Hydrocarbons

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Electron configuration of carbon atoms

- position of carbon in the Periodic table of elements:
  2nd period, group IVA

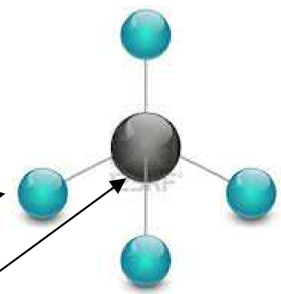
$_6C \Rightarrow 6\ p^+ \Rightarrow 6\ e^- \Rightarrow$ orbitals: **$1s^2\ 2s^2\ 2p^2$** (4 valence e^-)

- electrons in different orbitals have *different energy*
  (it rises in the order: $1s < 2s < 2p$)
- electrons in *s-orbitals* move in a *spherical space*
- electrons in *p-orbitals* move in a *space of 2 opposite drops*

electrons of a separate carbon atom and a carbon found in a molecule are arrangend differently:
the process of **hybridization** changes energy of electrons

- example: *sp^3 hybridization* = s p_x p_y p_z orbitals have the same energy

Bonds in hydrocarbons



- *hydrogen atom* (H): $1s^1$
- 1 electron of hydrogen and 1 electron of carbon make pair of electrons: *covalent bond* (sharing electrons)
- pairing of electrons from s-orbitals (or hybride orbitals) makes *sigma-bond* (σ-bond)

  $\rightarrow$ *sigma electrons* move <u>around the axis</u> connecting two atoms involved in a covalent bond (H-C or C-C)
- pairing of electrons from p-orbitals makes *pi-bond* (π-bond)

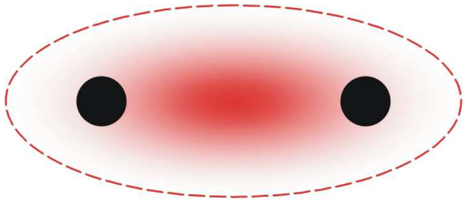
  $\rightarrow$ *pi electrons* move <u>above and under the axis</u> connecting two atoms (C-C) $\Rightarrow$ ***they are more reactive***

double bond = 1 σ-bond and 1 π-bond

triple bond = 1 σ-bond and 2 π-bonds

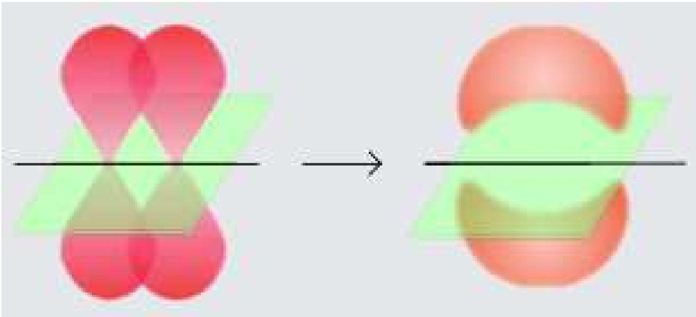
Shape of molecules

σ-bond C–C



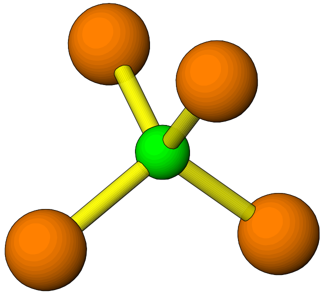
π-bond C=C

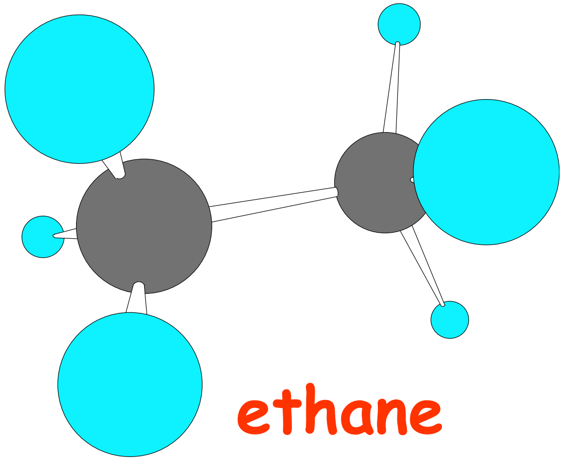
C≡C



Alkanes

- hybridization sp^3 – <u>tetrahedral shape</u> (4 σ bonds)

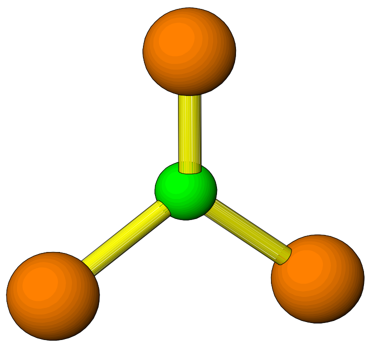


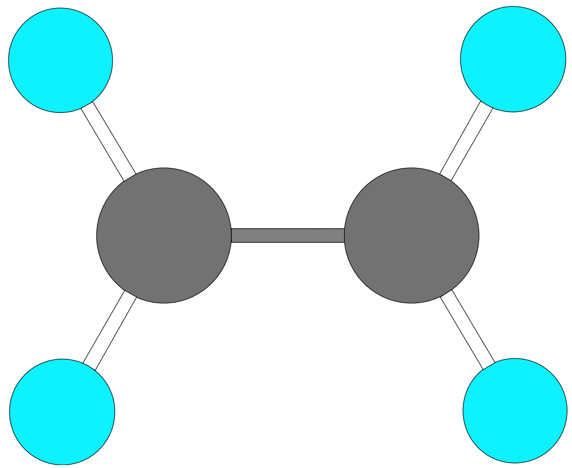


ethane

Alkenes

- hybridization sp^2 – <u>trigon</u> (each carbon: 3 σ and 1 π)

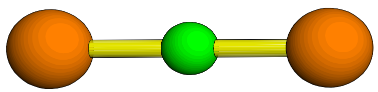


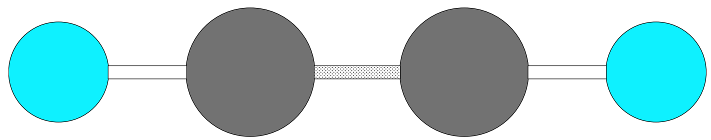


ethene

Alkynes

- hybridization sp – <u>linear</u> (each carbon: 2 σ and 2 π)





ethyne

Alkanes – saturated hydrocarbons

(C_nH_{2n+2})

main natural source:

- **natural gase**
  (up to 97% of methane; ethane, propane, CO_2, N_2)
- **petroleum**
  (mixture of aliphatic, alicyclic, and polycyclic hydrocarbons C_1-C_{50}; the composition varies with its location)

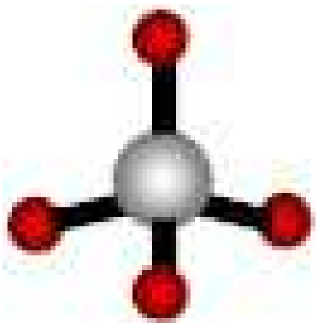
Alkanes – saturated hydrocarbons
(C_nH_{2n+2})

fractions of petroleum:

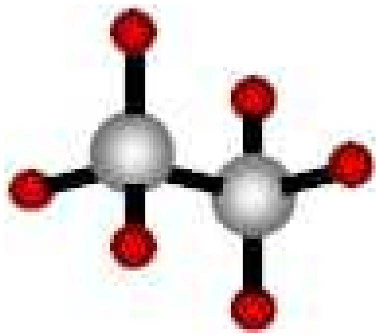
- gas (C1-C4) ~ cooking gas
- petroleum ether (C5-C6) ~ solvent for org. chemicals
- gasoline (C6-C12) ~ automobile fuel
- kerosene (C11-C16) ~ rocket and jet fuel
- fuel oil (C14-C18) ~ domestic heating
- lubricating oil (C15-C24) ~ lubricants for automobiles and machines

Alkanes – saturated hydrocarbons

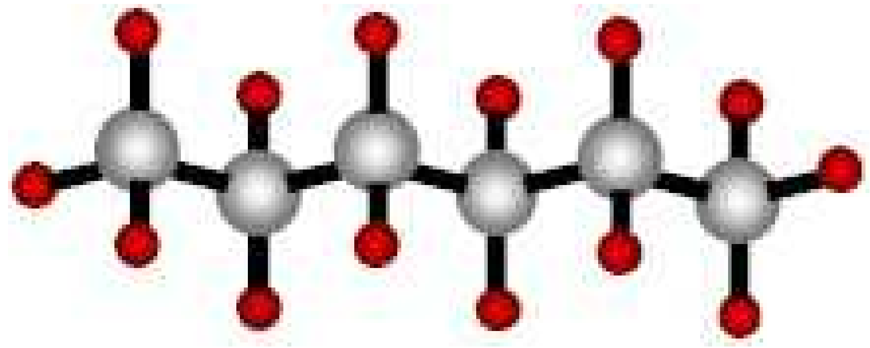
(C_nH_{2n+2})



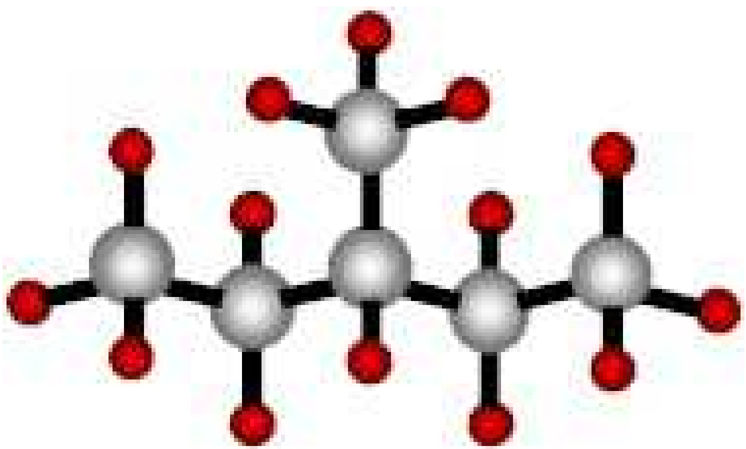
methane



ethane



hexane



3-methylpenthane

! Alkanes are not planar !

Alkanes – saturated hydrocarbons
(C_nH_{2n+2})

physical properties:

- **not soluble in water** (= hydrophobic)
- non polar bonds (similar electronegativity of C and H)
- densities between 0.6 and 0.8 g/cm^3 (= less than water)
- colorless, tasteless, nearly odorless
- boiling points increase with increasing MW, and decrease with branching (C1-C4 are gases)
- volatility decreases with molar weight (MW)
- **narcotic and irritant effects** increase with MW (! C5-C9)

Alkanes – saturated hydrocarbons

(C_nH_{2n+2})

alkanes and the human body:

- inhalation of alkane vapors (e.g. gasoline) causes severe damage to the **lung tissue** (it dissolves cellular membranes)
- liquid alkanes can also **harm the skin**: long-term contact between low MW alkanes and skin remove skin oils and can cause soreness and blisters
- high MW alkanes can be used to **protect the skin**: mixtures of C_{20}-C_{30} alkanes are used in skin and hair lotions to replace natural oils
- mineral oil purified mixture has been used as **a laxative**

Alkanes – saturated hydrocarbons
(C_nH_{2n+2})

reactivity:

- **not very reactive** *(„paraffins" ~ parum affinis = little activity)*
- **simple (sigma, σ) bonds:**

  C-C   bonding electrons tightly held between carbons, not readily available to other substances

  C-H   bonds around the carbon skeleton, more susceptible to reactions (usually under extreme conditions)

Alkanes – saturated hydrocarbons
(C_nH_{2n+2})

reactivity:

1. **oxidation** *(combustion)*

   - gases of any alkane form explosive mixtures with air
   - exergonic reaction: **heat is produced**

   e.g. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ + energy (192 kcal)

2. **halogenation** *(it is a substitution reaction, replacement)*

   - $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
   - $CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$ ....→ $CHCl_3$, CCl_4

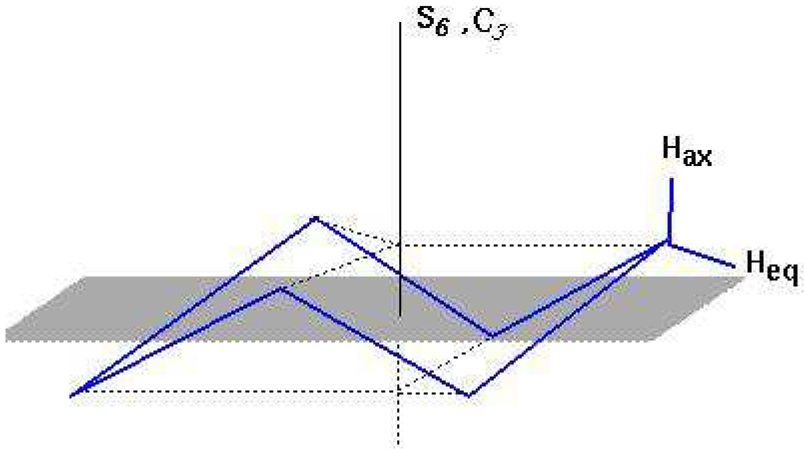
Cycloalkanes – cyclic saturated hydrocarbons

(C_nH_{2n})

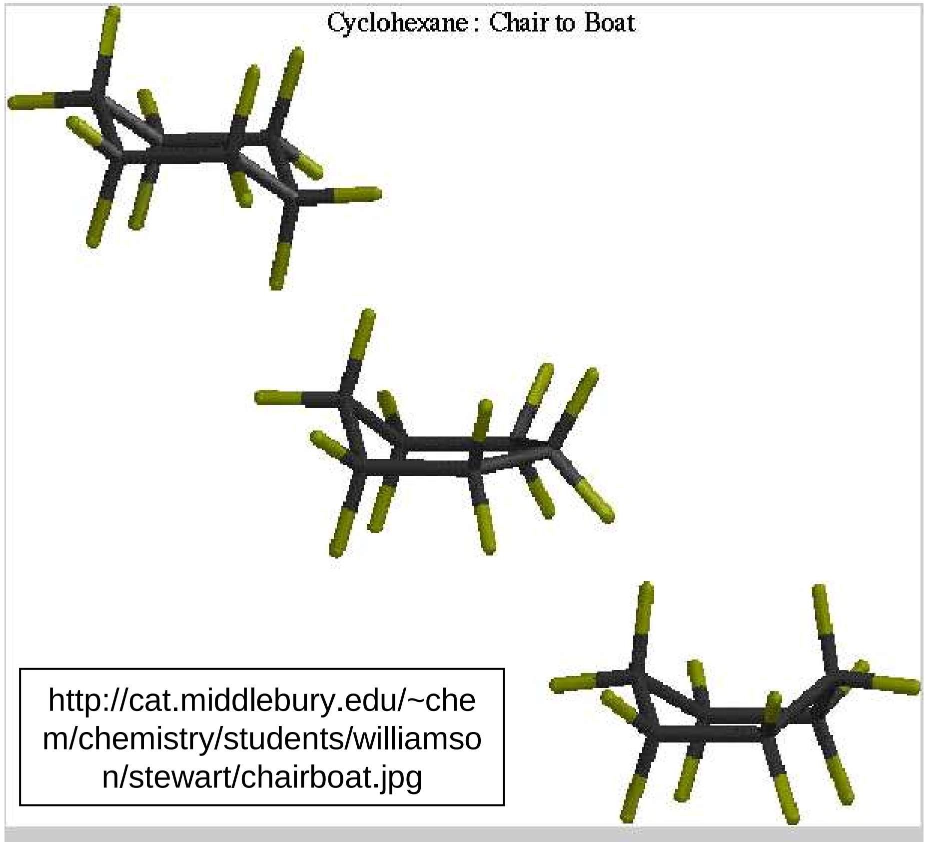
- carbon atoms in a ring (polygon)
- properties similar to alicyclic hydrocarbons
- C3 and C4 are higly reactive (ring strain)
- cyclopropane was used as a narcotics
- polycyclic (cyclopentano perhydrophenanthrene) is a parent structure of steroids
- C3, C4, C5 are planar molecules

Cycloalkanes – cyclic saturated hydrocarbons
(C_nH_{2n})

- C6: many conformations in space *(free rotation of C-C; the most stable at room temperature: CHAIR conformation)*



http://www.chemistry.nmsu.edu/studntres/chem539/answers/chexane_chair.jpg

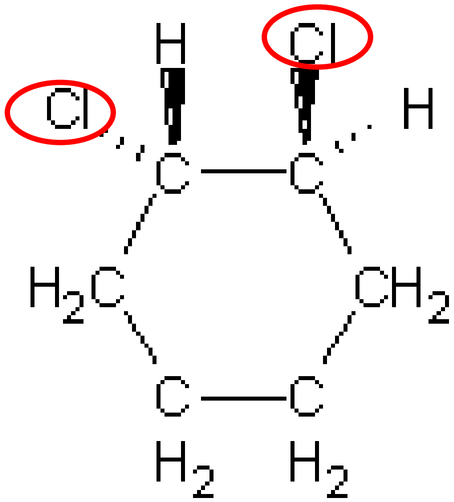


http://cat.middlebury.edu/~chem/chemistry/students/williamson/stewart/chairboat.jpg

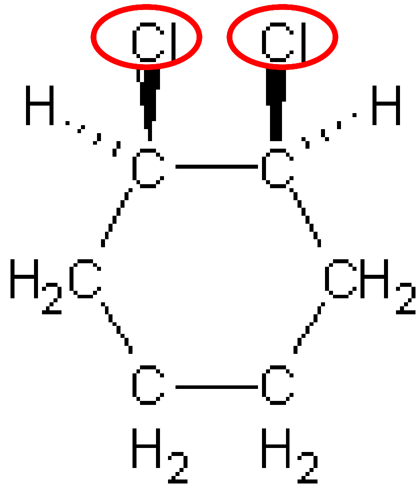
Cycloalkanes – cyclic saturated hydrocarbons
(C_nH_{2n})

➢ **geometric isomerism** = *the same sequential arrangement of atoms but different arrangement in space*

trans = E-



cis = Z-



http://www.arthistoryclub.com/art_history/Geometric_isomerism

Alkenes – unsaturated hydrocarbons
(C_nH_{2n})

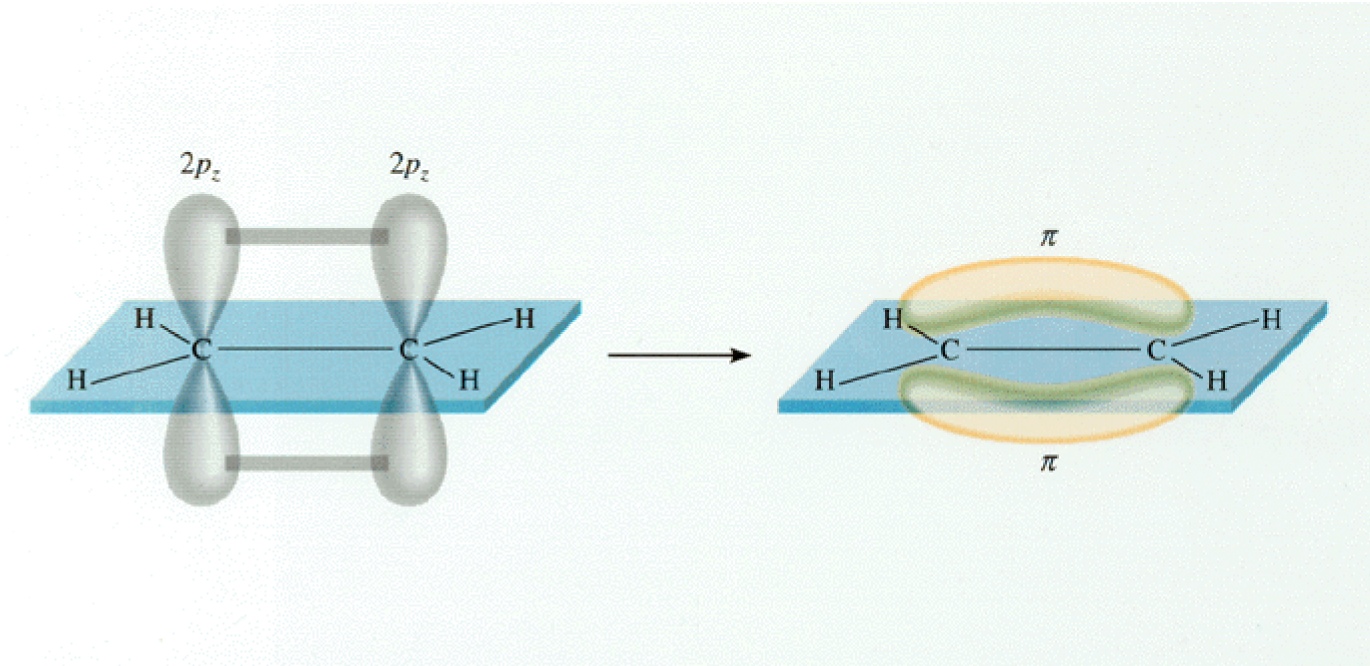
physical properties:

- **not soluble in water** (= hydrophobic)
- nonpolar bonds (similar electronegativity of C and H)
- low boiling points – lower than alkanes of the same length (C2-C4 are gases)
- double bond consist of **1σ and 1π bond**
- the double bond does not permit free rotation

→ geometric isomerism

Alkenes – unsaturated hydrocarbons
(C_nH_{2n})

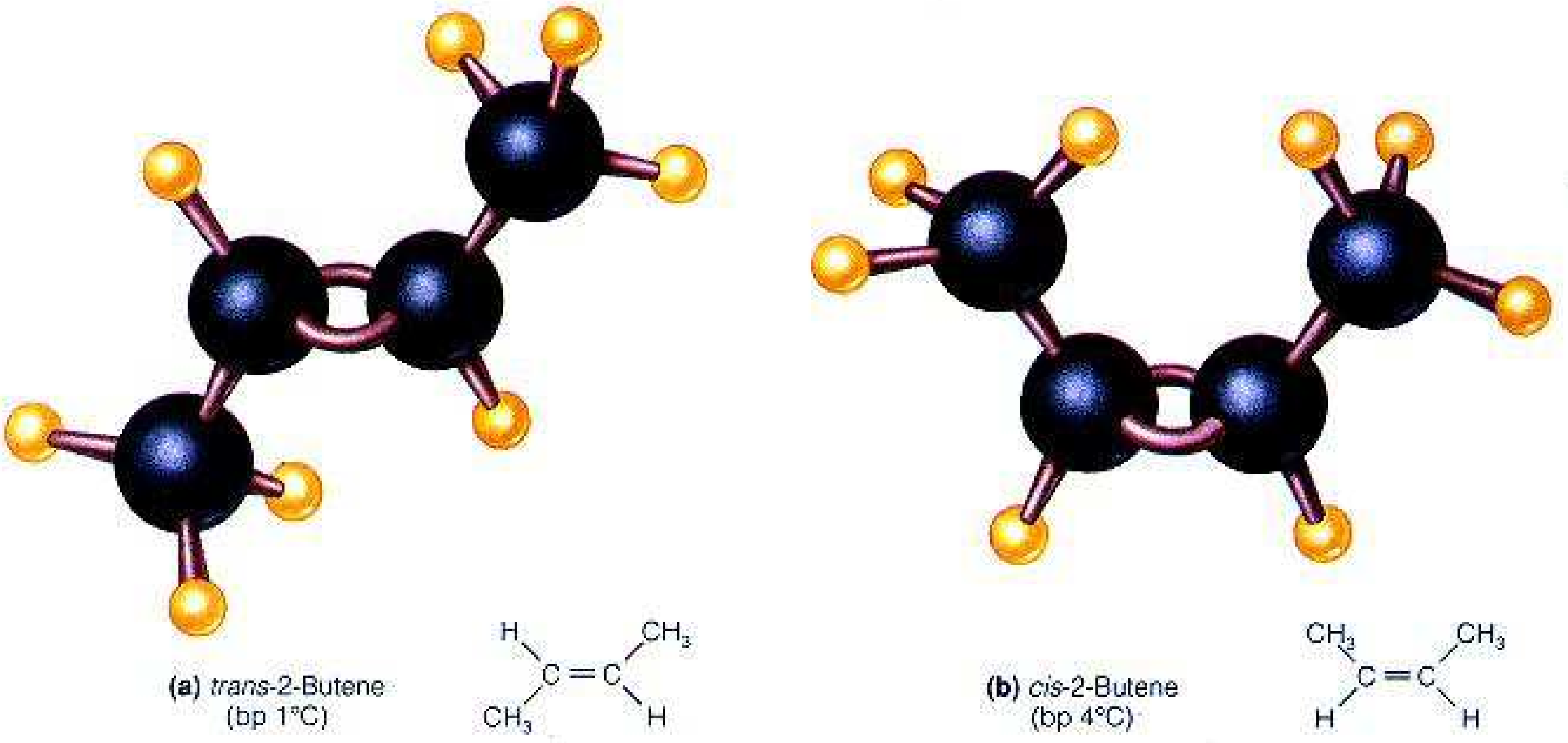
- ethene (= ethylene) is planar



http://www.chem.umass.edu/~rday/chem110/ethenepi.gif

Alkenes – unsaturated hydrocarbons
(C_nH_{2n})

- example of geometric isomers:



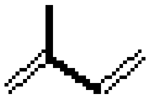
(a) *trans*-2-Butene (bp 1°C)

(b) *cis*-2-Butene (bp 4°C)

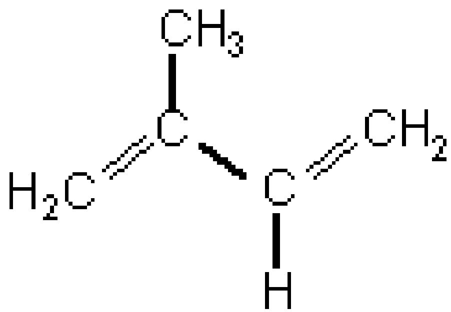
http://www.gunthersclass.com/24_10.jpg

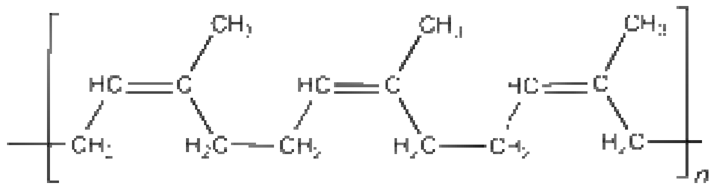
Alkenes – unsaturated hydrocarbons
(C_nH_{2n})

- alkenes have higher **biological efect** than alkanes
- their narcotic efect and toxicity increase with MW and with other unsaturated bonds
- 2 double bonds: **ALKADIENS**



or





polyisoprene
(natural rubber)

2-methylbuta-1,3-diene = **isoprene**

Alkenes – unsaturated hydrocarbons
(C_nH_{2n})

reactivity:

- the double bond is responsible for their reactivity

1. **oxidation** - π-bond is attacked by oxidizing agents

CH_3-CH=CH-CH_3 → CH_3-CH(OH)-CH(OH)-CH_3 *(e.g. by $KMnO_4$)*

2. **reduction = hydrogenation** = **saturation** of the molecule by hydrogen *(hydrogenation is a kind of addition reaction)*

CH_3-CH=CH-CH_3 + H_2 → CH_3-CH_2-CH_2-CH_3 *(catalyzed by Pt)*

Alkenes – unsaturated hydrocarbons
(C_nH_{2n})

reactivity:

3. **addition reaction** = two substances join together to form a compound containing all atoms present in the original substances

   - the double bond is transformed to the single bond, substituents are added

$CH_2{=}CH_2 + Br_2 \rightarrow Br\text{-}CH_2\text{-}CH_2\text{-}Br$ = halogenation

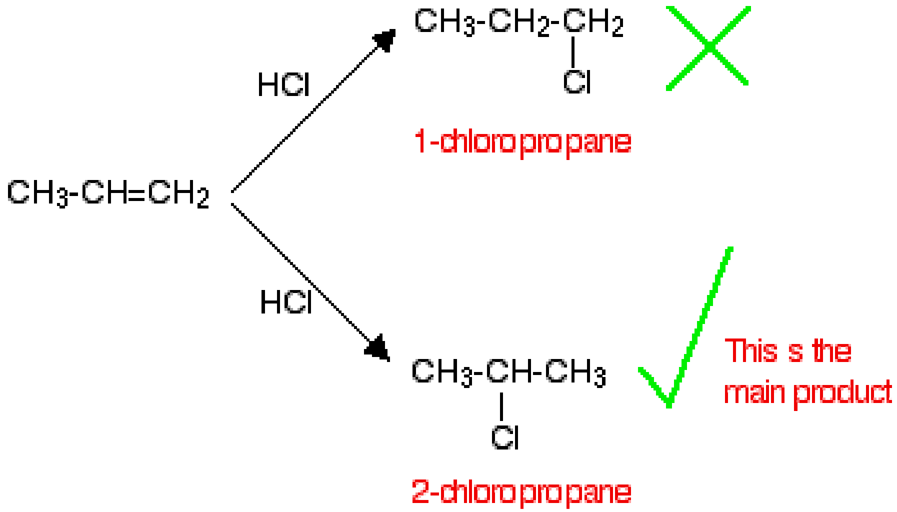
$CH_2{=}CH_2 + HCl \rightarrow CH_3\text{-}CH_2\text{-}Cl$ = halogenation

$CH_2{=}CH_2 + H_2O \rightarrow CH_3\text{-}CH_2\text{-}OH$ = hydration

Alkenes – unsaturated hydrocarbons
(C_nH_{2n})

! Markovnikov´s rule !

- for unsymmetrical reagents „HX“
- „hydrogen atom of the reagent HX binds to the unsaturated carbon that has the greater number of dirrectly bonded hydrogen atoms“



http://www.chemguide.co.uk/organicprops/alkenes/propenehcl.gif

Alkenes – unsaturated hydrocarbons
(C_nH_{2n})

4. polymerization

- „polymers" are high molecular weight molecules made from thousands of repeating units, which are low molecular weight molecules („monomers")
- it is a multiple addition reaction of alkenes

e.g. $n\ CH_2{=}CH_2 \rightarrow (-CH_2-CH_2-)_n$

- **properties** of polymers depend on the monomer used and MW of the product

Alkenes – unsaturated hydrocarbons
(C_nH_{2n})

4. **polymerization** - *examples of polymers:*

- polyethylene (PE)
- polyvinylchloride (PVC)
- polypropylene (PP)
- polytetrafluoroethylene (Teflon)
- polystyrene (PS)
- polymethylmetacrylate (Plexiglas)

Alkynes – unsaturated hydrocarbons
(C_nH_{2n-2})

physical properties:

- boiling points slightly higher than that of alkanes and alkenes
- specific gravity higher in comparision to alkenes
- the **triple bond = 1σ and 2π bonds**
  - it is shorter than the double bond
- **the reactivity** of the triple bond is similar to that of the double bond of alkenes (addition reactions)
- **ethyne** (= acetylene): all four atoms in a straight line

Aromatic hydrocarbons

benzene

- liquid of pleasant odour
- narcotic effect
- can damage the bone marrow
  (it can give rise to leukemia)

toluene and xylenes

- narcotic and irritant effect
- less dangerous than benzene

Aromatic hydrocarbons

biphenyl

- suspected from cancerogenesis

naphtalene

- irritant effect (skin, mucosa)
- causes methemoglobinemia and the kidney damage

benzo(a)pyrenes

- cancerogenic effect

Halogene Derivatives

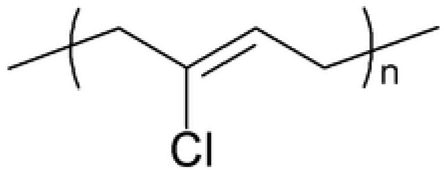
<u>majority of gas or liquid halogene derivatives</u>:

- narcotic effect
- irritate skin and mucosa
- some can cause liver and nervous system damage

- **solvents** (CCl_4, CCl_3CH_3, CCl_2=CCl_2)
- **cooling media** (CH_3Cl, freons, e.g. CCl_2F_2)
- **fire-extinguishing agents** ~~(CCl_4~~, $CBrF_3$,...)
- **insecticides** (DDT, $C_6H_6Cl_6$)

Halogene Derivatives

- **monomers**
  - $CF_2=CF_2$, $CH_2=CHCl$,
  - chloroprene: $CH_2=CH(Cl)CH=CH_2$



polychloroprene = NEOPRENE

- **anesthetics** (Halothane: $CF_3CHClBr$)
- **formerly used in the medicine**: bromoform (in cough sirups), iodoform (desinfectant)
- **polychlorinated biphenyls** (PCB)

Important common (trivial) names

- add structural formulas -

- ethene = ethylene
- ethyne = acetylene
- trichloromethane = chloroform
- chloroethene = vinylchloride
- 2-methylbut-1,3-diene = isoprene
- methylbenzene = toluene
- dimethylbenzenes = xylenes
- vinylbenzene = styrene

MEMORIZE THESE NAMES