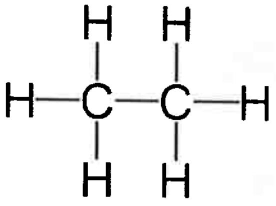
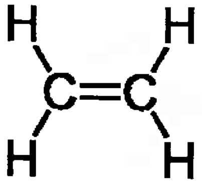
CHAPTER 3
ALKENES

3.1 Introduction.

Alkenes are molecules containing a C=C double bond. They are also sometimes referred to as olefins or as **unsaturated** compounds. They called unsaturated because the C atoms in a C=C double bond don't have as many hydrogens bonded to them as an alkane does. Molecules with one double bond are called **monounsaturated.** Molecules with multiple double bonds are called **polyunsaturated.** In contrast, alkane molecules with no double bonds are **saturated.**



Ethane (saturated)



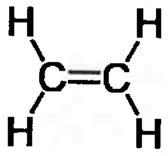
Ethene (unsaturated)

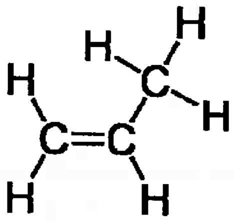
When we discuss the chemical reactions of alkenes, we will see that the primary site of reaction is the double bond and the most common type of reaction is the addition of atoms to the double bond to make a saturated molecule.

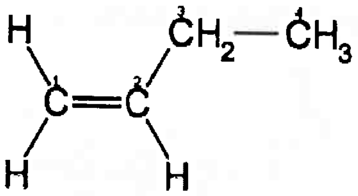
3.2 Naming Alkenes

To name alkenes, we count the number of C atoms in the longest unbranched chain, take the name of the corresponding alkane and change **–ane to -ene.**

Thus



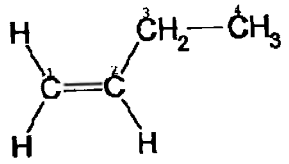


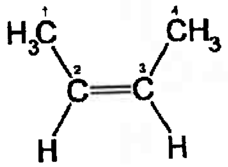


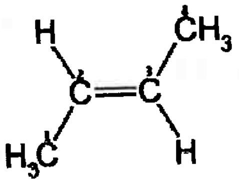
Systematic:	ethene	propene	butene
Common Name:	ethylene	propylene	butylene

When we put a double bond into butane, naming gets a little more complicated. There are two places where we can put a double bond: between the first and second carbons, or between the second and third C atoms. Furthermore we have the possibility for cis-trans isomers when the double bond is between the 2nd and 3rd C atoms. Can you see why there are no cis-trans isomers when the double bond is between 1st and 2nd C's? In order for cis-trans isomers to exist, there must be two different groups attached to both C atoms of the C-C double bond.

To name molecules with double bonds, pick out the longest chain containing the double bond. **Start numbering the chain from the end closest to the double bond** even if it results in larger numbers for other groups branching off the main chain.To indicate where the double bond is, specify the number of the **first** C in the double bond. The three isomeric butenes are:

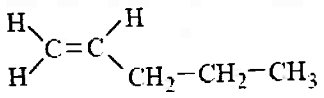

1-butene

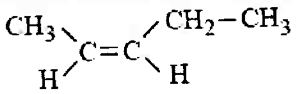

cis-2-butene

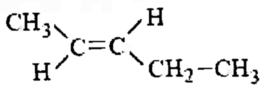

trans-2-butene

(Any cis/trans isomers on 1-butene?)

Let's take a second example; drawing all the isomeric pentenes:

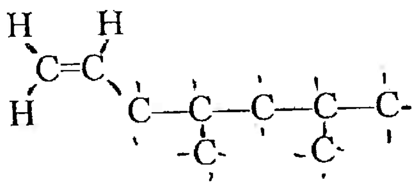

1-pentene

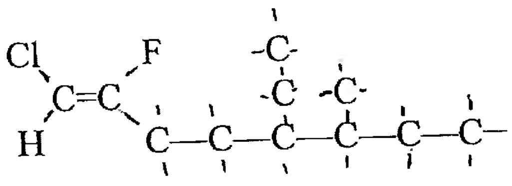

cis-2-pentene


trans-2-pentene

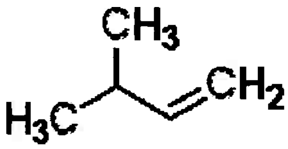
If we move the C=C between the #3 and # 4 C you will see that in fact it is the same molecule (flipped from left to right) as the 2-pentenes.

Naming Branched Alkenes

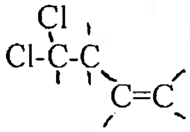

4,6-dimethyl-1-heptene

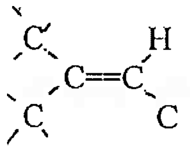

1-chloro-5-ethyl-2-fluoro-6-methyl-1-octene

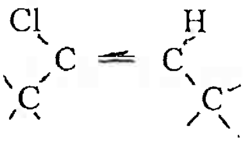
In the above examples, giving the smallest number to the C=C takes priority over giving a small number to the methyl branch.



The name for this molecule is 3 methyl-1-butene. Note we start numbering from right to left in this molecule to give the alkene the smallest value. As in the previous examples, giving the smallest number to the C=C takes priority over giving a small number to the methyl branch. Name the molecules below

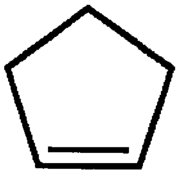




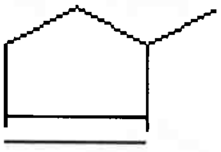


Are there geometric isomers of the above two structures?

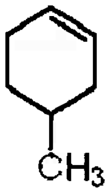
Double bonds commonly occur in rings. The numbering automatically starts from the double bond and goes around the ring so as to make the C=C numbering 1 and 2. If there are other groups on the ring, number around the ring in the direction that gives the smallest sumof numbers.



Cyclopentene



3 methyl cyclopentene

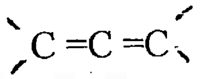


4-methylcyclohexene

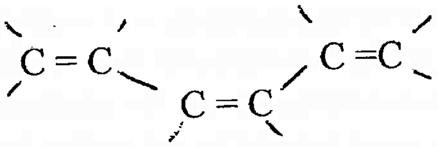
Some molecules think that if one double bond is good, two double bonds are better. We indicate this by putting a prefix directly in front of the -ene at the end of the name:

Two double bonds = -diene (You think you are diene!)
Three double bonds = -triene (But you should keep on triene!)
Four double bonds =-tetraene
Five double bonds = -pentaene

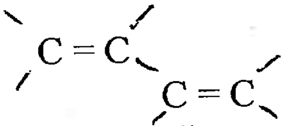
Six double bonds = -hexaene
Examples:



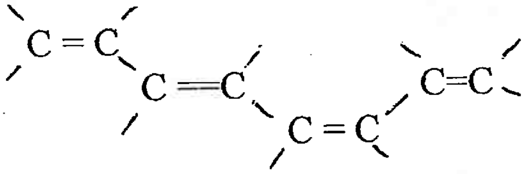
(1,2) propadiene



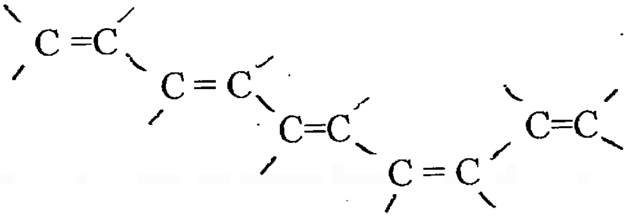
1, cis-3,5-hexatriene



1,3-butadiene

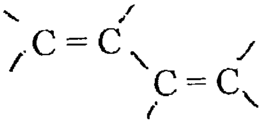


1, trans-3, cis-5, [illegible]-7-octatetraene



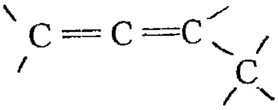
1,trans-3, trans-5,cis-7,9-decapentaene

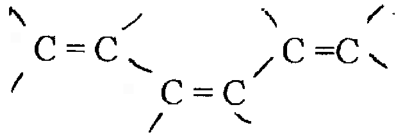
The shorthand notation for double bonds is shown below

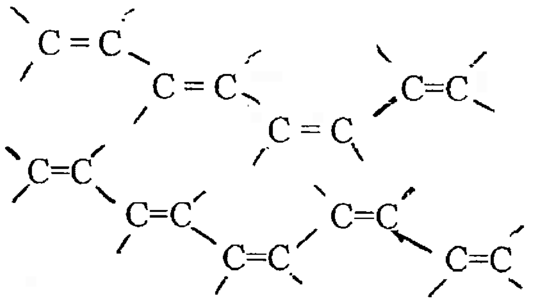


is written

Draw the shorthand notation and **name** the molecules shown below:







Alternate double and single bonds are called **conjugated** double bonds and are very common in nature; they have distinctive chemical properties, often absorb visible light, and as a result are often colored compounds.

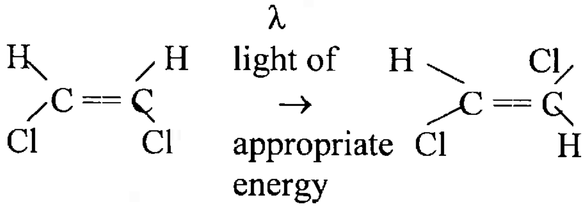
3.3 Chemical Reactions Of Alkenes

1. Photoisomerization
2. Hydrogenation
3. Addition of HCl
4. Addition of H_2O
5. Addition of alcohol
6. Polymerization
7. Oxidation

3.4 Photoisomerization reactions

A photoisomerization is the conversion of one isomer into another isomer by light. The examples we will look at involve exclusively the conversion between two <u>geometric</u> isomers.

Example:

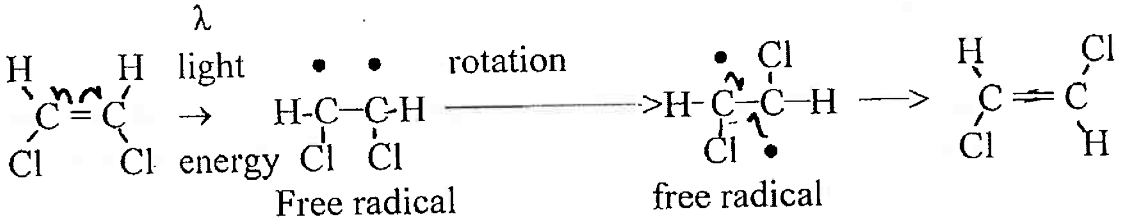


(The Greek letter λ signifies light.)

Reaction Pathway

How does this occur? Light energy (often abbreviated λ) can unpair the electrons in the pi bond so that only a single bond holds the 2 C atoms together. The resultant molecule has two unpaired electrons, and hence is not very stable. We call a molecule with unpaired electrons a **free radical** (no reference to its political status!). Since the free radical molecule has a C-C single bond, free rotation can occur about the C-C bond. After rotation through 180° the unpaired electrons can pair up again and in the process form the other geometric isomer.

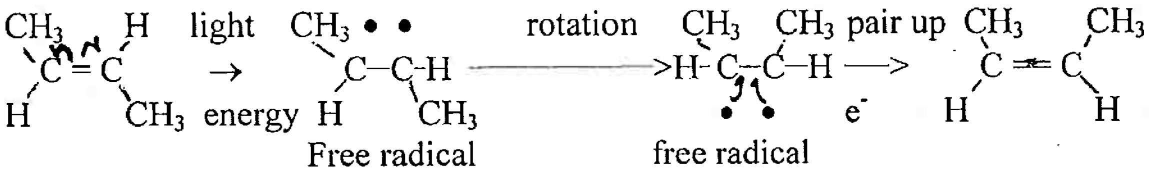
Let's look at a couple of specific examples:



The half arrows signify the movement of one electron from where the arrow starts to where the half arrow is pointing. In the first step of the above example, the two half arrows signify that light energy causes the **unpairing** of the pi electrons in the C=C double bond with one electron going to each of the C atoms. The unpaired electron is signified with a dot. The resulting single bond between the 2 C atoms can undergo free rotation. Eventually the two unpaired electrons can pair up and reform the double bond. This is indicated by the two half arrows that start at the unpaired electron on each separate C atoms and point back into the bond between them. This signifies the reforming of the pi bond.

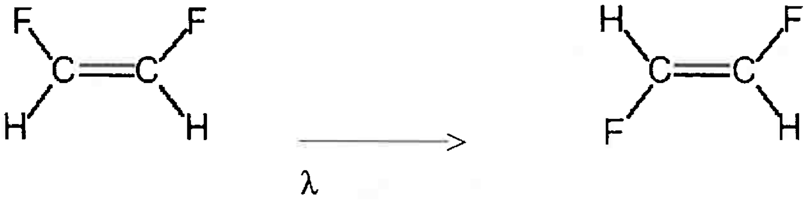
In the above reaction what sort of geometric isomer did we start with? What geometric isomer did we produce as a product?

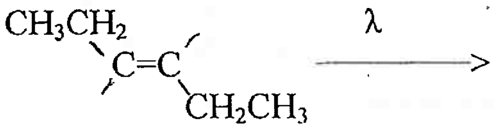
Example 2:



As before, the half arrows signify the movement of **one** electron from where the arrow starts to where the half arrow is pointing. In the first step of the above example, the two half arrows signify the unpairing of the pi electrons in the C=C double bond with one electron going to each of the C atoms. The unpaired electron is signified with a dot. The resulting single bond between the 2 C atoms can undergo free rotation. After a few rotations, the two unpaired electrons can pair up and reform the double bond. This is indicated by the two half arrows that start at the unpaired electron on each separate C atoms and point back into the bond between them. This results in the reformation of the pi bond and the end of free rotation.

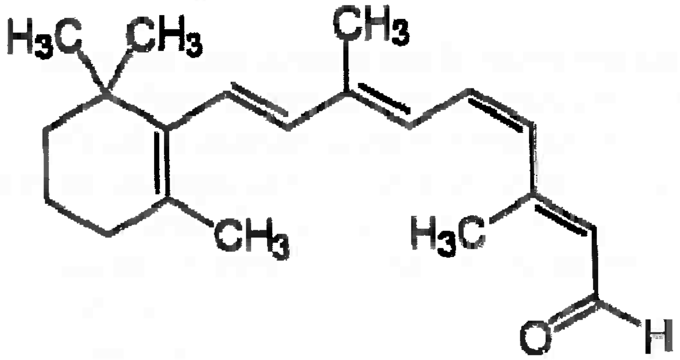
Try writing out the reaction pathway for the following reaction. Identify the beginning and final products as either cis or trans isomers.





Retinal photoisomerization

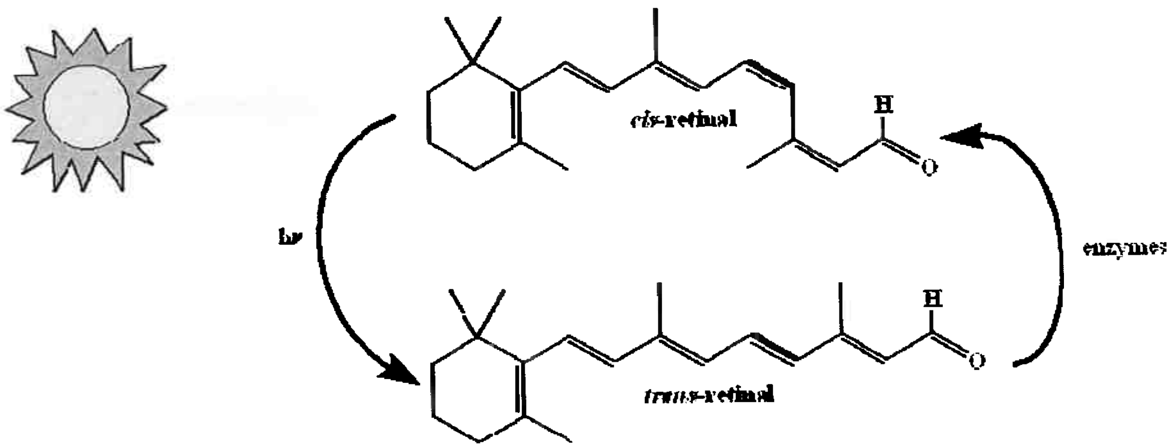
One molecule in which isomerization reactions are particularly important is cis-retinal (a form of vitamin A) shown below:



This complex molecule is known as cis-retinal or Vitamin A. Before we look at the isomerization of retinal (vitamin A), let's ask some questions about it.

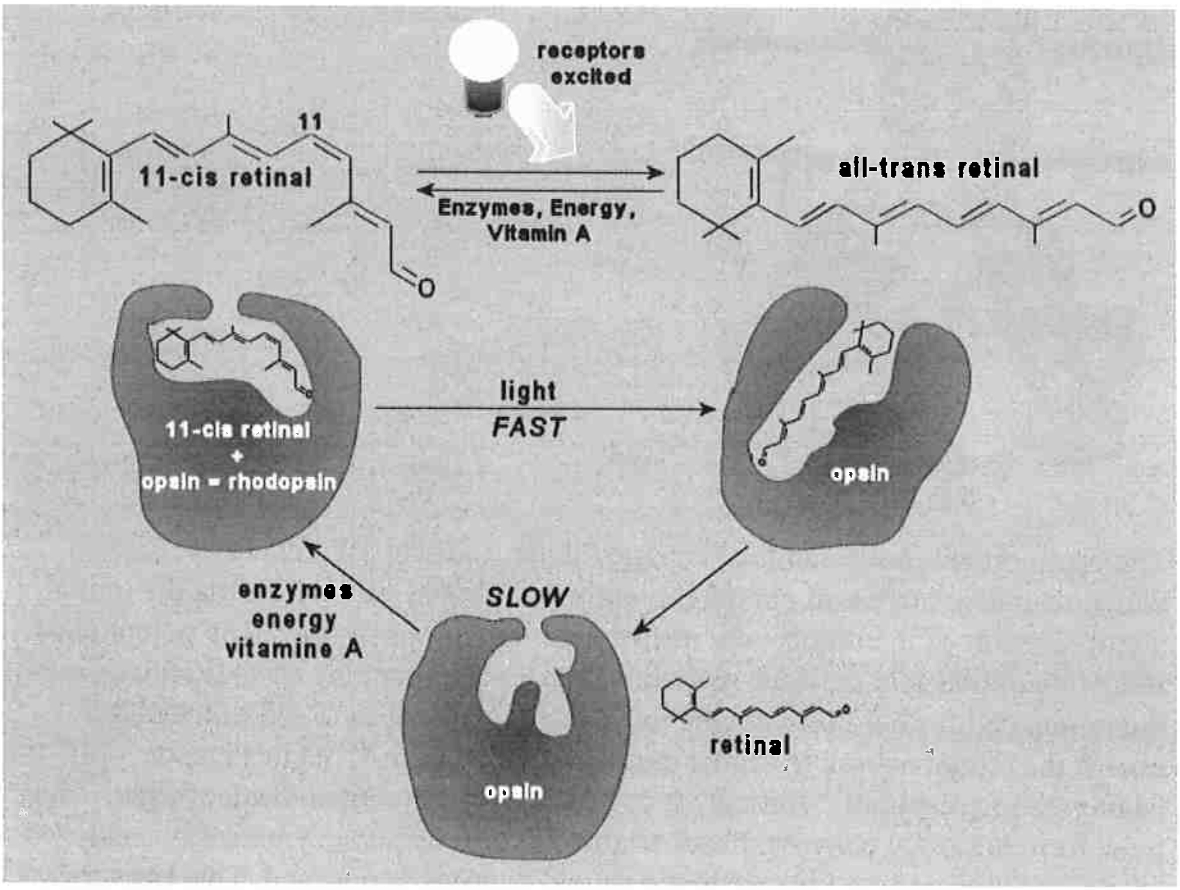
1. Will it be soluble in water?
2. Label each of the bonds in the chain as cis or trans.

Isomerization of Vitamin A (retinal) in the eye.

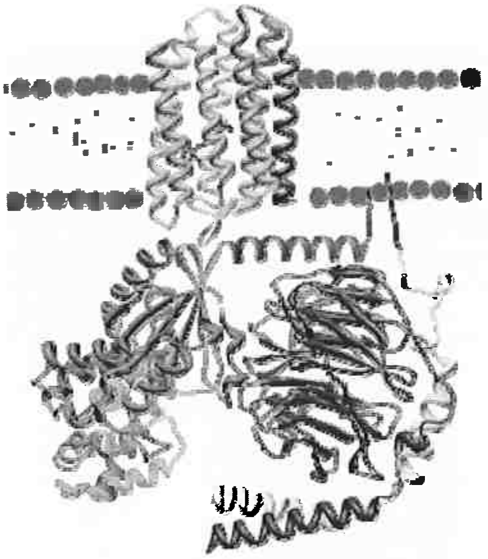


In this isomerization, the one cis bond in the polyunsaturated chain is converted into the trans form, which is referred to as trans retinal or all trans-retinal.

Cis retinal is bound to the protein **opsin** imbedded in cell membranes of the retinal cell. The retinal-opsin complex in rod cells is called **rhodopsin.**

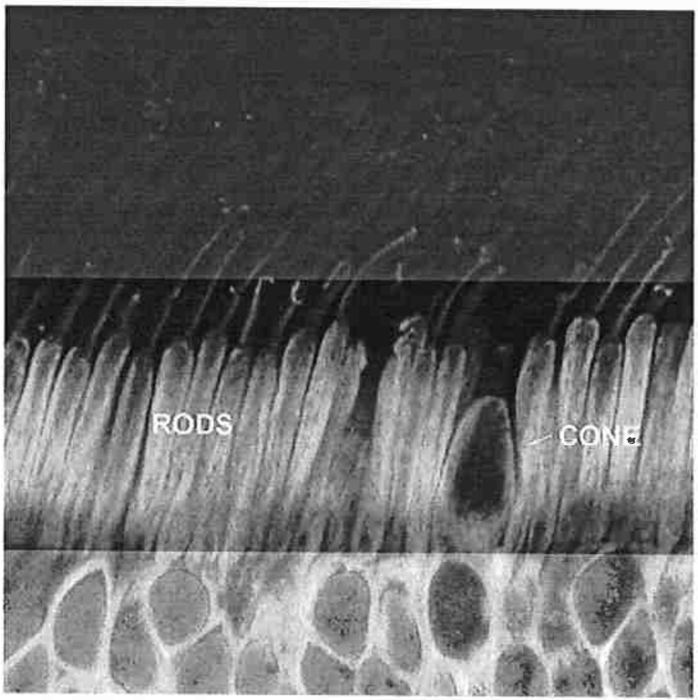


The energy of visible light unpairs the two electrons in the cis pi bond of retinal and when they are unpaired the C-C bond can rotate; when it rotates 180 degrees it converts the cis double bond into the trans geometric isomer. This photoisomerization occurs in about 2 (10^{-13}) seconds. (Now that's what I call fast!!) This chemical reaction causes the trans retinal to drop off of the opsin.



The opsin protein molecule then changes shape and sets off a chain of reaction which results in increased pumping positively charged Na ions across the retinal membrane **out** of the retinal cell, resulting in hyperpolarization. The potential of retinal membranes in the dark is about -30 mV. The pumping of sodium ions out of the retinal cell further polarizes the retinal cell membranes to -35 mV and this causes the retinal neuron to send a message to the brain: "I've just had an isomerization reaction!" Actually it comes across more like a flash of light. The trans form is slowly converted back to the cis form by an enzymatically catalyzed "dark" reaction and Na balance in the retinal neurons is returned. This conversion back to the cis form is much slower than the light induced cis–trans isomerization reaction. If there is a blinding flash of light that converts most of the cis retinal into trans retinal, one will not be able to see again until the trans retinal is converted back to cis and the cis retinal once again binds an opsin molecule. This reaction takes on the order of seconds to minutes rather than the fraction of a picosecond required for the forward photoisomerization reaction. (Although the free radical intermediates usually simply pair up again with each other, they occasionally react with other molecules and damage those molecules. This also reduces the supply of retinal, which must be continuously replaced with new vitamin A from the diet.)

Rhodopsin molecules in the **rod cells** are quite sensitive to light photons, and absorb maximally at 498 nm (green). They provide the black and white night vision in dim light. The **cone cells** are not as sensitive and hence are less useful in dim light, but they have three different forms of opsin protein which bind retinal to form three forms of the protein **photopsin**.



www.brps.org.uk/index.php?pageid=203&tln=aboutrp

The different **photopsin** proteins change the absorption spectrum of the retinal absorption spectrum. Maximally efficient activation of the blue form (short wavelength) of photopsin occurs at **420 nm**; maximally efficient activation of the middle wavelength (yellow) form of photopsin occurs at **534 nm** and long wavelengths (red) form of photopsin occurs at **564 nm;** the brain's sense of color is obtained by a comparison of the intensity of these three forms in a manner which is still not well understood.

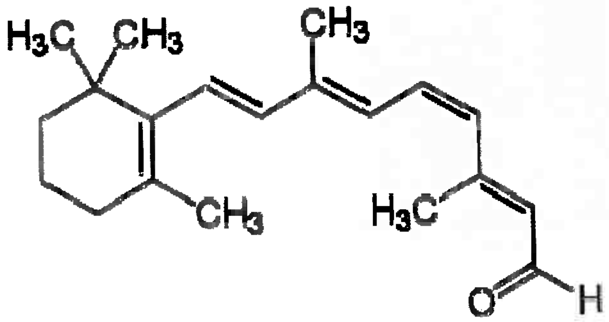
People who lack one of these forms of these cone photopsins will have color blindness with red color blindness being the most common (7% of the male population in the US). Most mammals only have 2 opsin forms in their cone cells, but humans, apes and some monkeys have 3. See "primate color vision" on the internet for more information.

Deficiency of vitamin A results in inability to quickly reform more cis retinal.

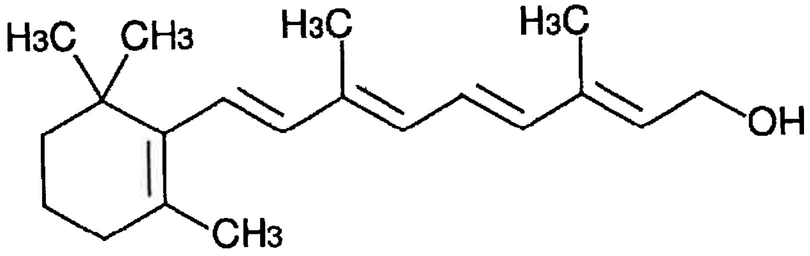
Still another form of retinal-bound opsin called **melanopsin** has been found in specialized cells of the retina where their activation appears to control pupil diameter; melanopsin is also thought to be part of the control of 24 hour circadian rhythms.

The retinal-opsin complex is also found in a salt-loving bacteria, Halobacterium , where it is found in a slightly different form as **bacteriorhodopsin**; these bacteria use bacteriorhodopsin to generate a voltage potential across their membrane. (They then use that voltage potential to make ATP, the energy currency of the cell.)

There are 3 chemical forms of vitamin A. They differ only in the functional group at the end of the polyunsaturated C chain. They are:

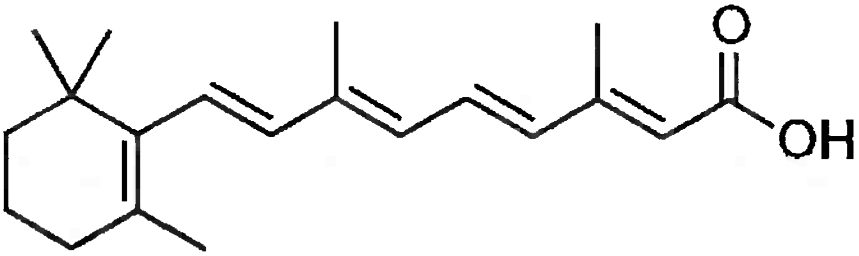


Retinal



Retinol

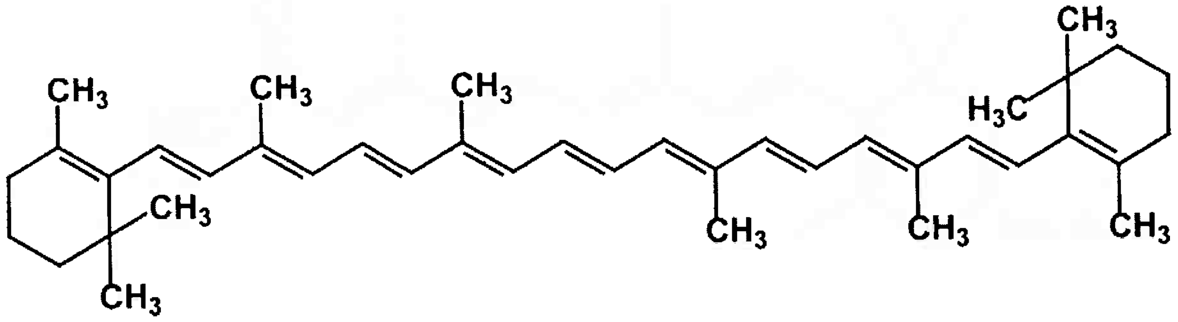
retinoic acid



This last form is of considerable pharmacological interest. It exists in the two forms, **cis retinoic acid** (marketed as **Accutane**) and **trans retinoic acid** (marketed as **Retin-A**).

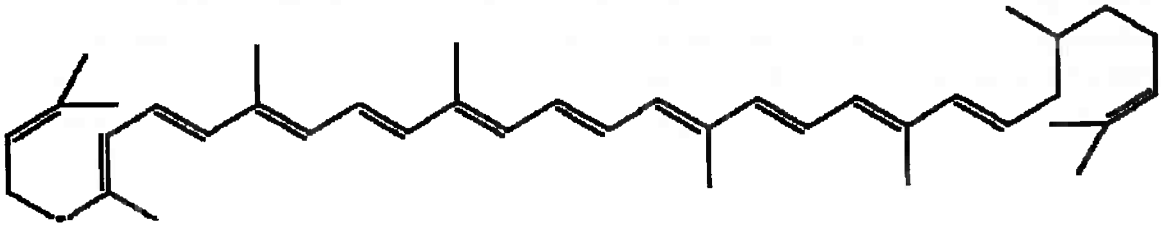
Both of these products are used for the treatment of acne. Retin-A is available as a cream, gel or solution which can be applied to skin for a 6 week course. It frequently causes redness, scaling, and sensitivity to sunlight. In addition to reducing acne, it decrease skin wrinkles slightly. This received publicity in the popular press and resulted in a large number of Retin-A prescriptions for middle aged women who had no problem with acne.

Accutane (cis retinoic acid) is the geometric isomer of Retin-A and is available in pill form. It is normally taken orally (P.O.) twice a day (bid) for a course of 15-20 weeks. Accutane is indicated for severe acne that is unresponsive to other forms of acne treatment. Like Retin-A, it can cause increased photosensitivity. One particular important adverse side effect is that Accutane is **teratogenic** -- it can cause birth defects. As a result, it is extremely important that women taking a course of Accutane should take effective measures to avoid pregnancy. By virtue of the fact that Retin-A is applied topically to the skin, there is much less absorption internally and it can be used during pregnancy.
Your mother may have told you to eat your carrots because they have lots of vitamin A. Carrots don't contain vitamin A, but they do contain the orange pigment β **carotene**, a precursor of Vitamin A, which can be cleaved in half to produce trans retinal.



Beta carotene

A very similar compound, lycopene, is the primary red pigment found in tomatoes and is claimed to reduce the risk of heart disease and cancer. How is the structure of lycopene different from beta-carotene?

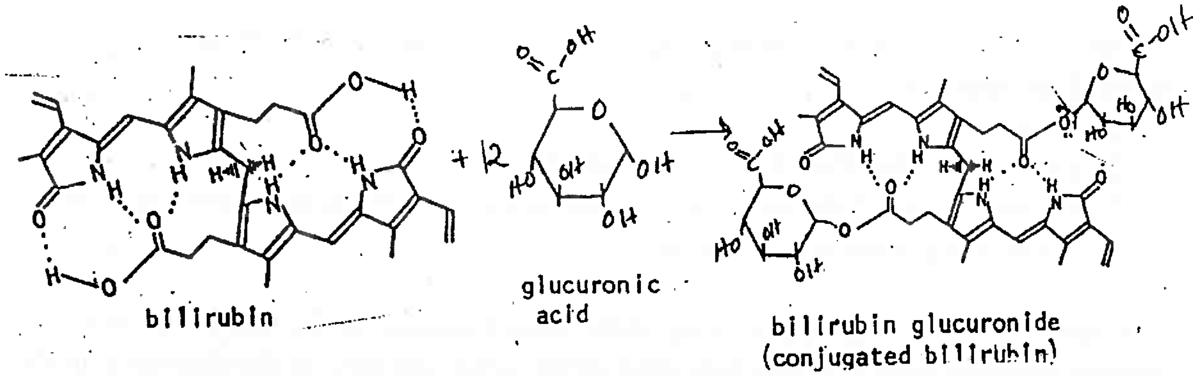


Lycopene

3.5 Photoisomerization Of Bilirubin

When red blood cells reach the end of their lifetime (about 3 months) they lyse and release red colored **hemoglobin**, the molecule that actually transports oxygen in the blood. The heme portion of hemoglobin is metabolized into orange colored **bilirubin.** A very small amount of bilirubin dissolves in urine and is responsible for the yellow color of urine, but the major route for excretion is more complex.

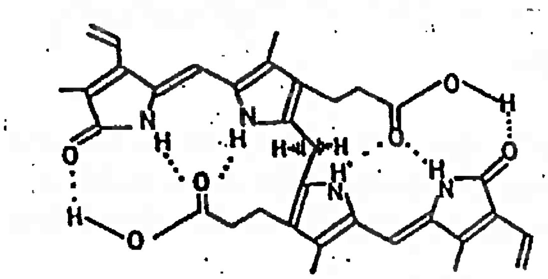
The major route for excretion of bilirubin is by excretion in bile into the small intestines and elimination in stools, but since stools are mostly water we have to make bilirubin more water soluble. The normal way of doing this is for the liver enzyme **glucuronyl transferase** to covalently attach two very polar molecules of **glucuronic acid (or glucuronate)** onto the nonpolar bilirubin molecule to make **bilirubin glucuronide**, commonly called **conjugated bilirubin**.



(What functional groups link the two glucuronic acid molecules to the bilirubin molecule? What functional groups in the original bilirubin and glucuronic acid molecules reacted to form that link?)

Conjugated bilirubin (bilirubin glucuronide) is much more water soluble and is excreted from the liver in bile and from there into the small intestine. In the large intestine bacteria metabolize it in a series of steps into **stercobilin (** from the Greek word sterco for poop), which has a brown color. However, if liver function is inadequate, there may be insufficient levels of the glucuronyl transferase enzyme to carry out the addition of glucuronic acid molecules to the bilirubin, and the bilirubin cannot be excreted in the stools;

There are some polar groups in the bilirubin molecule (OH, C=O, N-H) but the bilirubin folds up such that these polar groups are attracted to each other and internalized within a bilirubin molecule as shown below.

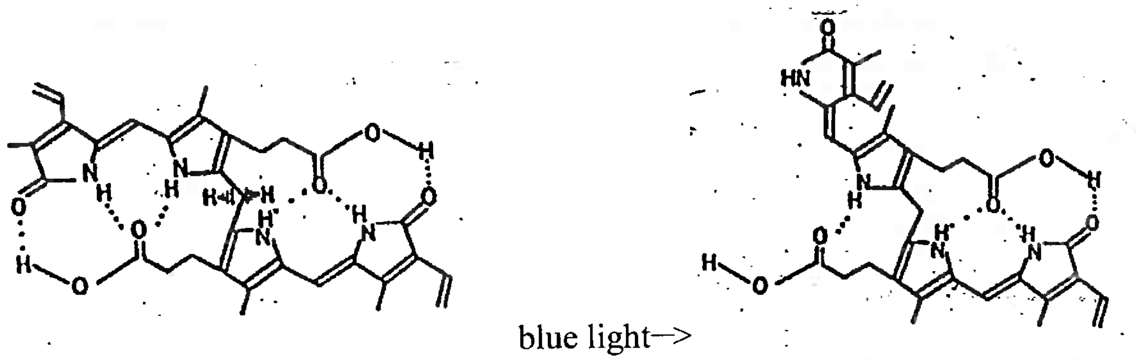


As a result, the surface of the bilirubin molecule is very nonpolar and bilirubin is not very soluble in water. Being nonpolar, high concentrations of bilirubin build up in the fatty tissues and membranes in the body. Since bilirubin is a yellow-orange colored compound, this produces **jaundice**.

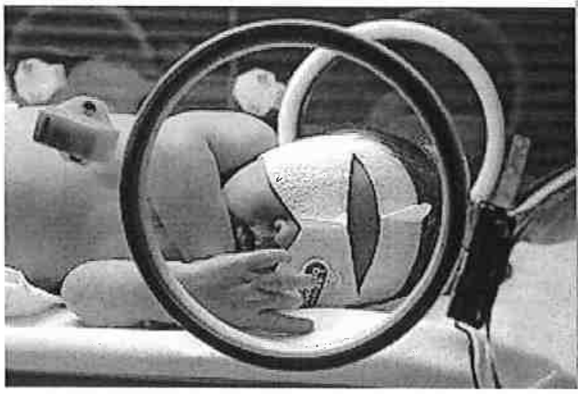
There are three common situations in which liver function is impaired sufficiently to produce jaundice.

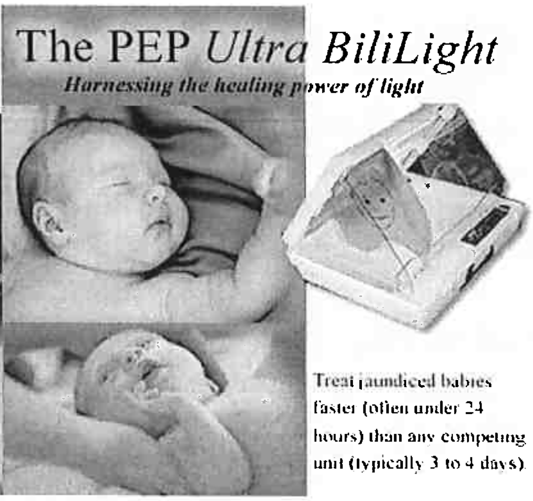
1. hepatitis
2. cirrhosis of the liver due to alcoholism
3. immature liver function in babies, especially common in premature babies resulting in **neonatal jaundice**

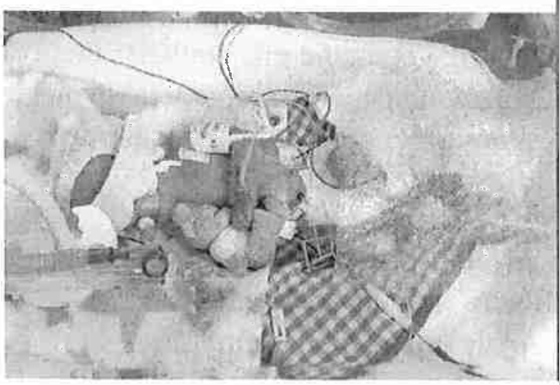
The third condition has serious long term consequences for the baby's mental growth because high levels of bilirubin in the brain can inhibit development of the baby's brain cells and cause permanent retardation. Consequently if blood bilirubin level gets too high (more than about 15 mg/dL for substantial lengths of time), measures are often taken to reduce blood bilirubin levels. This used to involve expensive blood transfusions, but it was noticed that babies with neonatal jaundice who were exposed to natural sunlight had increased urinary excretion rates of bilirubin. Further study showed that exposure to blue light causes the increased bilirubin excretion in the urine. Neonatal jaundice is treated with **a bili-light** that exposes the baby's skin to high intensity blue light. How does the bili-light work? Upon exposure to blue light, one of the C=C double bond adjacent to the 5-membered ring in bilirubin **photoisomerizes.**



In the process, more polar groups are exposed to the environment and the bilirubin is considerably more water soluble, even though the composition of the molecule has not changed. Bilirubin excretion in the urine and stools increases substantially and neonatal jaundice decreases!

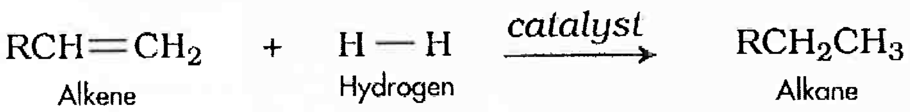




www.wellcomeimageawards.org/gallery.aspx

3.6. HYDROGENATION

Unsaturated alkenes can be converted into saturated alkanes by the addition of hydrogen atoms across the double bond. This reaction is usually catalyzed by a nickel or platinum catalyst, and the hydrogen is usually added in the form of diatomic hydrogen gas:



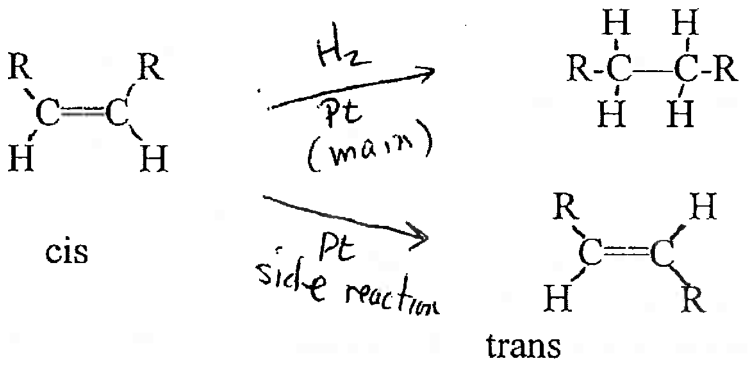
$$\underset{\text{Alkene}}{RCH{=}CH_2} + \underset{\text{Hydrogen}}{H{-}H} \xrightarrow{catalyst} \underset{\text{Alkane}}{RCH_2CH_3}$$

Pt, Pd or Ni

Wikimedia

Hydrogenation reactions are carried out on a variety of food molecules but particularly vegetable oils. Margarine, vegetable shortening and a majority of bakery products (crackers, cookies, pies, chips) contain partially hydrogenated vegetable oil. The vegetable oils are hydrogenated in order to raise their melting point above room temperature. Thus hydrogenating vegetable oils converts them into solids at room temperature. This is convenient, since it allows vegetable oils to be converted into such products as Crisco, margarine, etc. (In fact margarine is just Crisco with some food coloring and food flavoring added.)

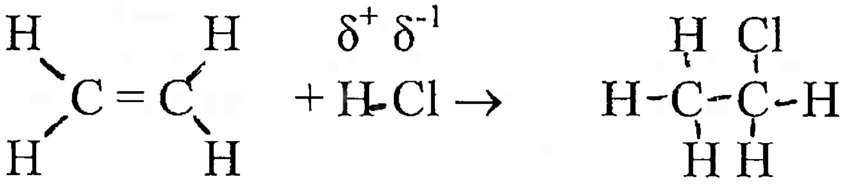
Small amounts of finely powdered Pt (platinum), Pd (palladium) or Ni (nickel) are added as catalysts to catalyze the hydrogenation of polyunsaturated oils. Manufacturers of partially hydrogenated vegetable oils do not attempt to hydrogenate **all** the double bonds in margarine: this would produce a hard brittle fat. They add enough hydrogen to partially hydrogenate the polyunsaturated vegetable triglycerides, leaving some of the double bonds in the triglyceride. This turns the oil into a soft solid, with melting point just slightly above room temperature. It was noticed many years ago that the metal catalysts act to catalyze the conversion of cis double bonds into trans double bonds on the unhydrogenated double bonds. Nearly all of the double bonds found in naturally occurring triglycerides are cis (i.e. the chain comes in and leaves the ring on the same side of the double bond). The presence of the Ni or Pt metal causes a cis-trans isomerization on many of the double bonds that do not get hydrogenated.



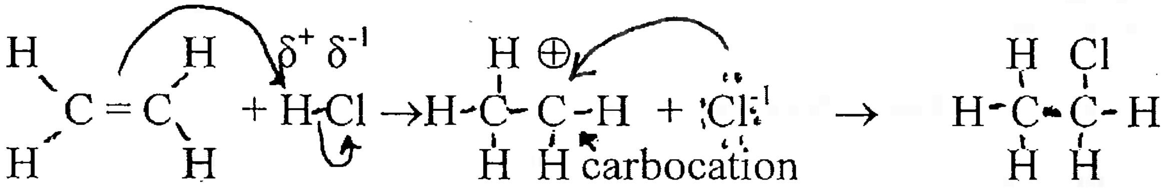
Thus margarine contains a significant number of trans double bonds which are not found in nature. There have been many studies done on the health ramifications of the presence of trans double bonds in partially hydrogenated fats. The consensus of most studies is that triglycerides containing trans double bonds increase the risk of atherosclerosis and coronary heart disease (CHD) even more than saturated triglycerides. This is rather ironic, since one of the selling points used by margarine manufacturers for years has been that margarine is less saturated than butter and hence reduces the risk of atherosclerosis compared with butter.

3.7 Addition Of HCl To An Alkene

An example is shown below.



The precise reaction pathway for this reaction is as follows:



Note that the pair of pi electrons in the alkene are relatively reactive. Next note that HCl is a polar bond: the H has a δ^+ and the Cl has a δ^{-1}. The reactive pi electrons of the alkene are attracted to the partially positively charged H. The H atom lets go of the pair of electrons it was sharing with the Cl (it was getting the "short end" of the deal anyway) and hops over and shares the pi electrons with one of the C atoms of the alkene. In the process, the other carbon atom of the alkene loses its share of the pi electrons. Since the second C atom has lost an electron, it now has a positive charge and we call a C atom with a positive charge a **carbocation**. Note that a carbocation does not have a full octet (8) of electrons. It only has 6. It is unstable because it does not have a full outer shell. In order to remedy the situation it needs to obtain an additional pair of electrons. Let's see how this happens.

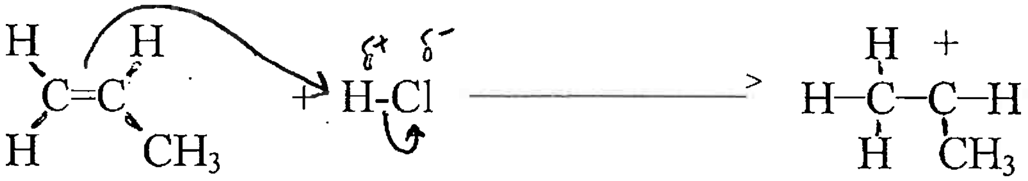
*The "double headed" arrow indicates that **both** electrons go with the arrow.*

When the H of HCl reacts with the pi electrons of the alkene, the Cl atom of HCl takes full possession of the pair of electrons it was formerly sharing with the H, essentially gaining an electron and becoming a negatively charged chloride ion (Cl^{-1}). Chloride ion can share one of its non-bonding pair of electrons with the carbocation and all the atoms once again regain their full outer shells.

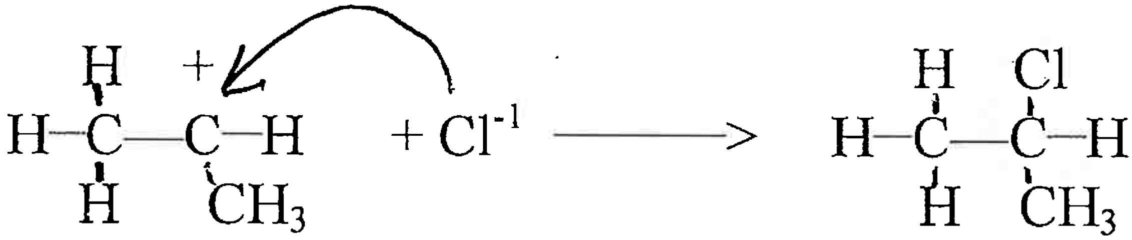
In the first step of the above reaction, the partially positively charged H is seeking out the negatively charged pi electrons of the C=C double bond the H is referred to as an **electrophile**. Since the pair of pi electrons is attracted to the partially positively charged H, the pair of pi electrons is referred to as a **nucleophile**. (Remember that atomic nuclei have a positive charge!) In the second step of the reaction the **carbocation acts as an electrophile** and the **chloride ion acts as a nucleophile.** These terms are commonly used by chemists.

"Ethyl chloride has been used as a refrigerant, an aerosol spray propellant, an anesthetic, and a blowing agent for foam packaging." Wikipedia. These are being phased out.

Here is a second example1-propene.



In the above first step the H is acting as the electrophile and the C=C is acting as the nucleophile.

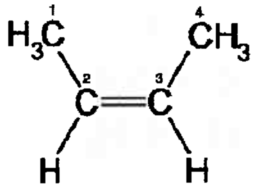


In the second step of the reaction pathway the carbocation acts as the electrophile and the chloride ion acts as the nucelophile. The final product is 2-chloropropane.

If you look at this first step of the above reaction carefully you might note that one could have added the H from the HCl onto the middle C atom rather than the end C, which would produce a different product. In fact, the H ion preferentially adds to whichever C has the most H atoms, which in this case is the end C. This is referred to as **Markovnikov's Rule** in honor of the Russian organic chemist, Vladimir Vasiliivich Markovnikov who formulated it in 1870.

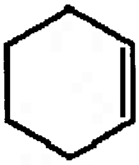
Show the reaction pathway, labeling all the intermediate steps as nucleophiles or electrophiles.

a)



+ H-Cl —>

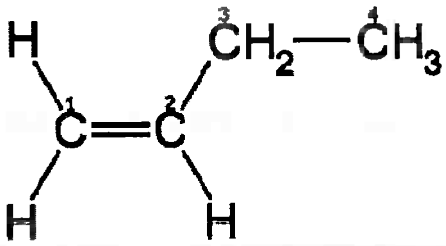
b)



+ H-Cl ———>

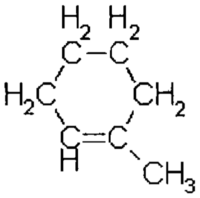
Think about Markovnikov's rule when you do the next two problems

c)



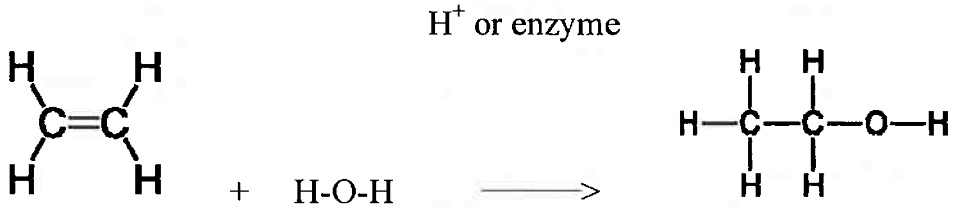
HCl—>

d)



+ HCl ———>

3.8 ADDITION OF WATER TO AN ALKENE



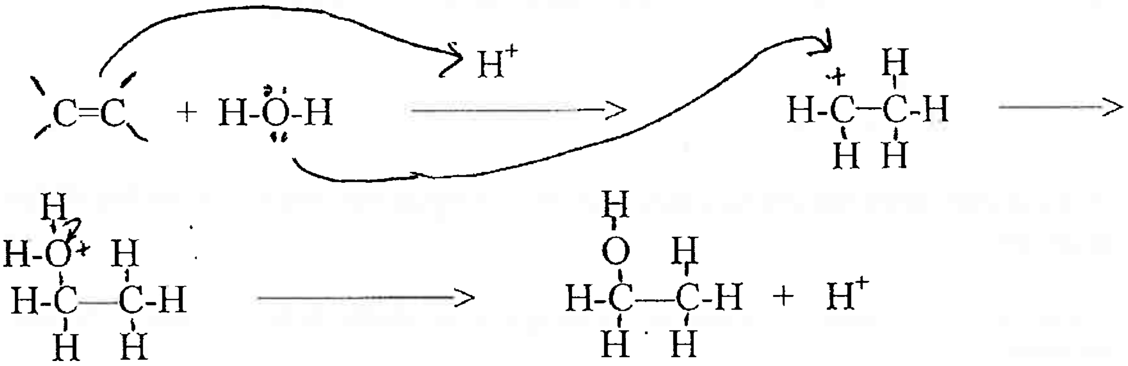
ethene(ethylene) ethanol

Much of the industrial (as opposed to beverage) ethanol in this country is actually made by this process. The ethene is a byproduct of the petroleum refineries.

Ethanol is frequently added to gasoline in this country as a way to increase the octane value and decrease pollution emissions of gasoline. Most of this ethanol is made from the fermentation of corn and helps support the corn industry, but it should be keep in mind that a lot of fossil fuel is used to grow corn and that this is driving up the price of food that directly or indirectly requires corn. Making ethanol by fermenting cellulose from wood is also being actively researched.

The reaction is catalyzed by the presence of a small amount of acid. Recall that a catalyst lowers the activation energy of a reaction and hence makes a reaction occur faster. The catalyst in this case is a hydrogen ion (H^+) from an acid such as sulfuric acid or hydrochloric acid and it initiates the reaction pathway, but is regenerated at the end of the pathway so that there is no net consumption of H^+ in the reaction. We indicate the need for a hydrogen ion catalyst by writing H^+ above the arrow between reactants and products.

The reaction pathway is similar to addition of HCl:



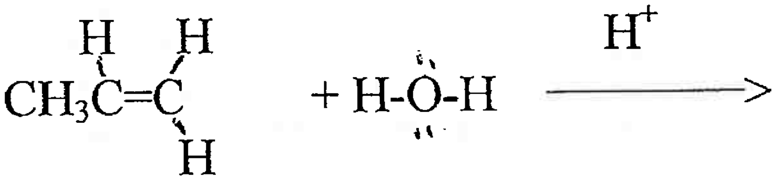
Note that the H^+ is a catalyst. In the absence of a small amount of acid, this reaction goes exceedingly slowly, but the addition of even a drop of acid causes the reaction to go much more rapidly. Since H^+ is regenerated at the end of the reaction pathway of one molecule, it can go on and catalyze the reaction pathway of another molecule.

Questions: Is the hydrogen ion a nucleophile or electrophile?

Is the pair of pi electrons a nucleophile or electrophile?

Is the carbocation in the second step a nucleophile or an electrophile?

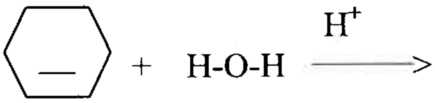
Show the reaction pathway:



(The middle carbon preferentially forms the carbocation.)

The above reaction has considerable economic importance. The reactant, 1-propene, is obtained as a byproduct of oil. When it is hydrated it produces 2- propanol, more commonly known as isopropyl or rubbing alcohol, which is commonly used to clean skin before giving an injection. The copious quantities of rubbing alcohol used in this country come from petroleum, just like our gasoline, motor oil, and most plastics!

Show the complete reaction pathway, labeling the intermediates:



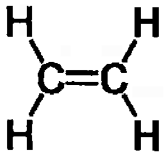
(You should draw out the full structure of cyclohexene when you do the reaction pathway.)

Several steps in the metabolism of glucose (Krebs cycle to be specific) in the body involve hydration reactions;

Fumarate ——> malate

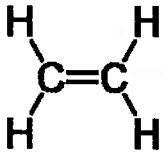
Aconitate $\longrightarrow$ isocitrate

3.9 ADDITION OF AN ALCOHOL TO AN ALKENE



$+ \mathbf{HOCH_3} \text{ - } H^+ \text{ -> } \mathbf{CH_3CH_2OCH_3}$

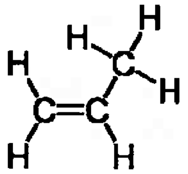
The reaction pathway is exactly like that of the addition of water, with the alcohol substituting for the water molecule. Show the complete reaction pathway:



$+ \text{ H-O-}CH_2CH_3 \text{ — } H^+ \text{——>}$

The product is diethyl ether, a molecule that was commonly used as an inhalation anesthetic for many years and that is used as a solvent to dissolve trimyristin from ground nutmeg. (It is typically prepared by a different reaction.)

Show the reaction pathway for:



$+ \text{ H-O-}CH_3 \xrightarrow{H^+}$

$+ \text{ HOCH}_3 \text{ — } H^+ \text{ ——>}$

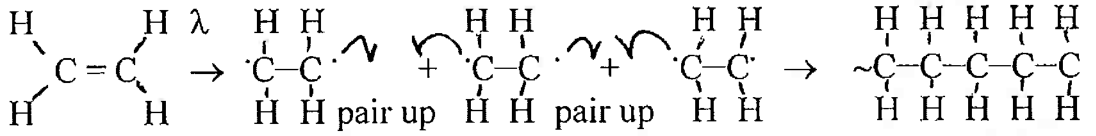
The last product has the common name methyl tertiary butyl ether(MTBE) and was used in gasoline for quite a few years. Use Google and find out what its function was and the problems with it.

3.10 POLYMERIZATION

Polymerization is the formation of extremely long molecules from small molecules called **monomers**. The plastics and rubber are examples of the most common polymers which are commonly used in both everyday life and in medical applications. The exact properties of polymers depends on a variety of chemical details and this unit will give you a brief introduction into some of the common polymers and how their properties depend on their specific chemical details.

Polymers can be formed by a variety of reaction pathways. In this unit we will look at those formed by the process of free radical polymerization. Suppose we have a container full of ethene (ethylene) monomers and we unpair the pi electrons by a suitable method, either by appropriate radiation, or a **free radical initiator** such as a peroxide molecule (the most common way of producing them industrially).

By one means or another, we produce free radical ethylene molecules which can pair up with each other to form a long chain:



Our example just shows one molecule of monomer as a reactant, although in fact there are large numbers of them that will react with each other to form the polymer:

The one sided arrows indicate that one electron goes to each C atom. This is in contrast to the previous reaction pathways where both electrons went to the same atom and we showed a double sided arrow. The ~ indicates that the chain can extend for many thousands (or even millions) of C atoms.

What sort of functional group have we produced in the product? It's an alkane. However, it is named on the basis of the fact that it is formed from polymerization of ethylene: polyethylene.

We can diagrammatically represent this polymerization reaction with a monomer, A, being polymerized into a long chain of A:

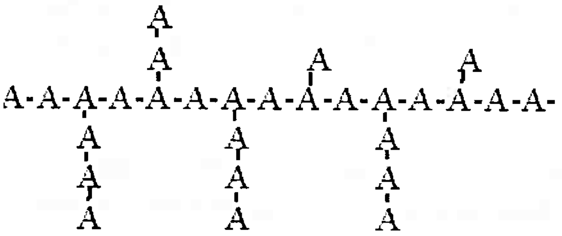
Many A monomers ⟶ ~A-A-A-A-A-A-A~

Polyethylene

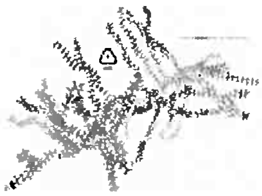
The long chains of A can line up to each other somewhat like adjacent strands of spaghetti in a very fairly compact mass and be extruded in thin sheets to make plastic. This form of polyethylene is called **high density polyethylene**, abbreviated **HDPE** and is labeled on the plastic recycling system as #2.

It is used for laundry detergent jugs, plastic milk bottles, fuel tanks, Tupperware and wood plastic composites which are resistant to rot.

Branches in this long polyethylene chain can be introduced so the chains look more like:



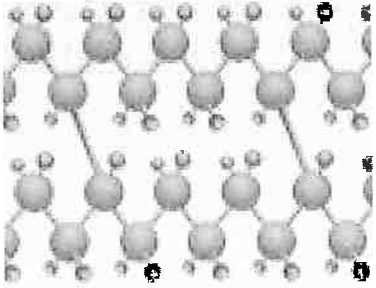
In this case the chains of somewhat branched polyethylene cannot snuggle as closely together and we have **low density polyethylene**, abbreviated **LDPE,** # 4 on the plastics recycling numbering system.



The attractions between the strands are not as strong since the chains are held somewhat apart by the branches, but the plastic is less opaque than HDPE. It is used in polyethylene bags, 6-pack plastic rings, and the inside coating of soda cans where it protects the aluminum can from corrosion by the acid of the soda.

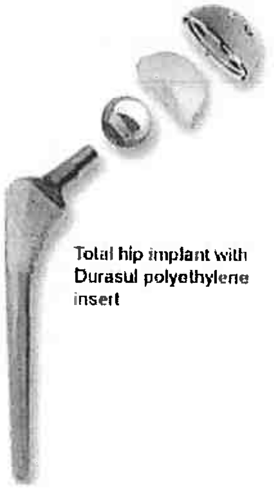
A third form of polyethylene has **extensive cross-linking** between the long chains of polyethylene and is called **PEX (polyethylene crosslinked)**

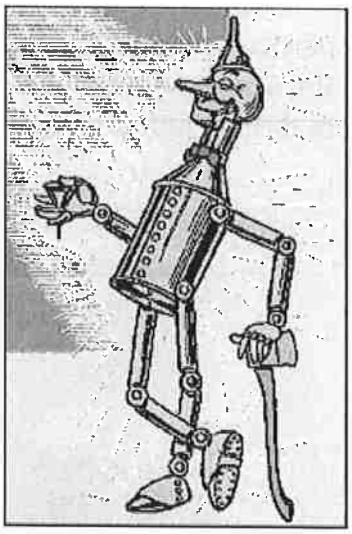
Schematically it looks like



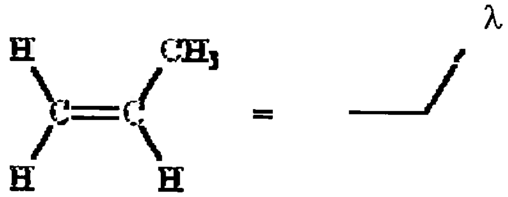
PEX is much stronger than HDPE or LDPE due to the cross-links and PEX is seeing increased use in water pipe systems. It is very strong (due to the cross-linking) but still has enough flexibility to expand if the water freezes inside it, so that PEX does not typically crack if the PEX pipes are frozen during cold weather. This is a distinct advantage over steel, copper, and PVC pipes which often crack if water freezes inside them.

In medical applications PEX is being used as a low-friction liner between the acetabulum and femoral head in total hip replacements. The PEX provides a very durable, low friction surface between the metal head (typically made of titanium or high grade stainless steel) and the acetabulum.(Can't just squirt some oil in like the Tin Woodman!)

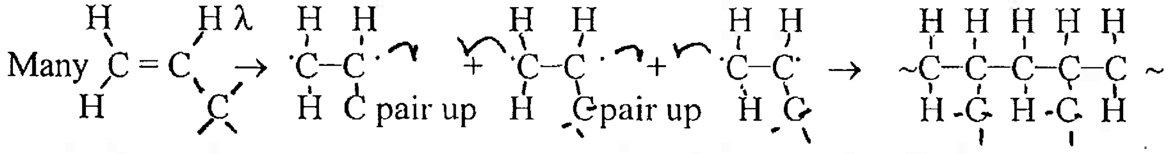

Total hip implant with Durasul polyethylene insert



Polypropylene



Propene
Propylene(common name)



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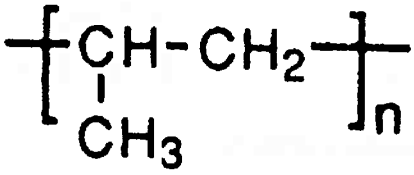
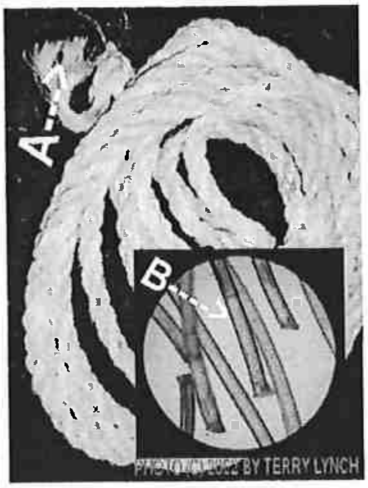


$$\left[\underset{\displaystyle CH_3}{CH}-CH_2 \right]_n$$

Polypropylene

Polypropylene is commonly used to make plastic rope This rope is commonly used in marine applications because it floats. (Can you suggest why?). It is also used for medical instruments that will be autoclaved at temperatures at 120°C. It is also seeing increased used in plastic containers such as yogurt containers. Polypropylene can withstand this temperature where polyethylene cannot. It is also used for making medical suture thread, although nylon is more common.

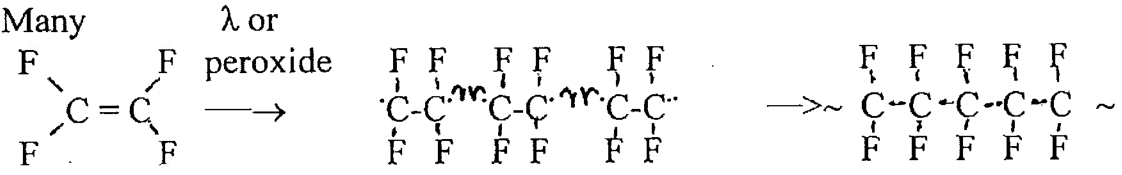


It does have the recycle designated number of 5, although polypropylene is not currently recycled very much.

Thought question: What effect will adding a small amount of 1- propene to a polymerization mixture of ethene have? What sort of polyethylene will result?

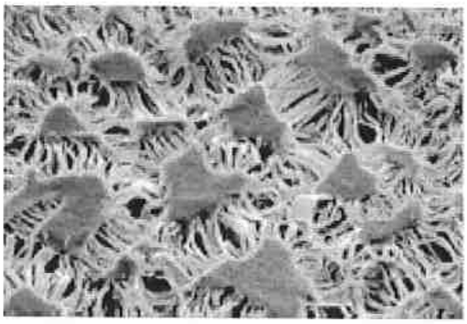
Teflon

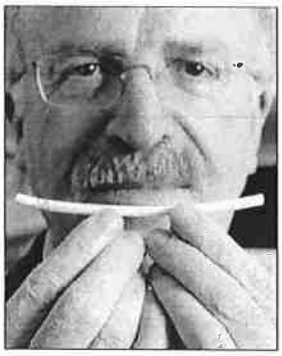
1)Many



1,1,2,2-tetrafluorethene polytetrafluoroethylene (PTFE orTeflon)

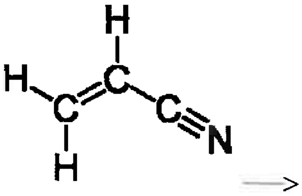
Besides use in coating non-stick cookware, PTFE membrane is the basis for Gore-tex outdoor clothing. The Gore-tex is woven in a microscopic level fabric that allows water vapor molecule to pass out, but is too small to allow water droplets to pass in, thus providing a raincoat that breathes.

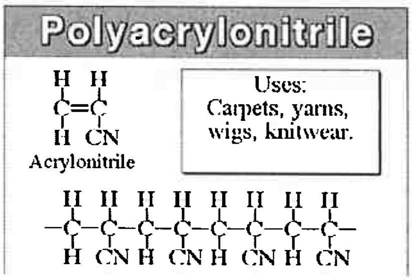




Gore-tex is also used in a variety of medical applications such as replacing portions of blood vessels that are damaged or clogged with atherosclerotic plaque with a piece of Gore-tex tube called a graft. (Normally surgeons prefer to take a piece of similar sized vein from the same patient but this is not always possible if the replacement is on a very large blood vessel such as the aorta or if multiple repairs are needed.)

Polyacrylonitrile





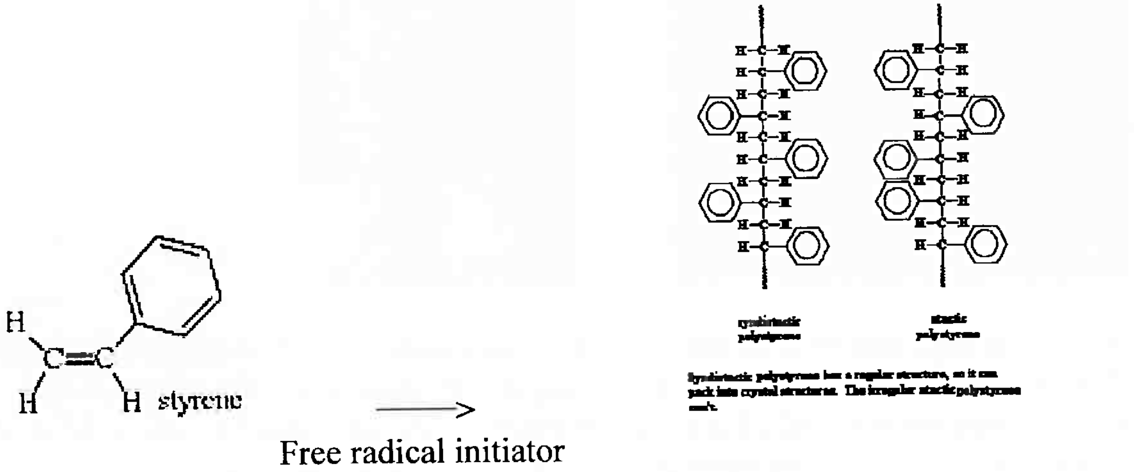
acrylonitrile

polyacrylonitrile (PAN)

(Orlon)

Polyacrylonitrile is being used to make rubber gloves that substitute for latex gloves.

Polystyrene

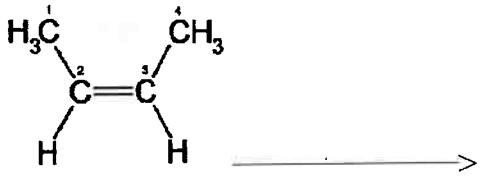


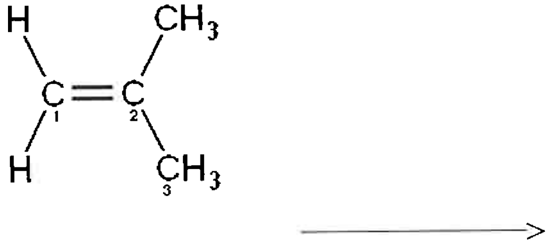
polystyrene

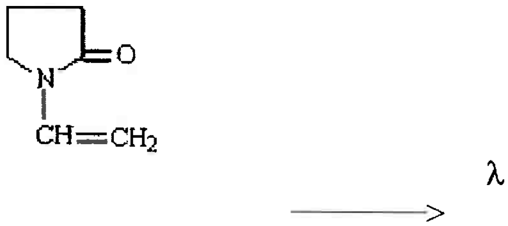
If air or other gases are blown into the polymer when it is synthesized we end up with **Styrofoam,** a very common insulating material used in packaging and in coffee cups, to name just a few uses.

Draw the structure of the polymerization product when the monomers shown below are polymerized:

Many:



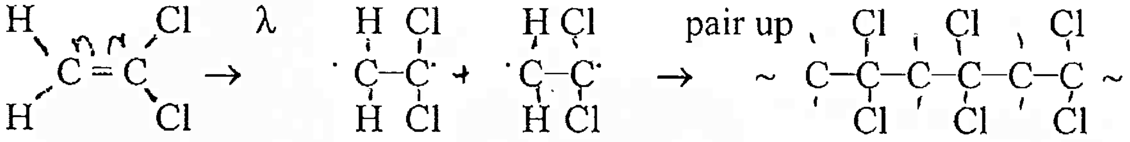




The common name of the last monomer above is vinyl pyrrolidone. The polyvinylpyrrolidone (PVP) polymer has many uses. Medical uses include combination with iodine to make Betadine, which releases iodine slowly into wounds and kills bacteria. It is also mixed with other polymers to make copolymers.

Polyvinylidene chloride (Saran)

Many

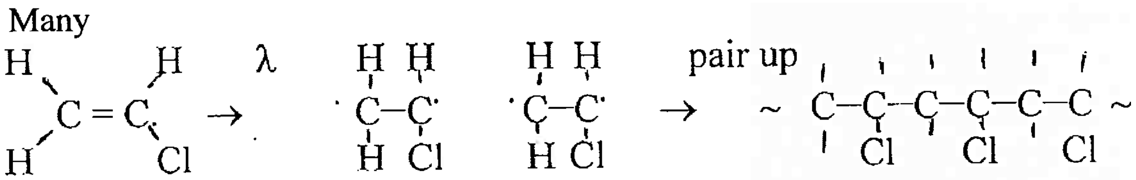


Vinylidene chloride
(1,1 dichloroethene)

polyvinylidene chloride
marketed as SaranR

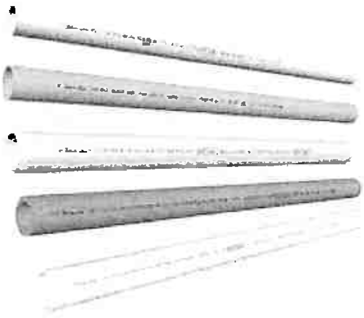
Sheets of polyvinylidene(Saran) are marketed for wrapping food and keeping it fresh. The Saran polymer is impermeable to oxygen in the air and hence limits oxygen from getting into the food reducing the rate at which it gets stale; also volatile aroma molecules typically don't get out of the wrapped food and this helps keep it tasting fresh. On the downside, **chlorinated polymer molecules break down only very slowly** and hence make a significant contribution to the buildup of non-biodegradable trash.

Polyvinylchloride (PVC)



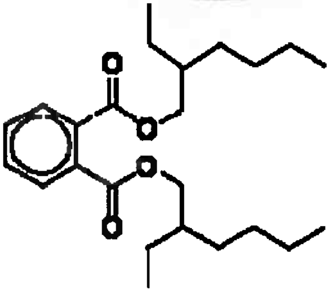
vinyl chloride

polyvinylchloride(PVC)



Plasticizers

Pure polyvinyl chloride (and some other plastics) can be quite brittle and non-flexible. In order to make it more flexible, small **plasticizer** molecules are added which slip in between long strands of polymer, lubricating them and making the whole mass more flexible. The most common plasticizer for PVC has been the molecule di (2-ethyl hexyl) phthalate, affectionately abbreviated DEHP.



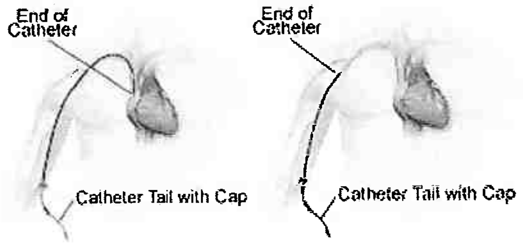
DEHP

Identify the functional groups found in DEHP. Can you identify the ethyl and hexyl goups in this structure?

DEHP makes PVC more flexible. Very small amounts added to PVC give it slight flexibility while still retaining a pretty rigid form. Addition of larger amounts increases flexibility still further. Concern has been raised by a variety of consumer advocate groups that very small amounts of the DEHP plasticizer may act as an **endocrine disruptor** and may alter biological hormone levels. This is of particular concern for pregnant women.

Concerns have also been raised about the plastics used for food containers especially during heating in microwave ovens. Heating food with plastic containers containing plasticizers can increase the amount of plasticizers that leach out into the food. The amount is fairly small and plastic manufacturers generally claim it is too small to be of concern. Some consumer advocates argue that even though the amounts are small some of these plasticizers can act as carcinogens or endocrine disruptors which can act as hormones and change biological activities in potentially very disruptive ways. There is particular concern about the effect of these chemicals on the fetus.

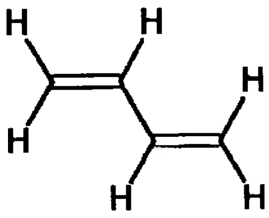
The addition of large amounts of DEHP produce a very flexible plastic which is used in a large variety of plastic applications including medical equipment such as catheters and IV bags.
Very small amounts of DEHP can dissolve into the contents of the catheter, IV bags and other medical devices and be transported directly into the bloodstream. Even though the amounts are very small, it is directly entering the bloodstream! This possibility has led to a lot of controversy and the reformulation of many medical plastic items to remove DEHP. Polyethylene, and polyurethane have been substituted as well as the use of plasticizers other than DEHP.



PICC Catheter **Midline Catheter**

[Smell of plasticizer in new cars]

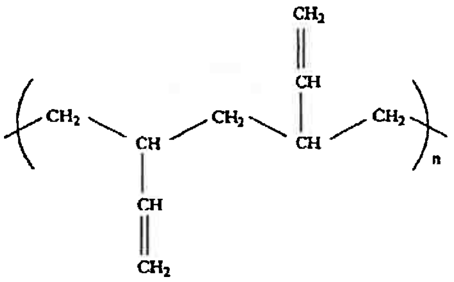
Polybutadiene(skip)



1.3 butadiene

Note that 1.3 butadiene has two double bonds rather than just one. This creates more options during the polymerization process.

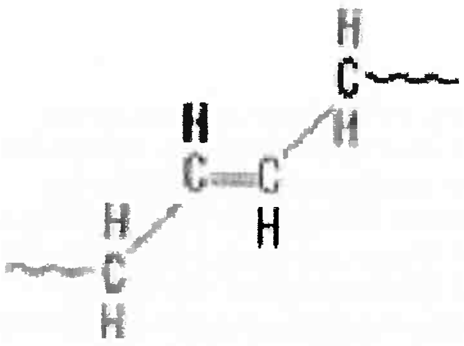
When the first double bond becomes a free radical, the free radical on the # 1 C atom can pair with another free radical on a butadiene. This leaves an unpaired electron on C # 2 which can react with another butadiene as shown below:



butadiene This type of reaction is called a 1,2 addition because the first and second C's on the molecule are the ones which react. It leaves a second double on the other end of the molecule which can react.

Actually this type of reaction only occurs about 20% of the time

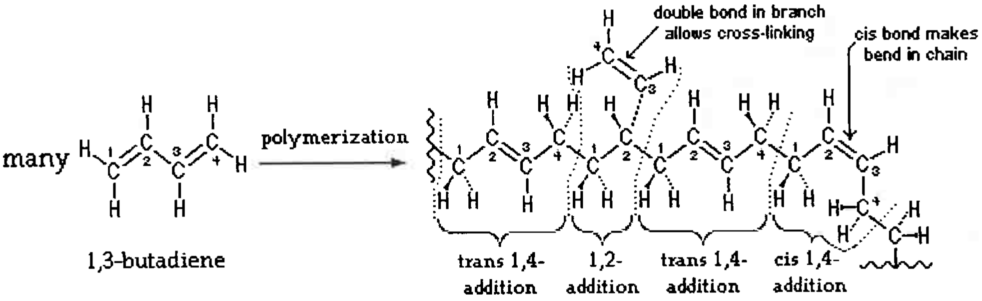
The reaction which occurs about 80% of the time (and one you would not have predicted) is shown below:



Polybutadiene

The second double bond unpairs its electrons and pairs up the unpaired electron on # 3 with the unpaired electron on C # 2. The unpaired electron on C # 4 can then react with an unpaired electron on another butadiene molecule to form a long polymer chain with C=C. Since an unpaired electron on C#1 reacts with an unpaired electron on C #4, it is referred to as a 1,4 addition polymerization.

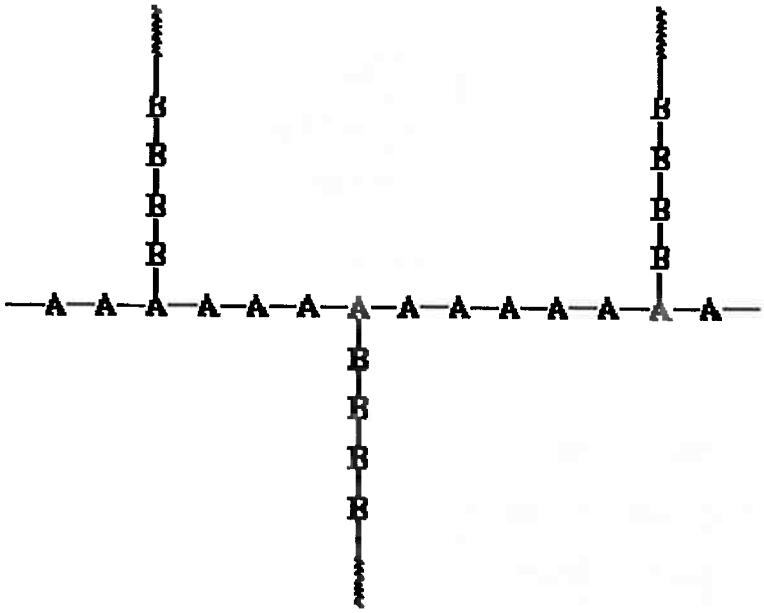
Under most common conditions a polymer is produced that is a mixture of both of the above reactions.



Notice that the presence of a double bond in the resulting polymer provides the opportunity for a polymer with either cis double bonds or trans double bonds (or a mixture. The initial work on this polymerization occurred in the 1930's when chemists were searching for a substitute for natural rubber. Initial experiments produced random cis and trans isomers, producing polymers which were not very useful. Further research produced specialized catalysts which result in either pure (or nearly pure) cis isomers or trans isomers. The resulting pure cis isomeric polymer is very elastic, but too soft to be useful as a replacement for tires.

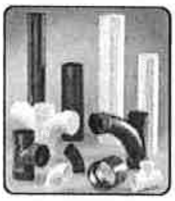
Copolymers

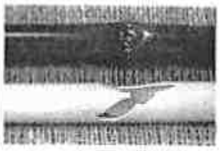
Chemists ended up making polybutadiene and then carrying out a polymerization of styrene mixed with the polybutadiene. In addition to reacting with other styrene molecules, styrene free radicals could react with the remaining double bonds of the polybutadiene, crosslinking the polybutadiene chains producing an SBS **copolymer**. This cross linking reduces the flexibility of the polybutadiene chains and makes the rubber harder and stronger, producing a rubber that can be used to make tires. The general name for this process is **graft copolymer.** It is called a copolymer to indicate that we are mixing two (or more) types of polymer, and graft indicates that we are grafting (or crosslinking) stretches of one polymer onto another type of polymer.



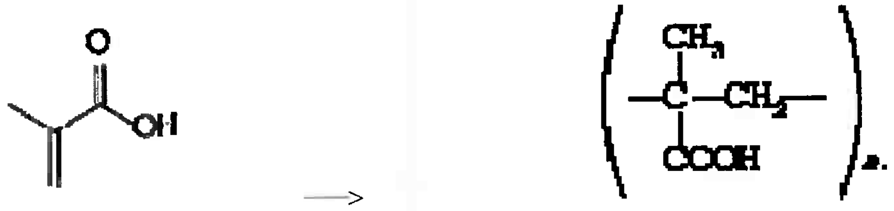
graft copolymer

Acrylonitrile is combined with polybutadiene and styrene to make acrylonitrile/butadiene/styrene (ABS) copolymer that consists of long chains of polybutadiene crosslinked with chains of styrene and acrylonitrile. The ABS plastic is commonly used in plastic piping (black ABS piping) as well as protective head gear, toys, autobody parts. Finely ground (~ 1 mcm diameter) colored ABS granules are used in some bright colors used in tattoos.



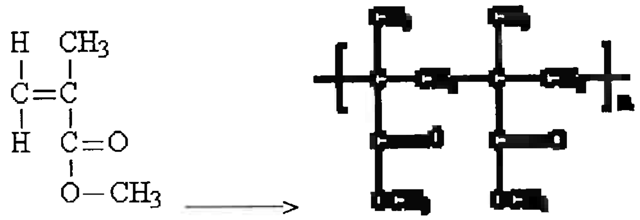


Polymethacrylate



Many
Methacrylic acid —> polymethacrylate

Polymethylmethacrylate



Many

Methyl methacrylate ———> Polymethylmethacrylate(PMMA)

The polymer PMMA has a huge variety of uses in both medical and non-medical applications. In sheet form it is better known by the trade name products Plexiglass and Lucite. Plexiglass is used as a substitute for glass. It is half the density of glass, and it is more resistant to breakage. It is more easily scratched than glass although hard coatings can be applied to its surface. It does not absorb ultraviolet radiation, in contrast to glass, which does. It is commonly used in aquariums and auto headlights. It is also used to make acrylic paints.

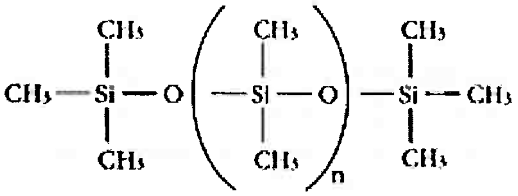
Medical uses include the manufacture of **dentures** and its use as **bone cement** when putting in prosthetic implants (i.e. hip replacements). PMMA was used in some of the earliest hard contact lenses.

One of the problems with the original hard contact lenses made of PMMA was that they had very low oxygen permeability thus depriving the cornea of essential O_2. This problem has been addressed by making a more polar polymer from 2-hydroxyethyl methacrylate (HEMA) and producing a polyHEMA. The increased content of polar OH groups increases the water content of the contact lens, making it softer (more comfortable) and more oxygen permeable as well.

2-hydroxyethyl methacrylate (HEMA) —> polyHEMA

Silicone polymers

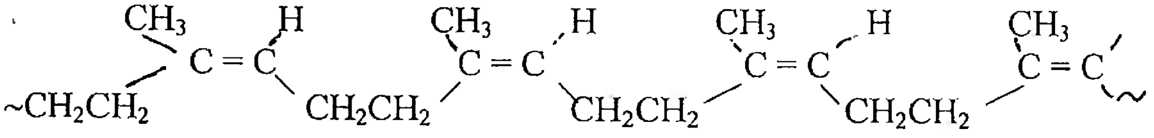
In 1999 silicone contact lenses, which are extremely oxygen permeable, were introduced.



$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O\left(-\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

Natural polymers:

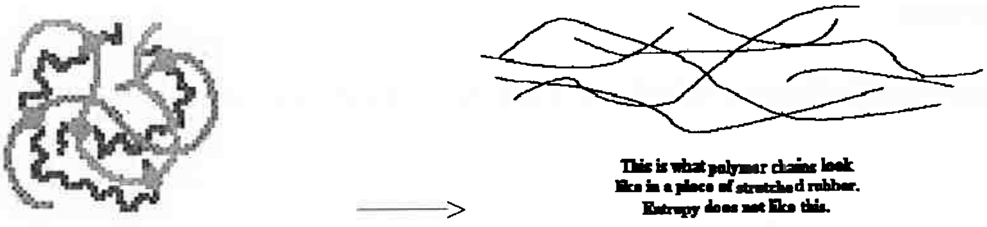
1)Latex Rubber comes from the sap of the tree, Hevea brasiliensis. It is a polymer containing cis geometric bonds



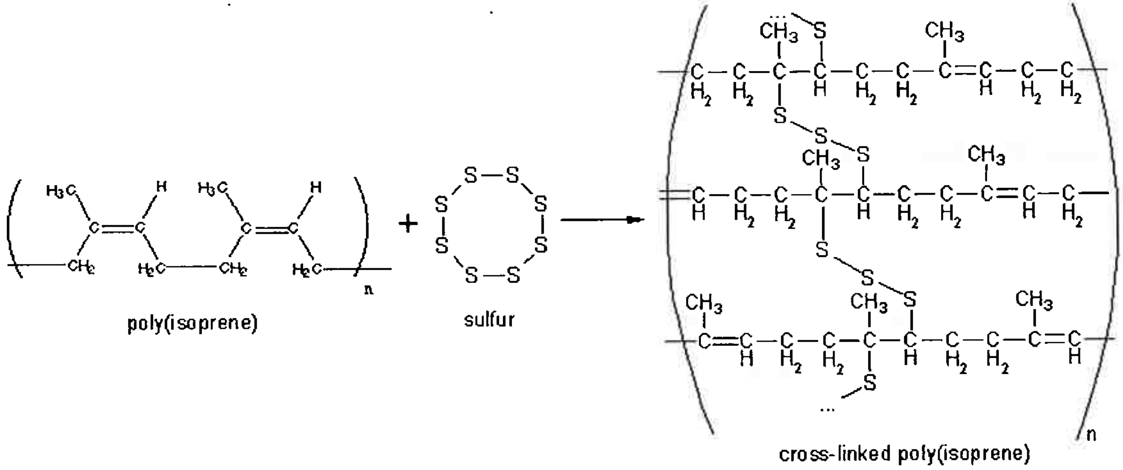
cis geometric isomer (latex rubber)

In the cis isomer the long polymer chain comes in and goes out on the same side of the C-C double bond.

The long chains of rubber are partially coiled up with occasional cross-links. As one puts tension on the rubber, it takes the slack out of the partially coiled polymer chains until they are nearly rigid. If there are very few cross-links, further tension will cause the long chains to slide past each other, similar to what happens with silly putty. Adding increasing cross-linking will limit or entirely stop this sliding of polymers past each other. When the tension is released, the extended chains will tend to reform their coiled forms, giving the rubber its characteristic and valued property of elasticity. (Further elongation after the slack is taken out of the chains will cause rupture and tearing of the material.)

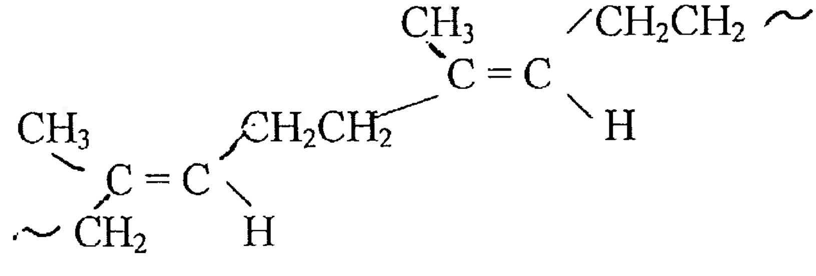


Cross-linking is done in a process called **vulcanization**, which adds disulfide and trisulfide bonds across various chains and reduces the amount of slippage that can occur between polymer chains. In effect, vulcanization turns all the polymers into one huge molecule.



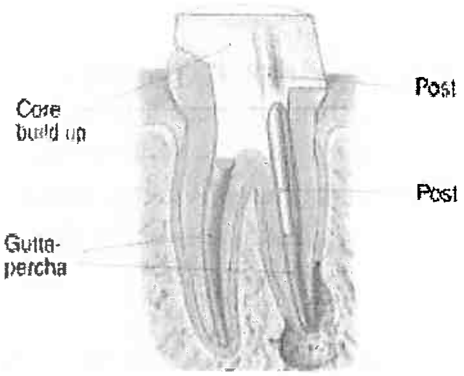
(corrected structure)

2)Gutta percha is a geometric isomer of latex with trans bonds



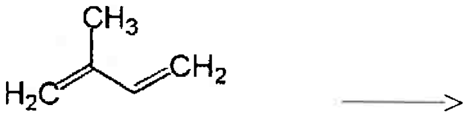
trans geometric isomer (gutta percha)

In gutta percha, the long chain comes in and goes out on opposite sides of the C=C double bond, hence making a trans geometric isomer. It is a polymer that is similar, but less elastic, than latex rubber. In the gutta percha tree one gets all-trans isomer, producing a hard material with less elasticity; it is used in golf balls and in root canal fillings.

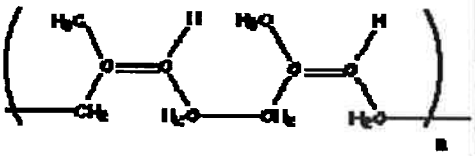


In the rubber tree, pure cis isomers produce elastic rubber When Japan invaded Indonesia in World War II, it took over the major supplier of natural latex rubber. Organic chemists were asked to make synthetic rubber from petroleum in a factory. Their first efforts produced a polymer with random mixture of cis and trans isomers which did not have the desired elastic properties. Organic chemists eventually came up with a reasonable substitute.

Synthetic latex rubber is now made by the polymerization of **isoprene** (2-methyl-1,3-butadiene) from petroleum.



Isoprene (2-methyl-1,3-butadiene)



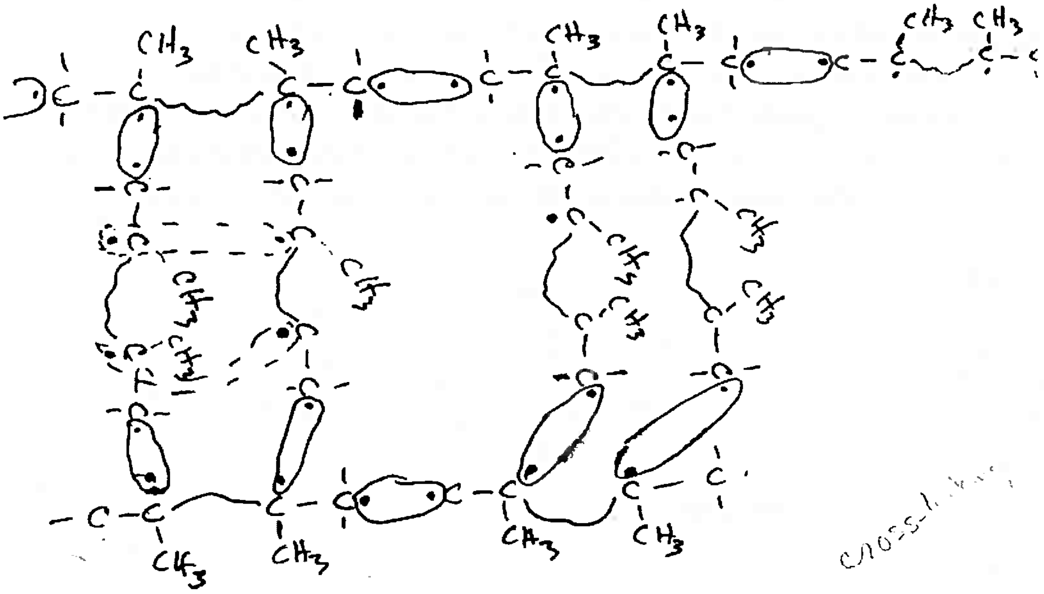
Latex is commonly used in latex gloves that are commonly used by medical and dental personnel. It is also used for the dental dams that dentists used to isolate a tooth from the rest of the mouth during their work..

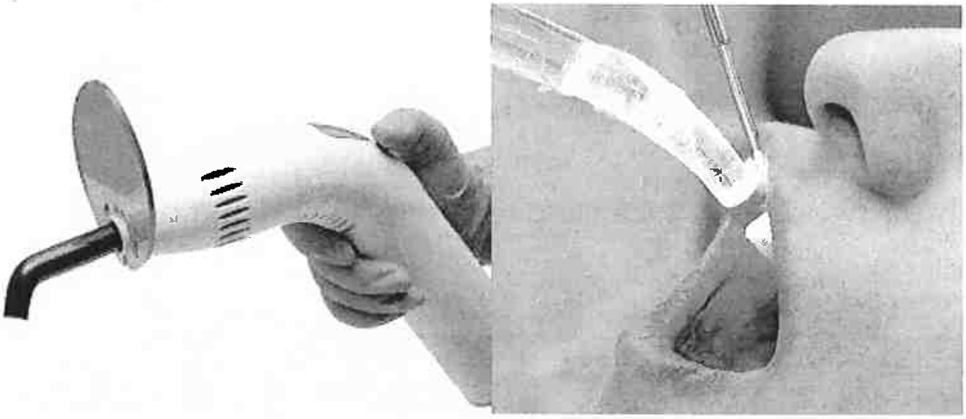
Increasing publicity about allergic reactions to latex is resulting in increasing use of gloves made from **acrylonitrile** or other chemicals. (Although there are problems reported with nitrile gloves also!) Low grade rash is most common type of allergic reaction, but some individuals may actually go into anaphylactic shock. The more severe reactions are thought to be due to some residual proteins in the latex rubber.

A latex gum called **chicle** from a different tree was the original latex gum used for making chewing gum, but other natural gums and polymers from petroleum sources are cheaper and have replaced chicle in virtually all chewing gum.

Dental sealants and filling materials

Dental sealants and some filling materials are made from a molecule that is abbreviated **bis-GMA.** Notice that this molecule has 2 double bonds rather than just one as was the case in the previous molecules. Thus when light is shown on the molecule, both double bonds can form free radicals and react as shown:

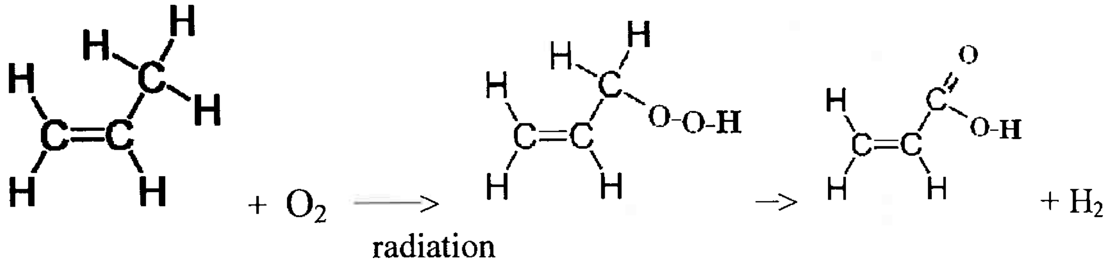


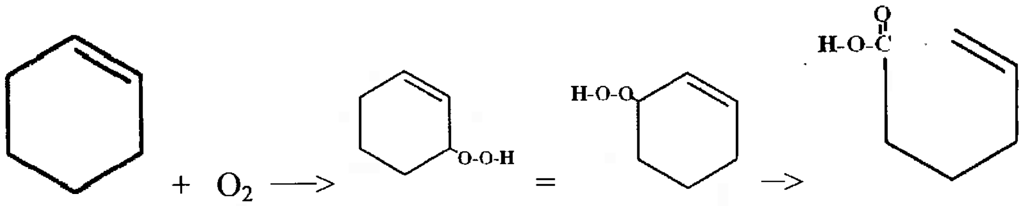


This **crosslinking** allows the formation of a 3 dimensional crosslinked polymeric material rather than a string. Like the situation with PEX (cross-linked polyethylene) and vulcanized rubber, cross-linking increases the hardness of the plastic at the expense of flexibility. This hardness and inflexibility are very desirable in dental sealants and dental filling materials. One can of course vary the flexibility of various plastic polymeric materials by varying the amount of cross-linking to meet particular needs.

3.11 OXIDATION

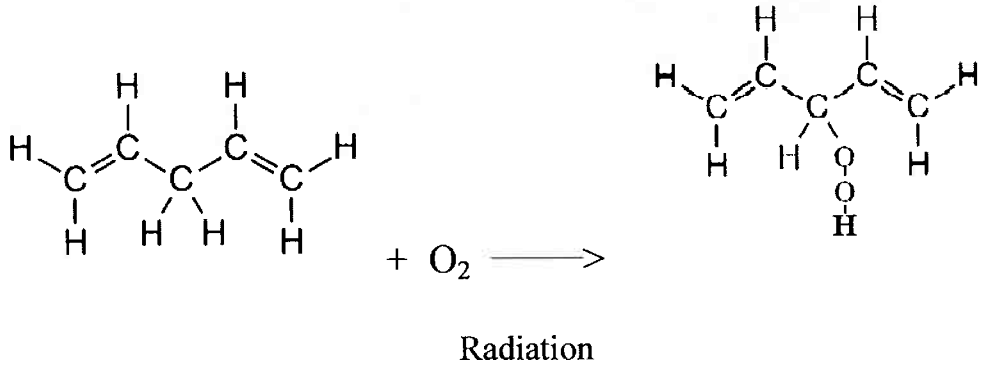
One last example of reactions of alkenes is oxidation, the addition of oxygen atoms to an alkene molecule. The exact nature of the oxidation products depends on what form of oxidizing agent is used. We will look at just one example, namely the oxidation of alkene molecules with molecular oxygen, O_2. Alkenes react with 0_2 to produce hydroperoxides which themselves are not very stable and can decompose to form two aldehyde or carboxylic acid functional groups. Oxidation of alkenes is speeded up by exposure to radiation which can produce free radicals and the addition of the O_2 molecule actually most commonly occurs at a C adjacent to the double bond (called an allylic C atom) as shown below.

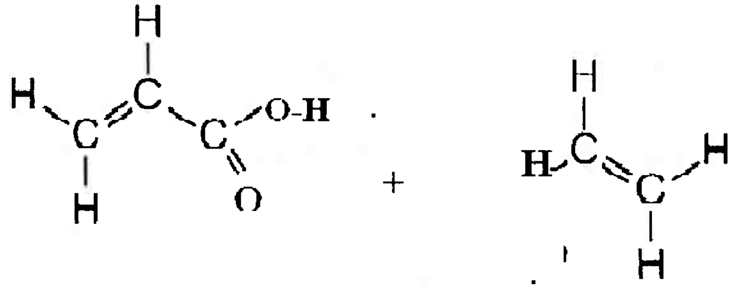




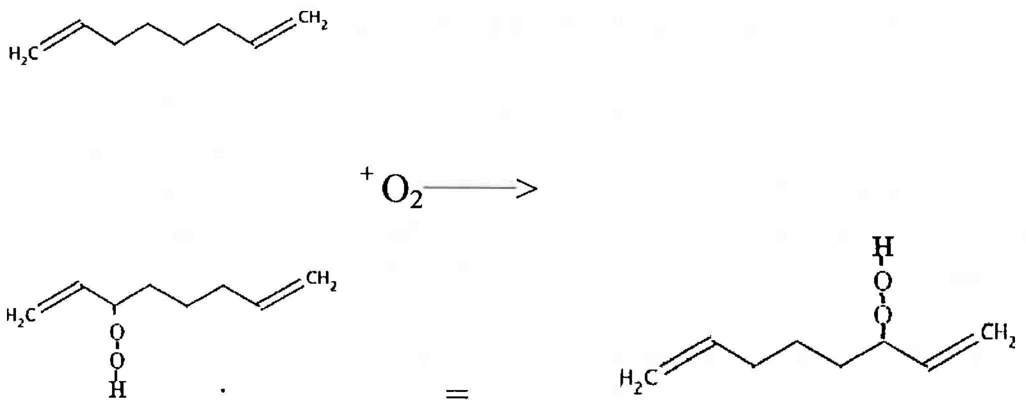
C atoms in between two C=C are even more susceptible to oxidation by O_2.

a)

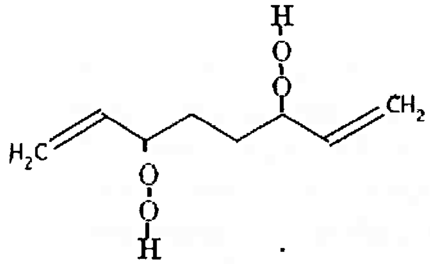




b)



If enough O_2 is around long enough you could get hydroperoxides formed at both of the C atoms adjacent to the C=C (allylic C atoms).



Examples where alkene oxidation is important in the real world:

1. When oxygen oxidizes the double bonds in polyunsaturated vegetable oils, they form hydroperoxides which can decompose further to form carboxylic acids and give it a rancid taste. When polyunsaturated oils sit around open to the air they become rancid due to the production of carboxylic acids.

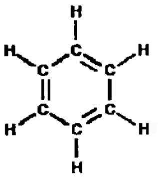
2. Polyunsaturated molecules in cell membranes can be oxidized during a cell's metabolism of food, causing damage to the membrane.

3. O_2 and 0_3(ozone) can also react with the C=C double bonds in latex rubber (see structure given previously) and break up the long chains of rubber molecules. The rubber molecules resemble long springs that "snap back" after being stretched. But when these springs are broken, the spring cannot snap back again and the rubber breaks. Cracks that appear in tires are an example of rubber oxidation.

3.12 AROMATIC MOLECULES: MOLECULES WITH *DELOCALIZED* ELECTRONS

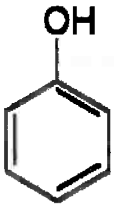
These molecules really are no more or less literally "aromatic" than other organic molecules. A really correct chemical definition of aromatic is beyond the scope of this course. The examples of aromatic molecules discussed in this course are cyclic alkenes containing 3 alternating conjugated double bonds which give them some unique electronic properties different from other alkenes.

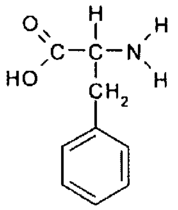
The primary aromatic molecule is benzene whose structure is shown below.

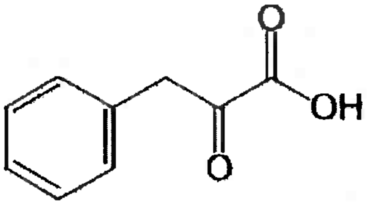


According to the naming rules we have given earlier, this would be named 1,3,5-cyclohexatriene. But it was named benzene by a German chemist at the time of its discover in 1833 and that name has been accepted as the systematic name.
When the benzene molecule was first isolated and studied, the Germans called it **benzene** while the French and British chemists called it **phene.** Although the German name won out, a benzene ring with an alcohol group is called phenol, and when we refer to a benzene ring as a side group of larger molecule it is referred to as a **phenyl** group.

Phenol phenylalanine phenylpyruvic acid

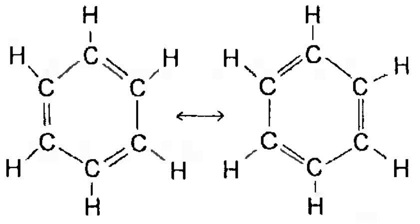






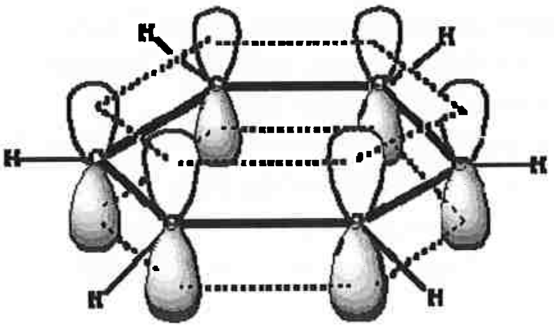
Notice the alternating conjugated double bonds in the ring structure. Because of the double bonds the C=C bonds have a trigonal planar geometry with a C-C-C bond angle of 120°. This is the angle found in a flat hexagon, and hence benzene forms a flat molecule, unlike cyclohexane which forms a chair or boat conformation. Also note that the presence of the double bonds results in just one H atom bonded to each C in the ring, and this H is in the plane of the ring. As a result there is no possibility of cis-trans isomers in benzene rings. (You can have cis-trans isomers in rings **or** on double bonds, but not on double bonds in rings!)

As organic chemists studied benzene and related compounds in more detail they discovered that the C-C bonds in the ring do not act like alternating double and single bonds. Double bonds are stronger than single bonds and tend to pull the two atoms closer together than single bonds. When chemists look at the actual structure of benzene, they find that all the bonds in the ring were the same length, intermediate between that of a single bond and a double bond. Linus Pauling, Nobel laureate in chemistry in 1954, suggested that the real benzene is intermediate between the two **resonance** structures:

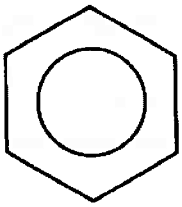


Linus Pauling

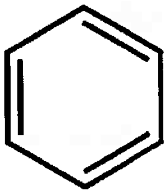
Another way of explaining this data is that the pi electrons are NOT localized between just two carbon atoms; instead they act like they're **delocalized** over the whole ring system. This comes about because of the way the pi orbitals overlap in the ring. All the pi orbitals overlap throughout the whole ring and as a result the pi electrons are free to spread themselves out in 2 donuts above and below the plane of the carbon atoms. The pi electron density between any 2 C atoms is the same, but at a lesser density than if it was a full C=C.



To indicate that the electrons in the alternating conjugated double bonds are really delocalized over the whole ring, the structure is frequently written as:

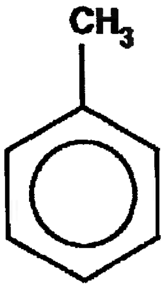


as well as

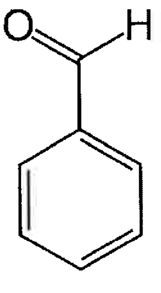


Some common benzene derivatives with names you should learn:

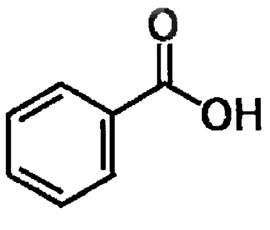
toluene



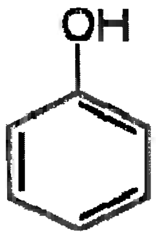
benzaldehyde



benzoic acid



phenol



Benzene was used as a common solvent in paint stripper until 1978. It was removed because epidemiologists had collected epidemiological data showing a positive statistical correlation between people working regularly with paint stripper and reduced levels of red blood cells (anemia) and elevated incidence of adult leukemia. As a result, benzene is no longer used as a solvent in paint stripper. Benzene is a naturally occurring component of gasoline where it increases the octane number of unleaded gasoline, and oil refineries often try to increase the benzene content to raise the octane value of their gasoline, but EPA requirements limit its content to 1% by weight of the gasoline. Human exposure to benzene due to gasoline spills at gas stations is regarded as a primary source of exposure to the general population and one (of many!) reasons why "topping off the gas tank" is officially discouraged.

Most of the gasoline sold in the Pacific Northwest is made from Alaskan crude oil which has a higher amount of benzene than oil from most other sources. As a result benzene from gas spills and incomplete combustion is found at higher than recommended levels in large metropolitan areas like Portland and Seattle especially near the major interstate freeways. The recommended EPA "benchmark" limit for ambient air is 0.13 mcg(micrograms) benzene per m^3 of air. Exposure at this level over a 70 year lifetime is estimated to increase the risk of death by 1 part in a million (.0001%)(Oregonian newspaper).

Benzene can be formed in trace amounts in other consumer products and although the amounts are extremely small, its presence has created concern in some quarters, as shown in the web site quoted below.

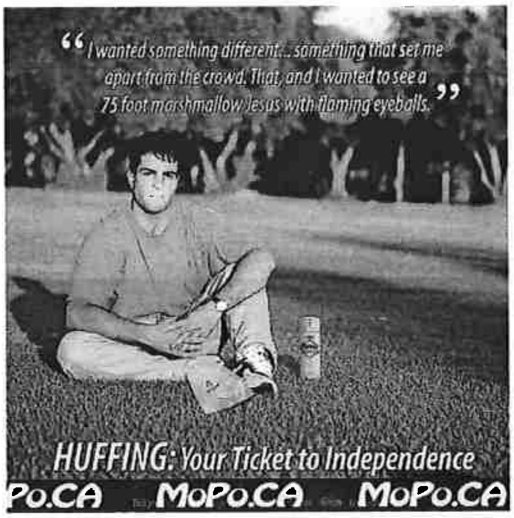
"Watch out, that next can of carbonated fizzy water you guzzle could turn your esophagus into a tumorous pipe oozing with cancer and bile. The carcinogen in question is Benzene and according to *Beverage Daily*, benzene levels in most soft drinks are up to five times the World Heath Organization's limit for drinking water.

Of course, the Coca Cola company isn't quite so stupid to purposely add benzene to their sodas. It's formed by a chemical reaction between ascorbic acid and potassium benzoate. Vitamin C and Preservatives, in other words. If you leave a can of pop out in the light, chances are it's already starting to become laced with traces of benzene.

Benzene exposure is commonly associated with leukemia and a swath of blood disease. The sodas that are most risky to drink include such favorites as Fanta Orange, Hawaiian Punch, Mug Root Beer and Tropicana Lemonade. Luckily, IBC Root Beer and Cherry Coke aren't on the list — we're not sure we could live without those."

www.consumerist.com/.../2006/03/mugrootbeer.gif

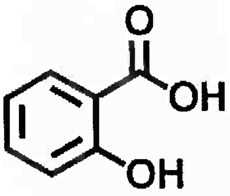
Toluene has replaced benzene as a common solvent in paint stripper and is also used in glue and in some types of "white-out". Although toluene does not appear to be carcinogenic, breathing large quantities of toluene can cause heart dysrhythmias (including **asystole!**) and brain damage. Glue sniffers and *huffers* are at risk for both of these health problems. (What is asystole? Check it out in a medical dictionary or on Google!)



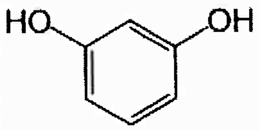
Benzaldehyde has an odor similar to that of almonds (benzaldehyde contributes to the smell of almond smell/flavor). Benzaldehyde is used in artificial flavored almond pastries, Maraschino cherries and other pastries.

Benzoic acid is very commonly used as a food preservative. It is particularly effective at inhibiting mold growth. As a result it is a routine food preservative in bread, pastries, and deli products like dips.

Phenol is an antiseptic. It was the original surgical antiseptic used by Lister and is still used in Chloroseptic and other disinfectants. It used to be called carbolic acid because of its acidic properties. Its chemical burning properties are used in facial peels to exfoliate (remove) the top layers of skin by people wishing to remove wrinkles and aging skin. Facial peels must be done with careful attention to the concentration of the phenol and the length of time it is allowed to remain on the skin. Too high a phenol concentration or too long a period of exposure can cause deep chemical burns. After a facial peel, patients should not expose their skin to direct sunlight or at least use a sun screen for at least a month, but this recommendation is often ignored. Facial peels are a big business in Hollywood. Facial peels may use several other phenolic compounds: salicylic acid (related to aspirin) and resorcinol. What do all three structures have in common?



Salicylic acid



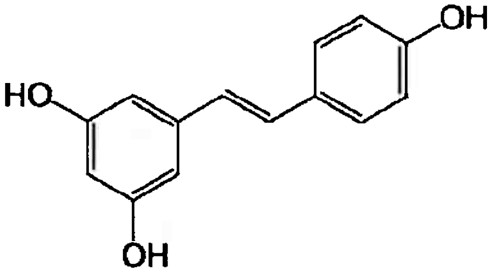
Resorcinol

The longer you use it, the better it works!

“AlphaMax left my skin clearer, smoother. It tightened up the pores. It took away the dryness that I felt I had before. It was quite a change!.”

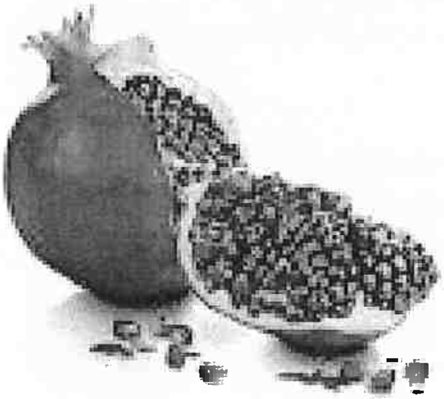
- Nancy Nason, Malvern, PA

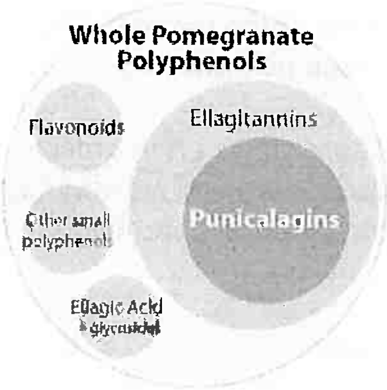
Polyphenolics are a diverse group of compounds containing 2 or more phenol rings. They are found in most plants, particularly fruits. Grapes and wine are a source of **polyphenolic** compounds that have received particular media attention recently. Epidemiological data suggests that consuming foods with polyphenolic compounds (grape juice, blueberries, pomegranites, wine) is associated with lower risk of cardiovascular disease and cancer. It is claimed that these correlations may be due to their antioxidant and free radical stabilizing properties of phenol compounds although direct data is limited. Speculative claims, especially by diet supplement companies, on the other hand are extensive.



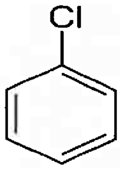
Resveratrol: ingredient in red grapes

www.helsinki.fi/.../research/polyphenolics.htm

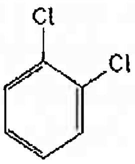




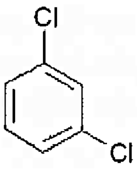
Naming substituted benzene rings



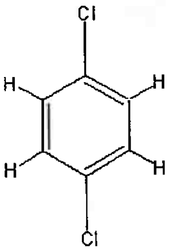
chlorobenzene



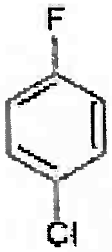
1,2-dichlorobenzene
ortho dichlorobenzene



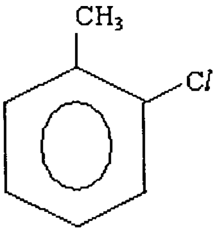
1,3-dichlorobenzene
meta dichlorobenzene



wikipedia
1,4-dichlorobenzene
para dichlorobenzene



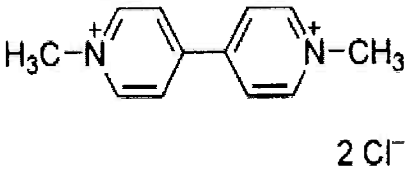
1-chloro-4-fluorobenzene
parachlorofluorobenzene
mothballs



2-chlorotoluene
orthochlorotoluene

There are no cis or trans isomers in benzene ring because there is only one additional bond to C outside the benzene ring. Because the benzene C has a (delocalized) double bond it has trigonal **planar** geometry and the bond is in the plane of the benzene ring. As a result there are **no** cis/trans possibilities on the flat planar benzene ring.

The prefixes ortho-, meta-, and para- are special names used **only** on benzene derivatives and are alternate names for 1,2; 1,3 and 1,4 respectively. Examples of these prefixes are found in the herbicide paraquat.



Based on the structure, comment on the basis for both the "para" and the "quat" in the herbicide's name.

Paraquat is an herbicide which works by inhibiting photosynthesis. It has been used by the US government to spray marijuana fields (especially in Latin America) to kill marijuana plantations. Small amounts of paraquat may be found in marijuana that was not killed by the spray and there has been concern about lung injury when volatilized paraquat is inhaled into the lungs. More recently strains of marijuana whose roots are resistant to paraquat have been reported.

Draw the structure and give an alternative name using numbers for

a) ortho dimethyl benzene b) meta-dibromobenzene c) para-difluorobenzene

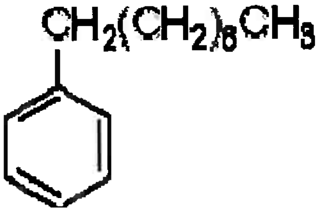
d)ortho-methyl benzoic acid e)para-chlorophenol

Draw the structure for 2,3,4,5,6-pentachlorophenol

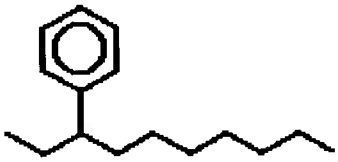
Pentachlorophenol was a commonly used wood preservative until the 1987 when its use was terminated for the general public because of public health concerns that it could cause damage to the central nervous system, reproductive system, and liver.

According to its revised risk assessment, EPA does not believe children play near utility poles. If you have pictures of children playing on or around utility poles, send them to EPA.

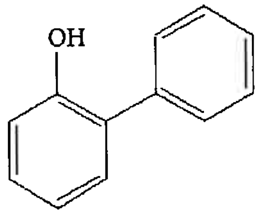
When a benzene ring is regarded as a group branching off of another chain, it is referred to as a phenyl group. This comes from the old British name for benzene: phene. Examples



1-phenyl octane



3-phenyl decane

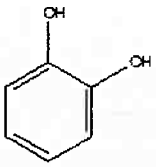


ortho-phenyl phenol
2-phenylphenol

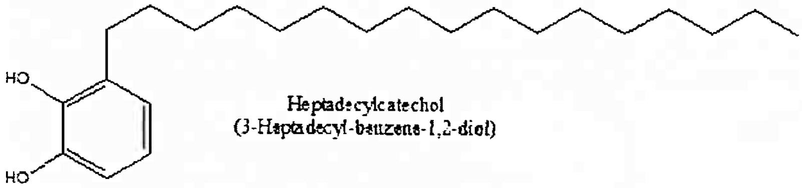
Orthophenylphenol is found in a variety of household disinfectants and is also applied to citrus peel as a fungicide.
There are many other closely related aromatic compounds.

Catechol (or pyrocatechol) is the common name for the benzene molecule with two alcohol functional groups in the ortho(1,2) configuration. Draw its structure.

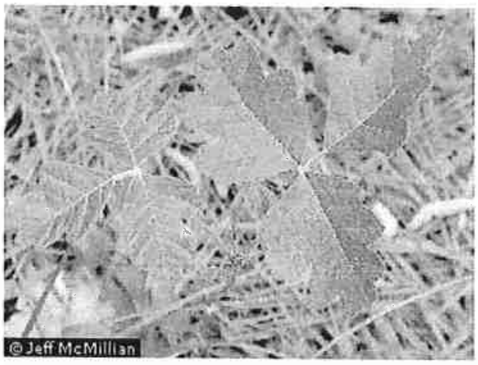
Urushiol is the active ingredient in poison ivy and poison oak that causes a rash and blistering (contact dermatitis) when it comes in contact with human skin. In poison oak it is a mixture of saturated 3-heptadecylcatechol and related compounds containing 1,2 or 3 double bonds in the 17 C chain. In poison ivy the alkyl chain off of the catechol molecule is 15 C long (3-pentadecylcatechol) and the chain can also be either saturated or unsaturated. The **unsaturated** molecules are the most irritating. The urushiol is quite hydrophobic (explain!) and dissolves into the epidermis and reacts with membrane proteins in epidermal cells. This changes the surface of those membrane proteins so that the body's T cells are tricked into thinking it is foreign and attack it. Washing with water will not remove the urushiol (why?), but most sources suggest that washing **quickly** after contact with a relatively non-polar solvent such as rubbing alcohol or with soap may dissolve the urushiol out of the top layer of skin before it reacts with membrane proteins.



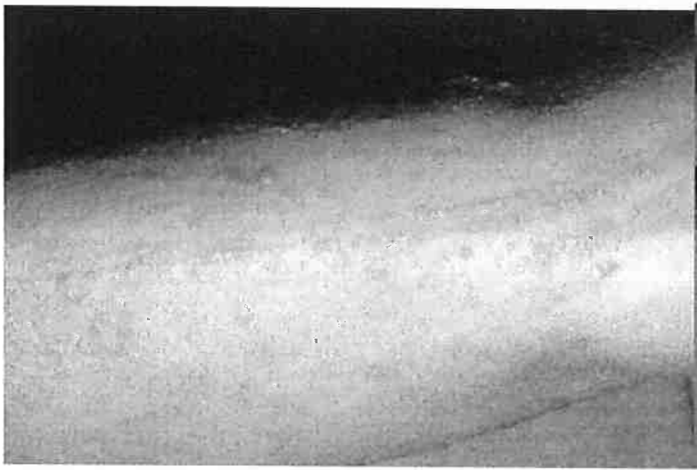
Catechol
(Benzene-1,2-diol)



Heptadecylcatechol
(3-Heptadecyl-benzene-1,2-diol)



Leaves of 3, let them be.

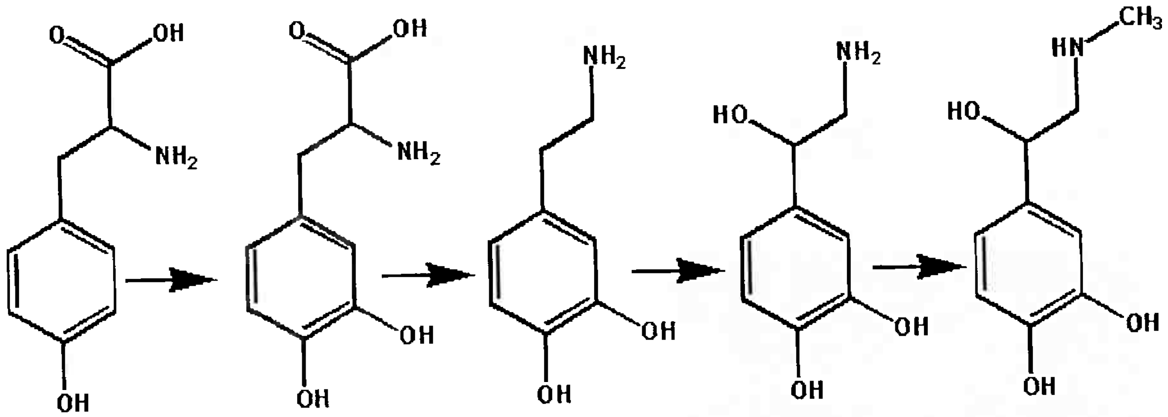


bayareahealth.org/PoisonIvy.html

serendip.brynmawr.edu/exchange/node/834

Catecholamines and Neurotransmitters

The amino acid tyrosine is metabolized first into DOPA (dihydroxyphenalanine) and then into the series of common **neurotransmitters dopamine, norepinephrine (noradrenaline) and epinephrine (adrenaline).** Because all three of these neurotransmitters have both a catechol ring system and an amine group they are collectively referred to as **catecholamines.**



L-Tyrosin DOPA Dopamin Noradrenalin Adrenalin
Norepinephrine Epinephrine
<———— catecholamines ————>

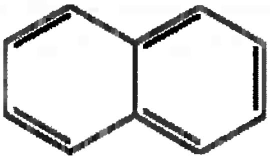
Epinephrine(adrenaline) is the neurotransmitter primarily responsible for the "adrenaline rush".

Dopamine has a large variety of roles in different parts of the brain stimulating everything from voluntary,motion, sleep, learning, memory, and mood. A lack of dopamine in the striatum produces Parkinson's; an excess of dopamine in the limbic center of brain can produce euphoria.

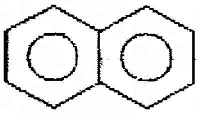
3.13 MOLECULES WITH MULTIPLE AROMATIC RINGS

Naphthalene was formerly used in some brands of mothballs because the crystals slowly evaporated (sublimed) and the pungent smell of naphthalene vapor repelsled moths from woolens. Concern about flammability have resulted in 1,4 dichlorobenzene being used instead. The chlorination reduces the flammability of the compound.

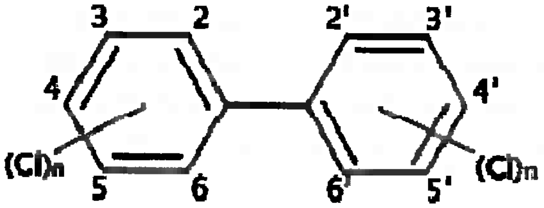
Naphthalene:



or

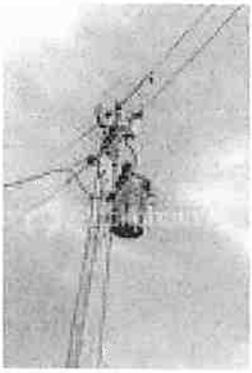


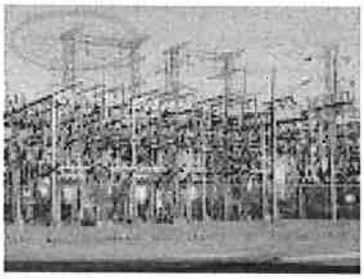
Polychlorinated Biphenyls(PCBs)



Polychlorinated biphenyls are a group of aromatic compounds with two ore more Cl atoms substituted on 2 benzene rings, as shown in the structure above. The number of Cl atoms and the position of those Cl atoms on the two benzene rings can vary considerably and that is indicated in the above structure by having the Cl bonding into the center of the ring and with the $(Cl)_n$ indicating a variable number of Cl's.

Polychlorinated biphenyl compounds (PCBs) are very stable (unreactive) non-flammable compounds that were used to absorb heat in electrical transformers and lubricants from 1929 until about 1977.

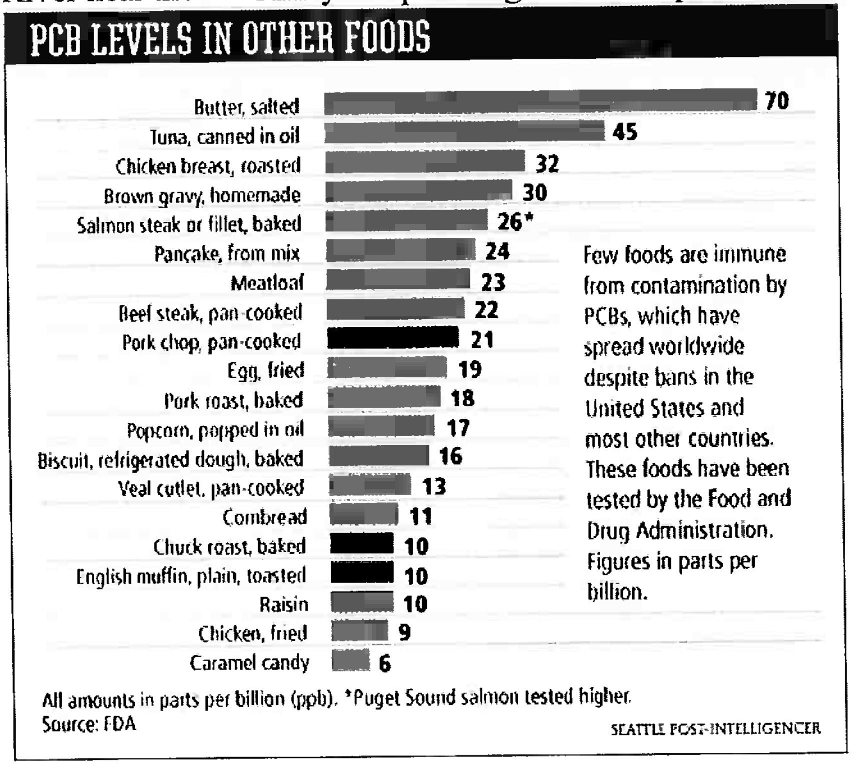




Sales of PCBs stopped in 1977, but disposal of PCB's has been a major problem. They are not readily destroyed. They require extremely high temperatures to decompose to harmless compounds and it has been difficult to find organisms that metabolize them effectively.

Unfortunately these compounds were sometimes dumped in landfills or streams when the transformers were replaced and PCB's have contaminated soils and waters throughout the world. Since these are non-polar compounds and are not metabolized, they tend to accumulate in fat and neural tissue at increasing concentrations as they work up the food chain (alga/small fish/big fish/eagle) Experimental laboratory data on animals (most commonly rats and monkeys) suggests that these compounds are carcinogens and that they can disrupt immune system and neurological systems. They may also disrupt the reproductive system and hormonal system (i.e. they may act as **endocrine disruptors**). Epidemiological data on humans exposed to PCBs suggest that humans are likewise at risk.

A substantial leak occurred from a powerhouse transformer near the Dalles, Oregon in January 2004 and PCBs have been found in sturgeon in the Columbia River near the US Army Corp of Engineers dumpsite.


PCB LEVELS IN OTHER FOODS

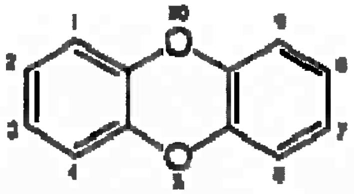
Few foods are immune from contamination by PCBs, which have spread worldwide despite bans in the United States and most other countries. These foods have been tested by the Food and Drug Administration. Figures in parts per billion.

All amounts in parts per billion (ppb). *Puget Sound salmon tested higher.
Source: FDA

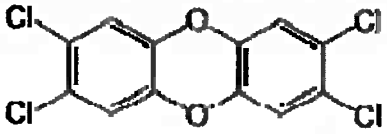
SEATTLE POST-INTELLIGENCER

Dioxin

Like the PCBs, the terms dioxin refers to a mixture of compounds containing varying amounts of Cl atoms on a basic 3-ring dibenzodioxin molecule.



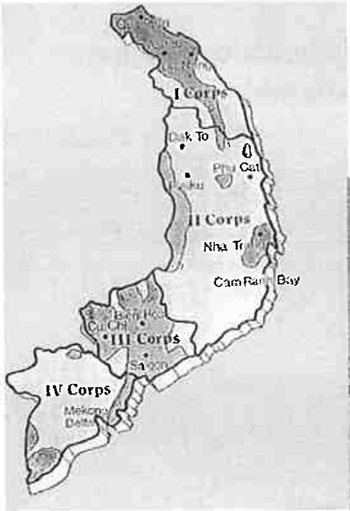
Dibenzodioxin



2,3,7,8-tetrachlorodibenzoparadioxin (TCDD)

The most toxic dioxin is the tetrachlorinated structure shown above whose full chemical name is 2,3,7,8-tetrachlorodibenzoparadioxin, abbreviated **TCDD.** Dioxin is a contaminant that is formed from the synthesis of certain chlorinated herbicides (particularly 2,4,5 trichlorophenoxyacetic acid or 2,4,5 T), bleaching of paper pulp, and incineration of chlorinated plastics. It is a fairly nonpolar molecule (C-Cl bonds are only slightly polar) and accumulates in the fat, being metabolized only slowly. One estimate has the half life of TCDD in fat as 8 years.

TCDD was a contaminant in **Agent Orange** defoliant (herbicide) that was widely sprayed (estimated 11 million gallons on 6 million acres) over tropical forests in Viet Nam from 1962 to 1971 to kill all vegetation and reduce the forest cover used by the Viet Cong guerilla fighters. Its toxicity is the subject of a great deal of controversy and has been the subject of lawsuits by veterans of the Viet Nam war.



http://www.vinylrecords.ch

Many veterans of the Viet Nam war alleged that dioxin was the cause of a variety of health problems, including skin rashes, neurological and psychological problems, and birth defects. In 1996 a National Academy of Science committee concluded there was suggestive evidence for slightly increased risk of Hodgkin's disease, soft-tissue sarcoma, and non-Hodgkin's lymphoma among American veterans heavily exposed to Agent Orange. It has been difficult to gather data, given the lack of quantitative information about the level of Agent Orange exposure and the possibility that other factors besides Agent Orange and its dioxin contaminant might be involved.

The small town of Time Beach, Missouri was evacuated in 1985 when oil made out of chemical wastes from a plant making Agent Orange was used for dust control on the town's streets. Sixty two horses died when oil was used to control dust in a horse stable. Eventually the whole town was evacuated, and compensated by the federal government to relocate elsewhere. The contaminated soil was incinerated (at a cost of $110 million) in an on-site incinerator which was then dismantled and removed. The former town is now a state park..

Incineration of urban waste containing chlorinated plastics (such as PVC and Saran and other compounds) can produce small quantities of dioxin that are released into the air and this has been a concern about waste incineration. Changes in the combustion conditions has greatly reduced the amount of dioxin produced in this manner.

Soldiers claim war zone contractors exposed them to toxins

Nashville lawsuit one of several over 'burn pits' in Iraq and Afghanistan alleged to contain dioxin, asbestos and human corpses

Email | Print By E. Thomas Wood

11-08-2009 11:06 PM —

Contractors working for the military in Iraq and Afghanistan are fouling the nests of U.S. soldiers with pollution, poisoning the troops in the very bases meant to be their sanctuaries.

That's the central allegation in a new set of lawsuits filed in Nashville and elsewhere across the country. The legal actions name as defendants the controversial contracting firm KBR Inc. (formerly Kellogg Brown and Root), as well as Halliburton Co., of which KBR used to be a subsidiary, and a Turkish general contracting firm, ERKA Ltd.

DEPARTMENT OF DEFENSE

DEPARTMENT OF DEFENSE

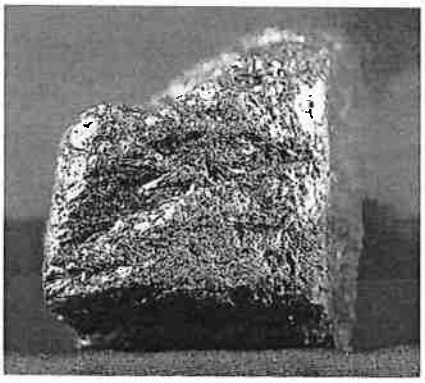
Chloracne

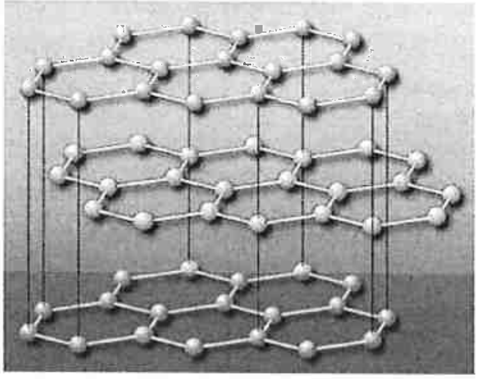
Acute exposure to large amounts of dioxin can cause a wide variety of symptoms including an unusual form of acne called **chloracne**. This got major media attention in 2004 in the case of Viktor Yushchenko, a presidential candidate in the Ukraine in 2004.

In September 2004 Yushchenko became ill during a very heated political campaign. He became very weak and was in great pain. Blood tests showed a high white blood cell count and elevated liver enzymes, but nothing specific. Disfiguring **chloracne** developed several weeks later and was the key to discovering the source of his health problems. His health has gradually improved and he won the election, but his face is very scarred and may remain so for years.

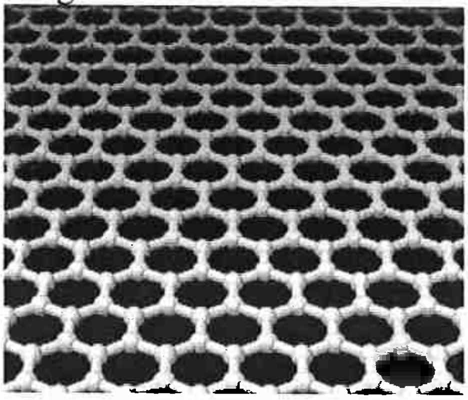
(AFP/AP PHOTOS)

Graphite is a large sheet of benzene rings that extend in large 2 dimensional sheets. It is a black powder with a greasy feeling and is used in "lead" pencils. (Although the Romans did use lead to make marks on papyrus, the discovery of pure deposits of graphite in 1564 gradually led to graphite replacing lead for this purpose. Graphite is often mixed and baked with clay to increase its hardness and then inserted into a wood or plastic/metal pencil to make it efficient to use.) Graphite is also used as a dry lubricant in machinery. Its lubricant properties result from the graphite sheets easily sliding over each other. It is also used in structural materials such as "high end" golf clubs, fishing rods, and bicycle frames.

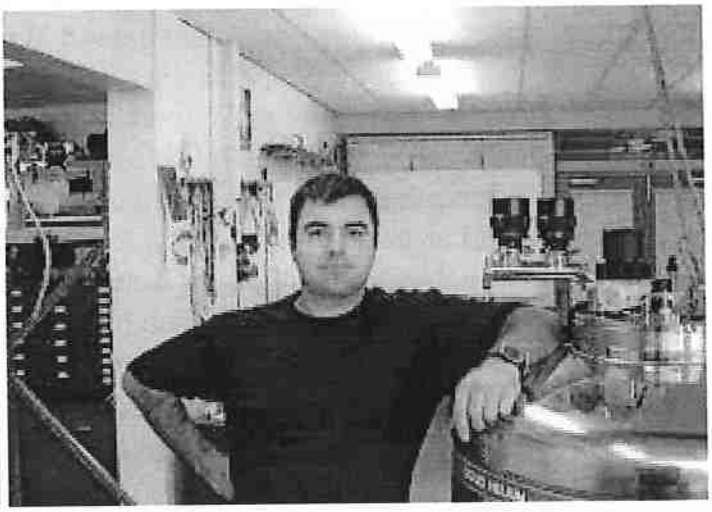




Single layers of graphite are referred to as **graphene** and are a subject of intense research interest for potential technical applications such as a component of integrated circuits.

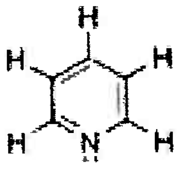


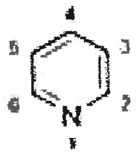
Andre Geim and Konstantin Novoselov won the physics Nobel Prize in 2010 for their work studying grapheme.



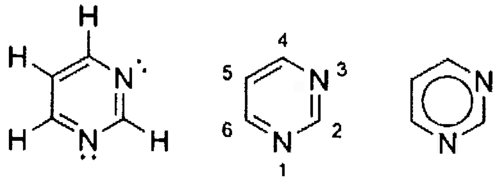
3.14 HETEROCYCLIC AROMATIC MOLECULES have aromatic rings in which 1 or more atoms are NOT C atoms. The most common heteroatoms are N and O. Some examples of biological importance include:

Pyridine

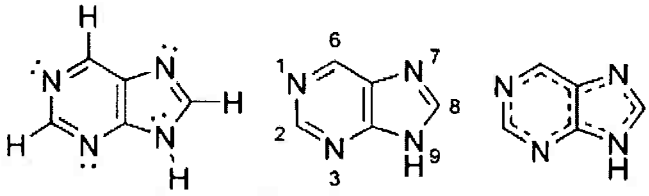




Pyrimidine

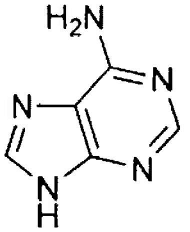


Purine

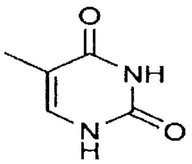


Derivatives of pyrimidine and purine rings are the bases that contain the "genetic code" found in **deoxyribonucleic acid (DNA)** double helix.

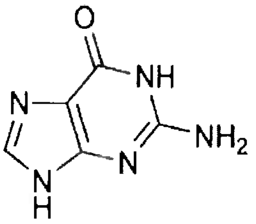
Adenine



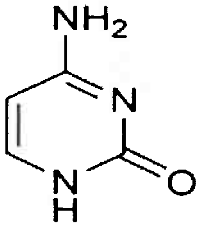
thymine



guanine

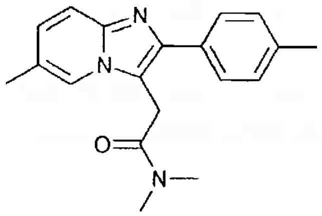


cytosine

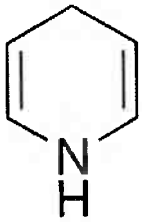


Which of the above DNA bases are purine bases? Pyrimidine bases?

Zolpidem (trade name **Ambien)** is one of the best-selling sleeping pills on the market these days. Its structure is shown below. There are two aromatic ring systems in the structure along with an additional functional group. Identify them.

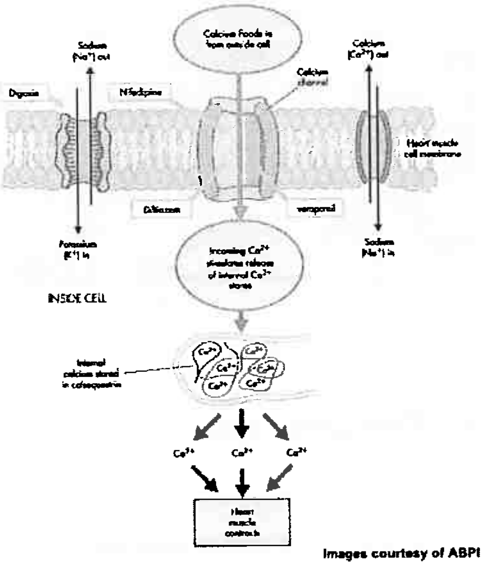


Dihydropyridine is a pyridine which has had two H atoms added to the ring. As a result it has only two double bonds in the ring rather than three and it is NOT aromatic.



The dihydropyridine ring is the basis for making several drugs which are commonly used for treating hypertension and angina.

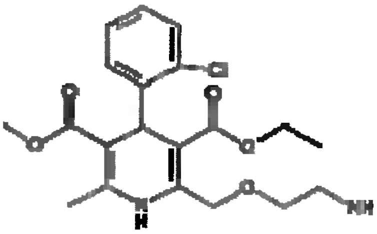
Drugs called calcium channel blockers block trans-membrane Ca channels in muscle cells and cause relaxation of the arteries.



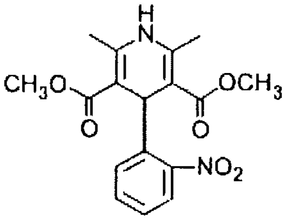
Images courtesy of ABPI

By increasing the volume (lumen) of the inside of the blood vessel, they lower blood pressure and reduce angina.

Several of the calcium channel blockers have a dihydropyridine ring as part of their structure. As a result they are sometimes referred to as **dihydropyridine** calcium channel blockers.



Amlodipine(Norvasc)



Nifedipine(Adalat, Procardia)

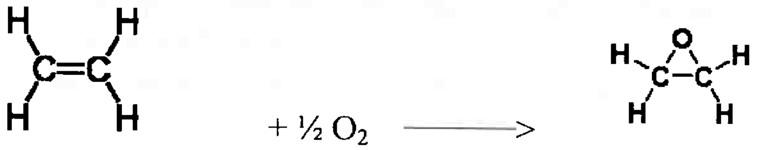
Amlodipine (Norvasc) is currently one of the most commonly prescribed drugs in the US for treating hypertension.

Label the dihydropyridine ring in each of the above calcium channel blocker molecules.

Identify the functional groups in each of these molecules.

3.15 FORMATION OF EPOXIDES AND CARCINOGENIC PRODUCTS

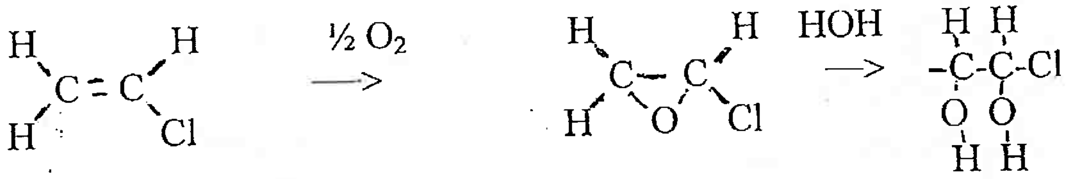
Ethylene oxide is made by treating ethylene (C_2H_4) with a limited supply of O_2 to make C_2H_4O, the basic epoxide molecule.



Ethylene oxide

It is unstable for the same reasons that cyclopropane: a huge bond angle strain. It has been used as a sterilizer for plastic medical equipment such as endoscopes which cannot withstand the high temperatures of an autoclave. The extremely reactive **epoxide ring** reacts and oxidizes and destroys most of the molecules in any biological organism or virus. It is however extremely toxic, potentially explosive as well as carcinogenic and requires very strict procedures and careful monitoring.

Vinyl chloride epoxide. Vinyl chlirde is the monomer used to make the very common plastic, polyvinylchloride (PVC). In the body vinyl chloride can undergo metabolism in the liver to form reactive and potentially mutagenic vinyl chloride epoxide.

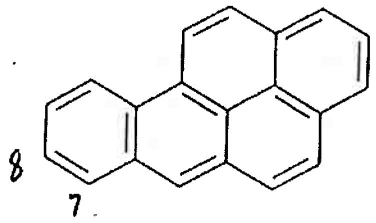


Ideally the epoxide will then react with a water molecule to form a diol (a molecule with 2 alcohol functional groups) and be excreted in the urine. But the reactive epoxide group also has the potential for reacting with DNA and causing a mutation.

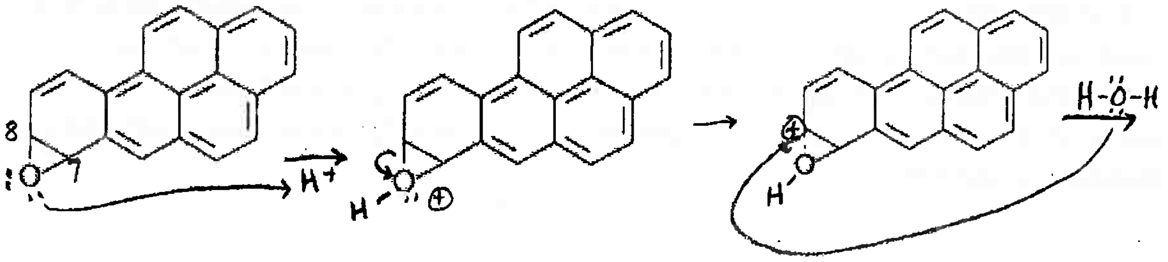
Exposure to vinyl chloride produces intoxication similar to that of ethanol. Long term exposure (i.e. workers in vinyl chloride manufacturing plants) is associated in particular with liver angiosarcoma, which is normally a very rare type of cancer. Human exposure to vinyl chloride is very strictly controlled in factories making polyvinylchloride (PVC). PVC itself is not a carcinogen because the reactive double bonds are removed in the process of making the PVC polymer.

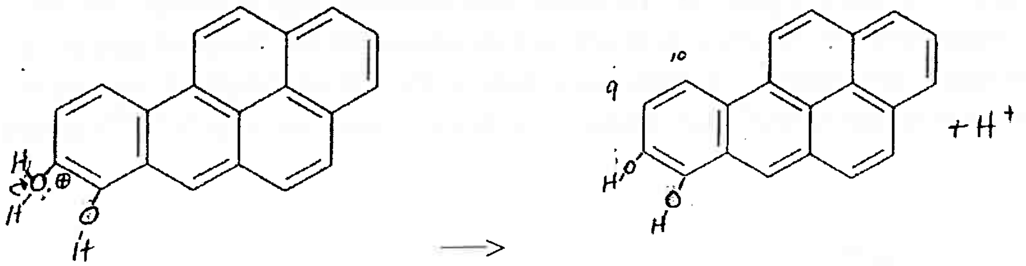
Benzopyrene (sometimes jokingly referred to as 2,4,6,8 “chickenwire”) is a carcinogen found in smoked and charred materials: cigarette smoke, marijuana smoke, wood smoke, and lesser amounts in char-broiled steaks. It appears to be the primary molecule responsible for the carcinogenic properties of tobacco smoke. (Even before cigarette smoking became popular in the early twentieth century, smoke was suspected as a carcinogen. A London surgeon, Percival Potts first noted in 1775 that young chimney sweeps were at increased risk of cancer of the scrotum (call “soot warts”).

Later the chimney sweeps guild in Denmark recommended that chimney sweeps take daily baths and this resulted in decreased incidence of this form of cancer, at least in Denmark according to a study published in the British Medical Journal in 1892. It should be noted that daily baths were not a routine activity in 19th century Europe!)

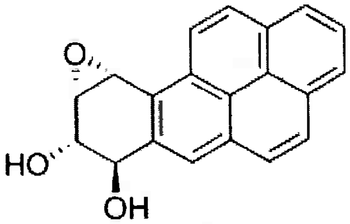


When a person breathes or absorbs benzopyrene, the benzopyrene cannot be utilized in the body and the body seeks to dispose of it. The primary route of excretion for unwanted substances in the body is to excrete them in the urine or feces. This requires that the substance be water soluble. The structure of benzopyrene is completely non-polar so it is not soluble in urine. The body's liver seeks to make it more water soluble by adding polar OH groups. The liver has a whole family of enzymes called the **cytochrome P-450** family, which adds polar groups (often OH) to molecules to increase their water solubility and prepare them for excretion. In the reaction pathway for benzopyrene an O atom is first added to the 7,8 position (see structure) creating an unstable intermediate, benzopyrene 7,8 epoxide. The O atom on the unstable 3-membered ring can pick up a hydrogen ion, followed by attack by a pair of electrons on the O of a water molecule as shown below.



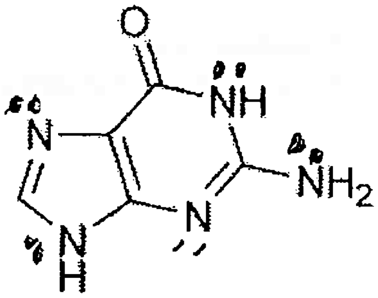


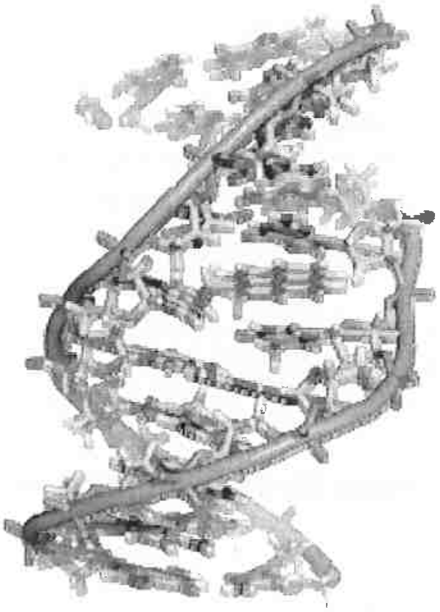
Adding a water molecule produces benzopyrene 7,8 dihydrodiol. A second epoxide is then added across the #9 and 10 C atoms to make benzopyrene 7,8 dihydrodiol 9,10 epoxide.



The second epoxide molecule may react with glucuronic acid (remember bilirubin metabolism!) or adds another water molecule. In either case the additional OH groups will result in increased water solubility and excretion in urine. This is all well and good, and exactly what Mother Nature intended. Unfortunately the "best laid plans of mice and men oft' go awry" to quote the Scottish poet Robert Burns.

The benzopyrene epoxide molecule has a tendency to slip in between the **purine** and **pyrimidine** bases in the DNA double helix, a process called **intercalation**. It reacts readily with available pairs of electrons on the DNA bases. It appears to have a preference for reacting with the amine group on guanine bases. (Can you guess what parts of the guanine might be most reactive?)This reaction will cause a mutation in the DNA.


guanine



This mutation will most likely be found by DNA repair enzymes and be repaired, but there is a small chance that it will not. The mutation may have different results depending on the exact location in the DNA.

Some of the many possibilities:

1) The mutation may occur in a portion of DNA that isn't critically important and produce no result.
2) The mutation may occur in a portion of DNA that is absolutely essential to the cell's health and cause the cell's death.
3) The mutation may occur in a portion of DNA that controls cell replication. As a result it may produce a cell that starts replicating and the replication cannot be "shut off". In this case the mutation has started the formation of a tumor.

(There is some evidence that benzopyrene epoxide preferentially **intercalates** into a portion of the DNA for a gene called P53, which controls the cell replication cycle.)

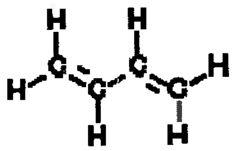
Alkenes Study Guide

1. How many different unbranched hexenes are there? (In other words, how many different places can one put a double bond in 6 C unbranched chain?) Draw the structure for each and give the systematic name for each molecule. Be on the watch for geometric isomers.

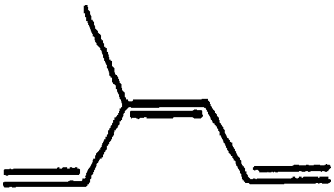
2. Draw structural formulas for:
a) 2,3-dimethyl-2-butene b) 1-methylcycopentene c) cis-2-heptene, trans-2-heptene d) 3-chloro-1-cyclobutene e) cyclohexene f)4-methyl-cis-2-pentene

3. Give the names for the following molecules:

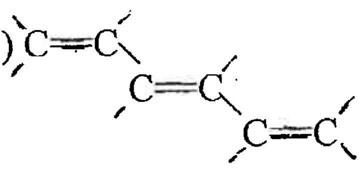
a)



b)



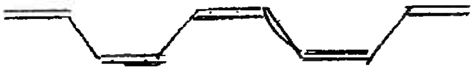
c)



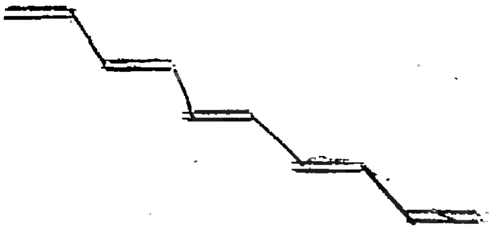
d)

e)

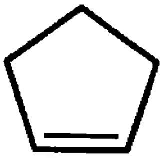
f)



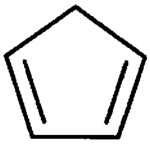
g)



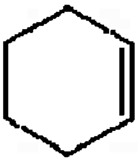
h.



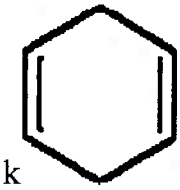
i.



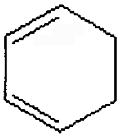
j.



k



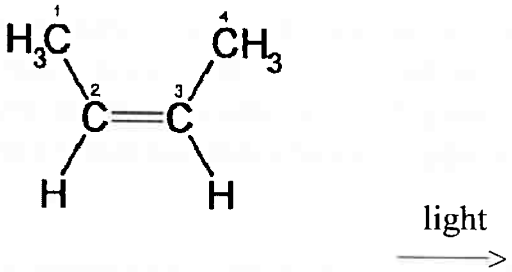
l.



4. Explain what is meant by the term polyunsaturated.

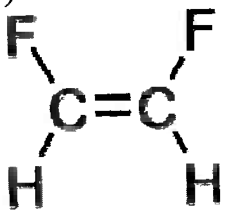
5. Show the complete reaction pathway for the photoisomerization of:

a)



b)  light ——>

c)

 —light—>

6. Given the structure of vitamin A , explain how the isomerization of retinal is important in vision. Also discuss the solubility of vitamin A in water and in non-polar solvents such as fat. What is the orange pigment in carrots? How is it related to vitamin A? Name the red pigment in tomatoes. How is its structure different from the pigment in carrots.?

7. a) How does retinal differ from retinol and retinoic acid in terms of chemical structure? These three molecules are three different forms of _______________.

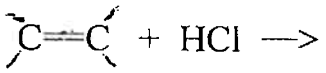
   b) How does Retin A differ from Accutane in terms of a)structure b) clinical use c) adverse effects.

8. Retinal binds to a protein called _______________ in the retinal cells of the eyes to form a complex called _______________. When light of appropriate wave length strikes the retina, it causes a _________________________ reaction which converts _______________ into __________. How does this isomerization result in the perception of light? Where is the bacterial form of retinal found and what is its biological function?
9. Explain what neonatal jaundice is and why it occurs. Explain how phototherapy can reduce neonatal jaundice. Be sure to include a) what molecule is absorbing the light? b) what type of reaction is occurring? c) why this changes the water solubility? d) how is the solubility of bilirubin in water increased in the normal liver?

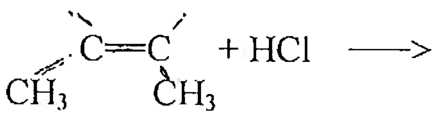
10. Give the reaction that occurs in the hydrogenation of alkenes and explain the reason it is so important in the margarine industry. Why is it done and what problems result from this reaction?

11. Show the complete reaction pathway:

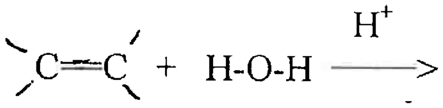
a)



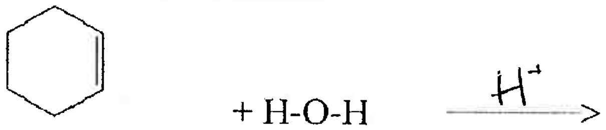
b)



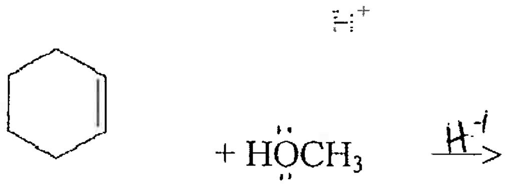
c)



d)



skip e)



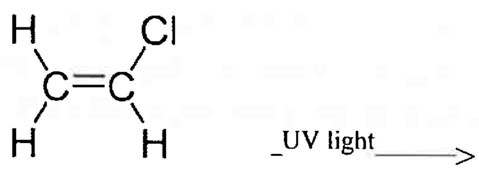
12.How do the structure of LDPE, HDPE and PEX differ? How do they differ in the way the polymer chains pack together and why? How do they differ in terms of physical properties? What sort of products are they used in?

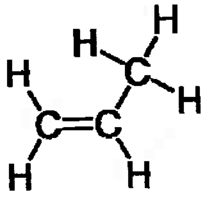
13. How does the structure of polypropylene differ from the structure of polyethylene? What sort of products is it used in? What advantage does it have over polyethylene in terms of heat stability?

14. What polymers allow Gore-tex to breathe and how do they do so? Give a medical use of Gore-tex.

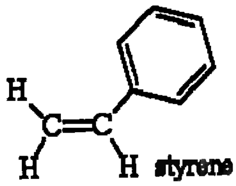
15.Given the structure of the monomer molecules below, draw the structure of the **polymer** product.

a) Many

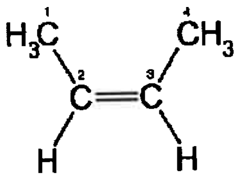


b)Many 

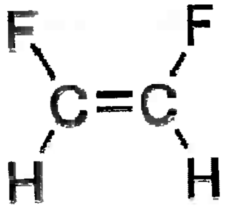
———> UV light

c) Many 

_UV light_____>

d) Many 

___UV>

e) Many 

__free radical initiator____>

16. What properties of polyvinylidene (Saran) are particular useful for storing food in Saran wrap?

17. What is the purpose of adding DEHP to PVC? What is the general term for molecules like DEHP? What sort of medical products have used PVC containing DEHP? What are the concerns about the use of DEHP?

18.
Discuss the role of branching and crosslinking and plasticizers in polymers

19. Polybutadiene was first made in the hopes of making synthetic __________. When and why was this regarded as important?

20. What two isomeric forms of polybutadiene can exist and how do their properties differ? Draw a representative short chain of each form.

21. How did chemists modify the original polybutadiene to give it more useful properties. What is the general and specific name for the resulting mixture?

22. How does the structure of polybutadiene differ from polyethylene?

23. What sort of products are commonly made out of polyacrylonitrile?

24. What does the term ABS stand for? Name some common products made of ABS plastic.

25. What does PMMA stand for. What are some practical everyday uses of PMMA? What are some medical uses of PMMA

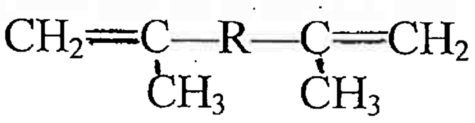
26. What problem occurs with using PMMA for hard contact lenses?

27. What materials are used for current contact lenses and how do they differ from PMMA.

28. What is meant by the term copolymer?

29. How is latex rubber different from gutta percha?

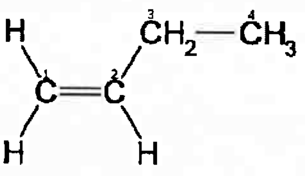
30. BIS-GMA (bis-phenol and glycidyl methacrylate) is mixed with inorganic materials and polymerized to form a composite material for dental pit and fissure sealants as well as fillings. What are two methods for polymerizing the BIS-GMA? How does the polymer formed in this polymerization differ from the polymers formed in question 11? Given the structure of dimethacrylate below, indicate how the presence of two double bonds in the structure accounts for this difference.

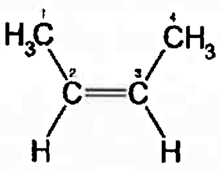


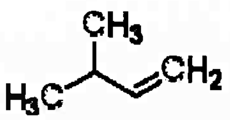
$$\mathrm{CH_2{=}\underset{CH_3}{C}{-}R{-}\underset{CH_3}{C}{=}CH_2}$$

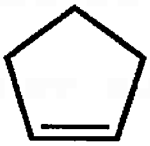
31. Discuss what chemical reaction explains 1) oils and fats going rancid 2) cell membrane damage and 2) cracking of rubber.

32. Draw the structure of the hydroperoxide product formed from the oxidation of the following molecules:

a) 

b) 

c) 

d) 

e) 

(2 possible products)

33. Draw the structure of benzene in two common notations. Draw the orbital overlap picture of benzene and label the delocalized electrons.

34. Draw the structure and give a use or medical/health fact about a) benzoic acid b) toluene c) benzene d)phenol e) benzaldehyde

35. Write the structural formula for a) paradichlorobenzene b) orthodichlorobenzene c) metabromotoluene d)ortho bromochlorobenzene e) orthochlorotoluene

36. What health effects can result from breathing benzene vapors? In what common product was benzene a major component? Where is benzene still found and why isn't it removed?

37. What health effects can result from breathing other organic solvents such as gasoline or paint stripper?

38. Draw the structure of naphthalene and explain what is meant by the term "fused rings". Name one practical use of naphthalene.

39. What was the industrial use for PCB's? What are some of the reasons they a health hazard? What does PCB stand for? Draw the generic structure of a PCB.

40. Name several industrial compounds where dioxins can be found as a contaminant. What sort of health concerns are there regarding exposure to dioxins. What problem results from acute exposure to high levels of dioxin? Name an incident where this received a lot of media exposure.

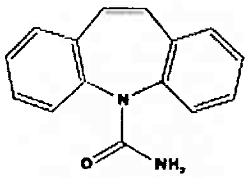
41. Describe the structure of graphite and indicate some uses of graphite. How does grapheme differ from graphite?

42. What is ethylene oxide used for and why is it so toxic?

43. What reactive molecule is vinyl chloride metabolized into and where in the body does this occur?

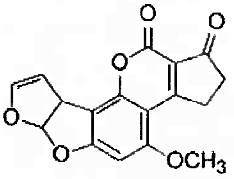
44. Draw the structure of benzopyrene and discuss how the formation of an epoxide group in the benzopyrene molecule results in the formation of a potent carcinogen. What functional groups in DNA can react with the reactive intermediate of the epoxide?

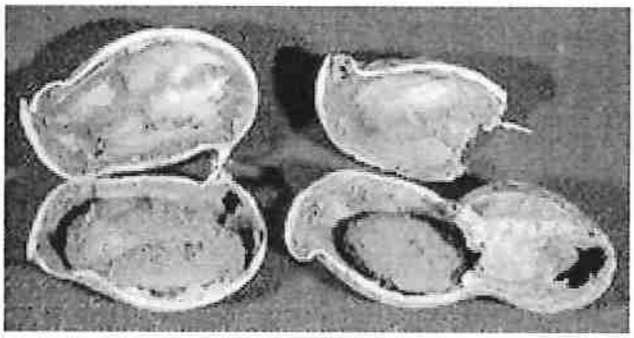
45.Carbamazepine (Tegretol) is a drug commonly used for treating seizures, manic depression, and other mood disorders. It is metabolized in a manner similar to that of benzopyrene, with the epoxide group being added to the double bond labeled in the middle 7-membered ring in the structure shown below. Show the epoxide and diol products that result from the metabolism of carbamazepine. What effect will these reactions have on the water solubility of carbamazepine? What health problems might be of concern based on what you've learned in this class?



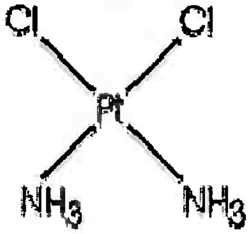
Carbamazepine

46.. Aflatoxin B is a potent carcinogenic toxin produced by a mold that can grow on peanuts and other grains, especially in humid conditions. The FDA and USDA mandates that aflatoxin in our peanut butter be at a level less than 20 parts per billion(ppb)! Contamination of aflatoxin occurred in several types of Diamond brand dog food in 2005 and was apparently responsible for the death of at least 70 dogs. The aflatoxin molecule is metabolized in a manner similar to benzopyrene. This metabolism occurs primarily in the liver and aflatoxin is particularly likely to cause liver damage and liver cancer. The epoxide reaction occurs on the double bonds in the 5-membered ring on the far left of the structure shown below. Show the epoxide and diol product.



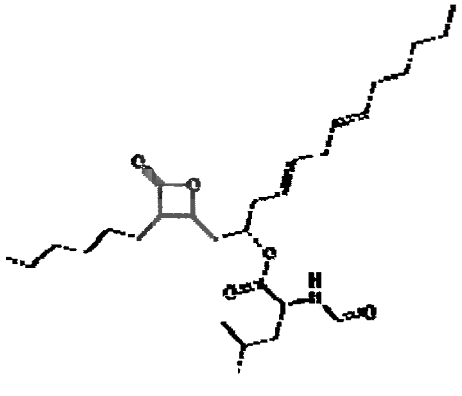


46. Cisplatin (cis-diaminedichloroplatinum) is used in chemotherapy of certain types of cancer. The cisplatin binds and crosslinks DNA, particularly replicating DNA and prevents DNA replication. The structure of cisplatin is shown below and the reason for the prefix cis should be clear. Draw the structure of transplatin, the geometric isomer of cisplatin. Only the cisplatin has any anti-cancer activity.



Cisplatin

Are the double bonds in lipstatin cis or trans?



Think questions: