube): "How to Prevent a Hangover"

Objective: Determine which alcohol is oxidized. Draw the structure of the product of the oxidation reaction.

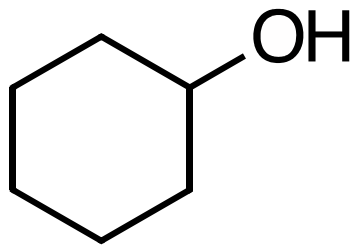


salicylic acid

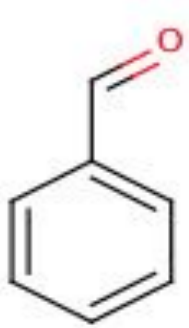




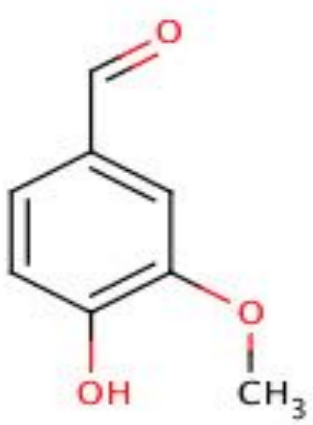
1-propene-3-ol



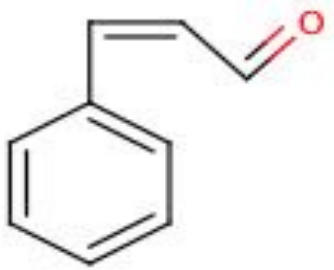
Plants Can Have Pleasant Odors



Almonds
(benzaldehyde)

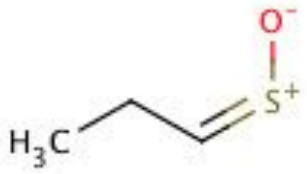


Vanilla
(vanillan)

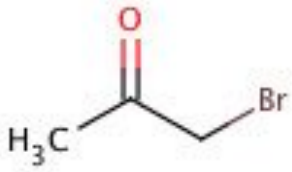


Cinnamon
(cinnemaldehyde)

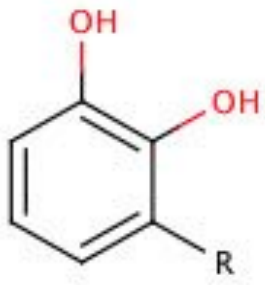
Or Unpleasant Consequences



syn-Propanethial S-oxide
onions
lachrymator

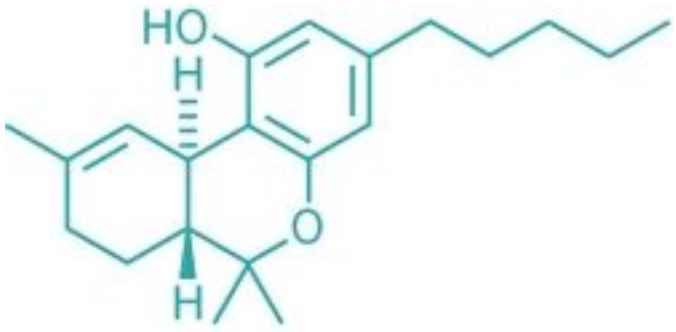


Bromoacetone
essential oil of a
Hawaiian seaweed
lachrymator



Urushiol
Poison oak: R = C17H27-33
Poison ivy/sumac: R = $C_{15}H_{25-31}$

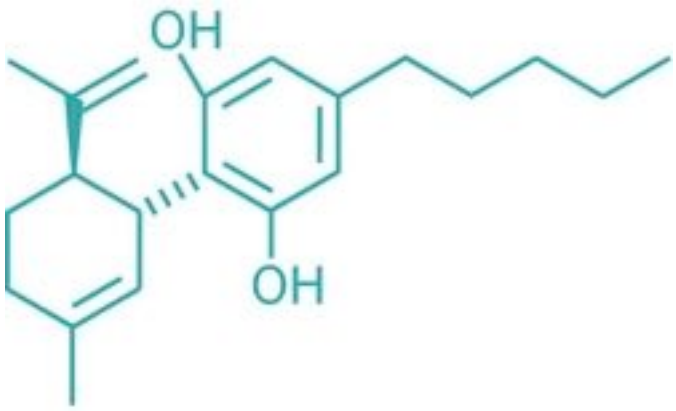
Stoner Memory Loss Explained
(http://cen.acs.org/articles/91/i48/Stoner-Memory-Loss-Explained.html)



Δ^9-Tetrahydrocannabinol

THC stimulates increased production of COX-2 (same enzyme inhibited by NSAIDs)
➔impaired working memory in mice

Medical marijuana is used to relieve nausea and vomiting, boost the appetites of chemotherapy patients, reduce seizure events, diminish neuropathic pain, and lower intraocular eye pressure.
http://cen.acs.org/articles/91/i49/Chemists-Analyze-Cannabis-Safety-Potency.html



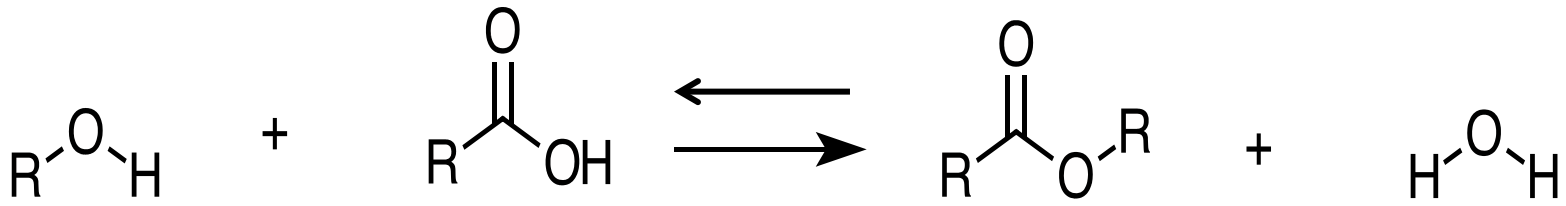
Cannabidiol (CBD)

Objective: Given reactants, predict products based on functional groups

The Product(s) of Organic Chemical Reactions Can Be Predicted By Looking at Functional Groups

Condensation reactions (reverse of condensation = hydrolysis):

Alcohol + acid --> ester + water (and reverse)
E.g., fatty acids + glycerol --> triglyceride + water



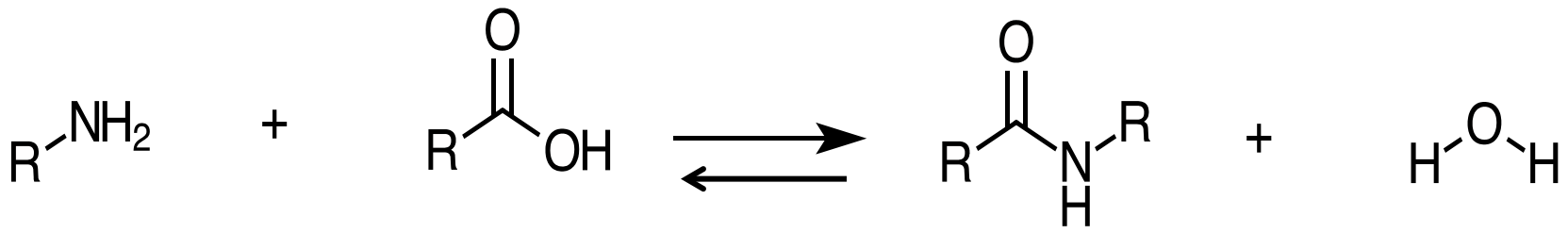
Objective: Given reactants, predict products based on functional groups

The Product(s) of Organic Chemical Reactions Can Be Predicted By Looking at Functional Groups

Condensation reactions (reverse of condensation = hydrolysis):

Amine + acid --> amide + water (and reverse)

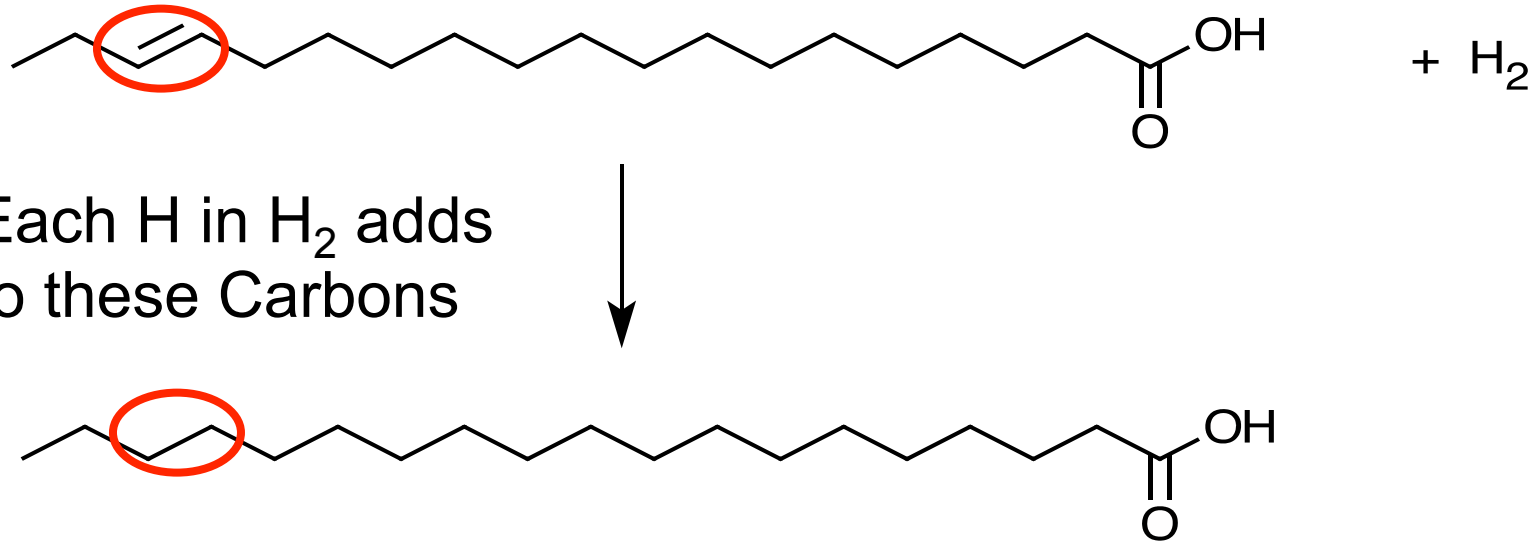
E.g., amino acid + amino acid --> protein + water



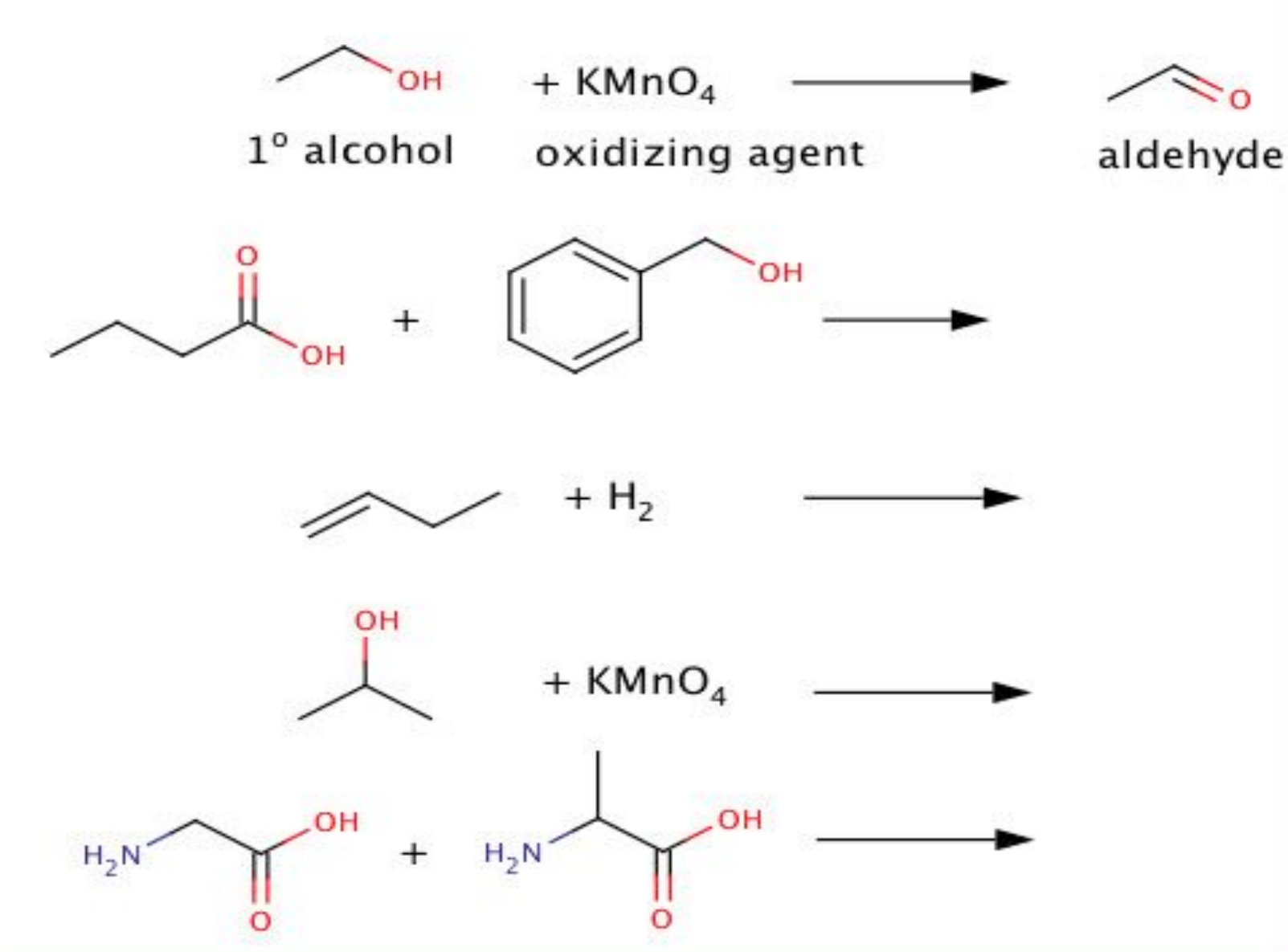
The Product(s) of Organic Chemical Reactions Can Be Predicted By Looking at Functional Groups

Alkene addition reactions:

Alkene + H_2 --> alkane *hydrogenation*
E.g., unsaturated fat + H_2 --> saturated fat



Objective: Identify the functional group(s). Determine the product(s) of the following reactions:



“I just want to say one word to you. Just one word.”

“***Plastics***”

What movie was this line made famous?

Plastics Are Polymers From Alkenes

Polymer is a long chain of repeating units (monomers)

Symbol	Acronym	Full name and uses
	PET	Polyethylene terephthalate - Fizzy drink bottles and frozen ready meal packages.
	HDPE	High-density polyethylene - Milk and washing-up liquid bottles
	PVC	Polyvinyl chloride - Food trays, cling film, bottles for squash, mineral water and shampoo.
	LDPE	Low density polyethylene - Carrier bags and bin liners.
	PP	Polypropylene - Margarine tubs, microwave-able meal trays.
	PS	Polystyrene - Yoghurt pots, foam meat or fish trays, hamburger boxes and egg cartons, vending cups, plastic cutlery, protective packaging for electronic goods and toys.
	Other	Any other plastics that do not fall into any of the above categories. For example melamine, often used in plastic plates and cups.

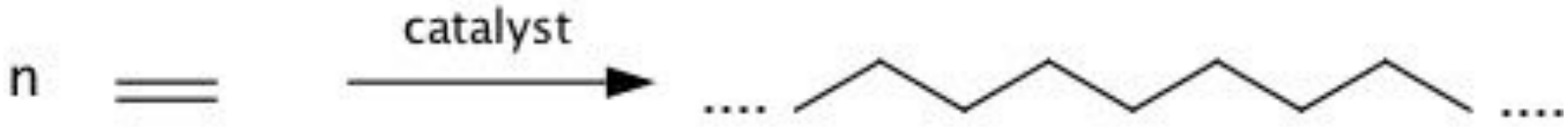
HowStuffWorks.com http://science.howstuffworks.com/plastic4.htm
Plastic recycling codes
http://www.chemheritage.org/EducationalServices/faces/poly/readings/rec.htm

Polyethylene (PE) is a common plastic.

1. What is the monomeric unit?

a. methane b. ethane c. ethylene

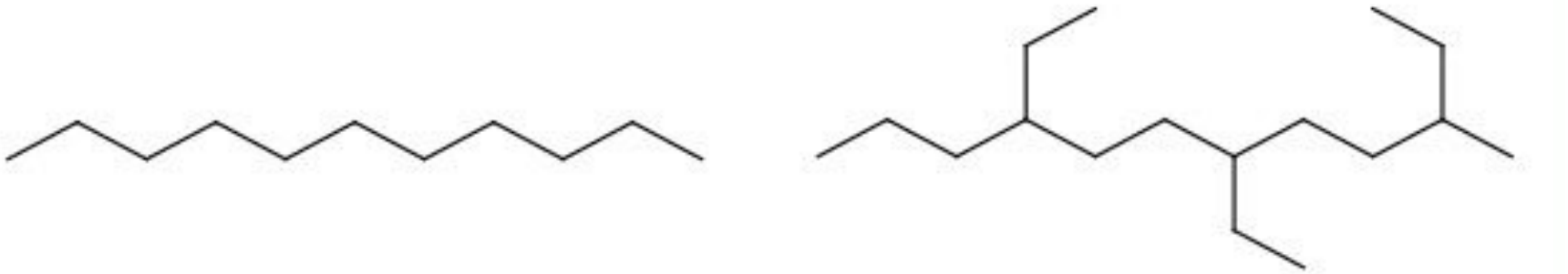
2. How is polyethylene made?



a. addition reaction
b. oxidation reaction
c. condensation reaction

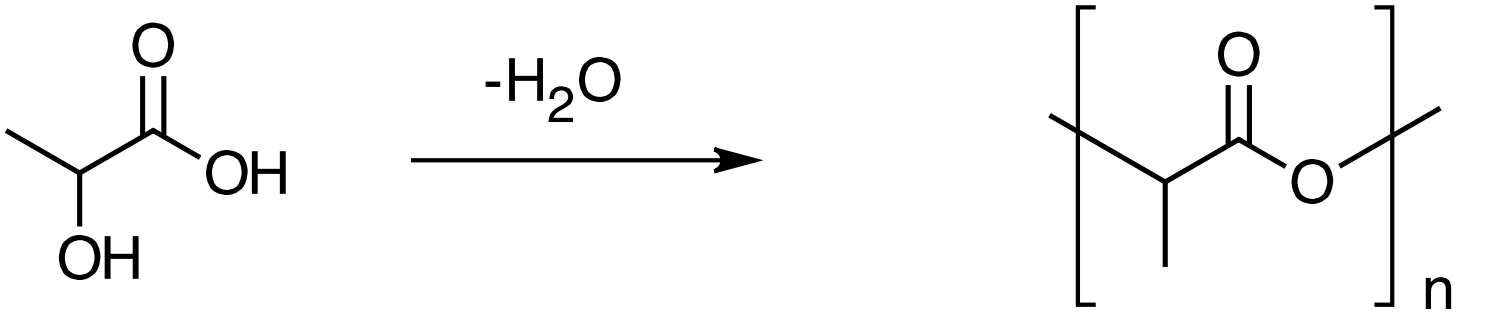
Polyethylene (PE) is a common plastic.
There are 2 types of polyethylene: HDPE and LDPE. What structural feature determines the properties of each type?

a. branches off main chain affect density
b. C-C single bonds affect softness
c. long hydrocarbon chain affect m.p.



3D printer filament:
PLA (polylactic acid)

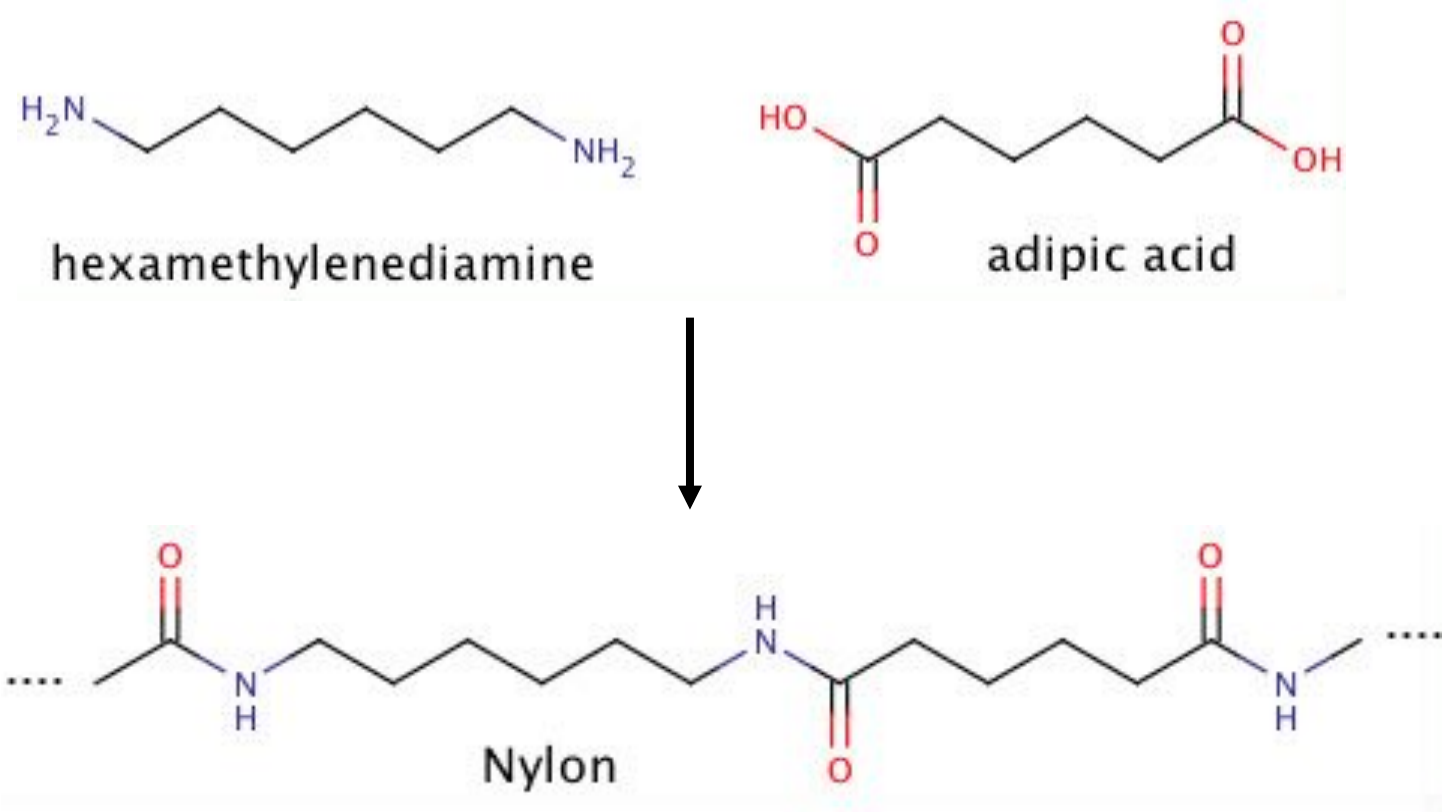
https://ae01.alicdn.com/kf/HTB1E0owRXXXXXaDXVXXq6xXFXXXT/High-Quality-Infitary-M508-3d-printer-Electronic-Kit-with-60-Meters-PLA-Filaments-Original-Arduino-Mega2560.jpg



lactic acid

polylactic acid (PLA)

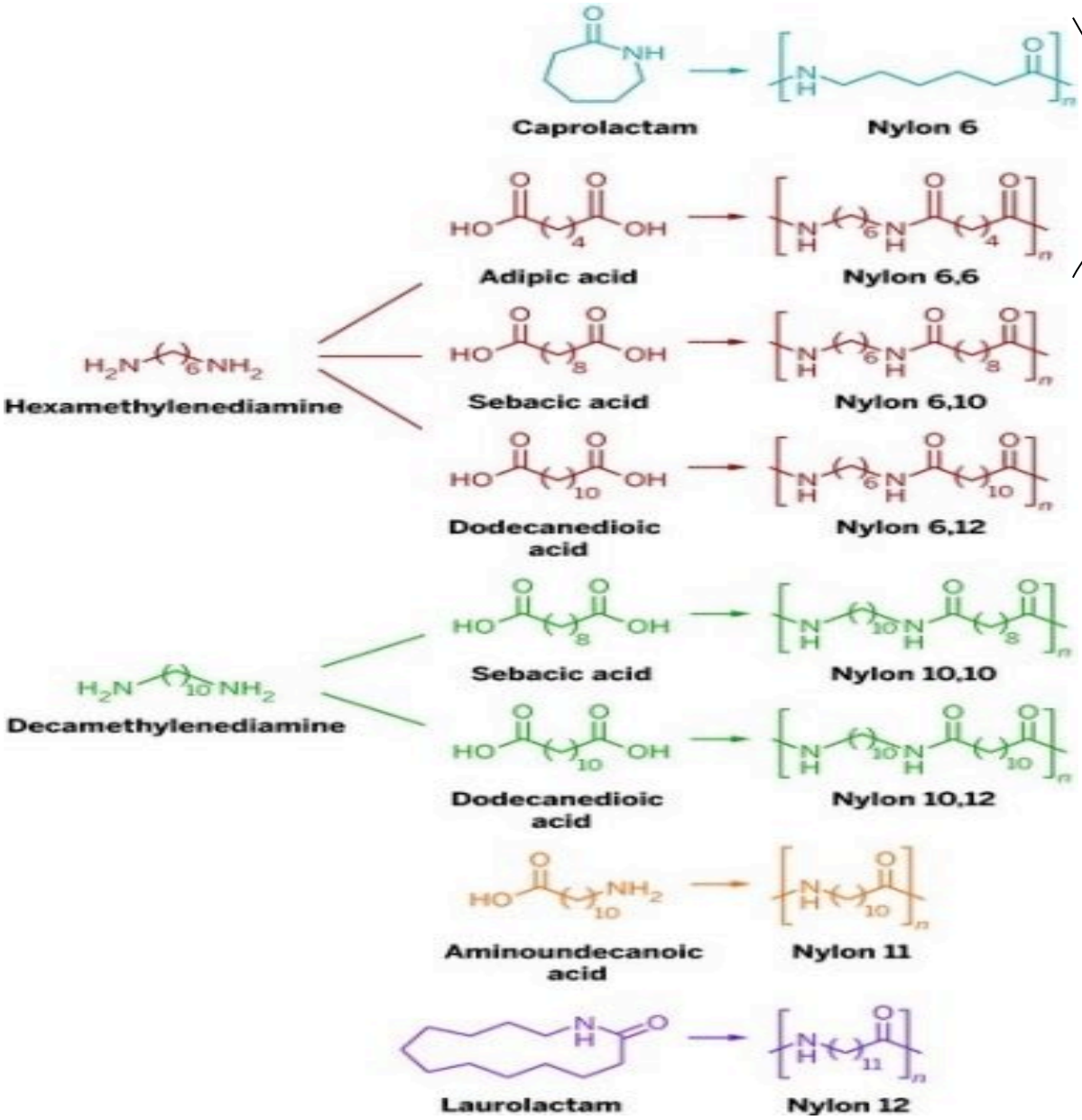
How is PLA made from lactic acid?



Nylon is a common plastic. (See Chang, 6th ed., Fig. 22.4, p. 765)

1. Identify the functional group(s) in nylon.
2. How is nylon made? Or How is this functional group made?
    a. Condensation (or reverse)
    b. alkene addition
    c. alcohol oxidation

Many Types of Nylon for Many Uses (CEN, 2/18/13, p. 28)



Carpets, fabric, food packaging, balloons

Flexible tubing in autos

As # of C's increase, chemical resistance and flexibility increase, specific gravity decreases

Brake and gas lines in cars

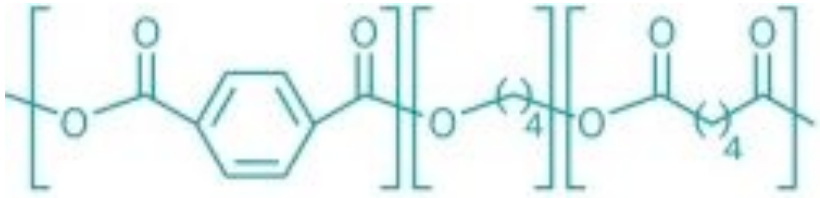
http://cen.acs.org/articles/90/i12/Old-Plastics-Fresh-Dirt.html

3/19/12, CEN, p. 12 "Old Plastics, Fresh Dirt"

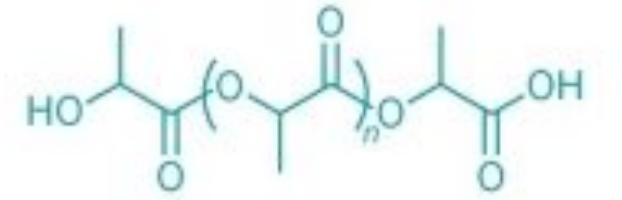
2010: 250 million tons of trash generated by Americans:

12% = Plastics

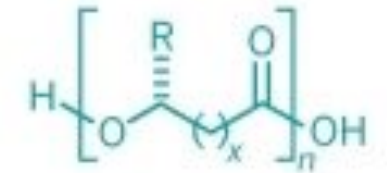
27% = Food waste and yard trimmings



BASF's Ecoflex (copolyester)



NatureWorks' Ingeo (polylactic acid)



Polyhydroxyalkanoate

Compostable Plastics biodegrade in a specific environment in a relatively short period of time.

Biomolecules Are Organic Compounds

Biomolecule	Elements	Functional Groups	Function	Polymer/ Bond Type
Carbohydrate	C, H, O	Alcohol, ether Aldehyde, ketone	fuel	Yes glycosidic
Protein	C, H, O, N, S	Amine, acid various	fuel	Yes peptide
Lipid	C, H, O, P	Acid, ester alkene	Fuel protection	no
Nucleic Acid	C, H, O, N, P	Sugar, base, phosphate	Transcription Protein synthesis	Yes Phospho-diester

Biomolecules are Important in Life

1. Why is glucose important? http://en.wikipedia.org/wiki/Glucose

a. It is sweet.

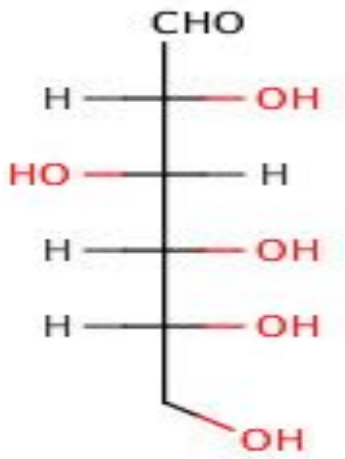
b. It is metabolized by our body as a fuel.

c. It is found in blood.

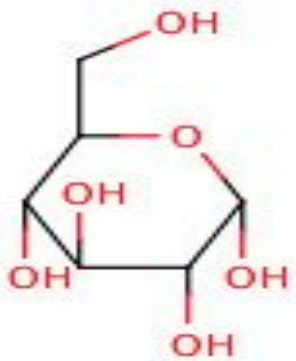
2. Two forms of glucose exists in our body. These structures are:

(i)Structural isomers (ii) stereoisomers (iii) different compounds

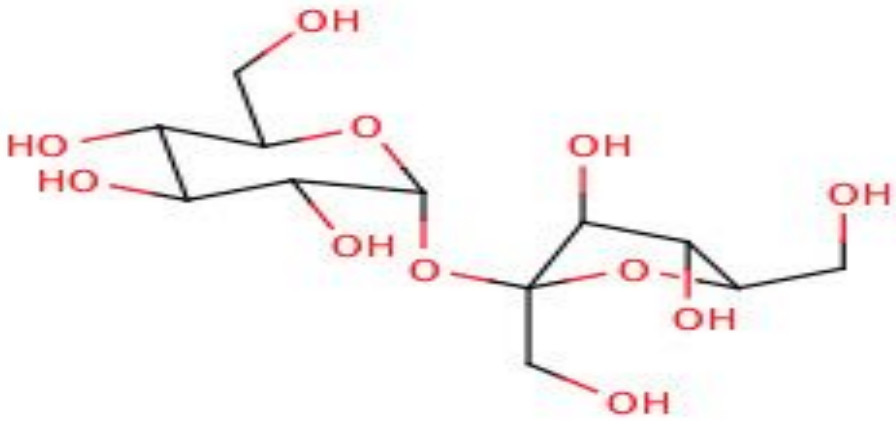
3. Locate the glycosidic bond in sucrose.



glucose



glucose

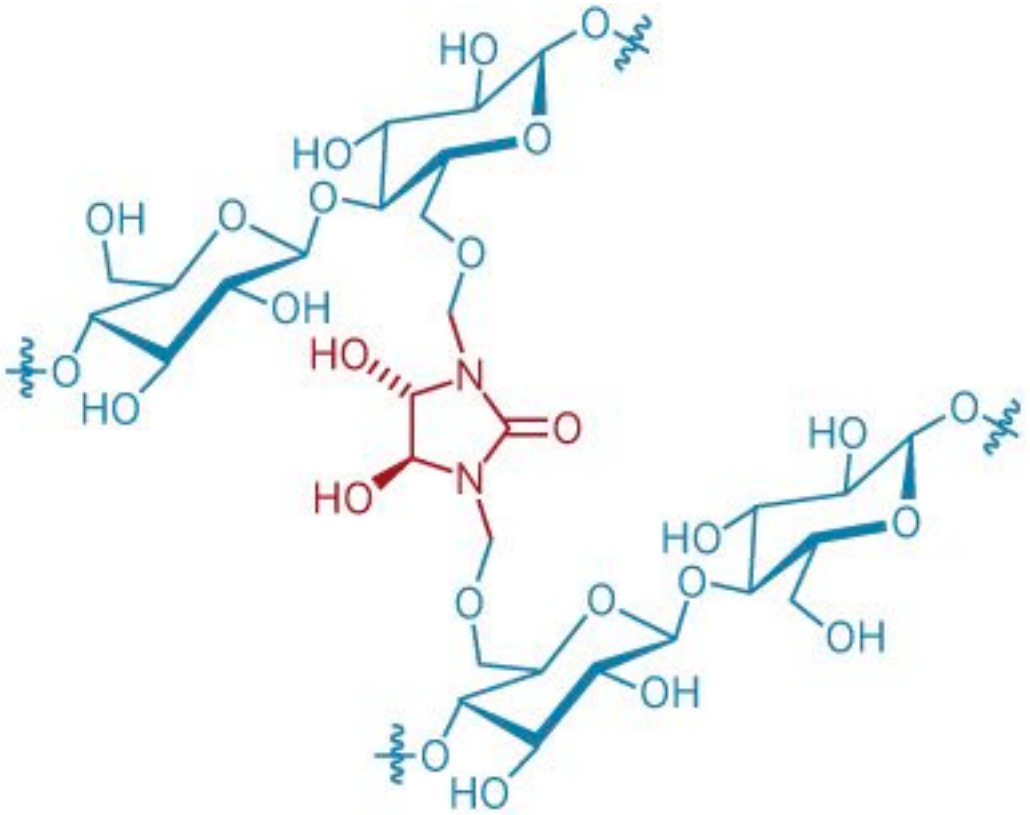


sucrose

Wrinkle-Free Cotton (C&EN, 12/2/13, p. 32)

http://cen.acs.org/articles/91/i48/Wrinkle-Free-Cotton.html

Cotton is made of numerous parallel chains of cellulose.
These chains are held together by weak **hydrogen bonds**.
H bonds break in warm dryer and re-form as chains shift into new positions.



Treat fabric with molecules that ***cross-link*** the chains to permanently hold them in place. (DMDHEU = dimethylol dihydroxyethylene urea)

Bio-Based Polymers

http://cen.acs.org/articles/92/i43/Biobased-Polymers.html

http://www.thinglink.com/scene/581585983141576706

Rubber

Plastic bottles

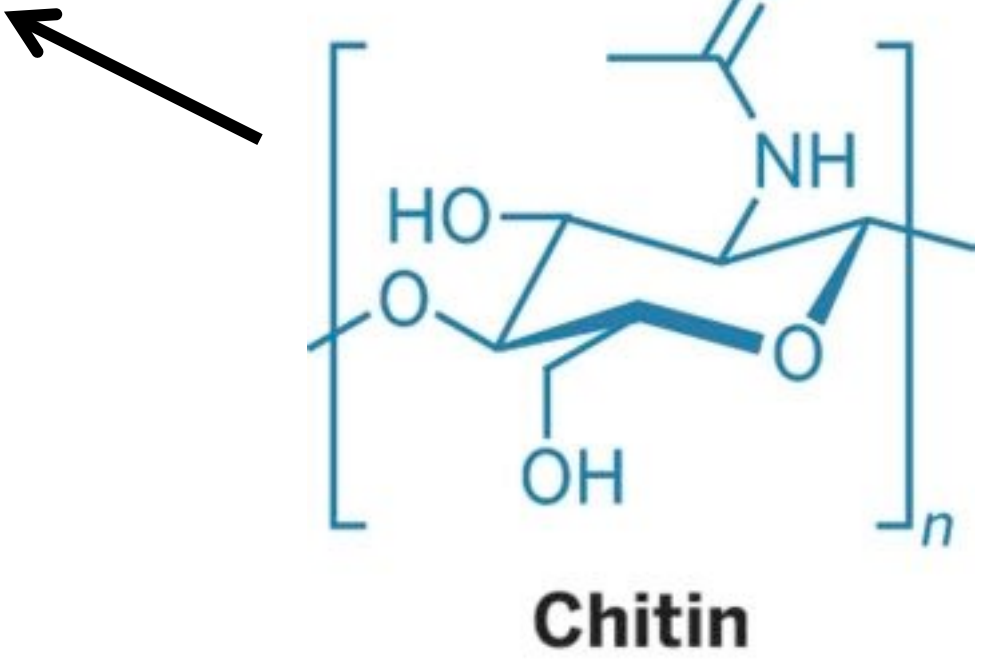
Nylon

Synthetic fibers

Etc.

Fungus-based materials – Plastics from Mushrooms

http://cen.acs.org/content/cen/articles/92/i40/Making-Mushrooms.html



Chitin

Chitin is the most common biopolymer found in nature.
Chitin is a:

a. Polysaccharide
b. Protein
c. Nucleic acid
d. Fat

Protein Shape (folding) Determines its Activity and Function

http://lectures.molgen.mpg.de/ProteinStructure/Levels/index.html

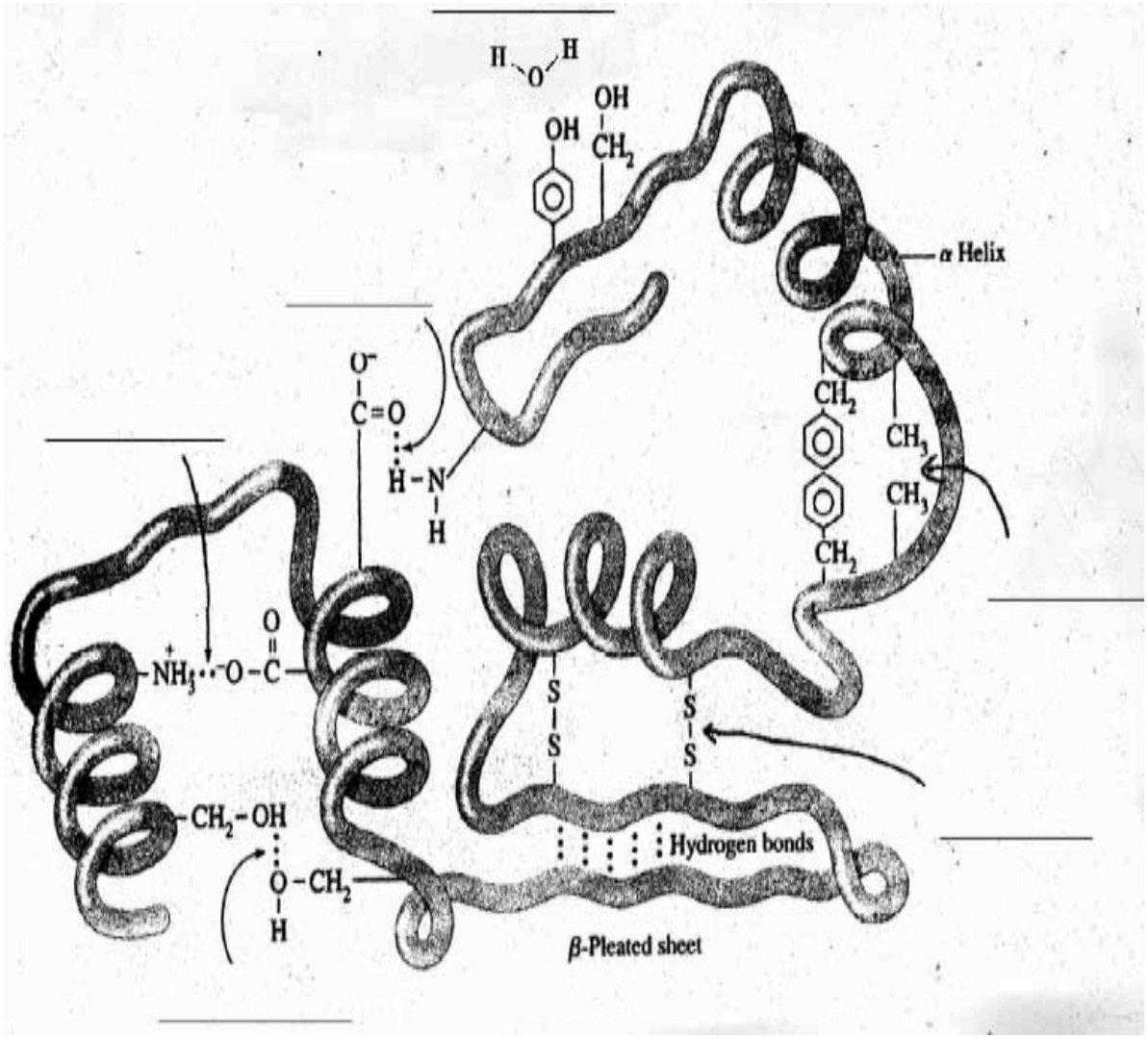
Which structural level determines its activity and function?

Primary (1°) = amino acid sequence

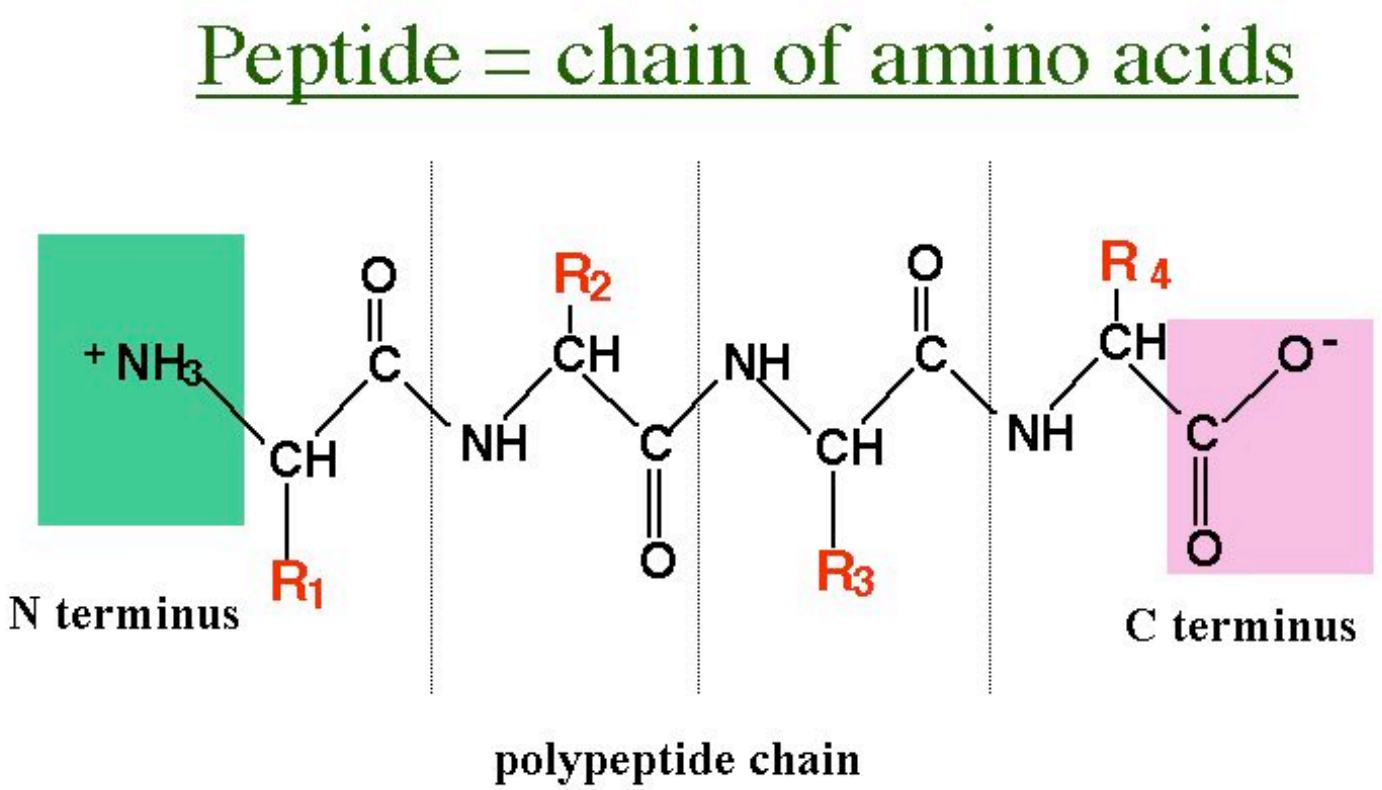
Secondary (2°) = shape of a *part* of a protein due to H bonds, e.g., α helix, β-pleated sheet

Tertiary (3°) = 3-D shape of *entire* protein molecule, e.g., fibrous, globular

Quaternary (4°) = 3-D shape of two or more protein subunits



A Peptide bond connects amino acids.
Where is the peptide bond?

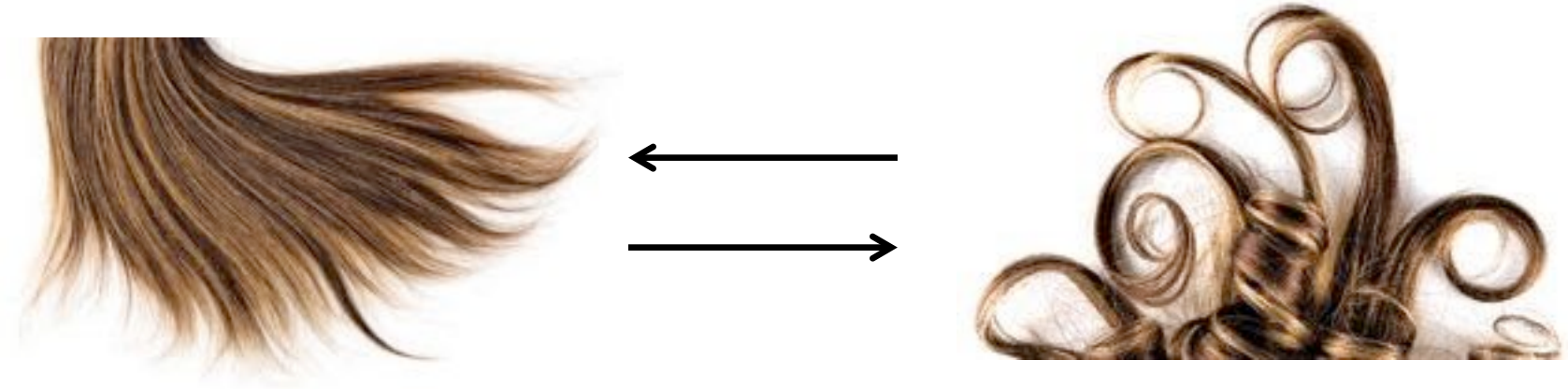


http://www.ucl.ac.uk/~sjjgsca/ProteinStructure.html

Hair Staighteners

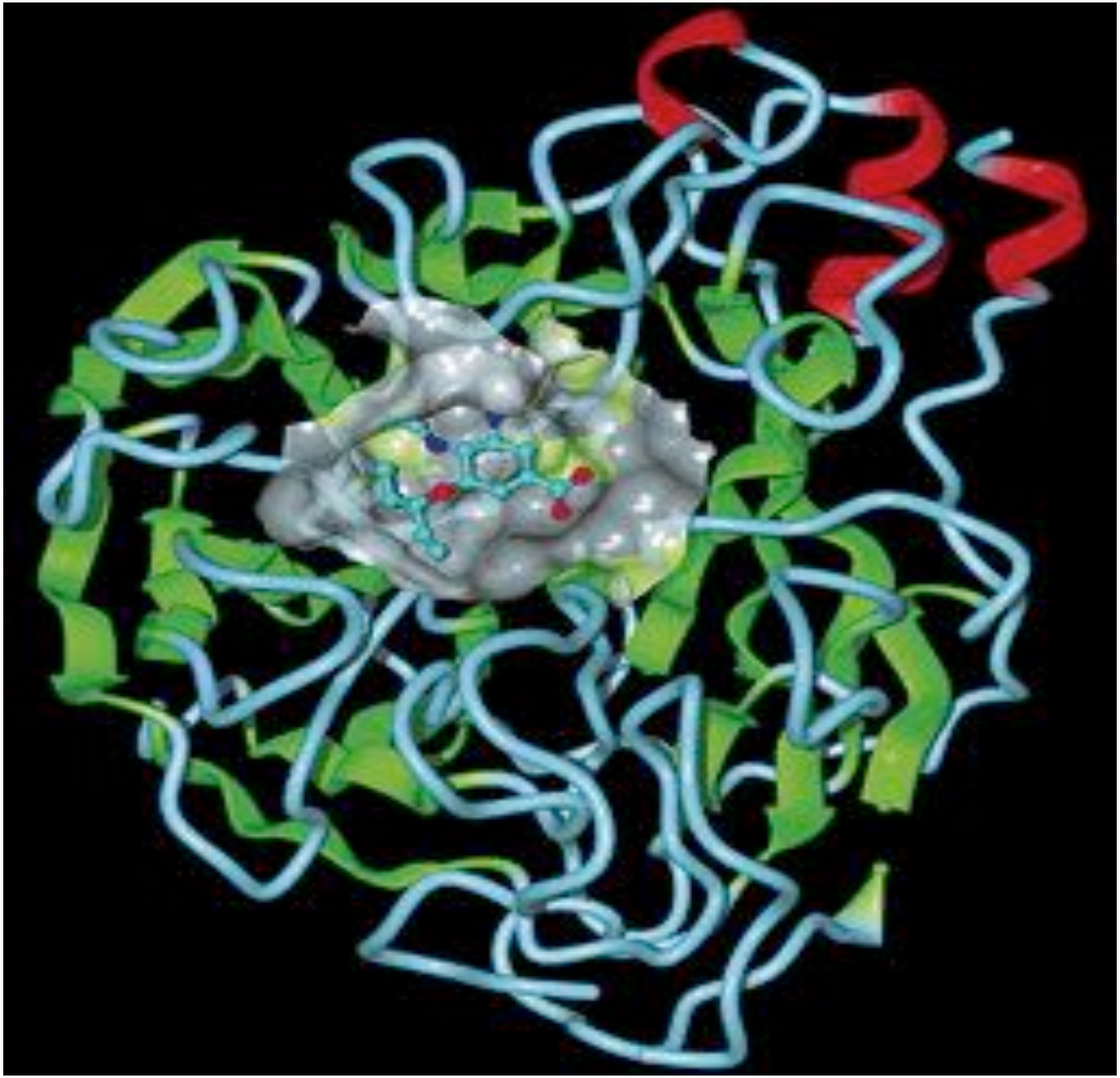
http://cen.acs.org/articles/88/i45/Hair-Straighteners.html

Break bonds to change shape



Hair is a fiber made of keratin (a protein).
Hair gets its structure from two types of bonds in Keratin:
1. Disulfide bonds (covalent)
2. Hydrogen bonds (intermolecular)

Cross-link amino acids in hair fibers to keep shape.
Straighteners: formaldehyde (Brazilian Blowout)
Ammonium thioglycolate (Japan)



Tamiflu (ball and stick) fights flu by blocking the active site of neuraminidase, a viral enzyme that cleaves terminal sialic acids from the surface of infected cells in order to enhance the release of newly assembled viruses.

CEN, August 29, 2005, pp. 20-22

Fats and Oils are Found in Nature as Triglycerides

Cooking oils are mixtures of fatty acids.

Fatty acid compositon: http://www.scientificpsychic.com/fitness/fattyacids1.html

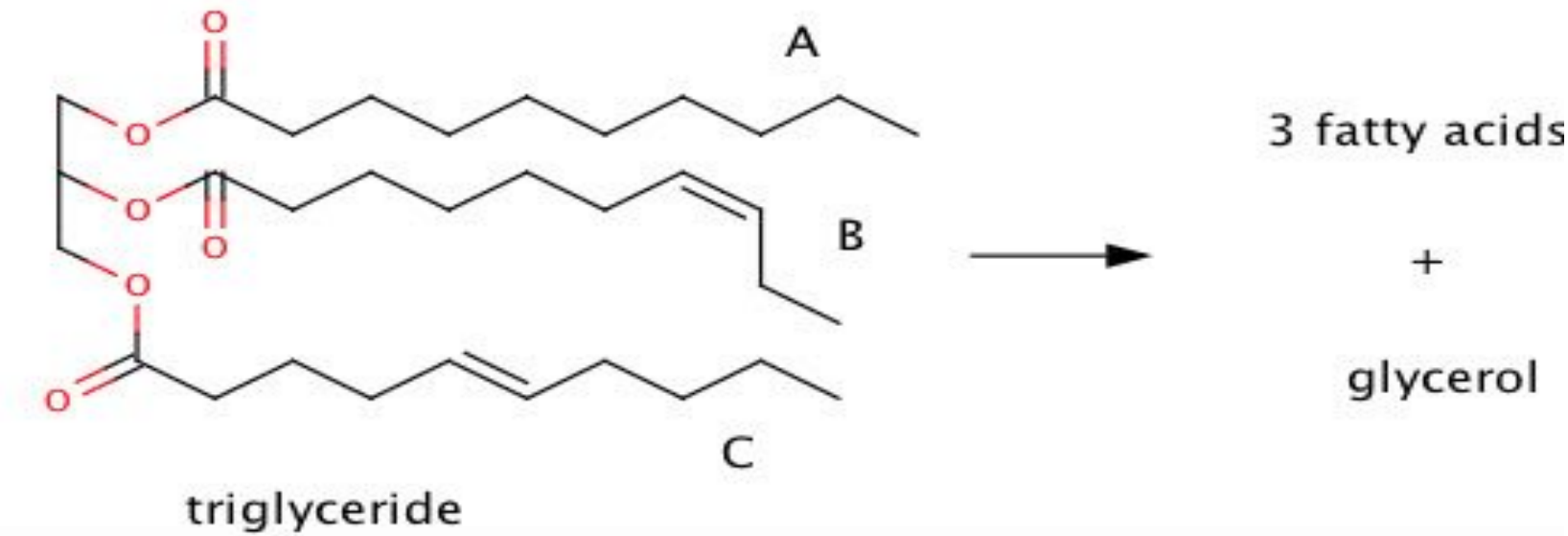
Oil properties: http://en.wikipedia.org/wiki/Cooking_oil

How to choose a good oil: http://www.healthcastle.com/cooking-oils.shtml

1. In the triglyceride shown below,

a. locate the saturated fatty acid chain: A or B or C

b. Locate the cis, unsaturated fat chain: A or B or C



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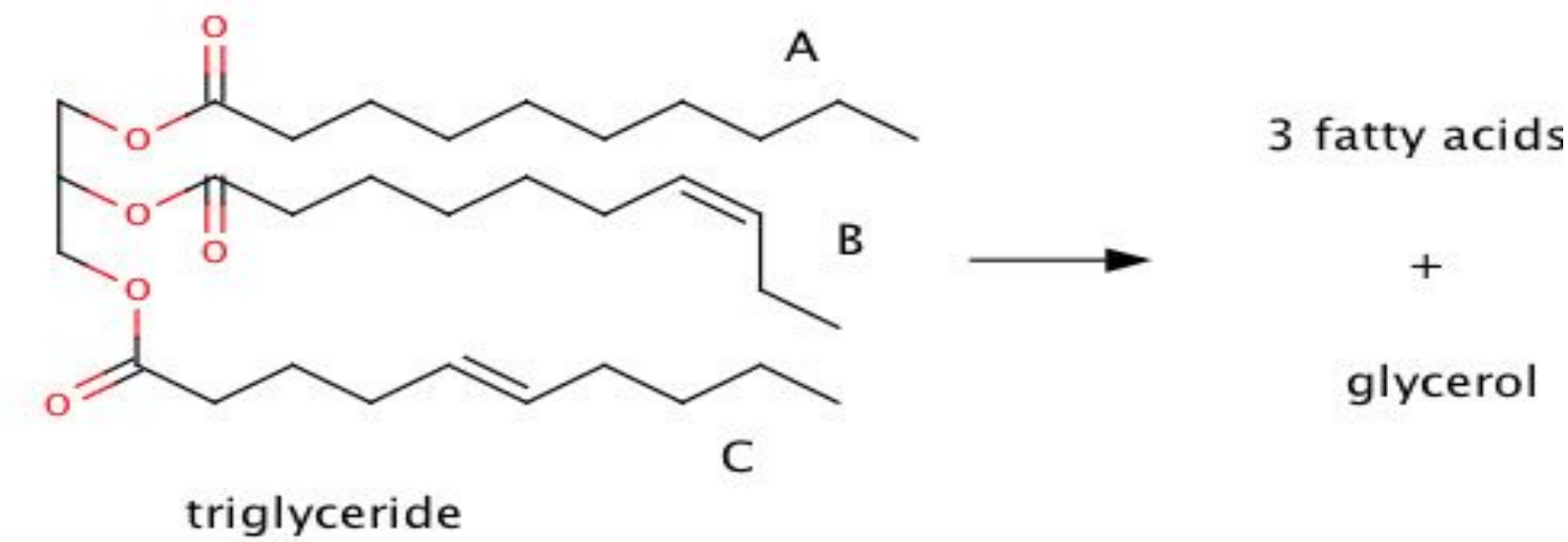
2. What type of fat is better to eat?

(i) saturated, straight (ii) unsaturated, straight (iii) unsaturated, bent

3. Explain how saturated fats and trans fats are similar.

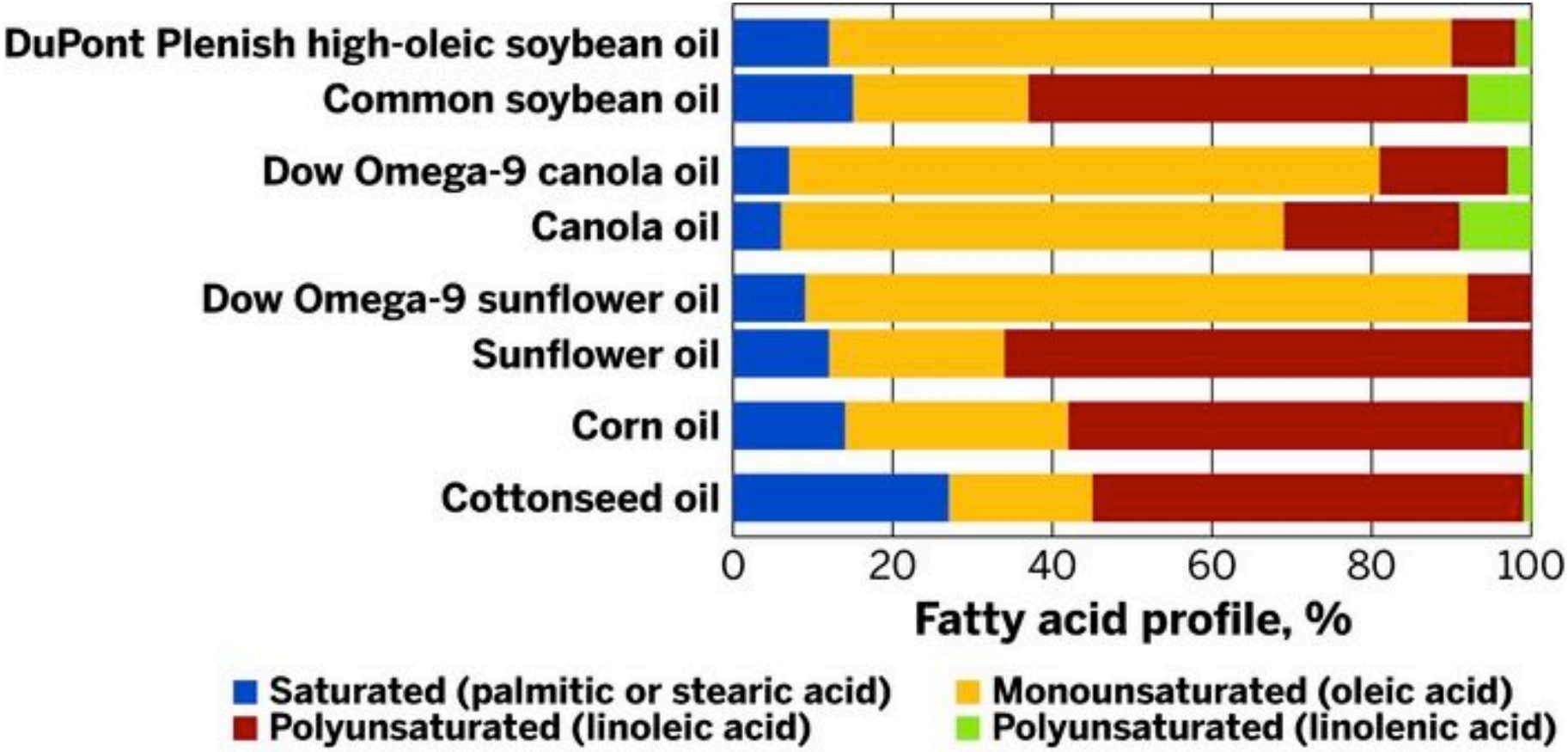


http://cen.acs.org/articles/90/i11/Replacing-Trans-Fat.html

3/12/12, CEN, p. 30 Replacing Trans Fat

New crops from Dow Chemical and DuPont target food makers looking for stable, heart-healthy oils

New seeds yield crops with higher proportion of monounsaturated oleic acid.



DNA is more than a bunch of letters (A, T, C, G).

1. What do the letters represent?

a) Random letters

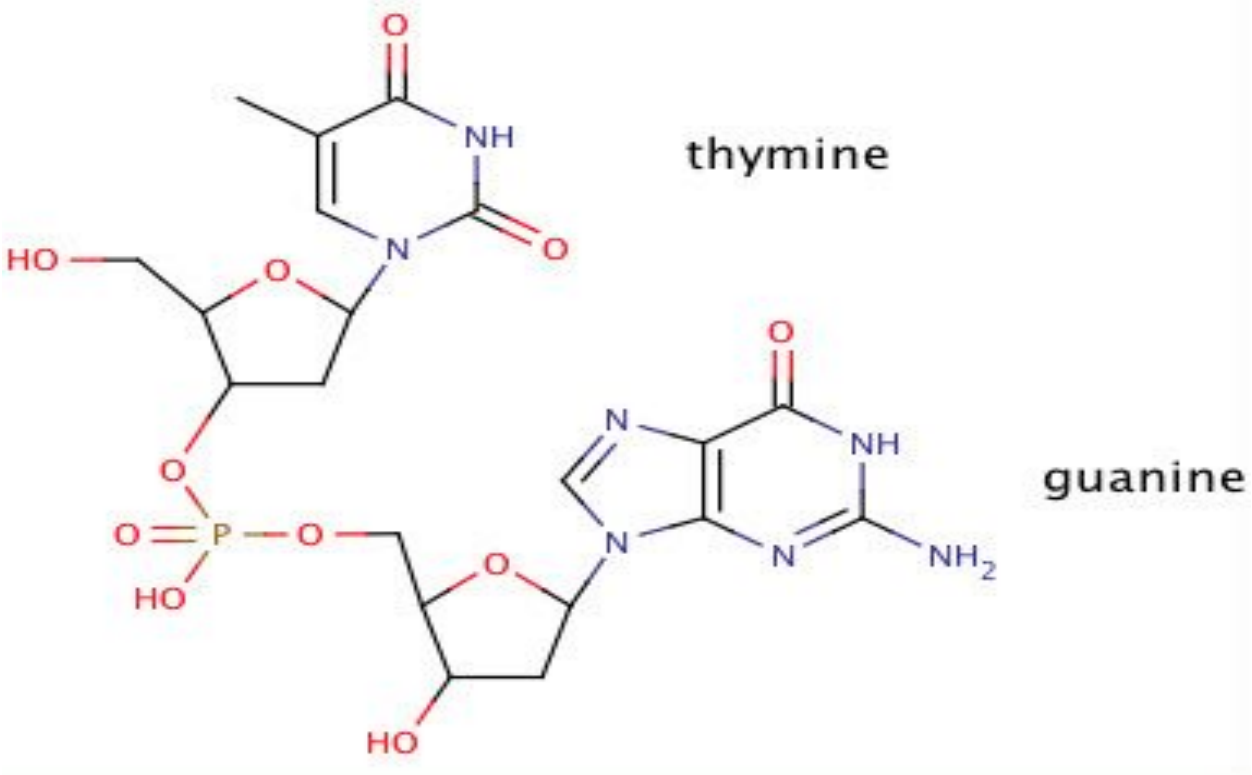
b) Bases on separate DNA strands that pair together

c) Genetic code

2. The TG dinucleotide is shown below.

a) Identify the base, sugar, and phosphate.

b) Locate the phosphodiester bond.



Valence Bond Theory and Molecular Orbital Theory are the Two Main Bonding Theories

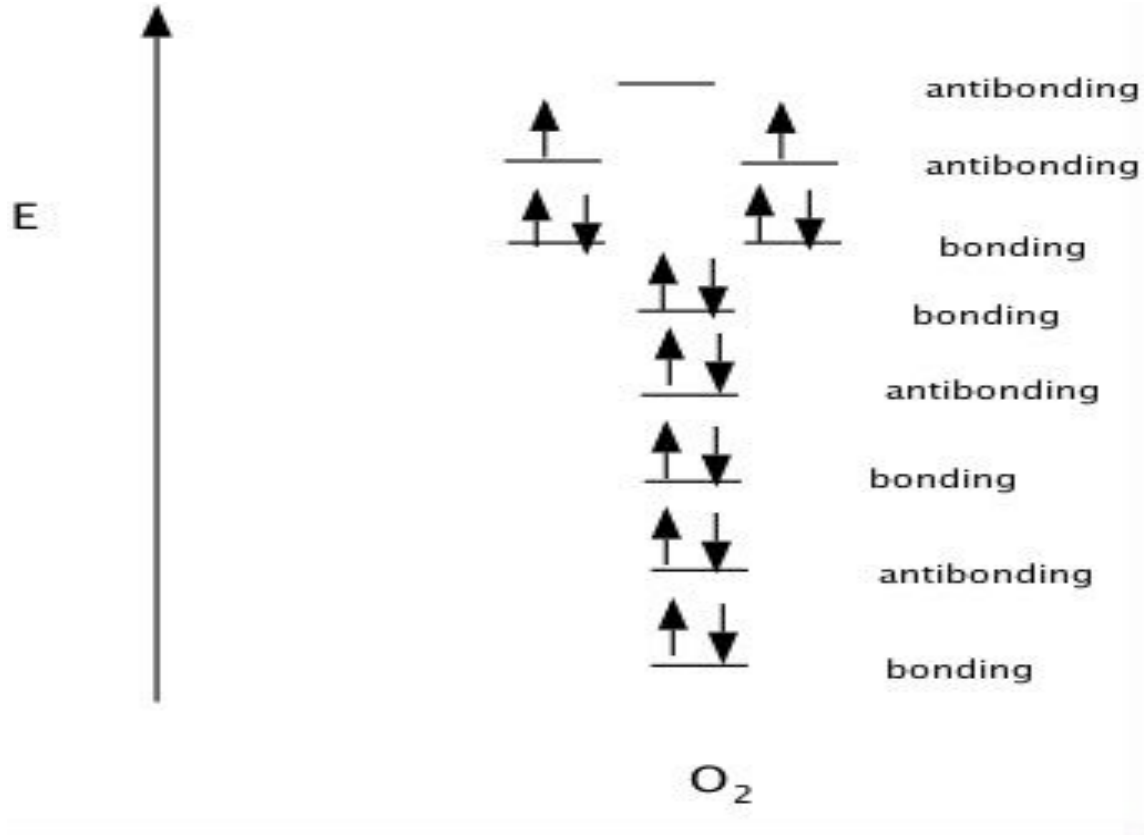
Bonding Theories are used to explain _____.

Valence Bond Theory	Molecular Orbital Theory
Describes geometry and shape	Describes magnetism, spectra, bond order
Localized electrons	Delocalized electrons if > 3 atoms
Hybrid orbitals: AO's from the same atom mix together	Molecular orbitals: AO's from different atoms mix together
Each hybrid orbital has a specific shape and orientation --> directional bonding	Bonding MO's - low E Antibonding MO's - high E
Orbital overlap = bond strength	Orbital overlap = bond strength

Oxygen, O_2, is paramagnetic. A paramagnetic substance has at least one unpaired electron.

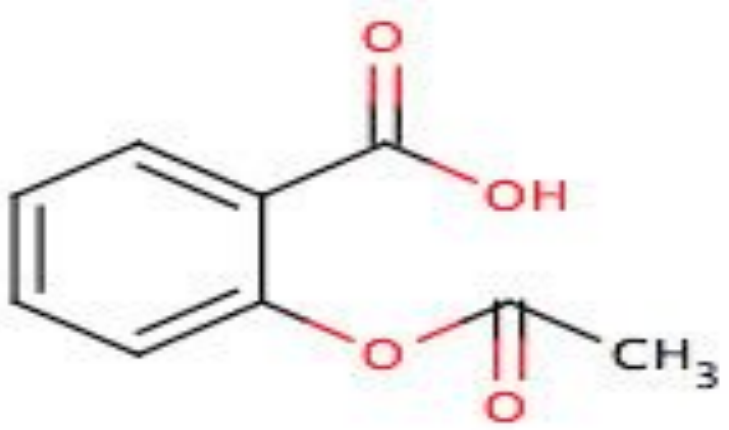
a. Draw the Lewis structure of O_2. Does the structure match the experimental data?

b. Draw the molecular orbital diagram of O_2. Does the diagram match the experimental data?



Practice Makes Perfect

1. a. Circle the functional group(s) in aspirin. Write the name of the functional group next to your circle.



b. Does aspirin react with ethanol, C_2H_5OH? If so, draw the structure of the organic product of this reaction.

2. a. Iso-amyl alcohol, $(CH_3)_2CHCH_2CH_2OH$, has at least one structural isomer. Draw the Lewis structure of <u>one</u> structural isomer of this alcohol.
b. What type of alcohol (1^o, 2^o, or 3^o) is iso-amyl alcohol?
c. Iso-amyl alcohol is treated with bleach. Draw the structure of the product of this reaction.