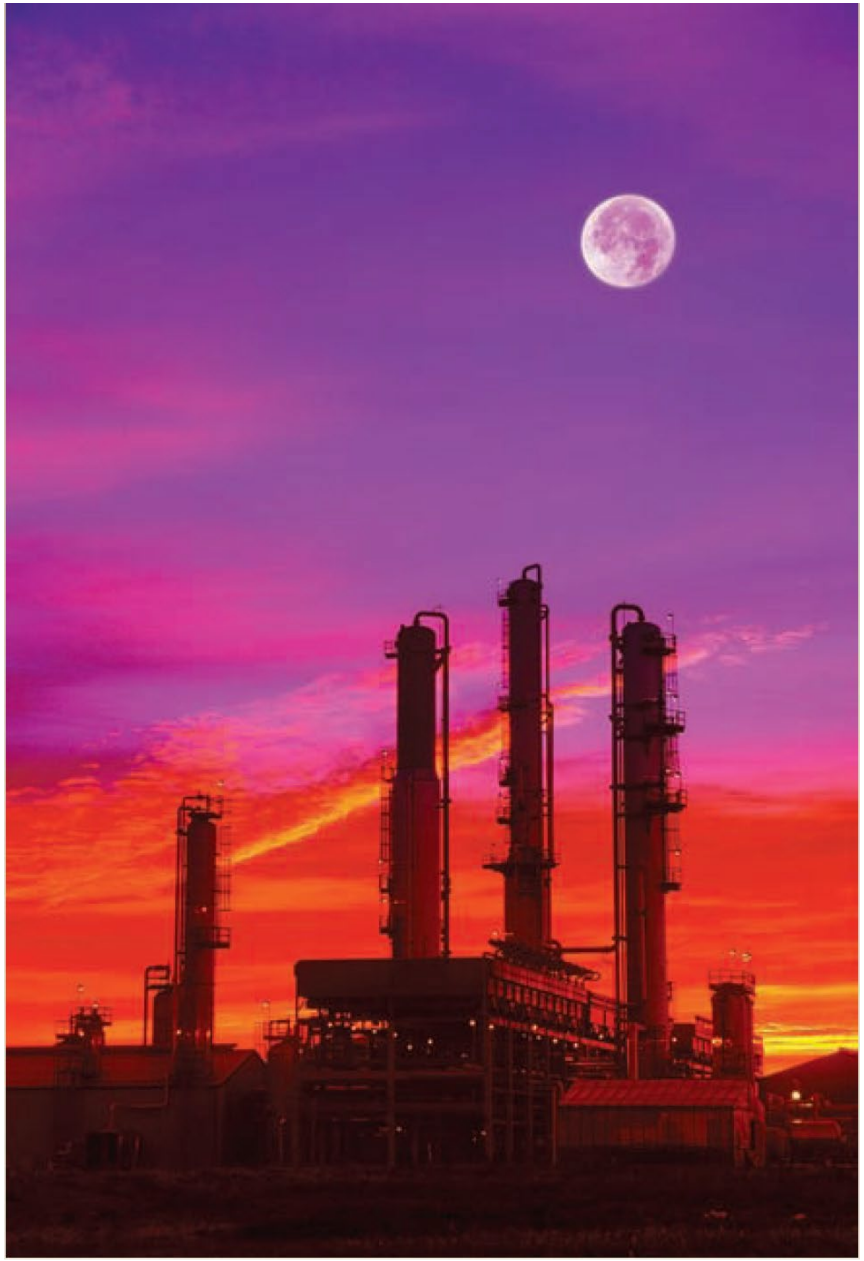
7

CHAPTER

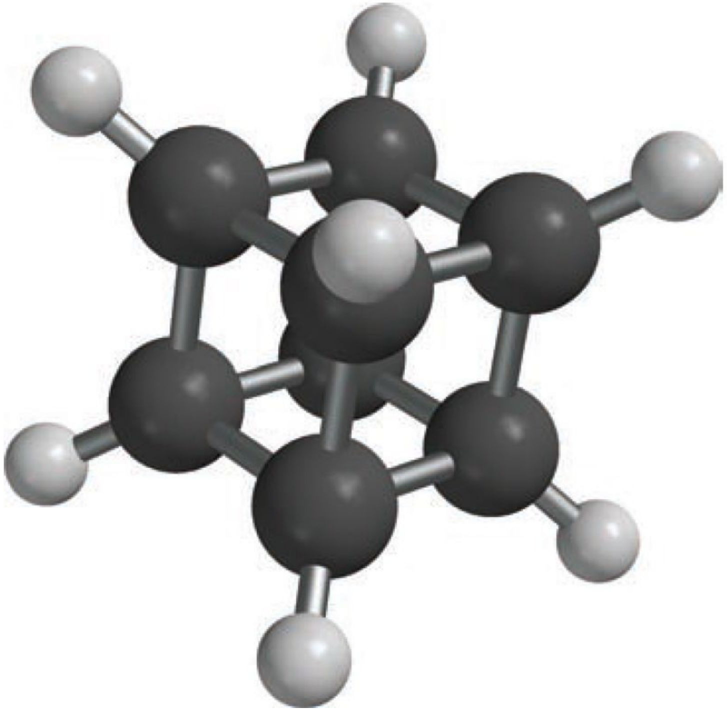
BONDING IN ORGANIC MOLEULES

1. Petroleum Refining and the Hydrocarbons
2. The Alkane
3. The Alkenes and Alkynes
4. Aromatic Hydrocarbons
5. Fullerenes
6. Functional Groups and Organic Reactions

   Connections to Biology: Functional Groups in Proteins
7. Pesticides and Pharmaceuticals



A petroleum refining tower



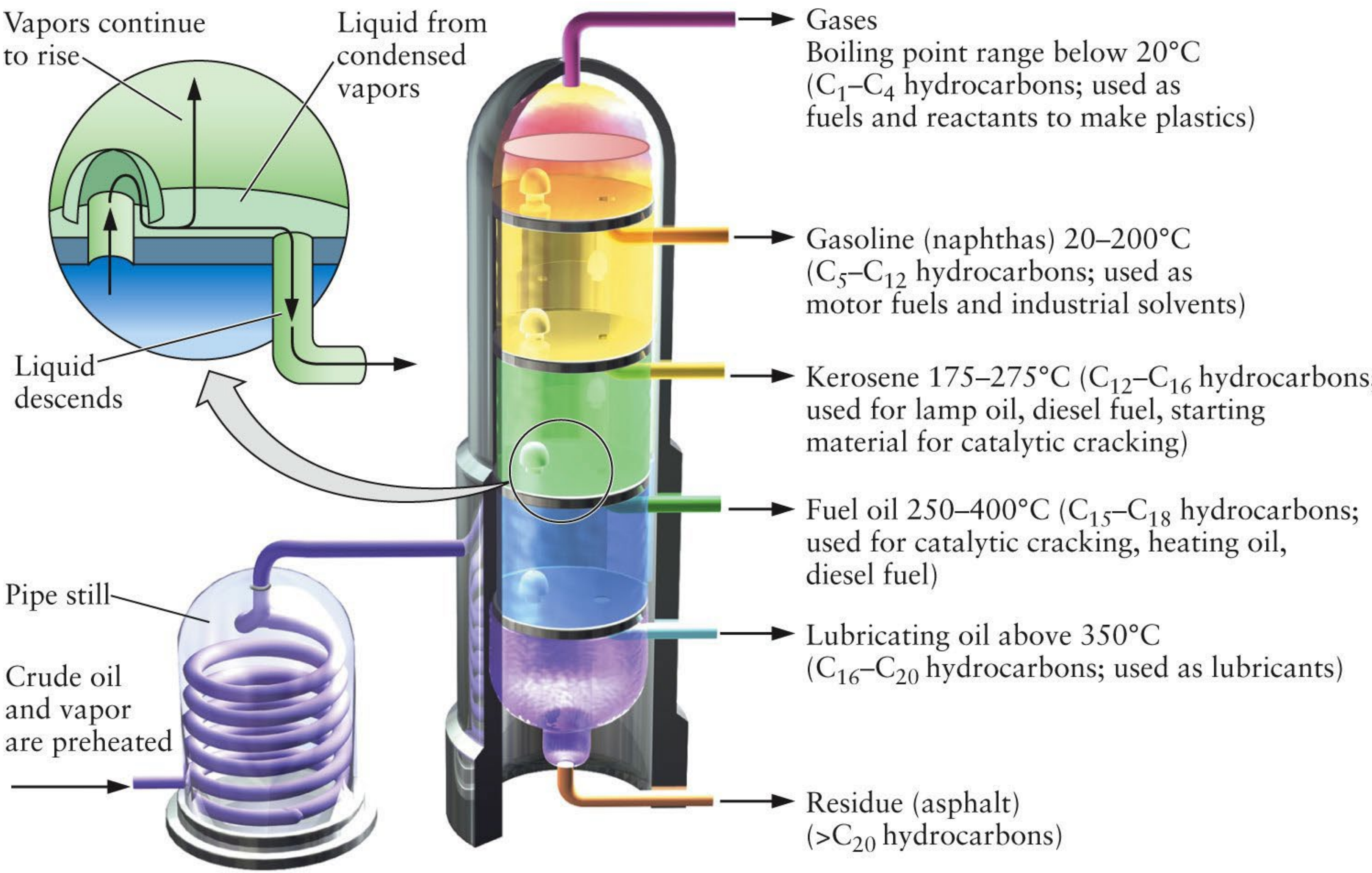
Cubane C_8H_8

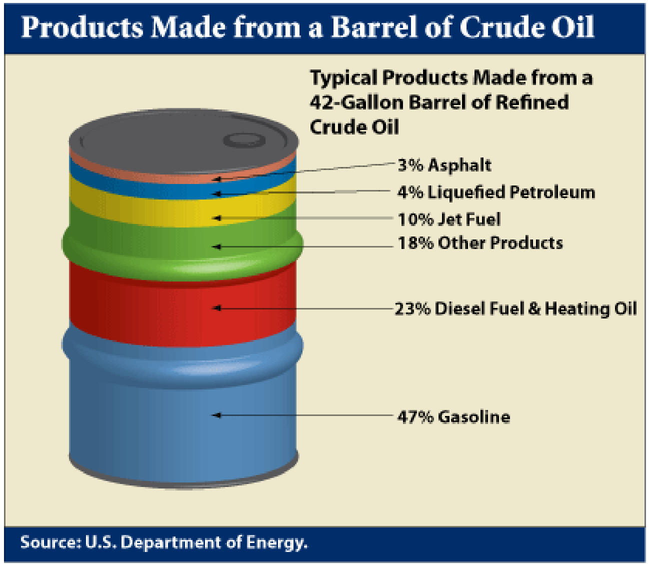
7.1 PETROLEUM REFINING AND THE HYDROCARBONS

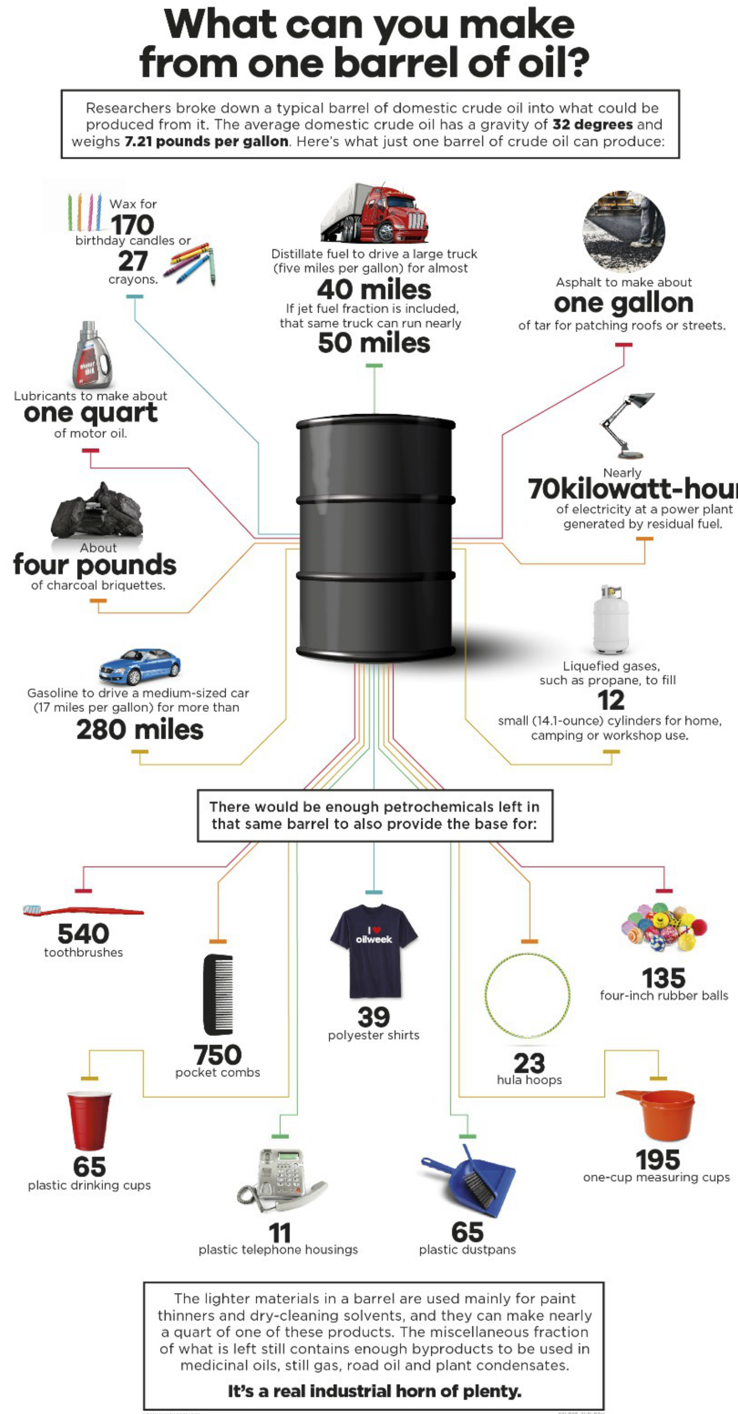
Petroleum: in latin ~ *petra (rock) + oleum (oil)* --- Crude Oil
Documented of usage 4000 yrs ago in Babylon.
Has been used as fuel in China since 400 B.C.
Has been used as a medicine since 15C. In Europe.
In 1854, world first modern oil well
In 1856, world first refinery
In 1859, world first actual modern oil well

Petroleum: major constituents are **hydrocarbons**
Hydrocarbon: compounds of hydrogen and carbon

Carbon - 83 to 87%, Hydrogen - 10 to 14%,
Nitrogen: 0.1 to 2%, Oxygen: 0.05 to 1.5%, Sulfur: 0.05 to 6.0%, Metals: < 0.1%


Vapors continue to rise
Liquid from condensed vapors
Liquid descends
Pipe still
Crude oil and vapor are preheated
Gases
Boiling point range below 20°C
(C_1–C_4 hydrocarbons; used as fuels and reactants to make plastics)
Gasoline (naphthas) 20–200°C
(C_5–C_{12} hydrocarbons; used as motor fuels and industrial solvents)
Kerosene 175–275°C (C_{12}–C_{16} hydrocarbons; used for lamp oil, diesel fuel, starting material for catalytic cracking)
Fuel oil 250–400°C (C_{15}–C_{18} hydrocarbons; used for catalytic cracking, heating oil, diesel fuel)
Lubricating oil above 350°C
(C_{16}–C_{20} hydrocarbons; used as lubricants)
Residue (asphalt)
(>C_{20} hydrocarbons)



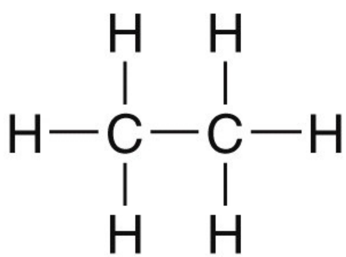


General Chemistry I

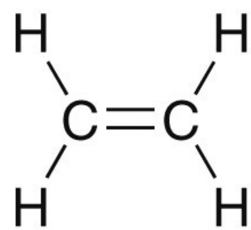
KAIST CHEMISTRY

7.2 THE ALKANES

- Hydrocarbons – compounds that are only compose d of hydrogen and carbon

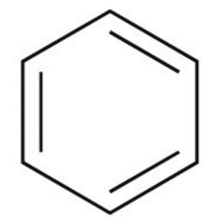


Ethane
C_2H_6



Ethylene
C_2H_4

Acetylene
C_2H_2



Benzene
C_6H_6

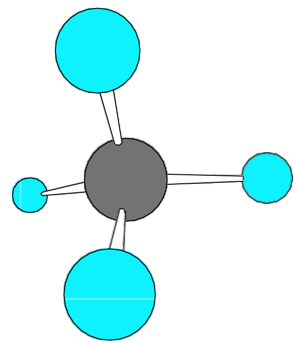
- Which of the molecules above is saturated with hyd rogen atoms?

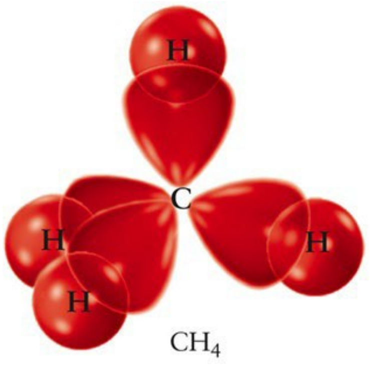
7.2 THE ALKANES

◆ **Normal Alkanes:** straight chain alkanes

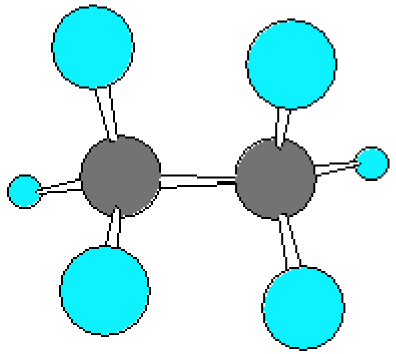
Alkanes: Saturated Hydrocarbons

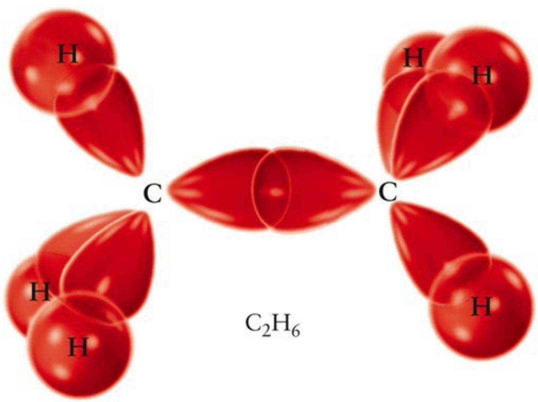
CH_4: sp^3 hybridized





C_2H_6





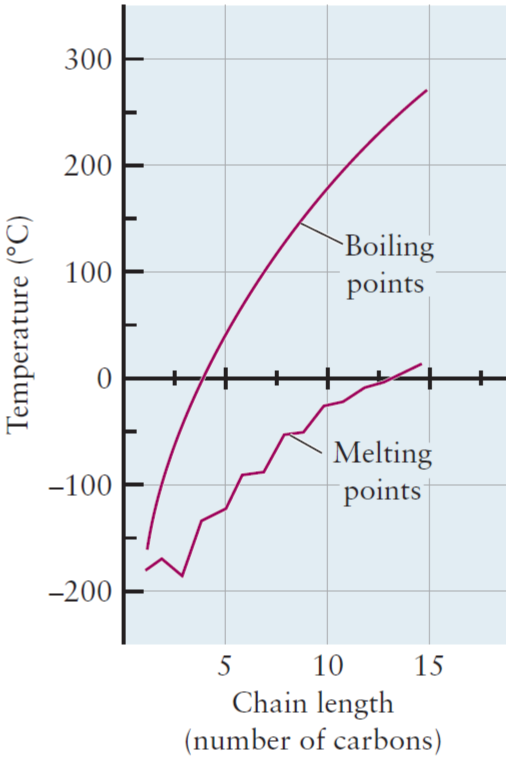
Saturated hydrocarbon : *all bonds are single bonds*

C_nH_{2n+2}

"Alkane" ***paraffin***

CH_4	methane
C_2H_6	ethane
C_3H_8	propane
C_4H_{10}	butane
C_5H_{12}	pentane
C_6H_{14}	hexane
C_7H_{16}	heptane
C_8H_{18}	octane
$C_{30}H_{62}$	triacontane

b.p. & m.p. increase



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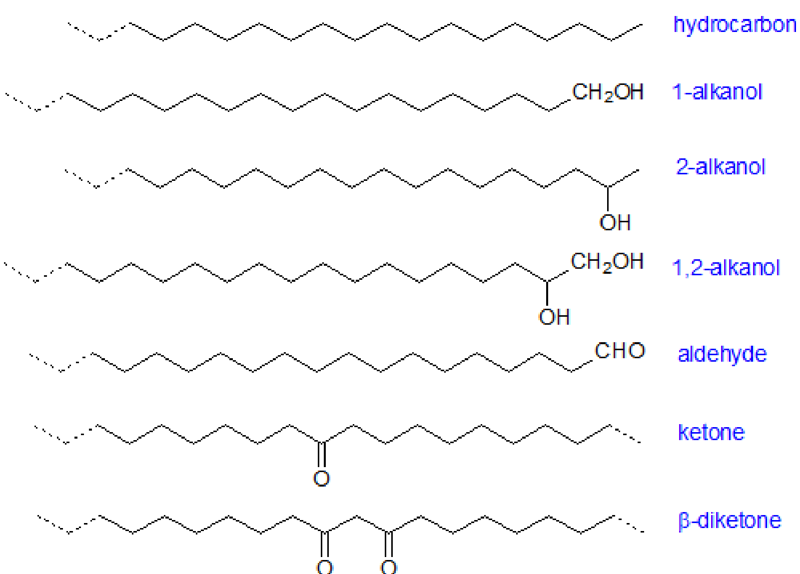
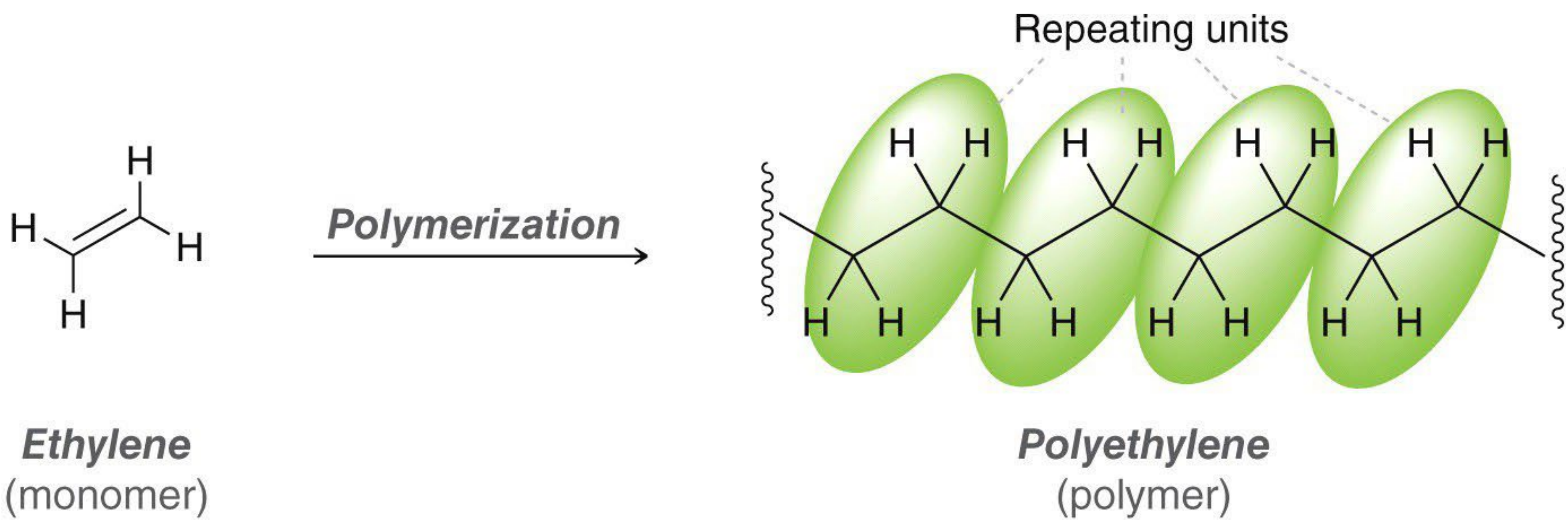
◆ Wax



Some common wax constituents

Polyethylene



Saturated hydrocarbon : *all bonds are single bonds*

"Alkane" ***paraffin***

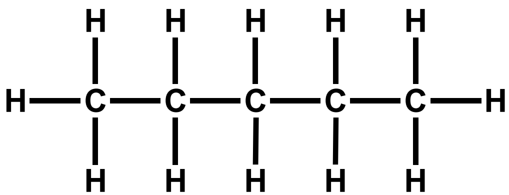
C_nH_{2n+2}

# of structures --- *isomers*

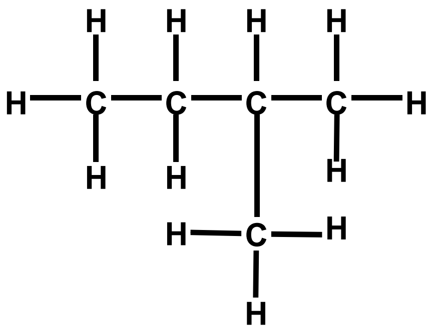
Branched-Chain Alkanes & Isomerism

CH_4	methane	1
C_2H_6	ethane	1
C_3H_8	propane	1
C_4H_{10}	butane	2
C_5H_{12}	pentane	3
C_6H_{14}	hexane	5
C_7H_{16}	heptane	9 → beginning of stereoisomerism (11)
C_8H_{18}	octane	18
$C_{30}H_{62}$	triacontane	4.11×10^9

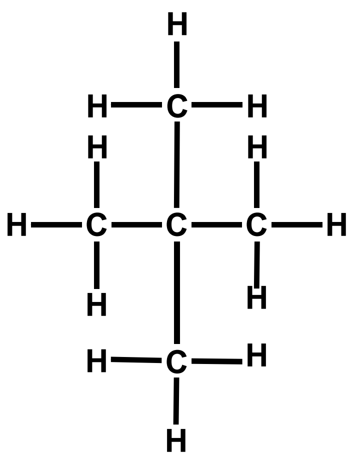
Example : C_5H_{12}



Pentane : b.p. 36°C

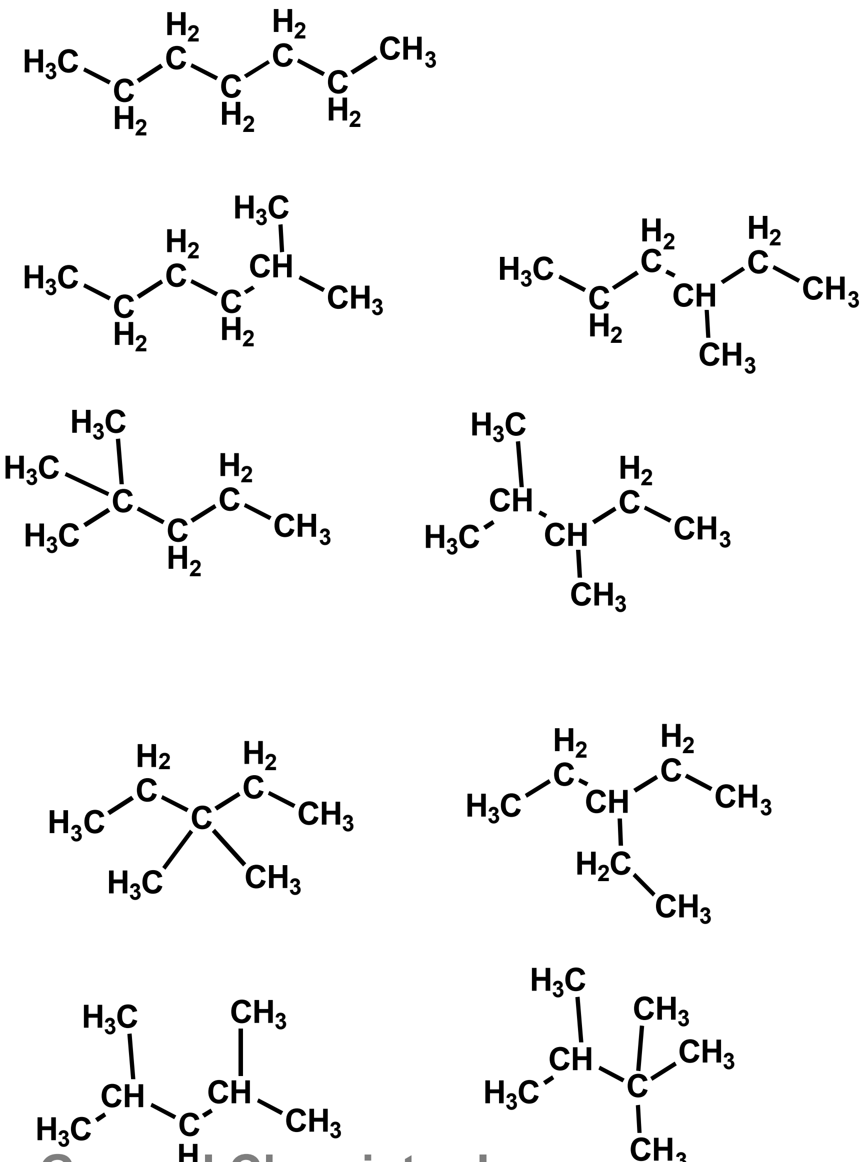


Isopentane : b.p. 28°C



Neopentane : b.p. 9.5°C

example : C_7H_{16} : Heptane



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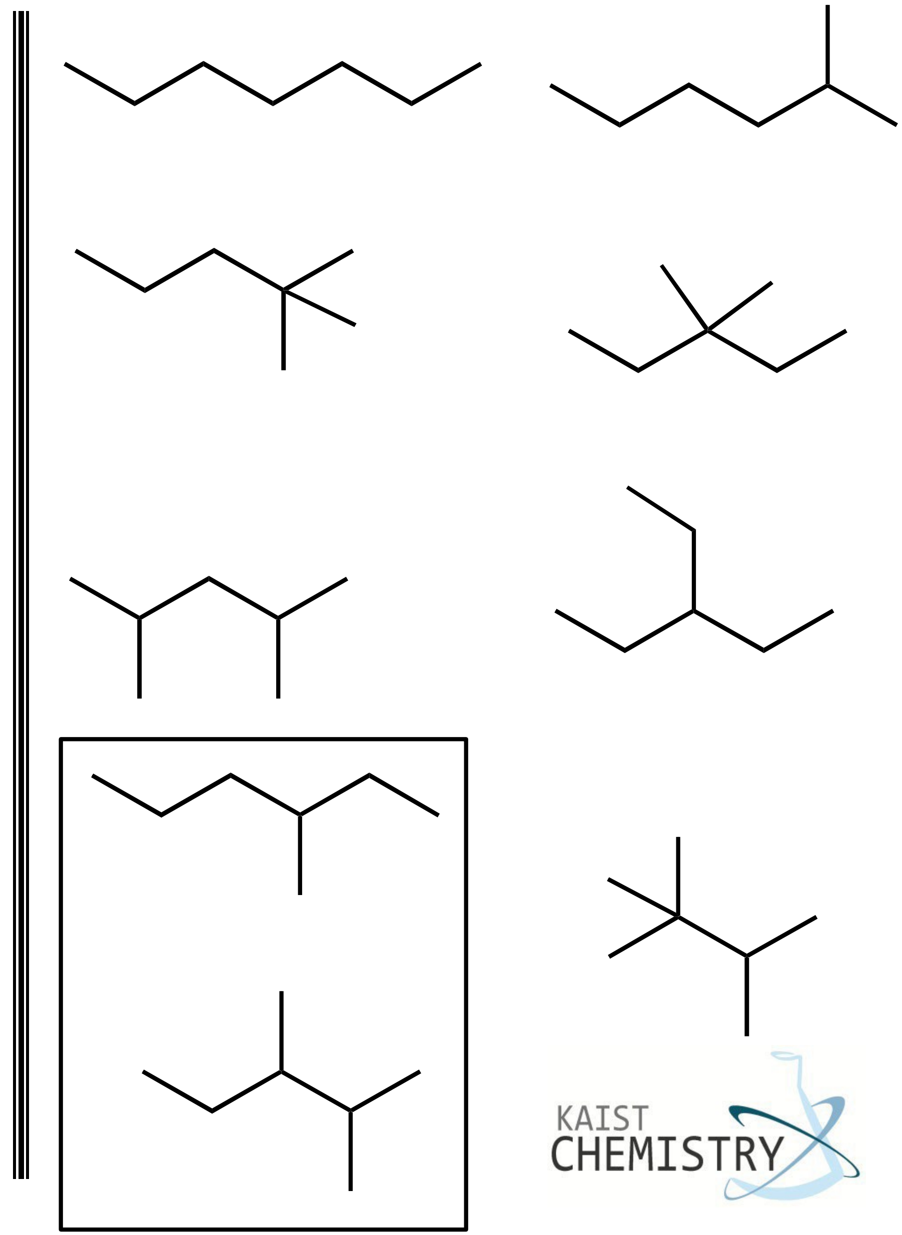
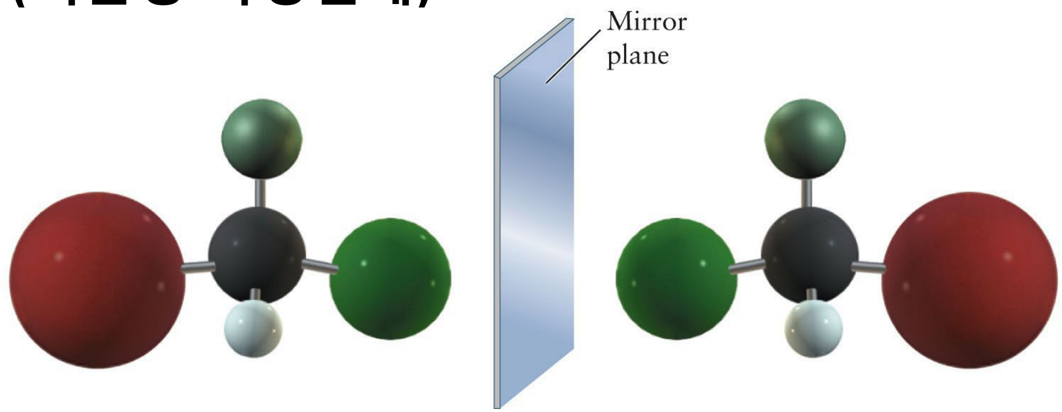


◆ Isomerism:

1. Structural (constitutional) isomer: different bonding arrangements of the same atoms.
   구조이성질체

2. Stereoisomer: same bonding arrangement, different spatial positions.
   입체 이성질체

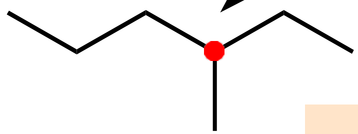
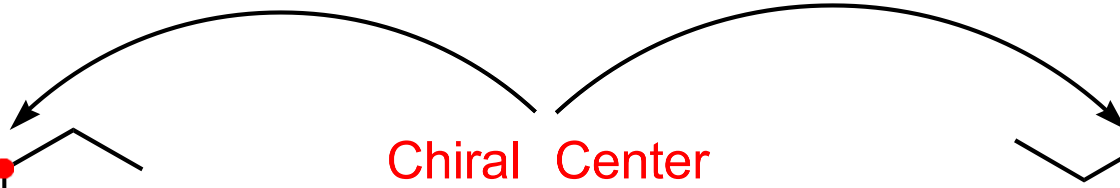
-- enantiomer (거울상 이성질체)

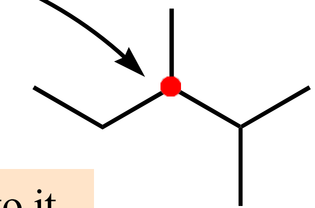


These are mirror images and not superimposable i.e. different compounds.

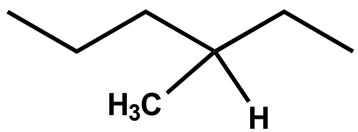
Different but have same physical properties except optical rotation. i.e. inseparable

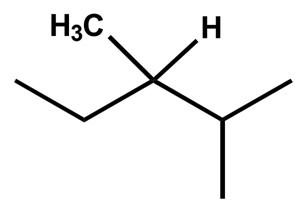
Stereoisomers

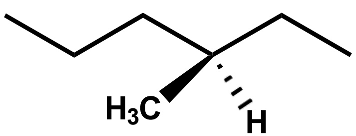



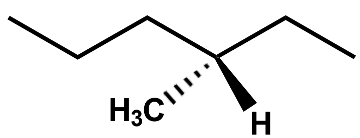


an atom that has all four different groups attached to it.

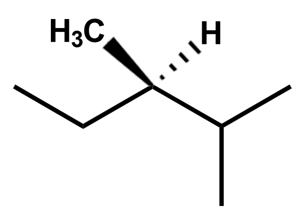


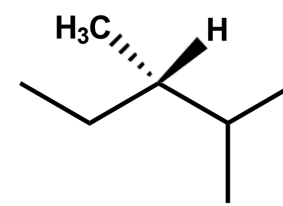






enantiomers





enantiomers

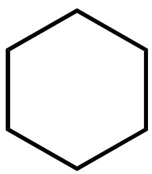
◆ Cyclic Alkanes:

Satruated hydrocarbon : *Ring structures* C_nH_{2n}

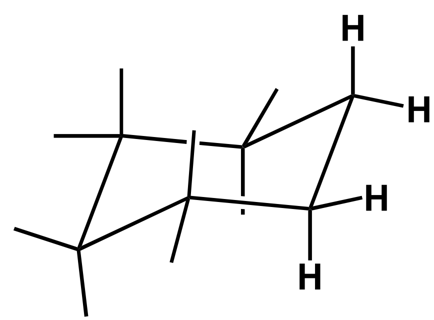
Cyclic Compounds

Usually unstable when it's small
Associate with strain energy

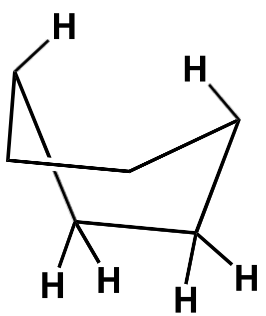
Most stable cyclic compound



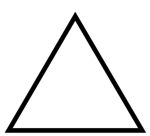
Cyclohexane



chair form



boat form



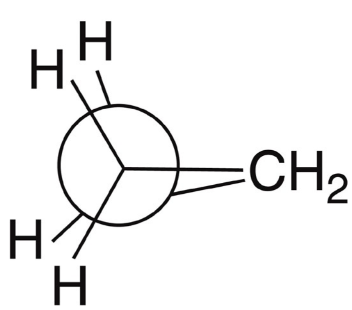
Cyclopropane

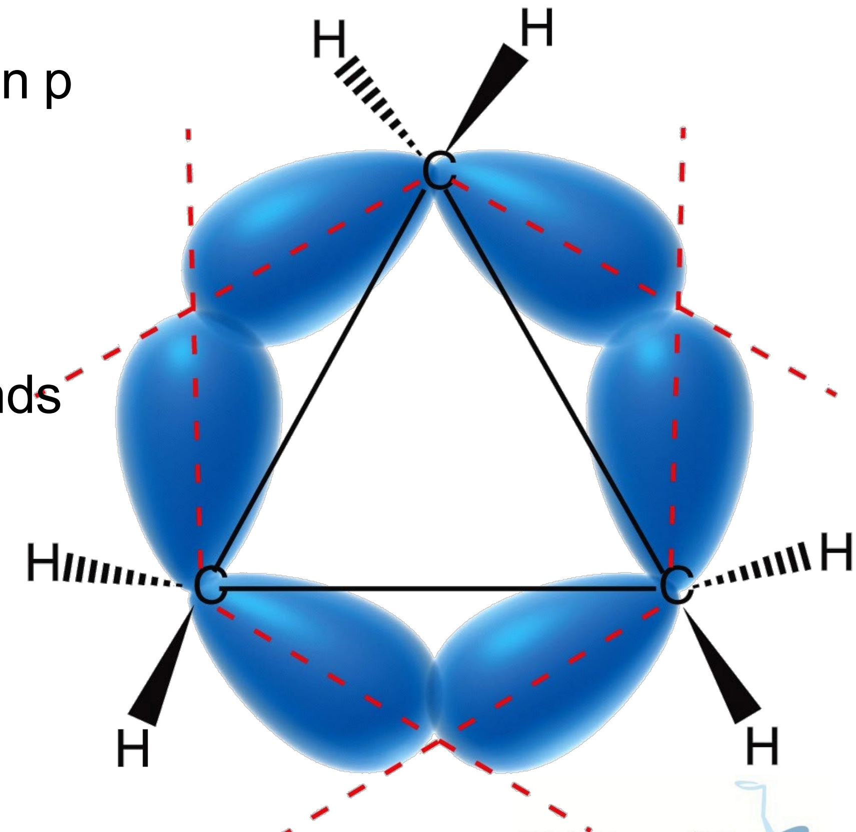
Most strained
reactive

Cyclopropane

- Cyclopropane is 44 kJ/mol less stable than cyclohexane per CH_2 group. It is highly strained and very reactive

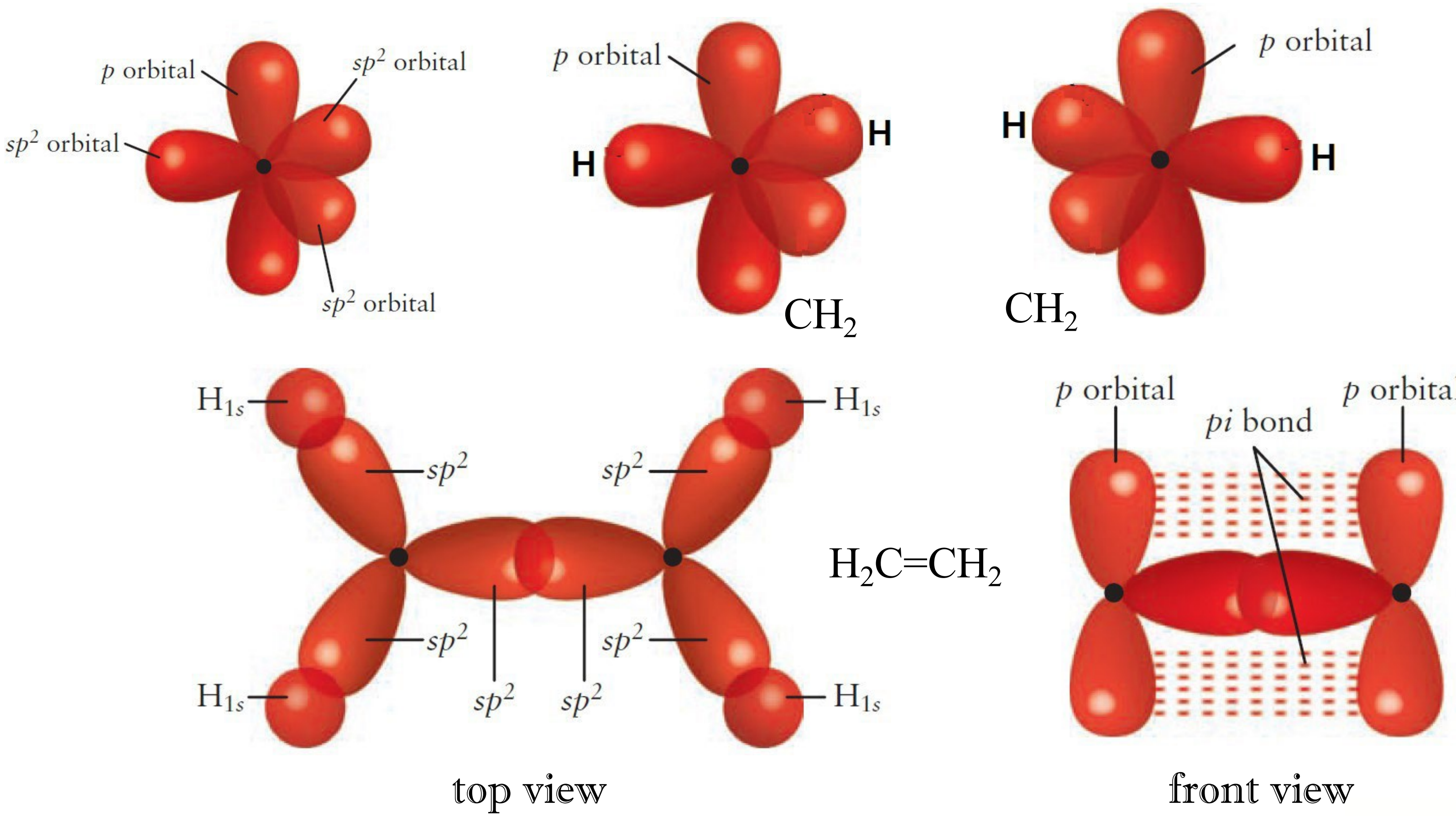
1. Angle strain
   - Bond angles of 60° cause electron pair repulsion in adjacent bonds
   - Inefficient sigma bond overlap
2. **Torsional strain** – eclipsing C-H bonds all the way around the ring



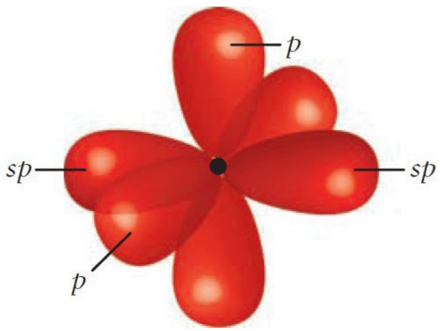


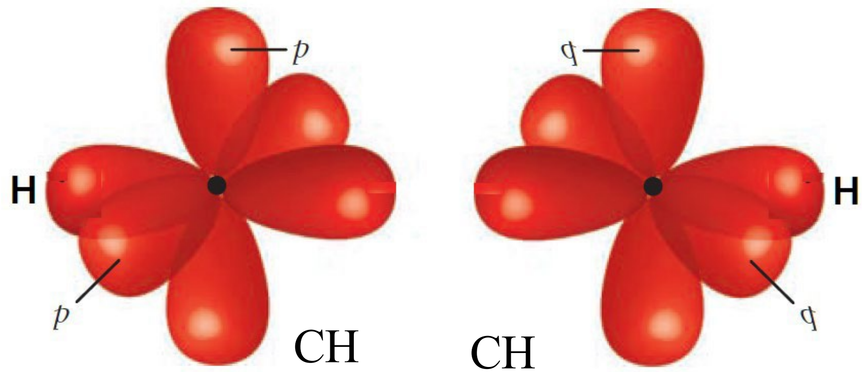
7.3 THE ALKENES AND ALKYNES

Alkenes

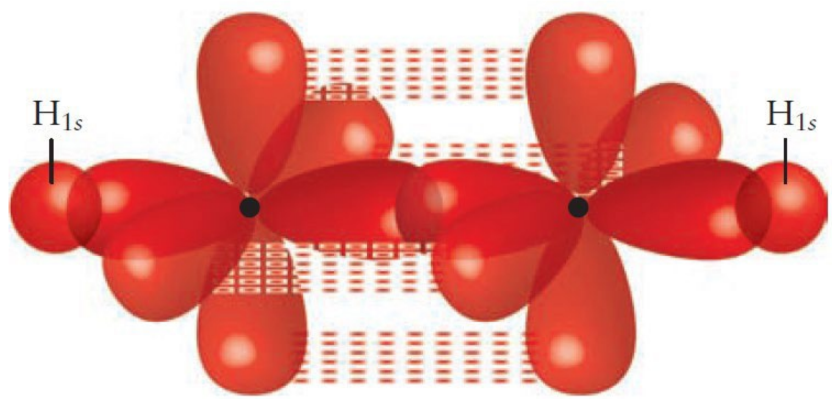


ALKYNES





HC≡CH



The Alkenes and Alkynes

- **Unsaturated hydrocarbons**

  Alkene ~ double bonds   ex. Ethene (Ethylene), C_2H_4

  Alkyne ~ triple bonds   ex. Ethyne (Acetylene), C_2H_2

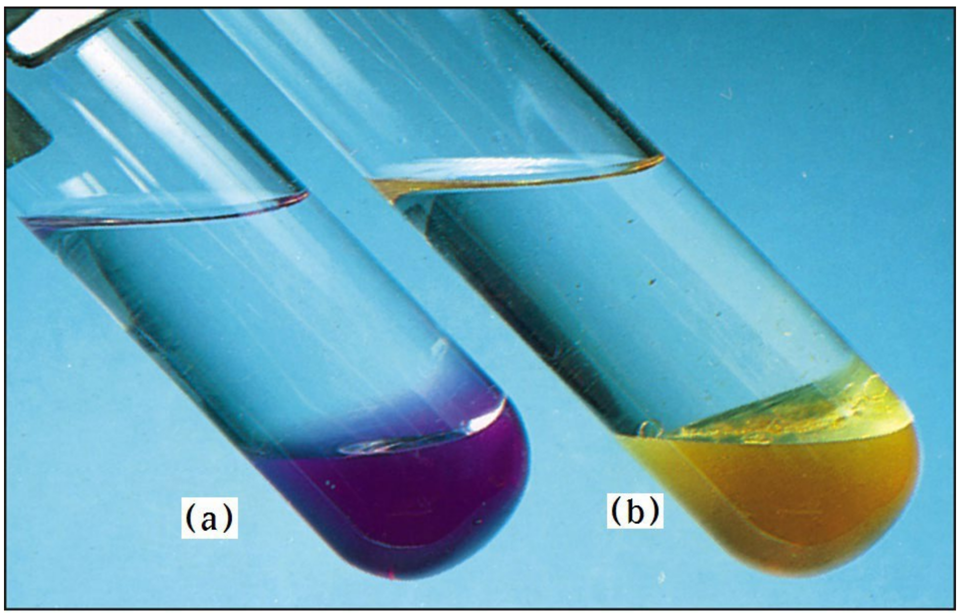


Fig. 7.10. Reaction with $KMnO_4$.
(a) No reaction with hexane.
(b) Redox reaction with 1-hexene.
Products: MnO_2 and $CH_3(CH_2)_3CH(OH)CH_2OH$

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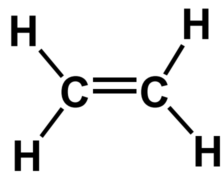
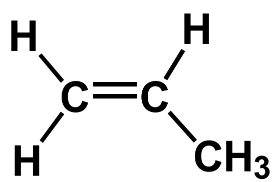
Unsaturated hydrocarbon : *Alkenes, Alkynes*

Alkene : C_nH_{2n}

C_2H_4

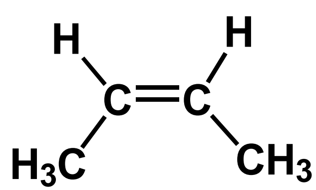


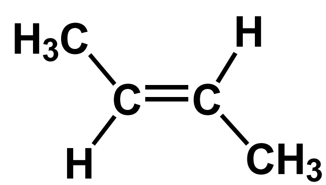
C_3H_6



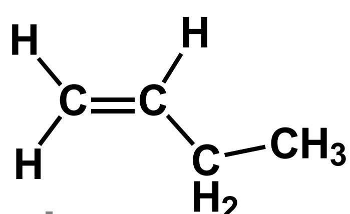
Pi bonds are more reactive than sigma bonds

C_4H_8



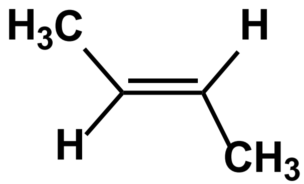


Trans isomer is more stable due to steric effect

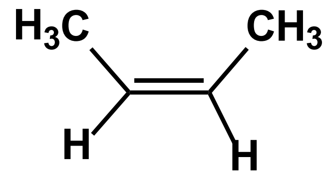


2. Stereoisomer: same bonding arrangement, different spatial positions.
입체 이성질체

geometrical isomer



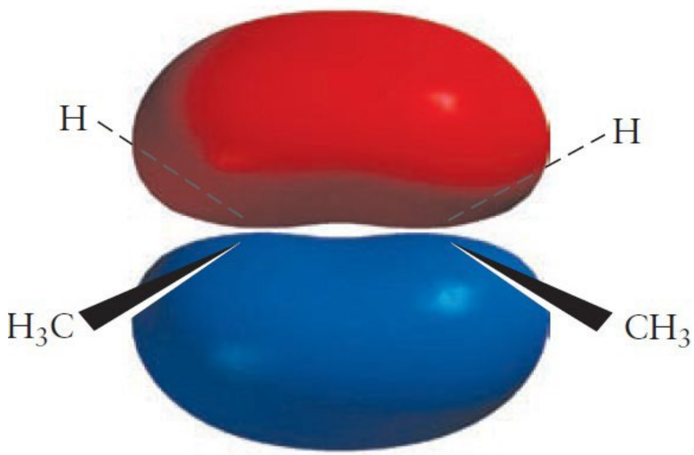
trans

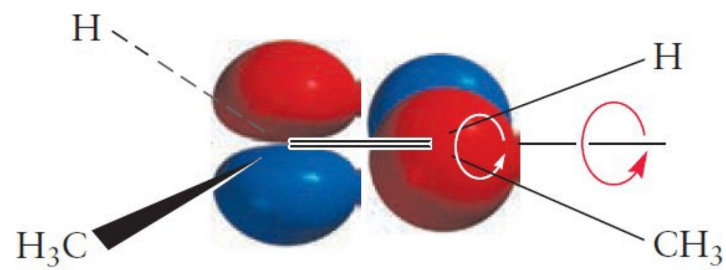


cis

rotation around the double bond requires **60 kcal/mol**

Different compounds different physical, chemical properties





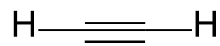
High-energy structure

p- bonding

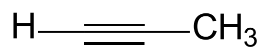
Unsaturated hydrocarbon : *Alkenes, Alkynes*

$_{n}H_{2n-2}$

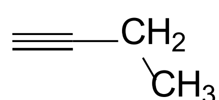
C_2H_2 :



C_3H_4 :

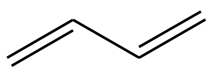


C_4H_6 :

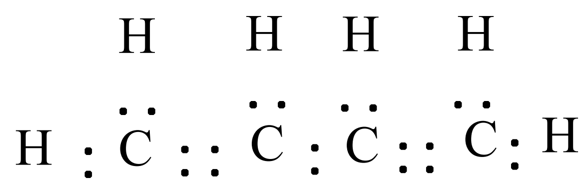


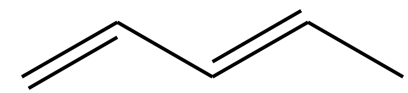
Unsaturated hydrocarbon : *Alkenes, Alkynes*

Polyenes

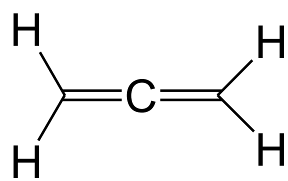


(butadiene)



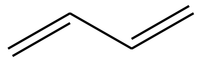


1, 3-pentadiene



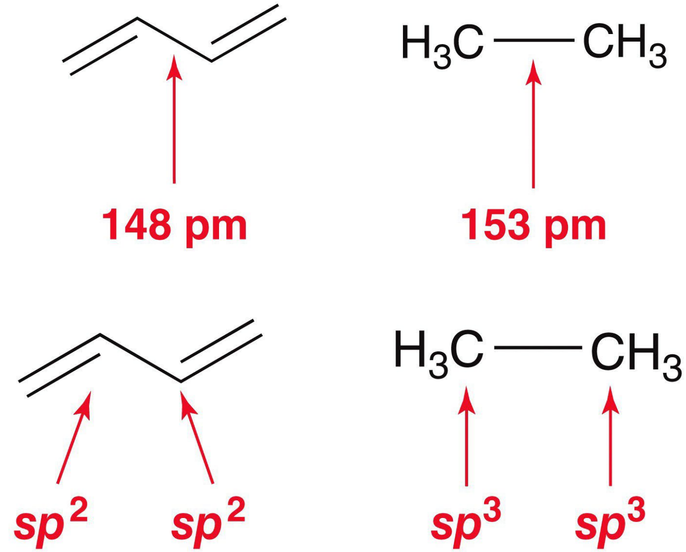
(Allene)

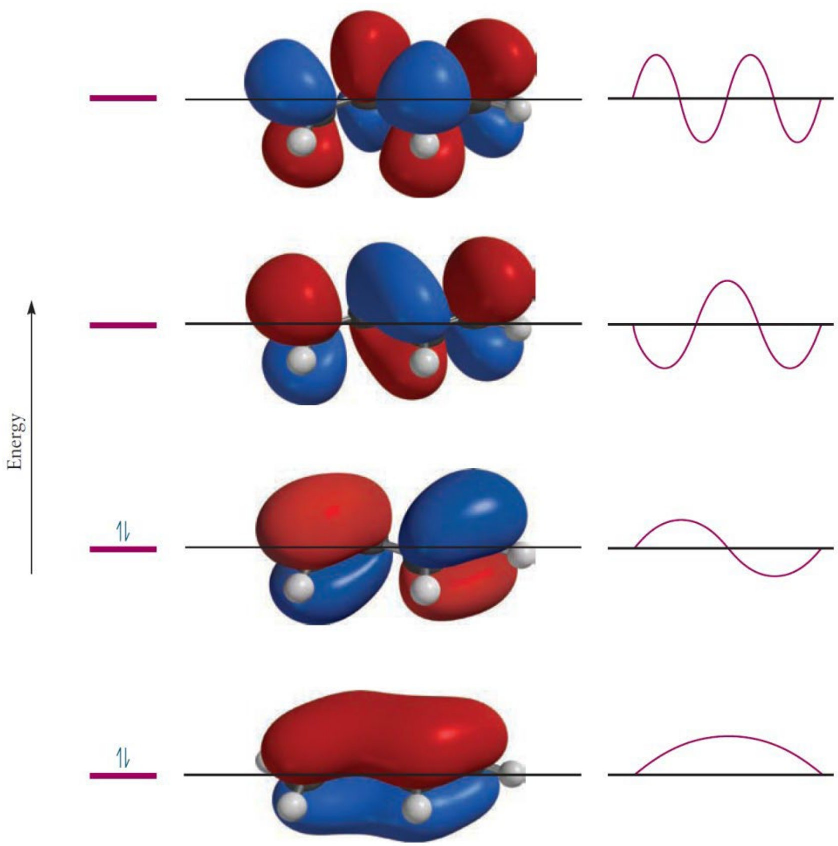
p molecular orbitals of butadiene; see chapter 20 p976



(butadiene)

Conjugated p bonding





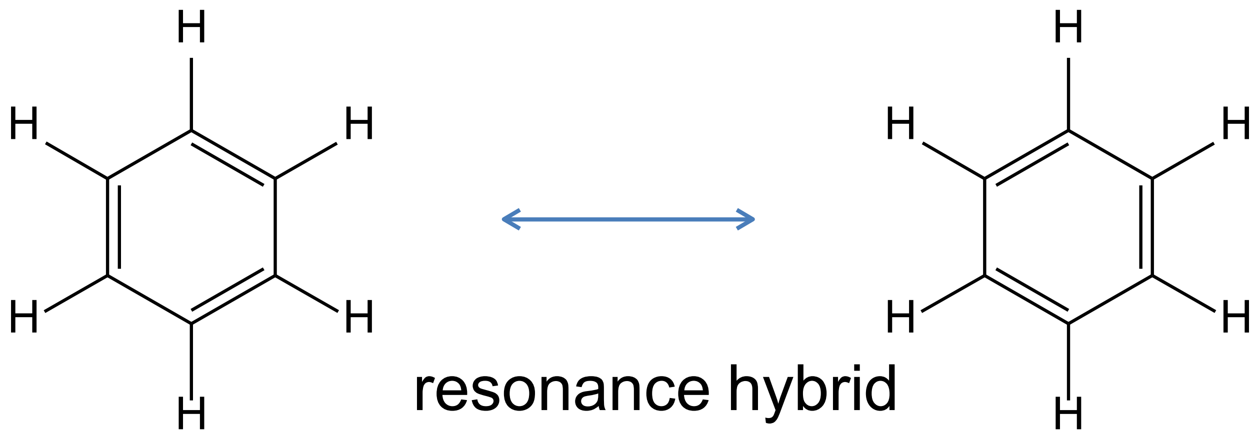
More stable than isolated two double bonds

KAIST CHEMISTRY

7.4 AROMATIC HYDROCARBONS

Hydrocarbons with $C_{4n+2}H_{2n+4}$

Benzene: simplest example C_6H_6



resonance hybrid

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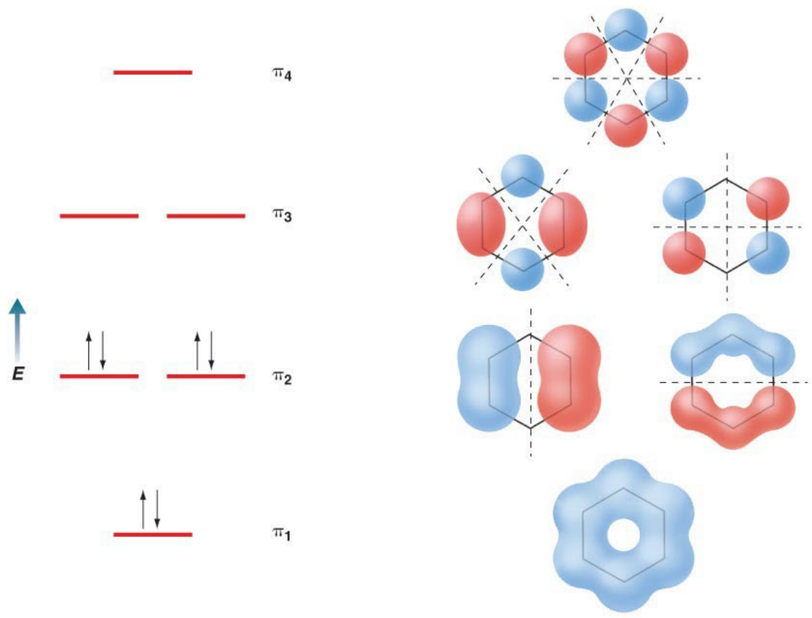
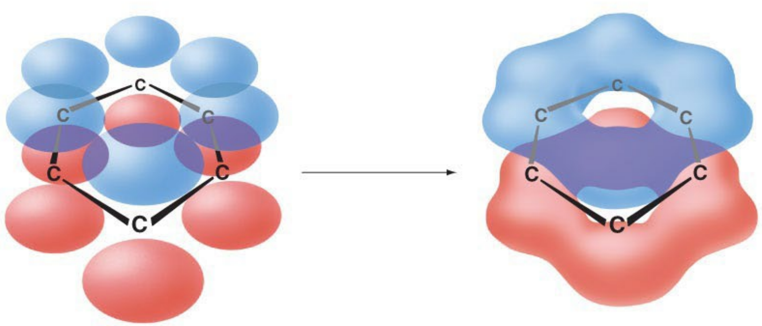
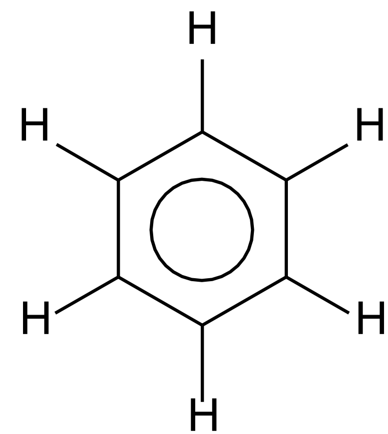
Modern view of three double bonds: *delocalized*

p molecular orbitals; view from the top





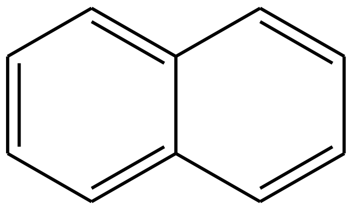


represented as circle inside

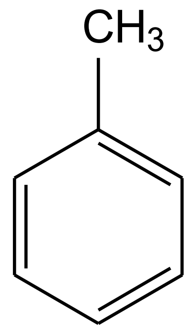
more stable than trienes

i.e. much less reactive

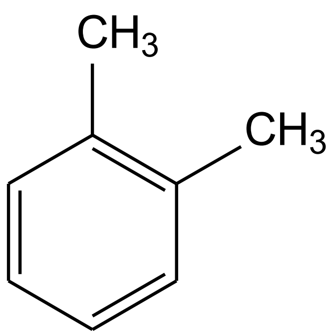
Aromatics from petroleum



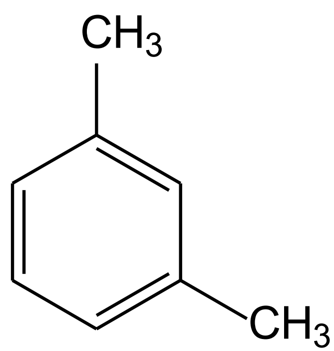
naphthalene



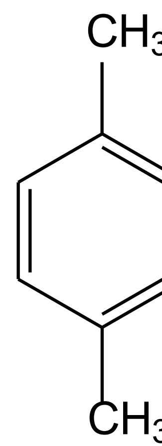
toluene



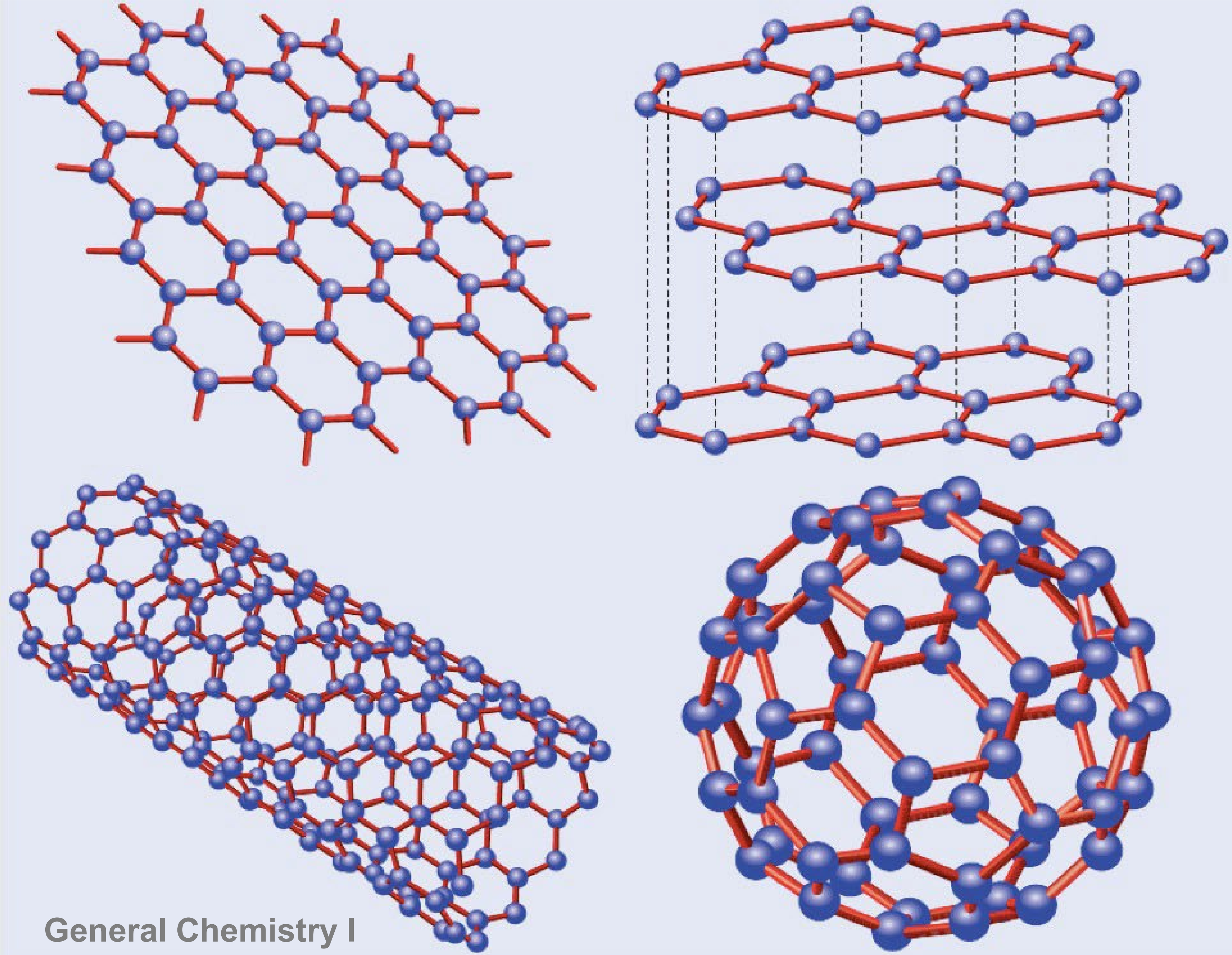
***o*-xylene**



***m*-xylene**



***p*-xylene**



7.6 FUNCTIONAL GROUPS AND ORGANIC REACTIONS

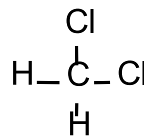
TABLE 18.4

Common hydrocarbon derivatives

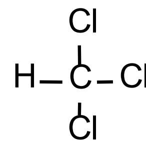
Derivative	Functional group	General formula	Examples	
Halide	—Cl, —Br	R—Cl	CH_2Cl_2, methylene choride (dichloromethane)	$CH_3CHClCH_3$ isopropyl chloride (2-chloropropane)
Alcohol	—OH	R—OH	CH_3OH methanol	CH_3CH_2OH ethanol
Ether	—O—	R—O—R′	CH_3CH_2—O—CH_2CH_3 Diethyl ether	CH_3—O—$C(CH_3)_3$ Methyl *t*-butyl ether (MTBE)
Ketone	—C(=O)—	R—C(=O)—R′	CH_3—C(=O)—CH_3 Acetone (propanone)	CH_3—C(=O)—CH_2CH_3 Methyl ethyl ketone (MEK) (butanone)
Aldehyde	—C(=O)—H	R—C(=O)—H	H—C(=O)—H Formaldehyde (methanal)	CH_3—C(=O)—H Acetaldehyde (ethanal)
Carboxylic acid	—C(=O)—OH	R—C(=O)—OH	CH_3—C(=O)—OH Acetic acid (ethanoic acid)	CH_3CH_2—C(=O)—OH Propionic acid (propanoic acid)

$\overset{\delta+}{C}$ —— $\overset{\delta-}{X}$

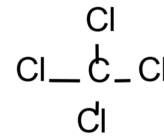
Alkyl halides



Methylene chloride



Chloroform

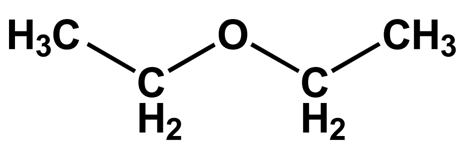


Carbon tetrachloride

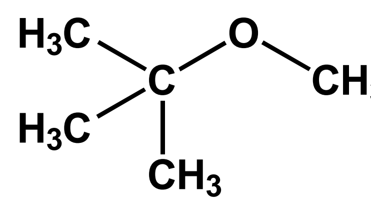
$\overset{\delta+}{C}$ —— $\overset{\delta-}{OH}$

1. Alcohol : R—OH

2. Ether : R—O—R'

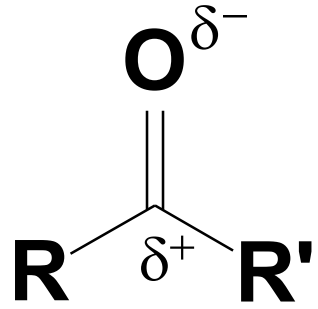


Diethyl ether -- "Ether"



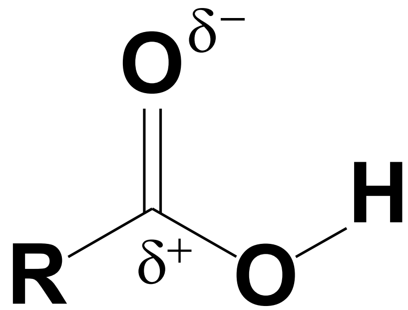
MTBE

3. Aldehyde, Ketone :

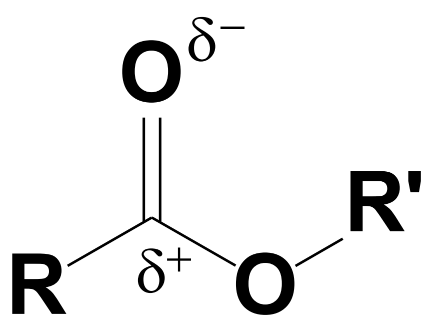


R’ = H : aldehyde

4. Carboxylic Acid :



5. Ester :



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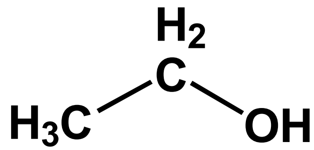
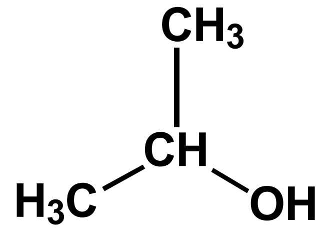
Alcohol   R-OH

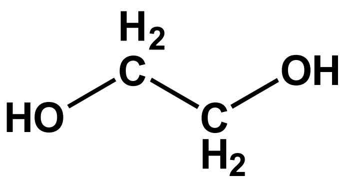
Methanol



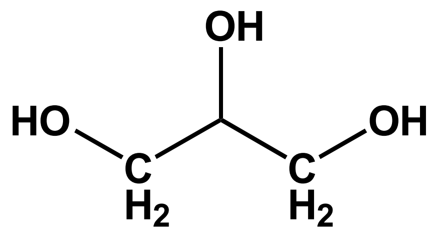
Ethanol
(primary alcohol)



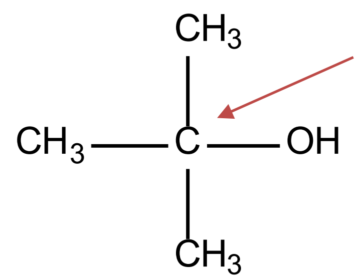
iso-Propanol
(secondary alcohol)



Ethylene Glycol

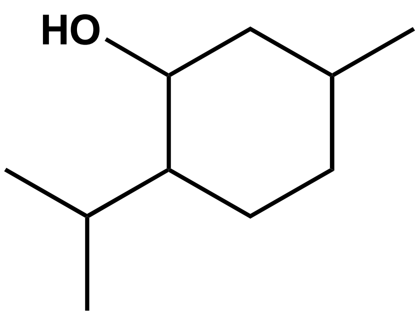


Glycerol

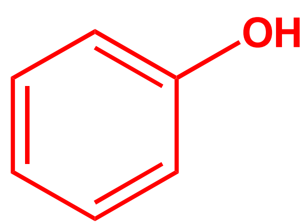


(tertiary alcohol)

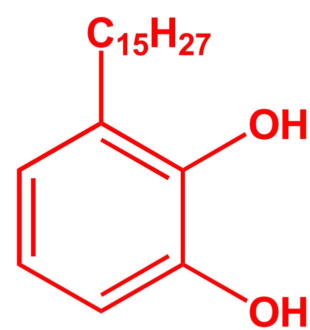
t-butyl alcohol



Menthol

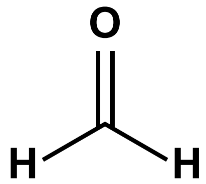


Phenol

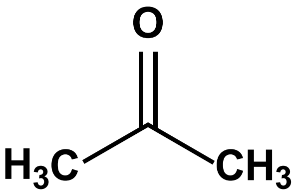


Urushiol

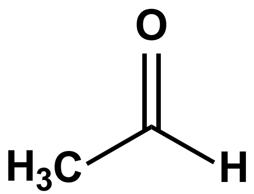
Aldehyde, Ketone



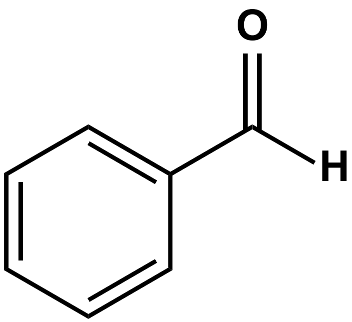
Formaldehyde



Acetone

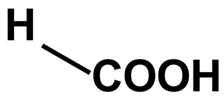


Acetaldehyde

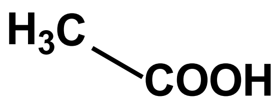


Benzaldehyde
(cherry flavor)

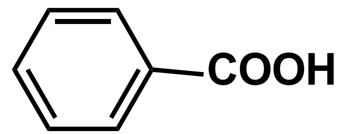
Carboxylic acid



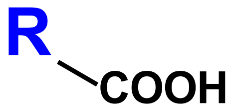
Formic acid



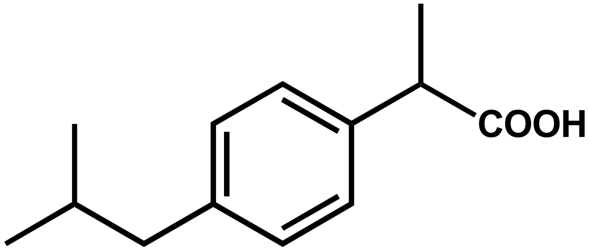
Acetic acid



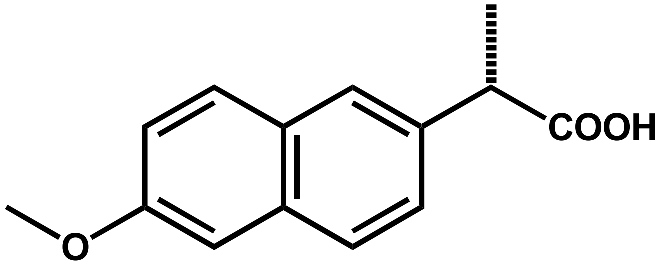
Benzoic acid



(more acidic with more electron withdrawing R group)

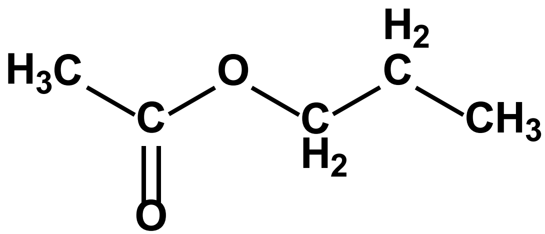


Ibuprofen (부루펜)

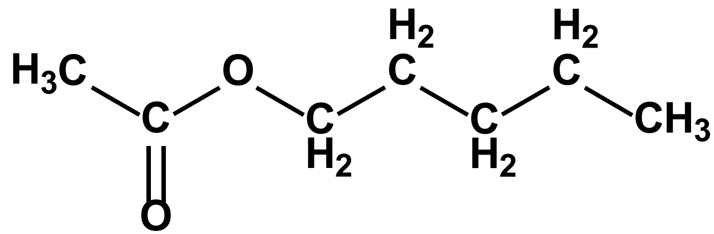


Naproxen (낙센)

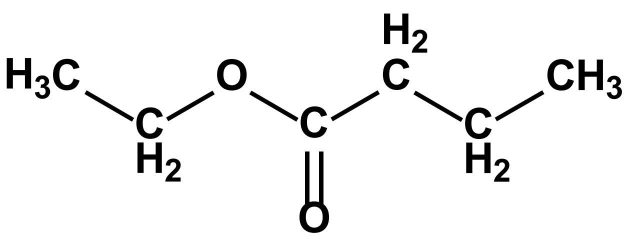
Ester



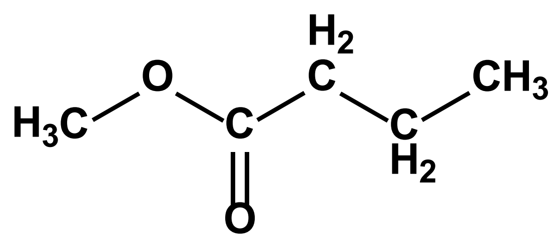
Pear



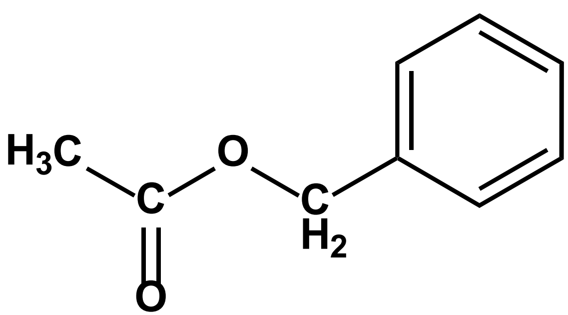
Banana



Pineapple

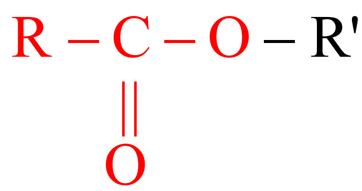


Apple

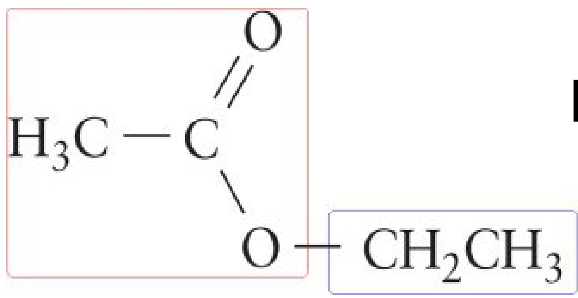


Jasmine

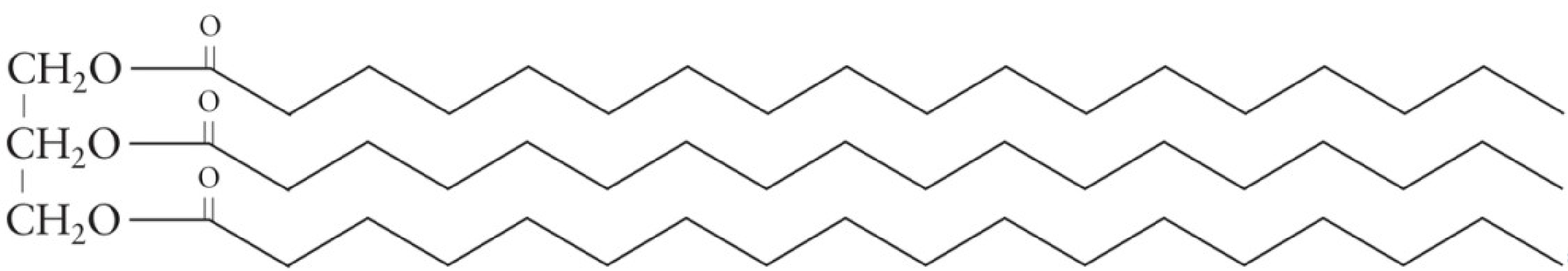
Esters, –oate,



- Product of the reaction between a carboxylic acid and an alcohol
- Fragrant odors, flavors of fruits

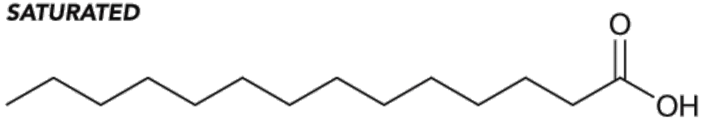
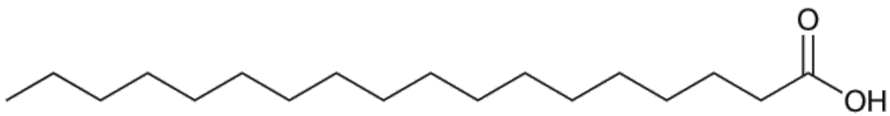
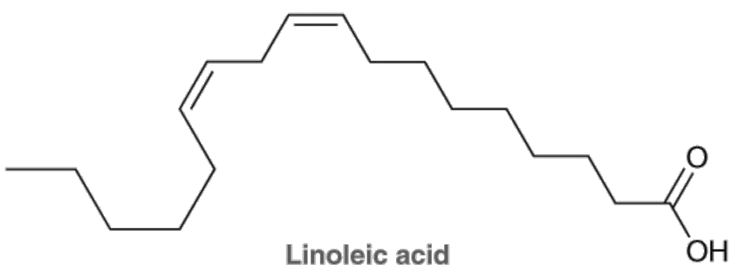
❖ 

Ethyl ethanoate (ethyl acetate)



Tristearin, $C_{57}H_{110}O_6$: animal fat

Triglycerides

STRUCTURE AND NAME	NUMBER OF CARBON ATOMS	NUMBER OF CARBON-CARBON DOUBLE BONDS	MELTING POINT (°C)
SATURATED			
 Myristic acid	14	0	54
 Stearic acid	18	0	69
UNSATURATED			
 Linoleic acid	18	2	–5

Trans fats (트랜스지방脂肪)

❖ Hydrogenation of oils (ester of cis-unsaturated fatty acids)

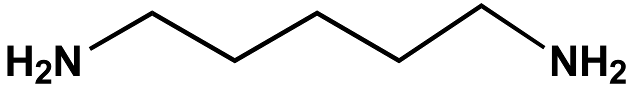
- Saturated fats with higher m. p.:

  → solid, good for baking and extended shelf-life

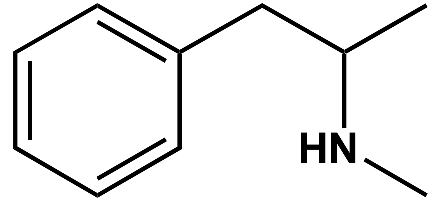
- Remaining double bonds converted from

  cis to trans isomers → bad for health!

●Amine●

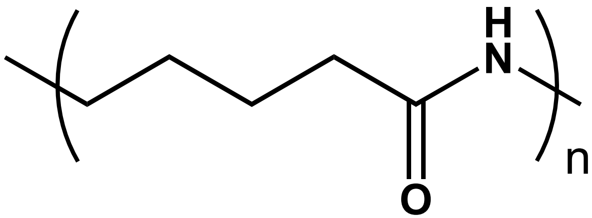


Cadaverine (시체썩는 냄새)

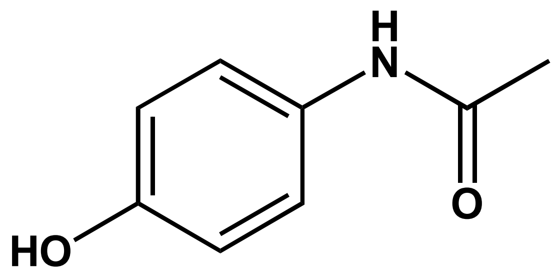


Methamphetamine (필로폰)

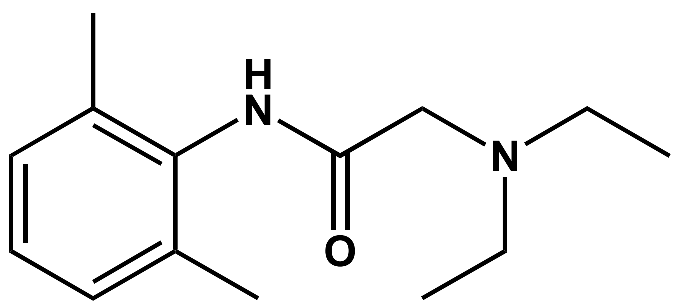
●Amide●



Nylon-6

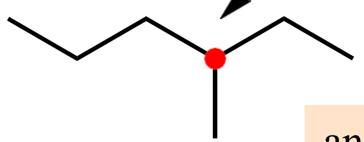


Acetaminophen (타이레놀)

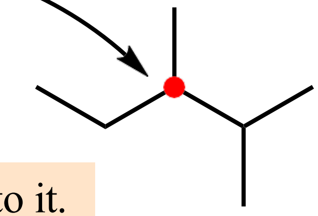


Lidocaine (국소마취제)

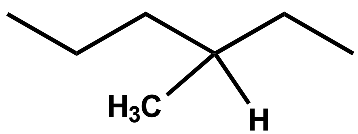
Stereoisomers

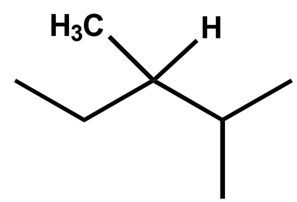


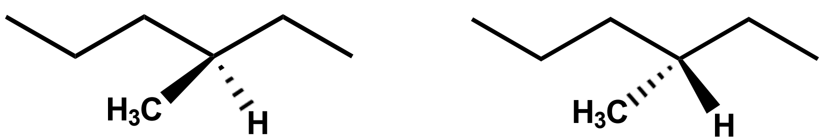
Chiral Center



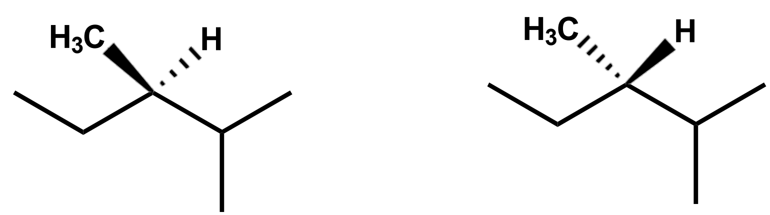
an atom that has all four different groups attached to it.





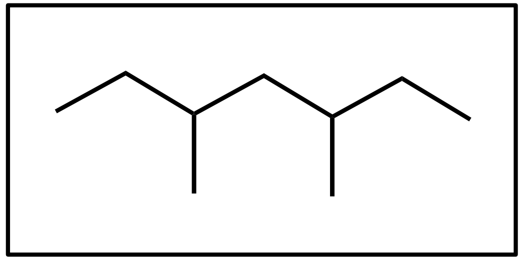


enantiomers

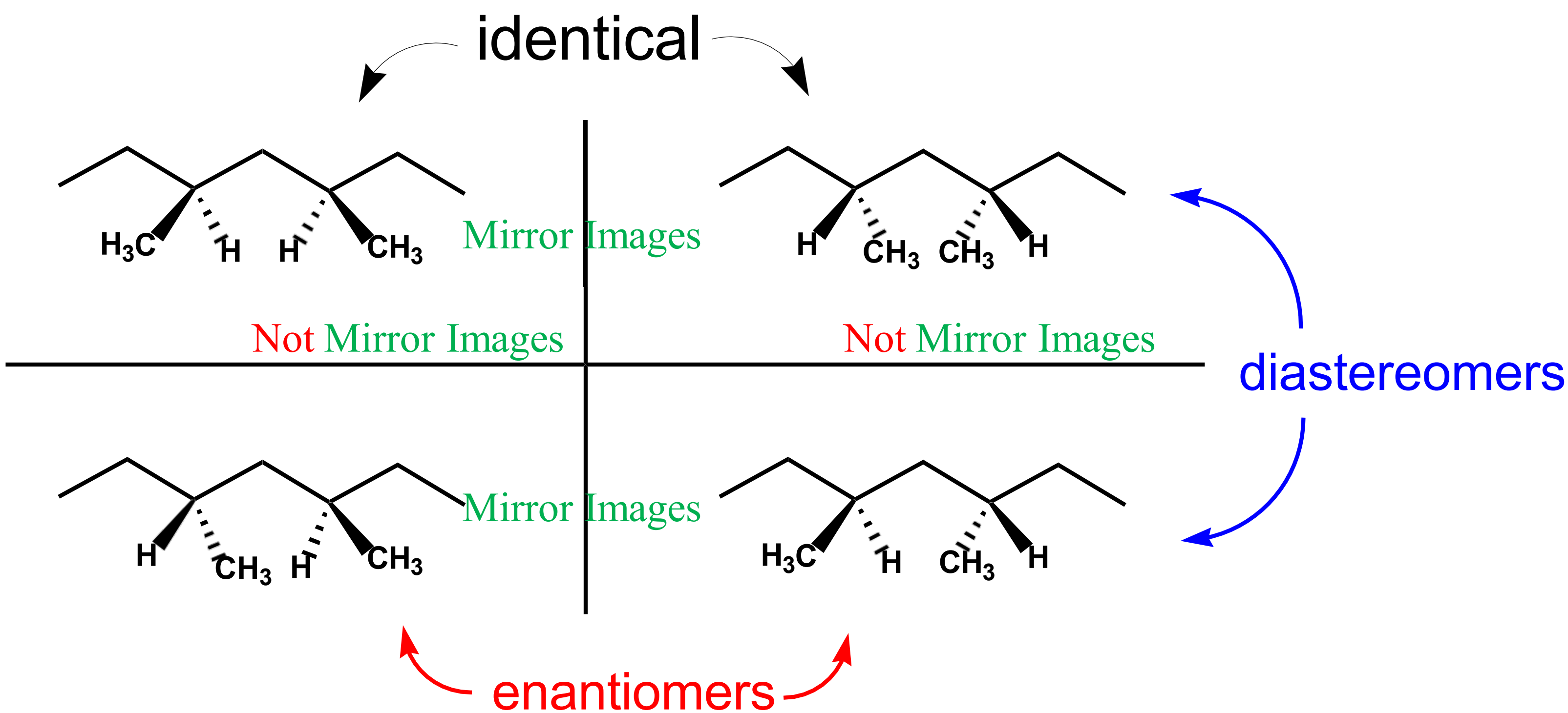


enantiomers

Stereoisomers

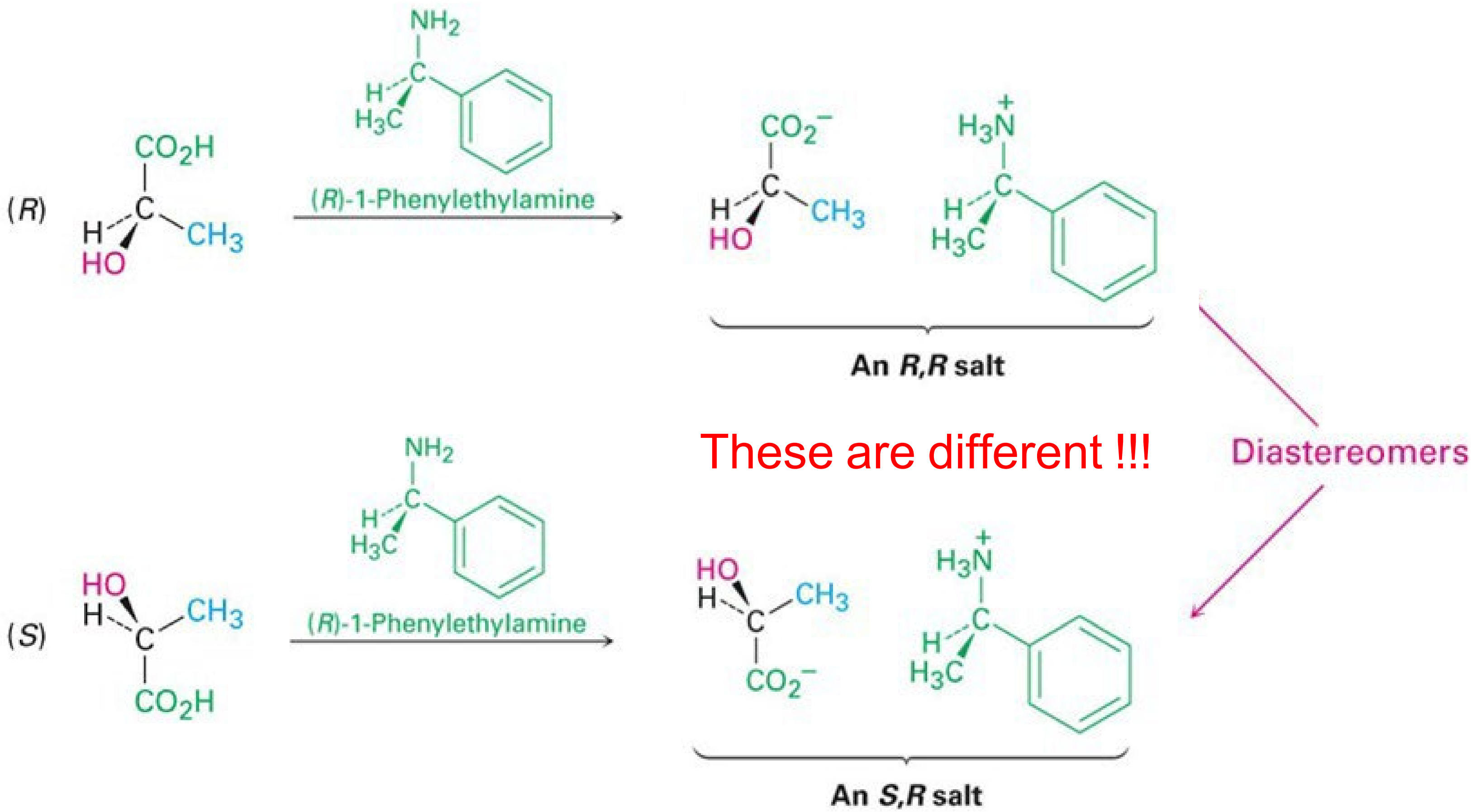


Two chiral centers make the situation complicated !



Diastereomers: Stereoisomers are not mirror images of one another and non-superimposable.

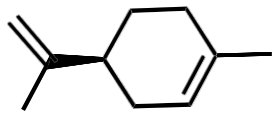
Stereochemistry



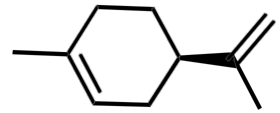
- Separation of enantiomers
- Recognition of enationmers differently

Importance of Stereochemistry

Limonene

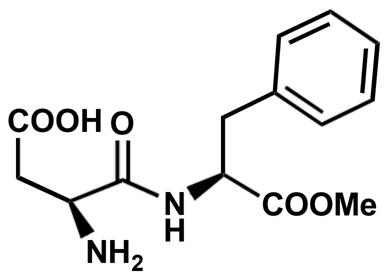


lemon

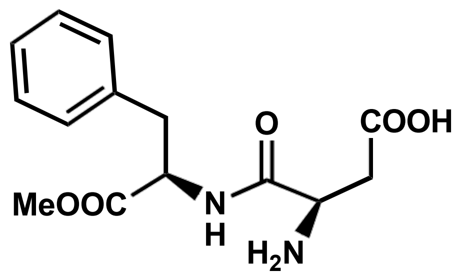


orange

Aspartame

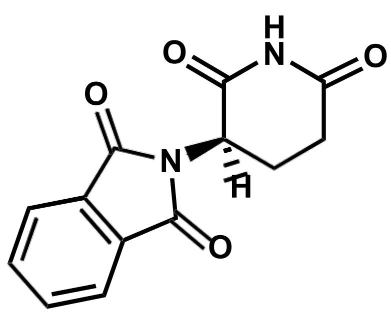


sweet

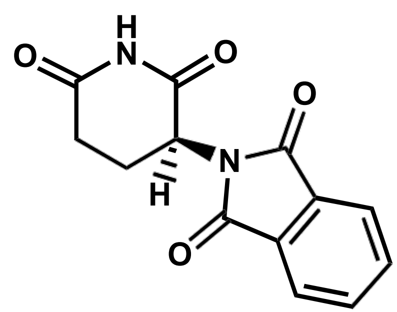


bitter

Thalidomide



sedative

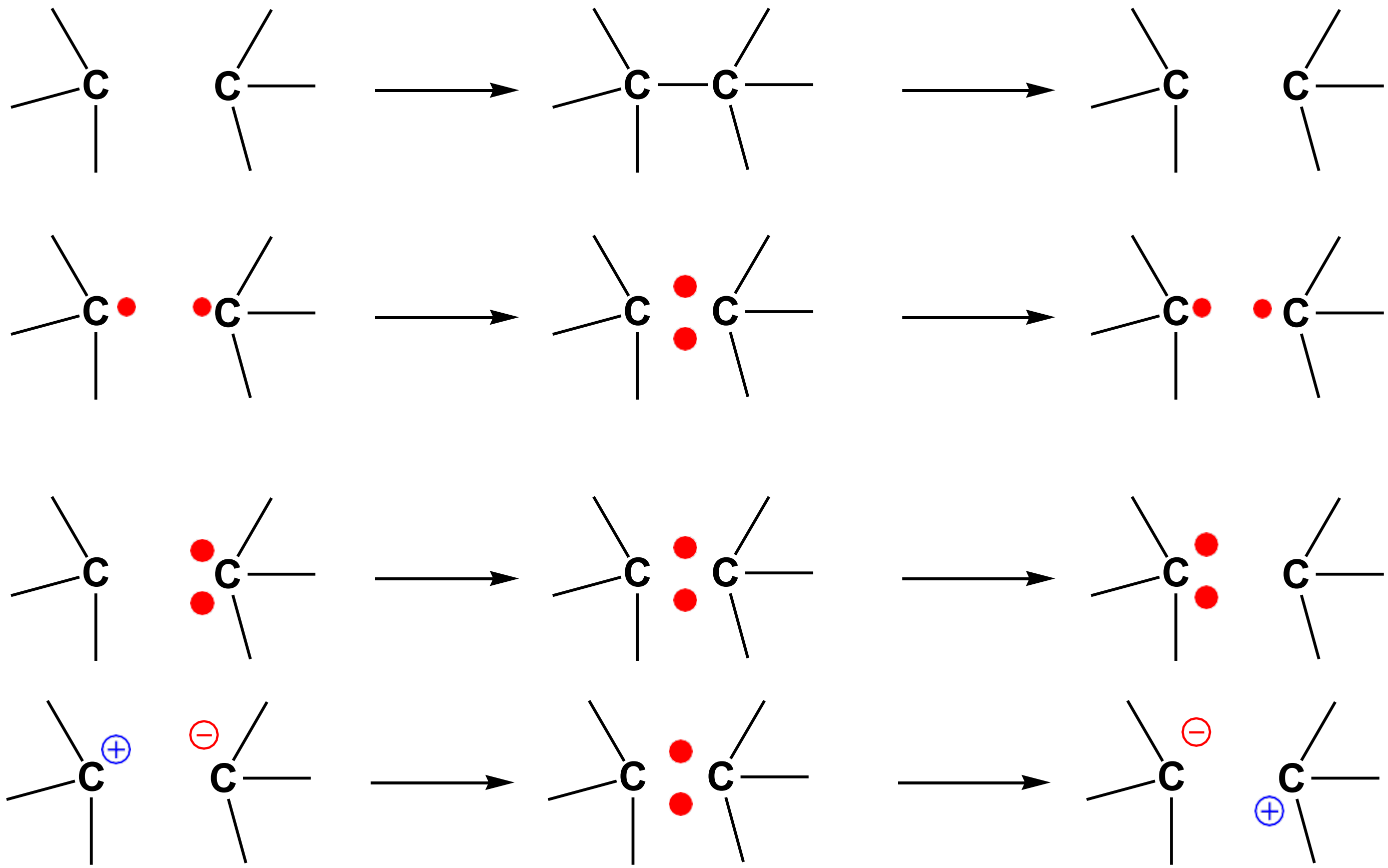


teratogenic

Reactions of organic compounds

1. carbon-carbon bond formation & cleavage

radical



Carbocation *Carbanion*

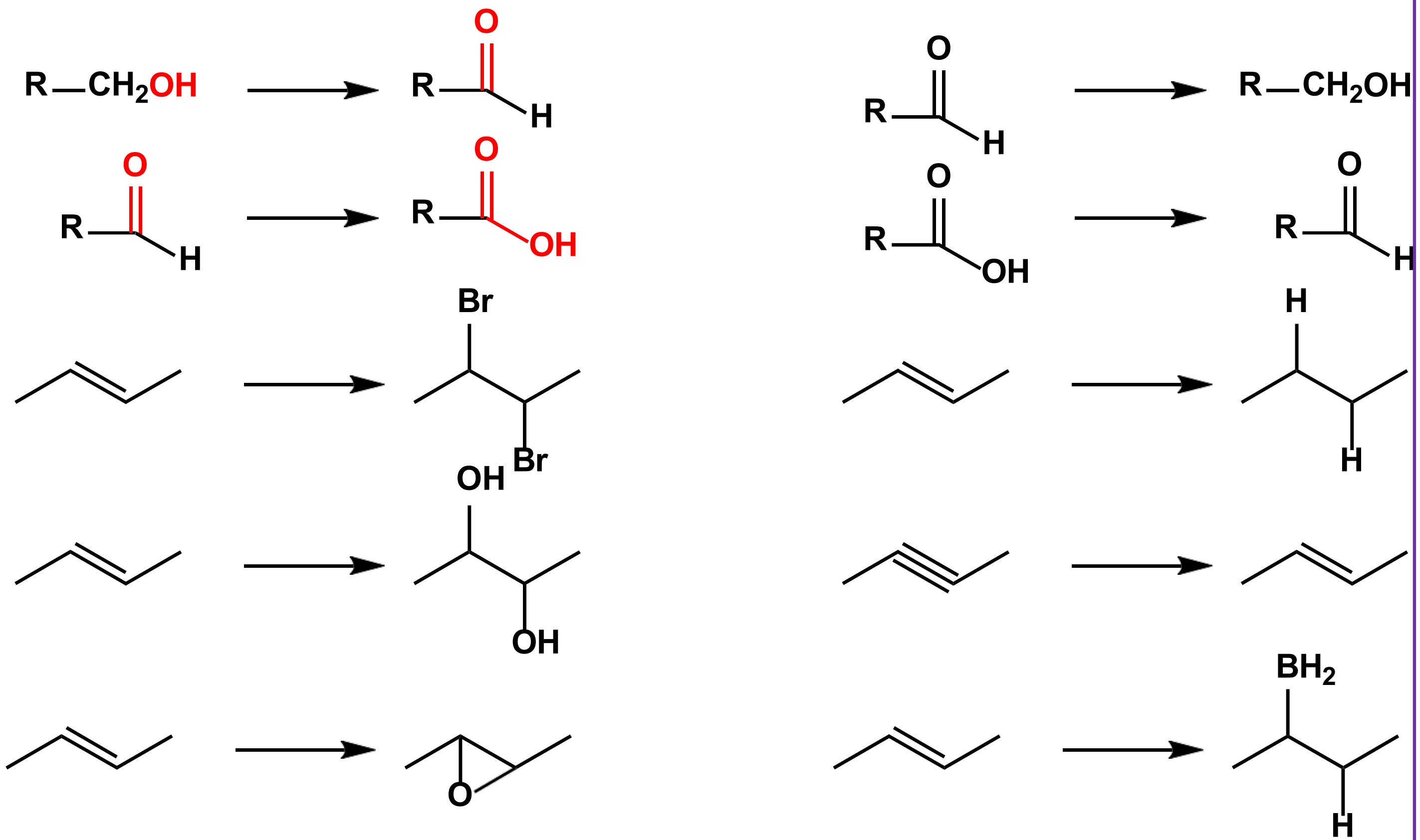
Lewis acid *Lewis base*

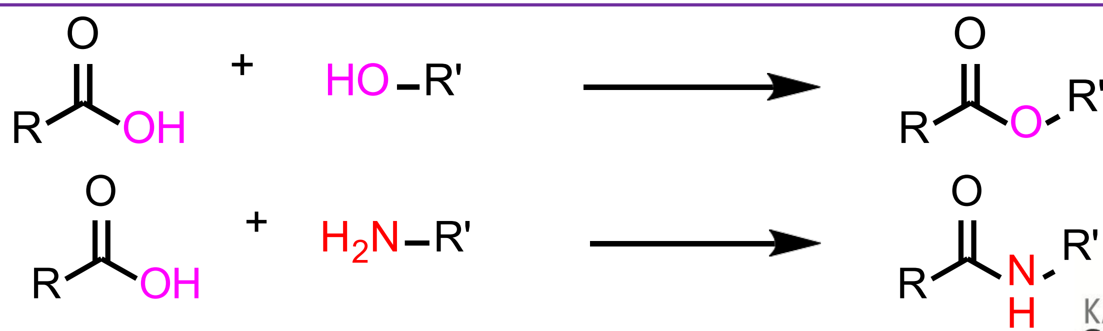
2. general reactive intermediates

A^{+} A^{-} $A^{\bullet}$

Conversion of organic functional groups

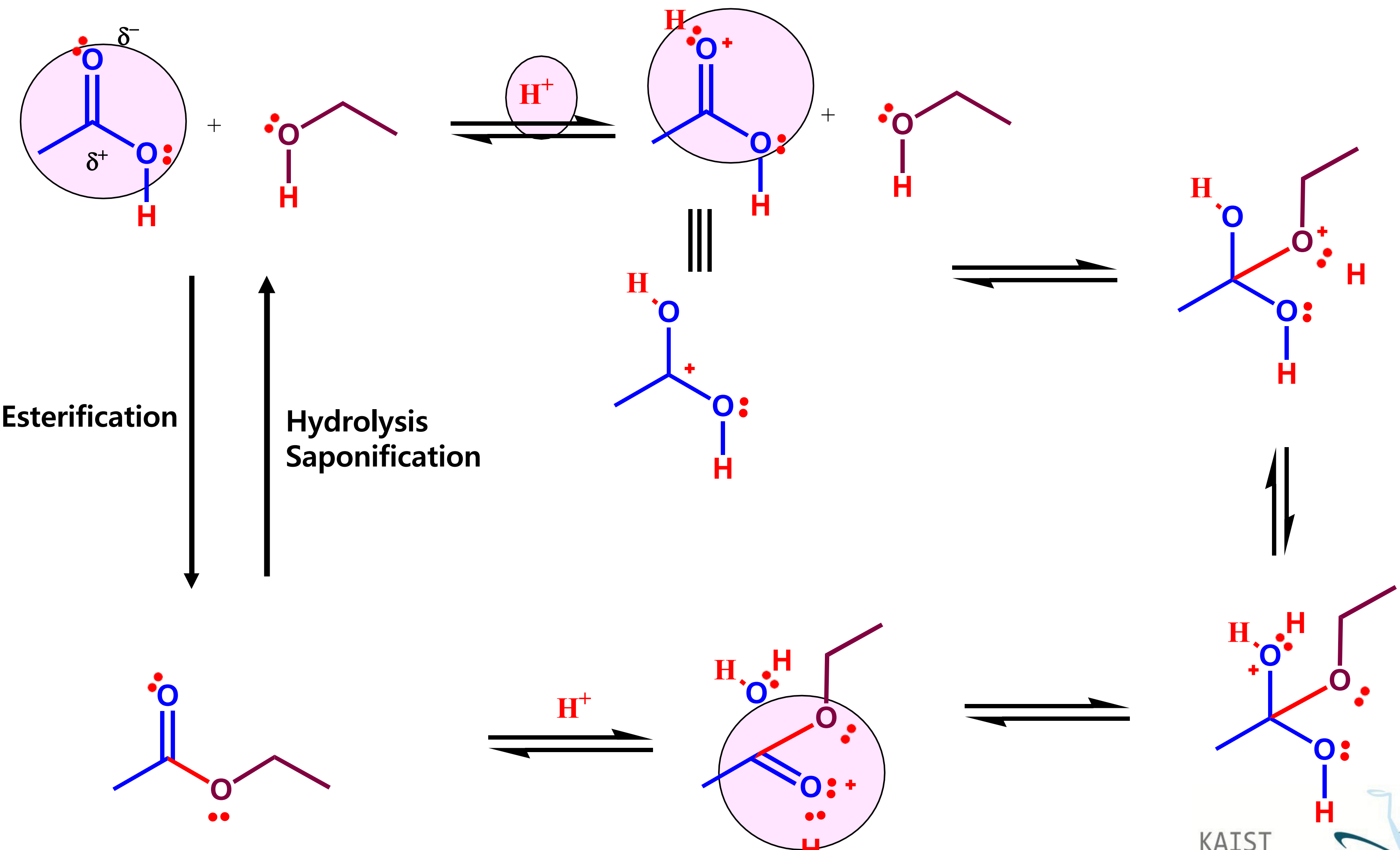
- Oxidation



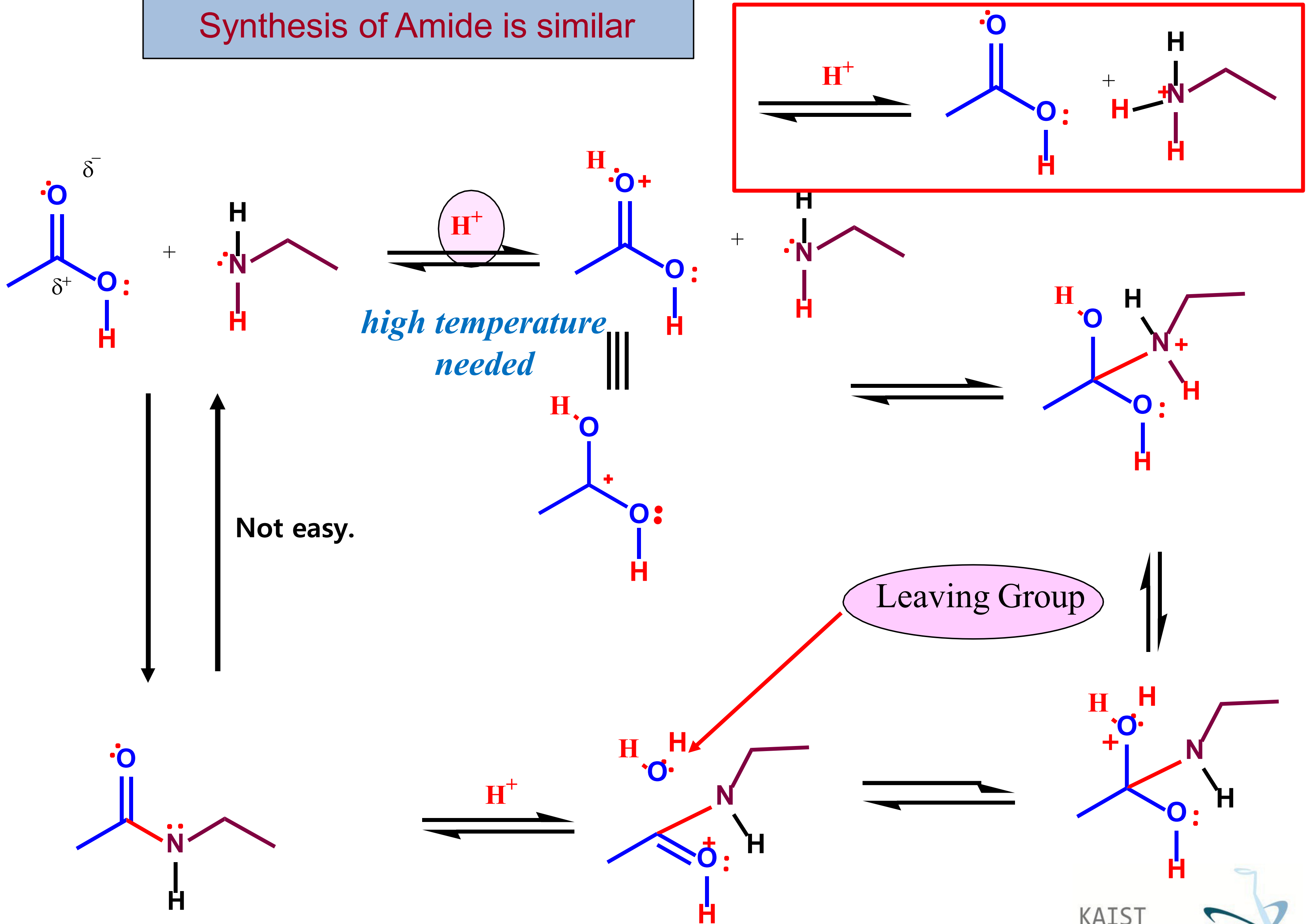


Synthesis & reactions of Esters
How does esters form?

Fischer Esterification



Synthesis of Amide is similar



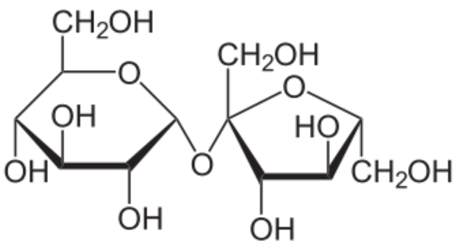
7.7 PESTICIDES AND PHARMACEUTICALS

Impact of Organic Compounds to the World

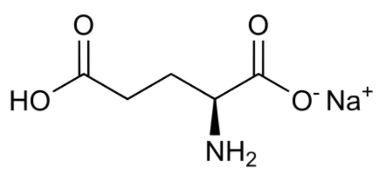
➢ 90% of matter on earth are organic!

i.e. organic compounds are everywhere around us.

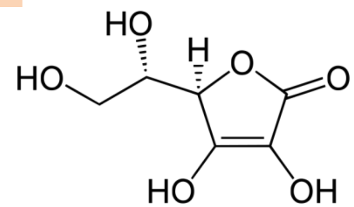
In food



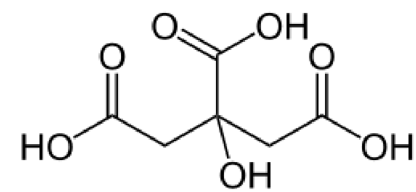
Sucrose (sugar)



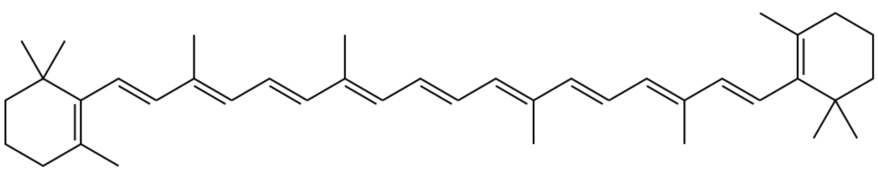
MSG (glutamic acid)



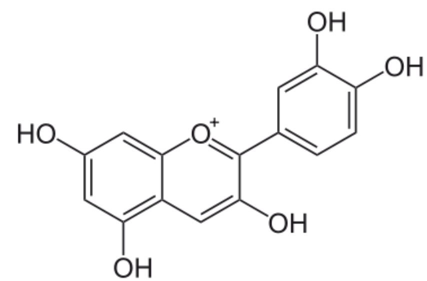
Vitamin C



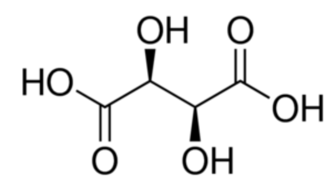
Citric acid (Lemon)



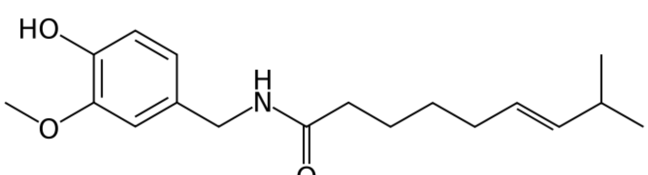
b-carotene (carrot)



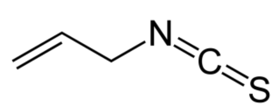
Cyanidin (anthocianin)



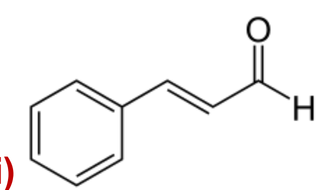
Tartaric acid (grape)



Capsaicin (pepper)

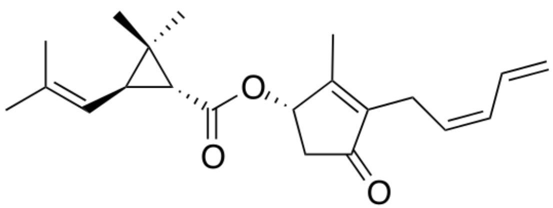


Isothiocyanate (wasabi)

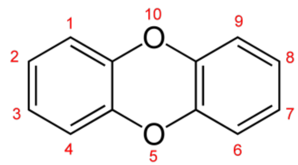


Cinnamaldehyde (cinnamon)

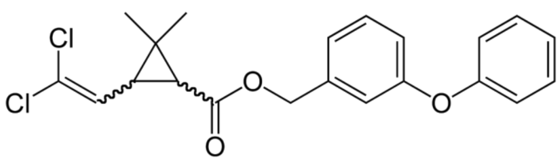
From nature (natural products) and beyond……



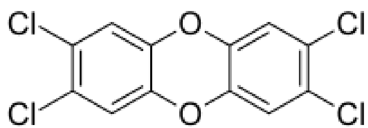
Pyrethrin I (from crysanthmum)
weak insecticide



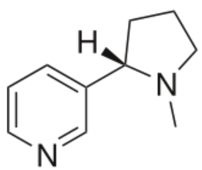
Dioxin



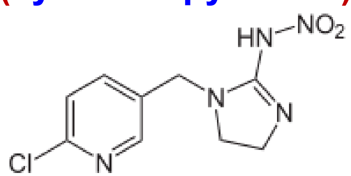
Permethrin (synthetic pyrethrin)



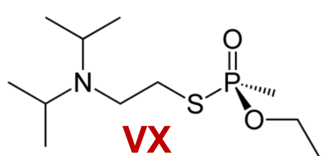
TCDD
(고엽제성분)



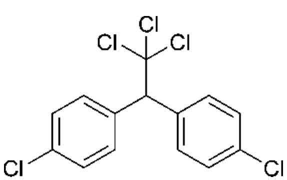
nicotine



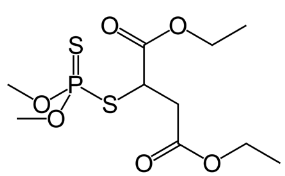
imidacloprid



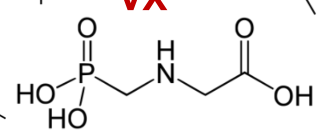
VX



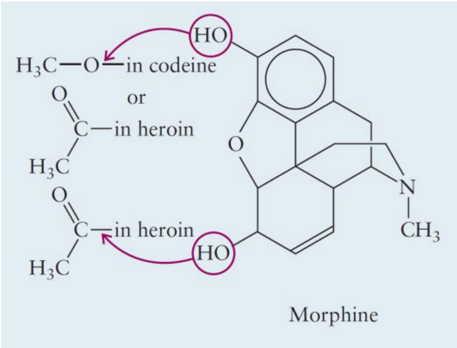
DDT

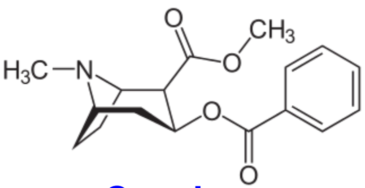


malathion

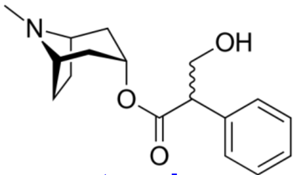


Glyphosate (weed killer)

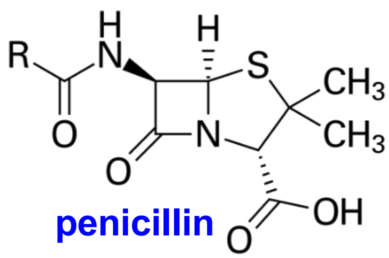




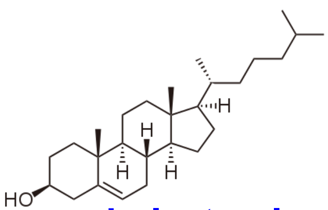
Cocaine



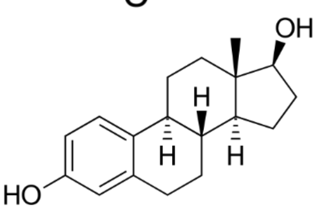
atropine



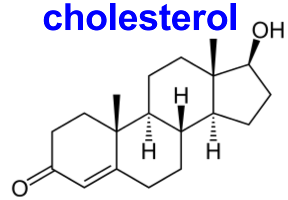
penicillin



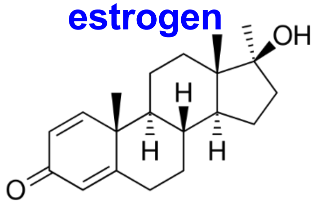
cholesterol



estrogen

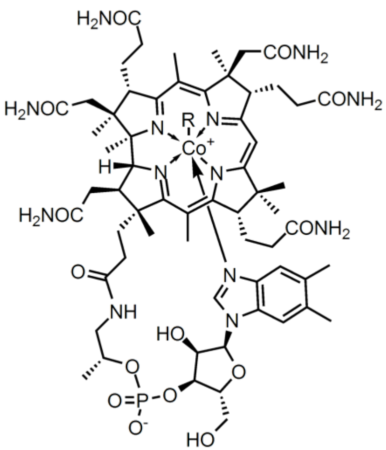


testosterone



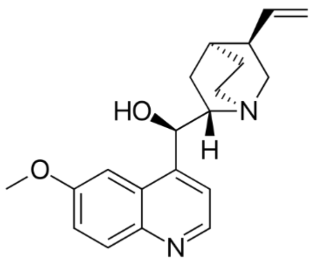
Dianabol

More natural products

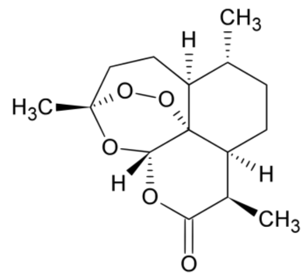


R = 5'-deoxyadenosyl, Me, OH, CN

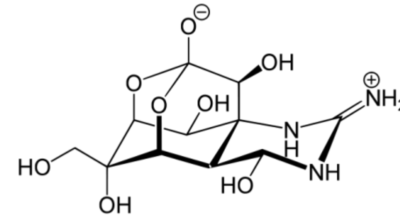
Vitamin B12



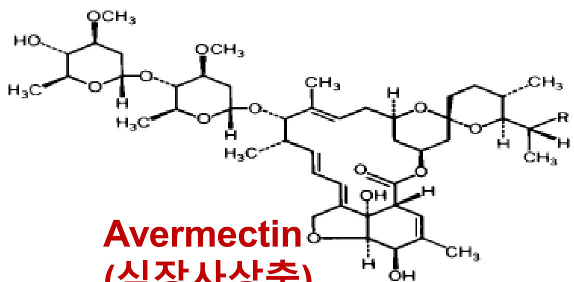
quinine



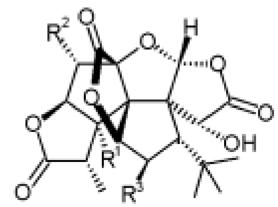
artemisinine



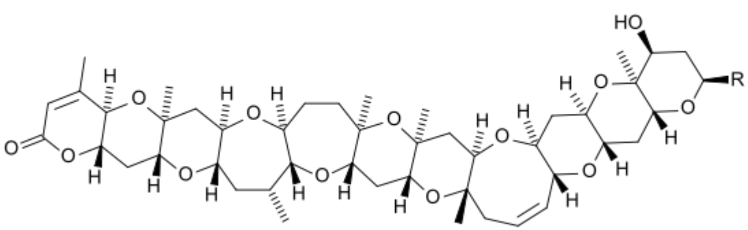
Tetrodotoxin (fugu fish, 복어)



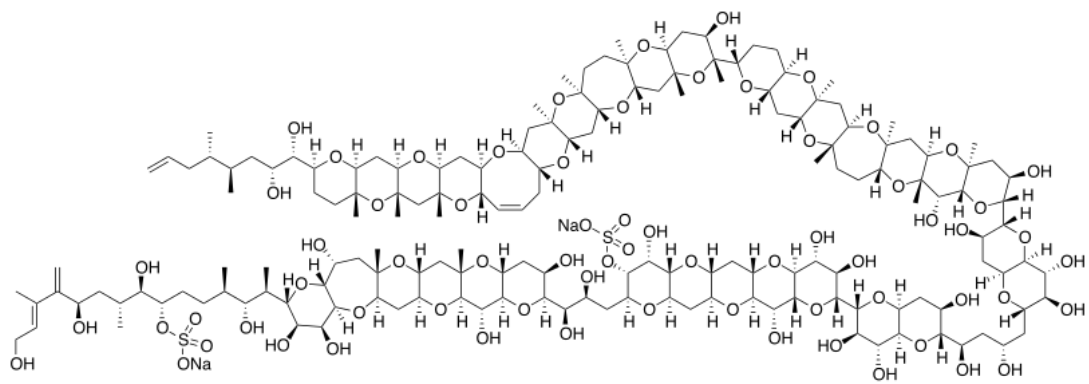
Avermectin (심장사상충)



Ginkolide (은행)

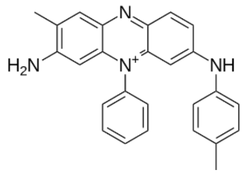


brevetoxin (red tide, 적조)

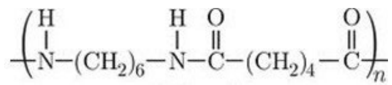


Maitotoxin, $C_{164}H_{256}O_{68}S_2Na_2$, M.W.= 3422

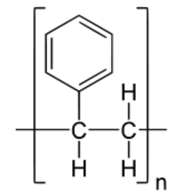
Significant organic molecules made by chemists



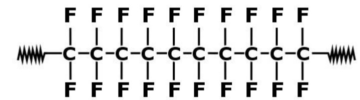
Mauveine (dye, purple)



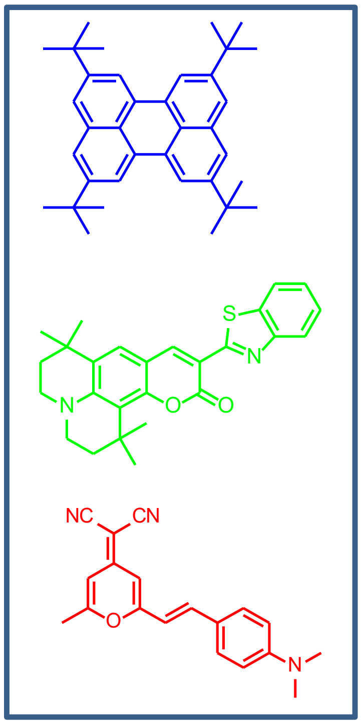
Nylon 66



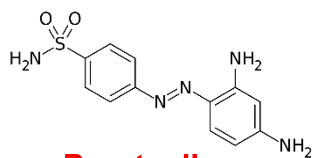
polystyrene



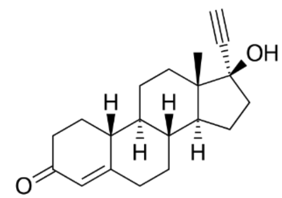
teflon



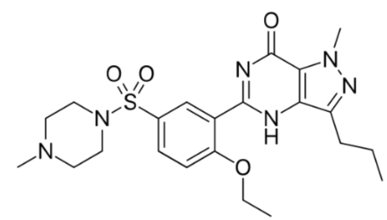
OLED materials



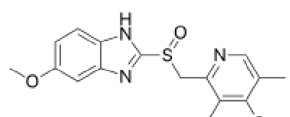
Prontosil (antibiotic)



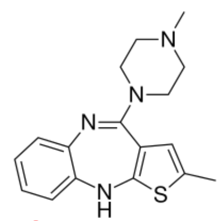
Norethisterone (contraceptive)



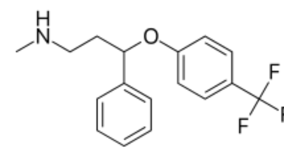
viagra



Omeprazole (antiulcer)



Olanzapine (schizoprenia)



Prozac (antidepressant)