

HALOGEN ELEMENTS (XVII GROUP PSE)

Fluorine (F)
Chlorine (Cl),
Bromine (Br),
Iodine (I)
Astat (At)
Tennesine (Ts)

117
Ts
Tennesine
[294]

9	17	10
F Fluorine 3.2×10^{-5}		
17		18
Cl Chlorine 1.5×10^{-3}		
35		36
Br Bromine 2.9×10^{-6}		
53		54
I Iodine 1.60×10^{-7}		
85		86
At Astatine		
117		118
Ts Tennesine		

Prof. Dr. Nedeljko Manojlović

HALOGEN ELEMENTS (XVII GROUP PSE)

Fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At).

Halos and gen in translation means **forms salts**.

The elements of this group **are non-metals**, they are colored and have similar chemical properties and physical characteristics.

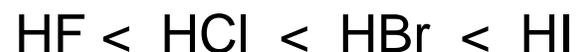
They are very reactive.

Halogenation with chlorine is called chlorination, with bromine is called bromination.

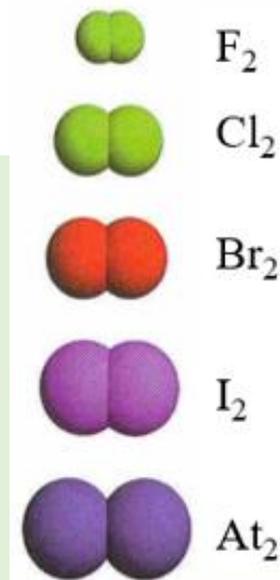
Halogen elements are oxidizing agents. The reactivity of the halogen elements decreases in the group going from top to bottom:



Halides form acids of the HX type (HF, HCl, HBr and HI). Acid strength increases in the following order:



Hydrofluoric acid (HF) salts are fluorides, **hydrogen chloride** (HCl) salts are called chlorides, **hydrogen bromide** (HBr) are bromides, and **hydrogen iodide** (HI) salts are iodides.



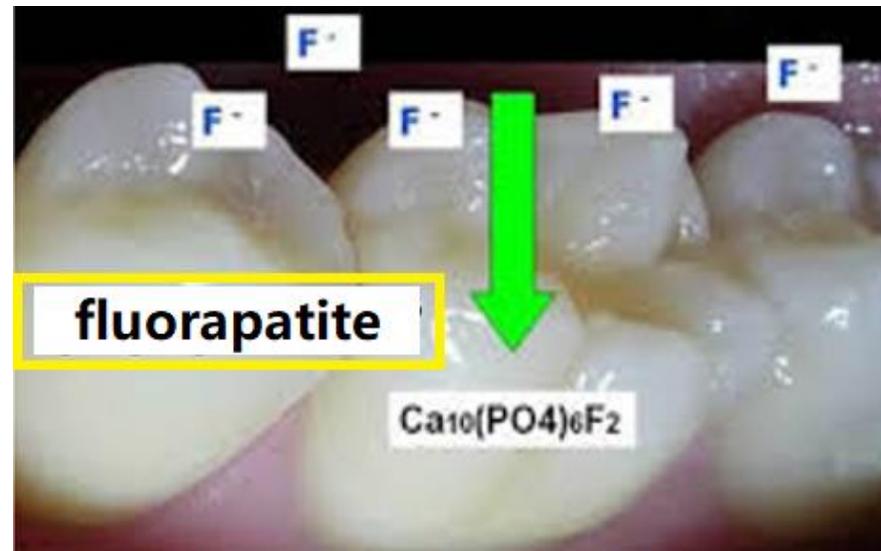
17		10
9	F Fluorine 3.2 x 10 ⁻⁵	10
17	Cl Chlorine 1.5 x 10 ⁻³	18
35	Br Bromine 2.9 x 10 ⁻⁶	36
53	I Iodine 1.60 x 10 ⁻⁷	54
85	At Astatine	86
117	Ts Tennessine	118

Fluorine (F) is a **poisonous gas**, yellow-green in color. Under normal conditions, it is found in the form of a diatomic molecule (F_2).

It is extremely reactive and **highly toxic**.

It has the highest electronegativity among all known chemical elements (**-4.0**) and is the strongest oxidizing agent.

Fluorapatite is a hard crystalline solid, a phosphate mineral of the formula $Ca_5(PO_4)_3F$. It is also **present in human teeth** that have been exposed to fluoride ions, for example, by fluoridating water or using fluoride toothpaste.



Chlorine (Cl₂)

is a very reactive gas, greenish-yellow, **poisonous**, with a sharp and irritating smell.

- The amount of chlorine in the human body is about 105 g (0.2%).
- It mainly occurs in the ionic state as chloride Cl⁻.

Chloride ions - can be activators of enzymes (eg amylase from saliva) and can be involved in transport processes O₂ and CO₂ in the blood.

Blood chloride concentration in plasma is 96-105 mmol/L.

A solution of chlorine in water is called **chlorine water**. Chlorine is important in the synthesis of compounds with bactericidal activity (eg hypochloric acid, HClO)

Chlorine is used in the production of paper and pulp, for bleaching, for sanitary purposes, for the production of hypochlorite, for the disinfection of drinking water, swimming pool water, for the sterilization of polluted water, etc.

Bromine (Br₂) is a dark brown liquid (van der Waals forces between molecules are weak) with an unpleasant odor.

It is very poisonous (lethal dose is 35 g). It causes burns and wounds on the skin that are difficult to heal.

Bromine vapors damage the mucous membranes of the respiratory organs. Bromine is used in the pharmaceutical and organic industries.

Bromine is a dark brown liquid

Iodine (I₂) is a solid aggregate, dark purple in color and has a metallic sheen. It dissolves in ethanol, giving a brown color (tincture of iodine).

Alcoholic solution of iodine has **antiseptic properties**.

It is added in small amounts of NaCl, which is used for human consumption (iodized salt).

Povidone iodine is a 10% solution and has **exceptional antimicrobial effects** and is used as an **antiseptic** for skin, mucous membranes, burns and wounds. It is a complex of iodine and polyvinylpyrrolidone (povidone).

There are 30-50 mg of iodine in the body of an adult (about 1% is found in the composition of **thyroid hormones**, triiodothyronine and thyroxine, produced by the thyroid gland).

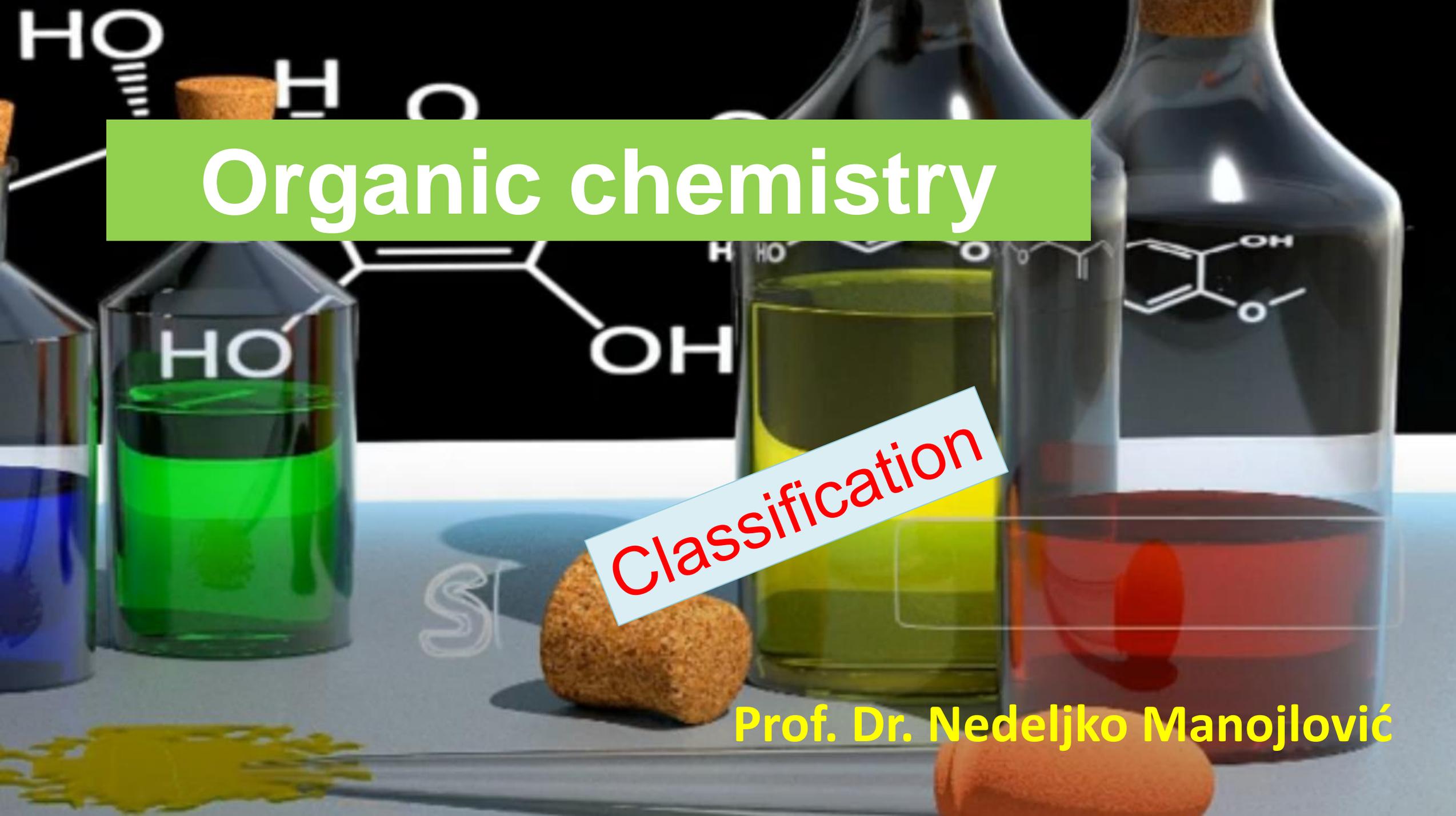
Lack of iodine leads to their reduced production, enlargement of the thyroid tissue and the appearance of a disease known as goiter.

Iodine is concentrated in the thyroid gland and it occurs in large quantities in other organs such as salivary glands, brain, cerebrospinal fluid, stomach lining, mammary gland, ovary and eye. Iodine is essential for normal growth and development of the body.

Iodine deficiency during intrauterine development and during growth can lead to cretinism.

thyroid gland

Organic chemistry



Classification

Prof. Dr. Nedeljko Manojlović

Organic chemistry is the study of the structure, properties, composition, reactions, and preparation of **carbon-containing compounds**.

Organic compounds **mainly contain carbon and hydrogen**, but also other elements such as: **nitrogen, oxygen, halogens, phosphorus, silicon, sulfur**.

There are two basic **classifications of organic compounds**:

- according to the structure of the hydrocarbon chain
- according to the existence of a functional group

The human body contains enough carbon to provide graphite for about 9000 pencils.

The number of organic compounds known so far is about 30,000,000

FUNCTIONAL GROUPS

Functional group is an atom or group of atoms that is part of an organic molecule and determines the chemical behavior of the entire molecule.

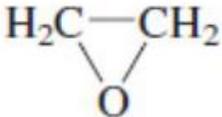
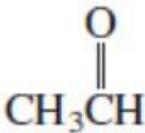
Based on functional groups, organic compounds are classified into classes.

	<i>Example</i>	<i>Example</i>
Hydrocarbons		
Alkanes	CH_3CH_3	Ethane
Alkenes	$\text{H}_2\text{C}=\text{CH}_2$	Ethene or ethylene
Alkynes	$\text{HC}\equiv\text{CH}$	Ethyne or acetylene
Dienes	$\text{H}_2\text{C}=\text{CHCH}=\text{CH}_2$	1,3-Butadiene
Arenes		Benzene

Halogen-substituted derivatives of hydrocarbons

Alkyl halides	$\text{CH}_3\text{CH}_2\text{Cl}$	Chloroethane or ethyl chloride
Alkenyl halides	$\text{H}_2\text{C}=\text{CHCl}$	Chloroethene or vinyl chloride
Aryl halides	$\text{C}_6\text{H}_5\text{Cl}$	Chlorobenzene

Oxygen-containing organic compounds

Alcohols	$\text{CH}_3\text{CH}_2\text{OH}$	Ethanol or ethyl alcohol
Phenols	$\text{C}_6\text{H}_5\text{OH}$	Phenol
Ethers	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	Ethoxyethane or diethyl ether
Epoxides		Epoxyethane or ethylene oxide or oxirane
Aldehydes		Ethanal or acetaldehyde

Carboxylic acids	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{COH} \end{array}$	Ethanoic acid or	Ionization of carboxyl;
Carboxylic acid derivatives			
Acyl halides	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCl} \end{array}$	Ethanoyl chloride or acetyl chloride	Nucleophilic acyl substitution
Acid anhydrides	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{CH}_3\text{COCCH}_3 \end{array}$	Ethanoic anhydride or acetic anhydride	Nucleophilic acyl substitution
Esters	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{COCH}_2\text{CH}_3 \end{array}$	Ethyl ethanoate or ethyl acetate	Nucleophilic acyl substitution
Amides	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CNHCH}_3 \end{array}$	<i>N</i> -Methylethanamide or <i>N</i> -methylacetamide	Nucleophilic acyl substitution

Nitrogen-containing organic compounds

Amines	$\text{CH}_3\text{CH}_2\text{NH}_2$	Ethanamine or ethylamine	Nitrogen acts as a base or as a nucleophile
Nitriles	$\text{CH}_3\text{C}\equiv\text{N}$	Ethanenitrile or acetonitrile	Nucleophilic addition to carbon–nitrogen triple bond
Nitro compounds	$\text{C}_6\text{H}_5\text{NO}_2$	Nitrobenzene	Reduction of nitro group to amine

Sulfur-containing organic compounds

Thiols	$\text{CH}_3\text{CH}_2\text{SH}$	Ethanethiol	Oxidation to a sulfenic, sulfinic, or sulfonic acid or to a disulfide
Sulfides	$\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$	Diethyl sulfide	Alkylation to a sulfonium salt; oxidation to a sulfoxide or sulfone

HYDROCARBONS

Hydrocarbons are organic compounds whose molecules contain only **carbon** and **hydrogen** atoms.

Hydrocarbons are divided into several groups

Aliphatic hydrocarbons including:

alkanes

alkenes

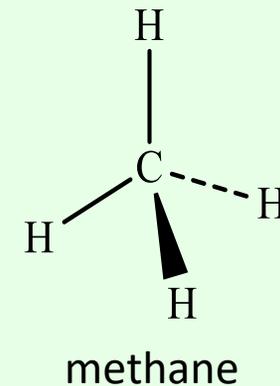
alkynes

alicyclic hydrocarbons

Aromatic hydrocarbons

Alkanes

- saturated (acyclic) hydrocarbons or paraffins (inactive)
- show weak reactivity
- they have no functional group!!!
- the general formula of alkane is C_nH_{2n+2}
- the simplest example of alkane – methane CH_4



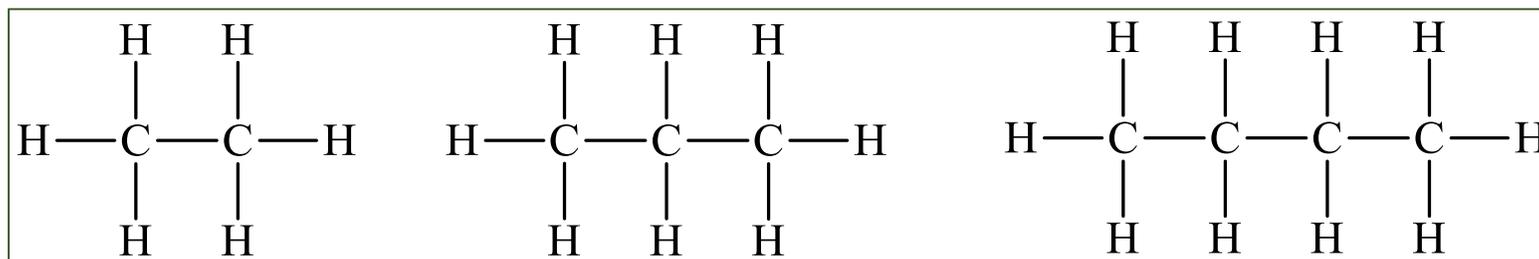
Homologous series of alkanes

Alkanes form a **homologous series** in which each member differs from the previous one by one methylene group **-CH₂-**

ethane

propane

butane

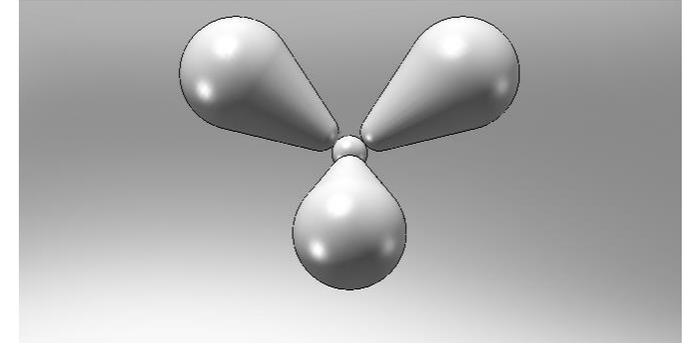


Hybridization of atomic orbitals

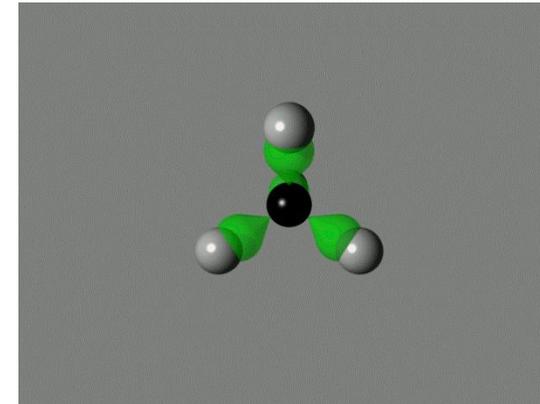
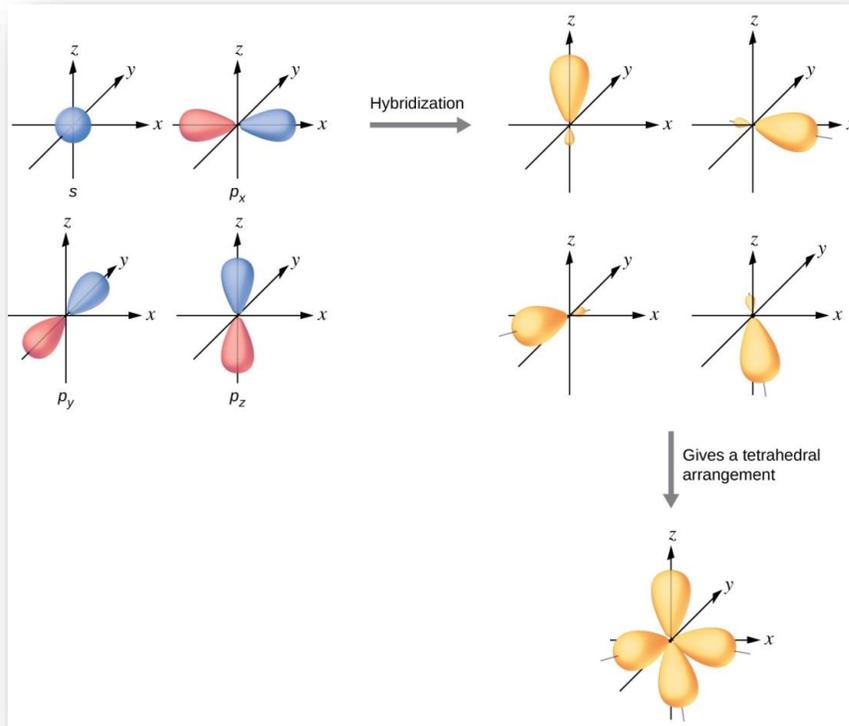
- **Hybridization** – combining atomic orbitals of the same or similar energies, resulting in new hybrid orbitals with new properties.
- **The number of hybrid orbitals** is equal to the number of atomic orbitals by which they are combined.
- Hybrid orbitals are of the same energy, i.e. degenerate.
- Hybridization of atomic orbitals does not exist in an isolated atom - it is only a quantum mechanical model.

sp^3 -hybridization

- One s- and three p-orbitals, give three sp^3 -hybrid orbitals
- sp^3 -hybrid orbitals are of the same shape and energy.
- The angle between sp^3 hybrid orbitals is $109,5^\circ$
- Tetrahedral geometry



sp^3 -hybridization – C_2H_6 (ethane)



methane

Single C—C bond in C_2H_6 :

σ bond – is formed by the frontal overlap of sp^3 orbitals of carbon

Single C—H bond in C_2H_6 :

σ bond – is formed by the frontal overlapping of sp^3 orbital of carbon and s orbital of hydrogen

IUPAC names of straight-chain alkanes

number of C-atoms	name	structure
1	methane	CH ₄
2	ethane	CH ₃ CH ₃
3	propane	CH ₃ CH ₂ CH ₃
4	butane	CH ₃ CH ₂ CH ₂ CH ₃
5	pentane	CH ₃ (CH ₂) ₃ CH ₃
6	hexane	CH ₃ (CH ₂) ₄ CH ₃
7	heptane	CH ₃ (CH ₂) ₅ CH ₃
8	octane	CH ₃ (CH ₂) ₆ CH ₃
9	nonane	CH ₃ (CH ₂) ₇ CH ₃
10	decane	CH ₃ (CH ₂) ₈ CH ₃
11	undecane	CH ₃ (CH ₂) ₉ CH ₃
12	dodecane	CH ₃ (CH ₂) ₁₀ CH ₃

Physical properties of alkanes

Polarity

- alkanes are **non-polar** (small difference in the electronegativity of C and H)
- the bonds are directed in a completely symmetrical way so that even the small polarity of the individual bonds is canceled
- **London forces** act between molecules (induced dipole-induced dipole interaction)
- forces act only on the contact surface and the larger the surface, the stronger the force

Chemical reactions of alkanes

- at room temperature they are **inert** - weakly reactive - compounds;
- also called **paraffins** (Latin: parumaffinis)
- they react under harsher conditions and according to certain reagents
- the reactions to which they are subject are not much used in laboratories, but have a large industrial application
- reactions of alkanes are carried out **via free radicals**
- basic type of reaction: **substitution**

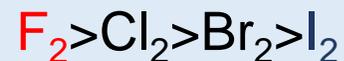
Halogenation

- reactions of mixtures of alkanes and halogens (most often Cl_2 and Br_2) in the presence of light, some other radiation or heat.

- this reaction proceeds by a **free-radical mechanism** in stages:

1. Initiation;
2. Propagation 1 and 2;
3. Termination

- relative reactivity of halogens according to substitution:



- iodination does not occur, and reactions with fluorine are very violent.

Cycloalkanes

Cycloalkanes are saturated cyclic hydrocarbons.

- carbon atoms connected in chains - open chain compounds
- carbon atoms connected to form a ring - cyclic compounds
- carbon atoms connected by an S-S bond to form a ring - cycloalkanes
- general formula C_nH_{2n}
- the chemistry of these compounds is similar to that of alkanes, however the ring form gives some of these compounds specific properties



cyclopropane



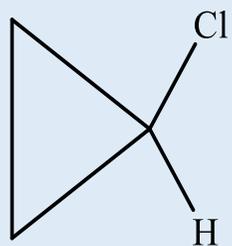
cyclobutane



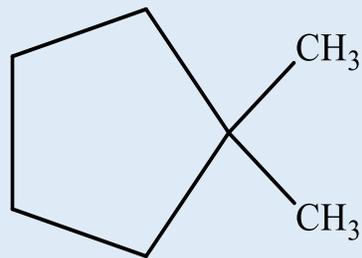
cyclopentane



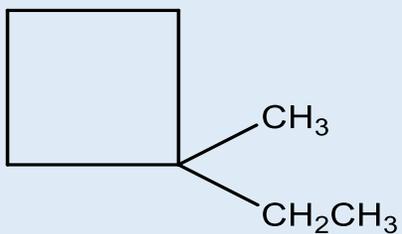
cyclohexane



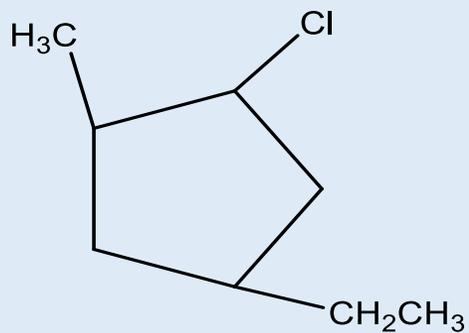
chlorocyclopropane



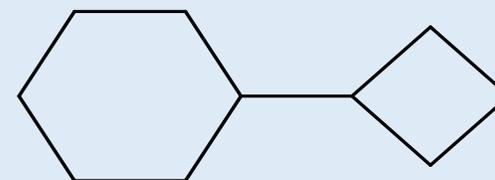
1,1-dimethylcyclopentane



1-ethyl-1-methylcyclobutane



1-chloro-4-ethyl-2-methylcyclopentane



cyclobutylcyclohexane

Alkenes

Alkenes are **unsaturated hydrocarbons** that have one double (unsaturated) bond in their molecule.

- the general formula of alkene is **C_nH_{2n}**

- double bond - the difference between an alkene and an alkane

- double bond is a **functional group**

- Homologous series: ethene (acetylene), propene, butene...

- alkenes are **very reactive compounds**

- dissolve in concentrated sulfuric acid

- react quickly with chlorine and bromine

- - subject to a large number of reactions

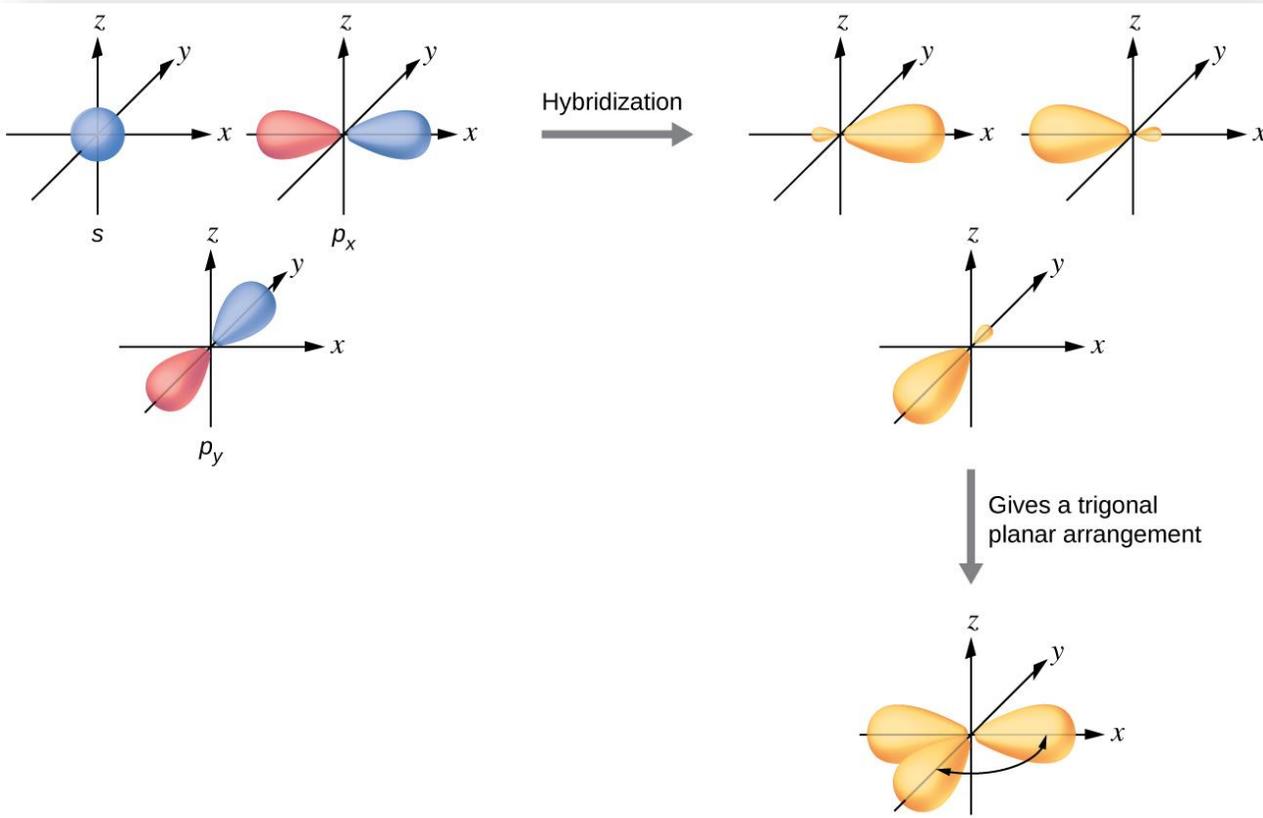
- **olefins** - another name for alkenes (oleum – oil, faceo – to make, make)

Physical properties of alkenes

- similar to the properties of alkanes
- the degree of solubility in water is slightly higher than that of alkanes
- soluble in non-polar solvents
- their density is lower than the density of water (as with alkanes)
- the double bond has no significant effect on the boiling and melting points

sp^2 -hybridization

- By combining one s- and two p-orbitals, three sp^2 -hybrid orbitals are formed.
- sp^2 -hybrid orbitals are of the same shape and energy.
- The angle between sp^2 -hybrid orbitals is 120°
- Trigonal-planar geometry



sp^2 -hybridization – C_2H_4 (ethene)

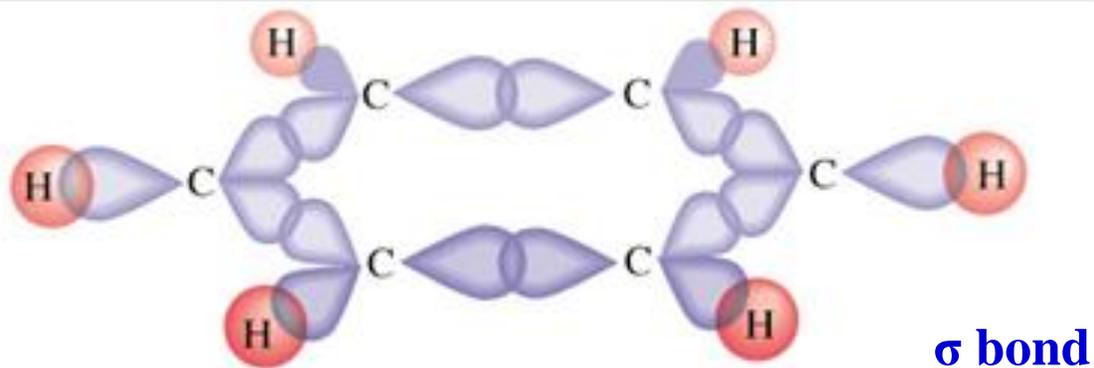
C=C double bond in C_2H_4 :

- 1) The σ bond is formed by the frontal overlapping of sp^2 -orbitals of carbon
- 2) π bond – is formed by lateral overlapping of unhybridized p-orbitals of carbon

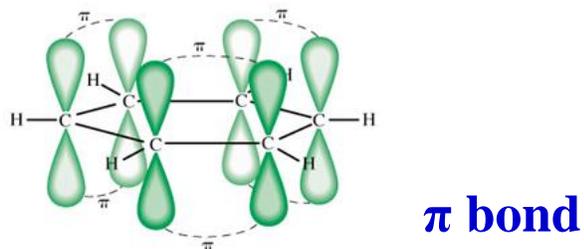
Single C—H bond in C_2H_4 :

σ bond is formed by the frontal overlapping of the sp^2 -orbital of carbon and the s-orbital of hydrogen

sp^2 -hybridization – C_6H_6 (benzene)



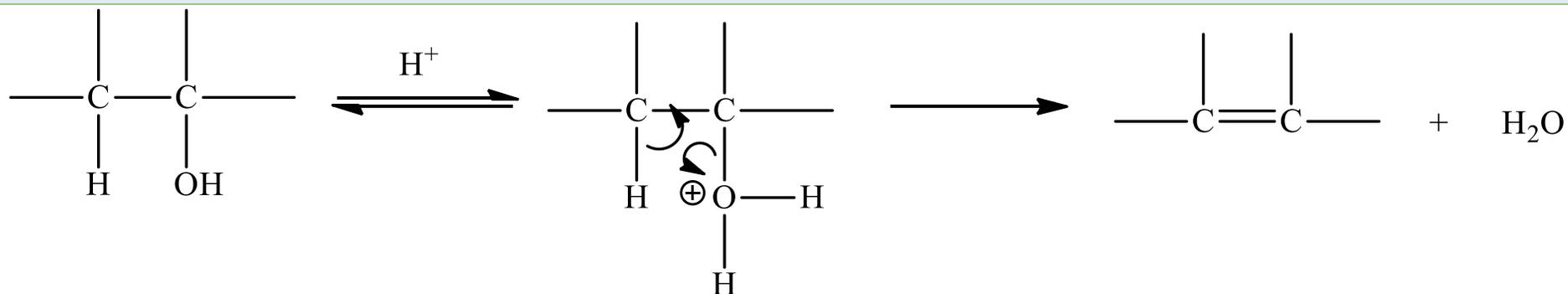
Delocalized π bond



Preparation of alkenes

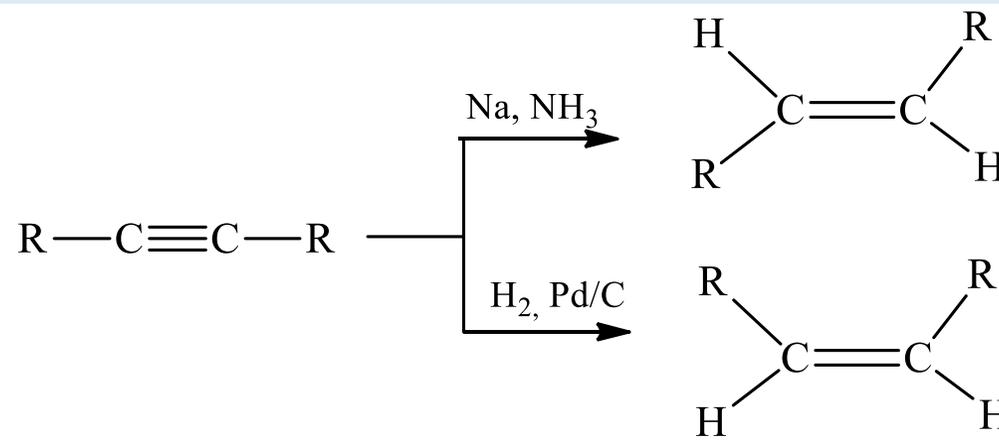
1. Dehydration of alcohol

- alkenes are obtained by dehydrating alcohol using sulfuric or phosphoric acid at a temperature of 200 °C, or by passing alcohol vapor over a catalyst, such as aluminum oxide, at 350-400 °C



- the ease of dehydration depends on the alcohol structure
- tertiary alcohols are the easiest to dehydrate, and primary alcohols are the hardest

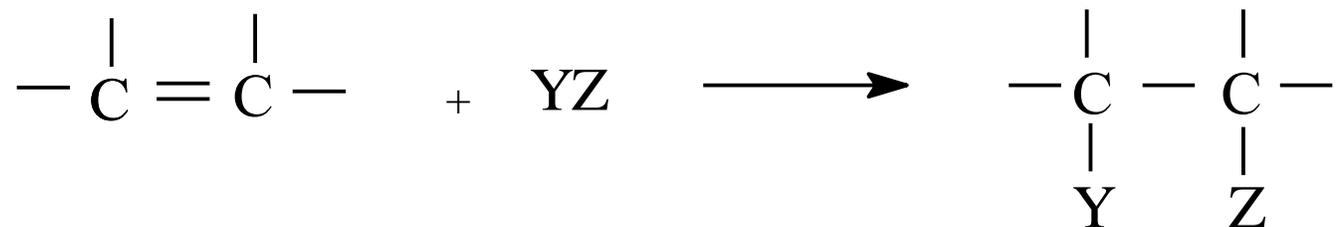
2. Alkyne reduction gives cis- or trans-alkene, depending on the reducing reagent



Alkene reactions

the double bond is composed of a **strong δ -** and **weak bond π -**везе

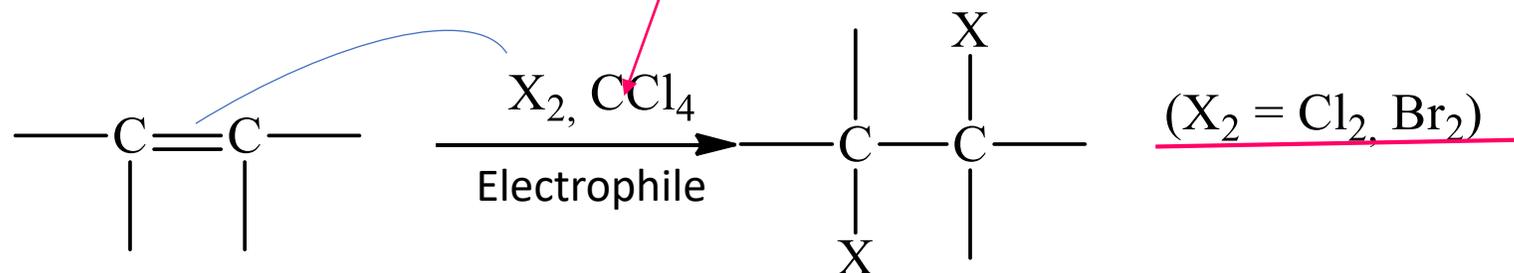
- in addition reactions with alkenes, the π -bond is broken, and a strong one is built δ -веза



1. Halogen addition

Halogens can act as electrophiles to attack a double bond in alkene.

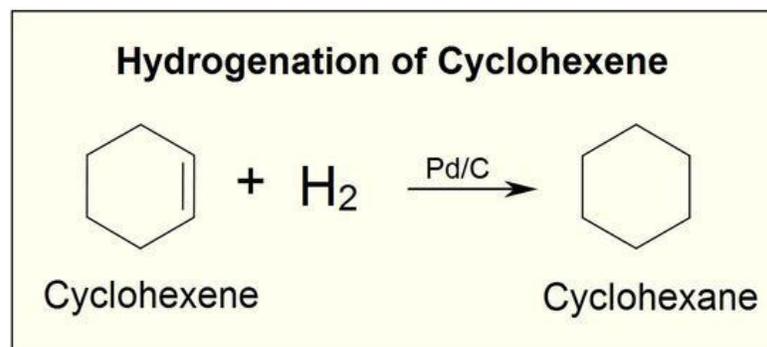
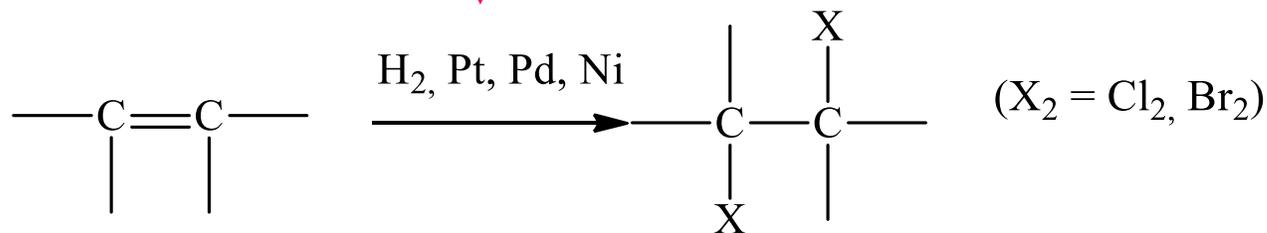
- when chlorine or bromine is added to the double bond of an alkene, a 1,2-dihalide is obtained



- **fluorine and iodine** practically do not react or give unstable compounds

2. Addition of Hydrogen

- the process is called **catalytic hydrogenation**
- olefins add hydrogen in the presence of a finely ground **metal catalyst** and give an **alkane**
- catalysts are usually nickel, platinum or palladium
- the reaction is a stereospecific syn-addition, i.e. both hydrogen atoms are attached from the same, less protected side of the double bond

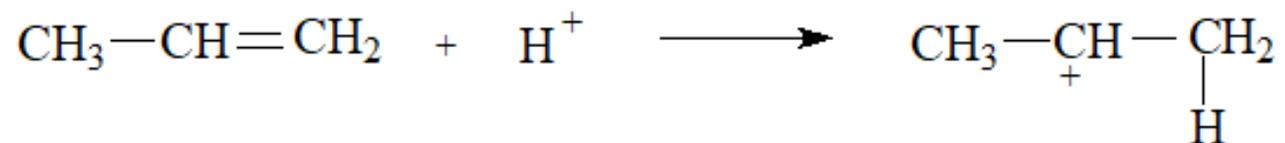


3. Addition of unsymmetrical adducts

1. Addition of hydrogen halide - Markovnikov's rule

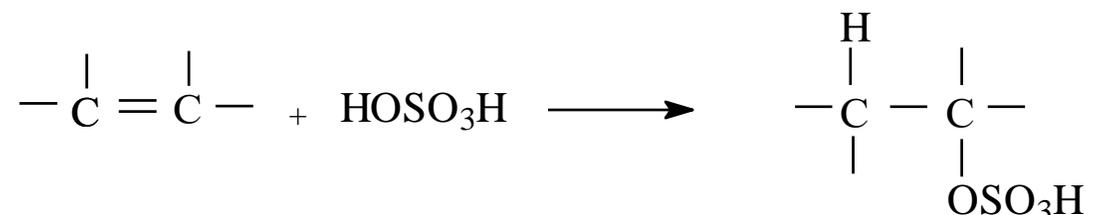
Markovnikov's rule:

- Hydrogen is added to the carbon with more hydrogens, and halogen is added to the carbon with less hydrogens.



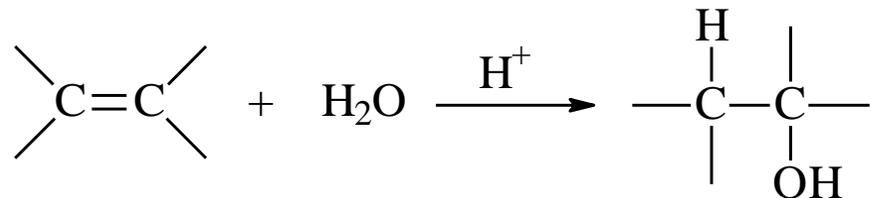
2. Addition of sulfuric acid

By the reaction of gaseous alkene and concentrated sulfuric acid, an addition compound is formed - alkyl-hydrogen-sulfate, ROSO_3H



4. Addition of water

by adding water to olefins, in the presence of acid, alcohols are obtained



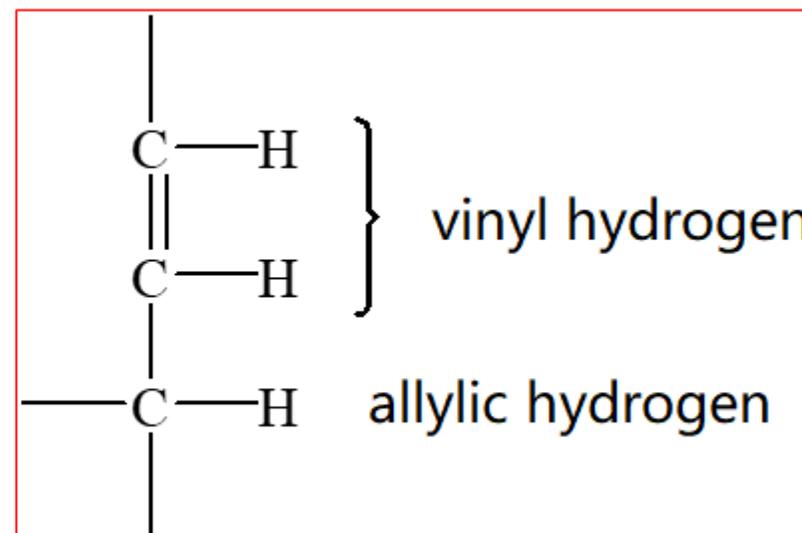
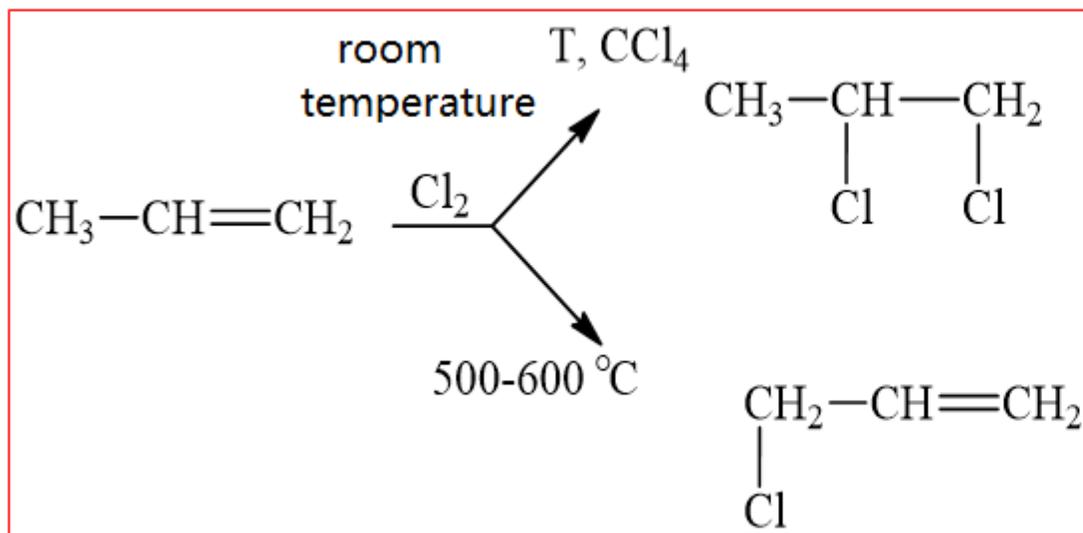
The reaction mechanism is the same as for the addition of sulfuric acid or hydrogen halide:

- electrophilic attack of protons from acid
- nucleophilic attack of water on the resulting carbonium ion



Alkene substitution

Necessary conditions for the reaction of the alkyl group (substitution): **high temperature** or exposure to light, i.e. radiation of a certain wavelength.



Allyl group

The reactivity depends on the stability of the radical, which increases in the following sequence:

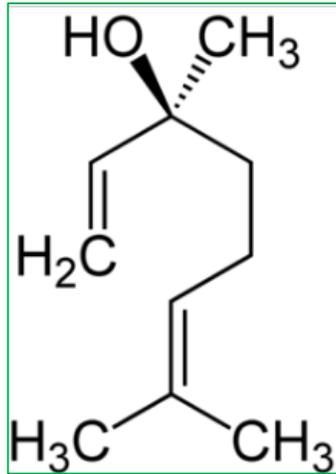


- the double bond increases the stability of the allyl radical and decreases the stability of the vinyl radical

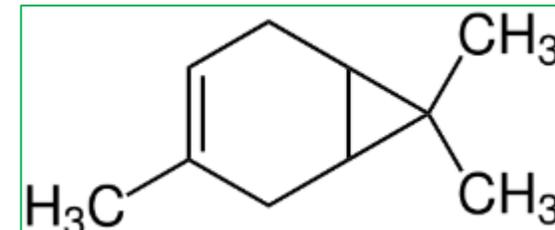
Terpenes: Naturally Occurring Alkenes

Terpenes are isoprene derivatives that determine the smell of many plants, such as menta, rosemary and lavender.

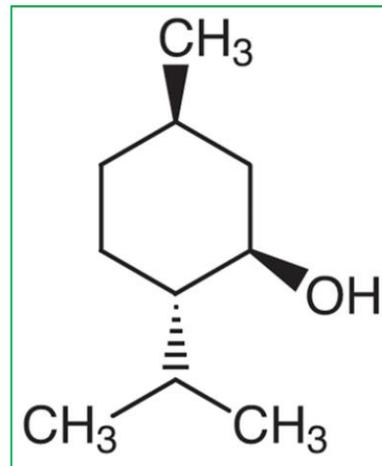
Linalool is a floral and spicy terpene alcohol (lavender).



linalool



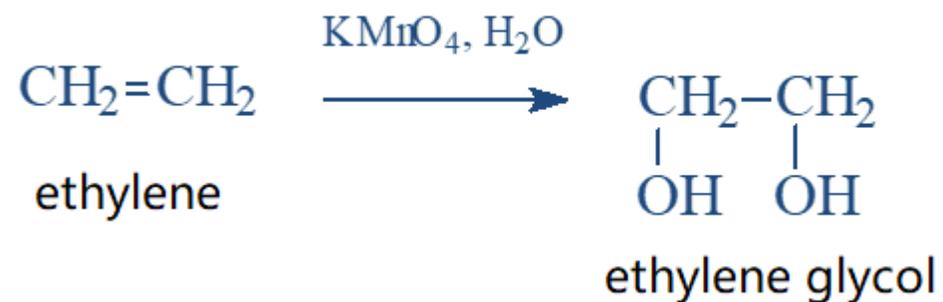
3-carene in rosemary



Menthol in *Menta piperita*

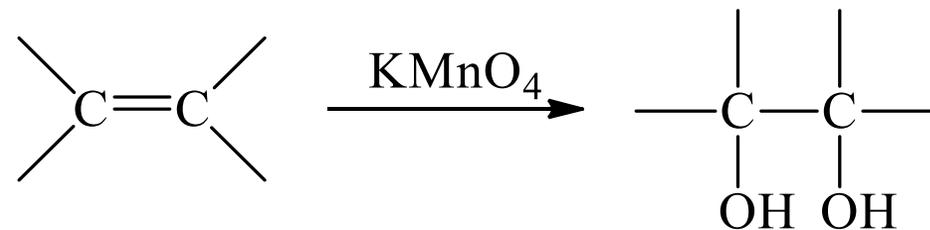
Alkene oxidation

- alkenes can be oxidized on the double bond using various reagents
- 1,2-diols (glycols) are obtained and epoxides



Oxidation with permanganate

Mild oxidation with permanganate leads to the binding of two hydroxyl groups, giving the corresponding 1,2-diols.



(at a temperature of 0-5 °C and in a neutral to slightly alkaline solution)

Alkynes

Alkynes are hydrocarbons that have at least one triple bond



internal (more stable)



terminal

functional group - triple bond

General formula of alkynes: $\text{C}_n\text{H}_{2n-2}$

- sp hybridization
- - linear arrangement of hybrid orbitals
- a triple bond consists of one σ and two π -bonds, which lie in mutually normal planes - the geometry of the part of the molecule that contains the triple bond is linear

σ - bond is strong, while π -bonds are weak

Physical properties of alkynes

- they are similar to the physical properties of alkanes and alkenes
- they do not dissolve in water, they dissolve in non-polar organic solvents such as benzene, carbon tetrachloride, ether
- their density is lower than the density of water
- boiling points increase with the increase in the number of carbon atoms and are similar to the boiling points of the corresponding alkanes and alkenes

2-4 C atoms – gases

5-13 C atoms - liquid

>13 C atoms - solid

sp-hybridization

- By combining s- and p-orbitals, **two *sp*-hybrid orbitals are formed**
- *sp*-hybrid orbitals are of the same shape and energy
- The angle between *sp*-hybrid orbitals is 180°
- Linear hybridization

sp-hybridization – C_2H_2 (ethyne or acetylene)

Triple bond $C\equiv C$ веза in C_2H_2 :

- 1) σ bond – is formed by the frontal overlapping of *sp*-orbitals of carbon
- 2) π bonds (two) – are formed by lateral overlapping of unhybridized p-orbitals of carbon
- 3) Single C–H bond in C_2H_2 :
 σ bond – is formed by the frontal overlapping of *sp*-orbital of carbon and s-orbital of hydrogen

Aromatic hydrocarbons (arenes)

cyclic hydrocarbons with a high degree of unsaturation, which in terms of their chemical properties are quite different from cycloalkanes and aliphatic compounds

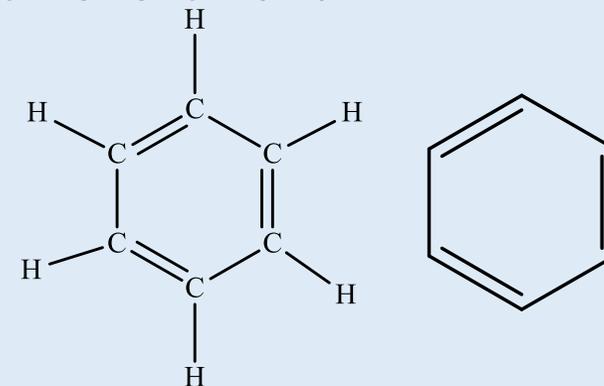
- carbon - carbon bond is between single and double in length
- they are resistant to oxidation and addition reactions
- they have a high resonance energy, that is, they are very stable

- compounds with a **characteristic (pleasant) smell**, isolated for the first time from essential oils

- the first representative of these compounds is **benzene**, from which all other aromatic hydrocarbons and its derivatives are derived.

- pure benzene was isolated in 1825 (Michael Faraday)

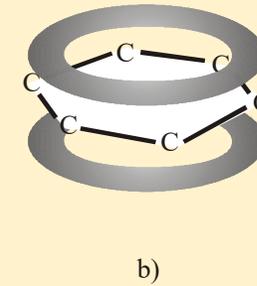
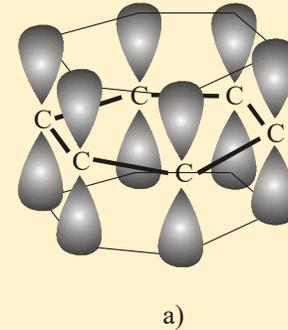
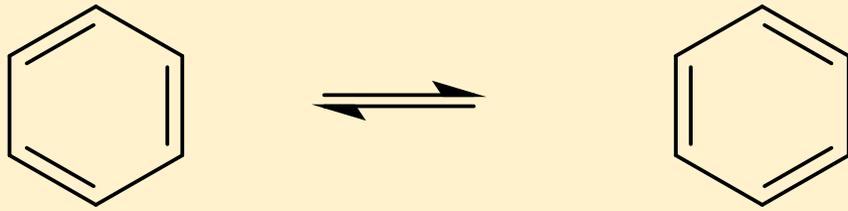
- the first structure of benzene was discovered in 1865 (August Kekule)



Kekule's formula of benzene

The structure of benzene is explained in two ways

- by the resonance method
- molecular-orbital theory



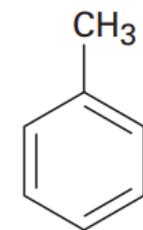
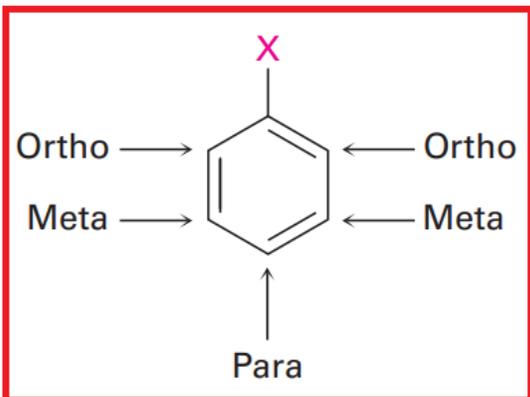
- according to the resonance method, the benzene molecule is a resonance hybrid that is represented by two boundary Kekule structures.

- molecular orbital theory assumes that all carbons are building atoms benzene molecule sp^2 hybridized, that they are connected to each other by the resulting σ bonds by overlapping hybridized orbitals and
- they are in one plane
- in that case, one unhybridized p -orbital with one unpaired electron remains on each C-atom

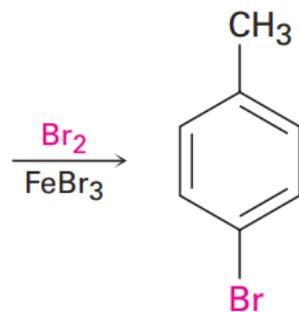
Properties of benzene

- mobile colorless liquid, which does not dissolve in water, and mixes well with organic solvents
- shows an **irritating effect on the skin**, and **its vapors are poisonous** (it is present in tobacco smoke, it is created when frying meat).
- benzene and its homologues are more easily subject to **substitution reactions**,
- **under drastic conditions**, benzene and its derivatives can also undergo some **addition reactions**.

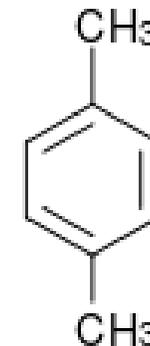
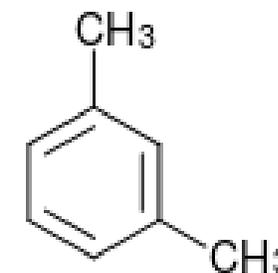
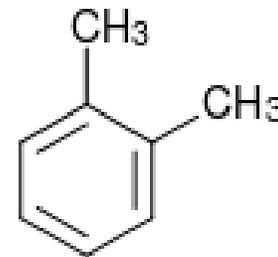
benzene



Toluene

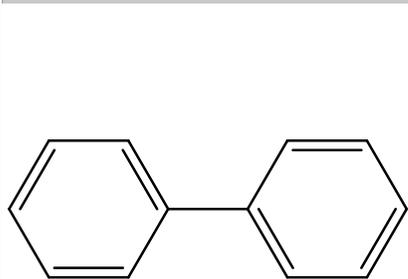


p-bromotoluene

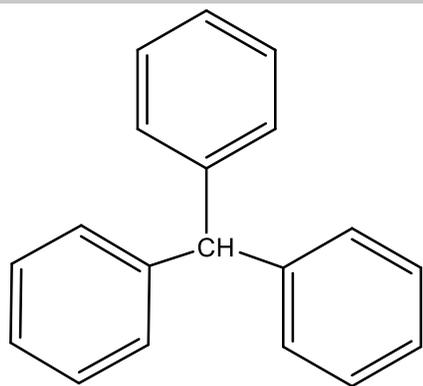


O-, m- и p-xylenes

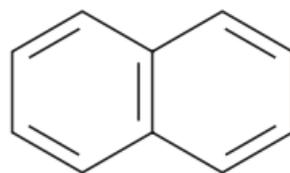
- arenes are classified into mononuclear and polynuclear (monocyclic and polycyclic)
- mononuclear are benzene and its alkyl-substituted derivatives, while polynuclear arenes are hydrocarbons that contain more benzene rings (nuclei) in their molecules.
- polynuclear arenes are hydrocarbons in which the benzene nuclei are attached directly (such as diphenyl, di- and polyarylalkanes (such as triphenylmethane)) and condensed arenes in which two rings have two common carbon atoms (naphthalene, anthracene, phenanthrene).



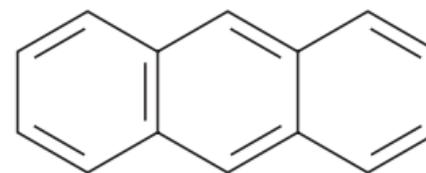
diphenyl



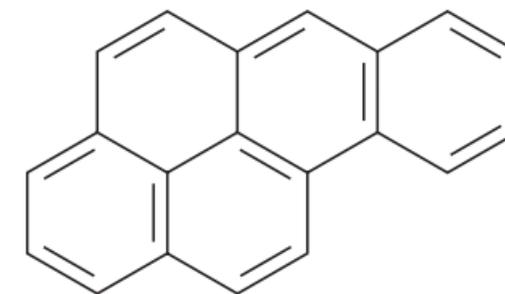
triphenylmethane



Naphthalene

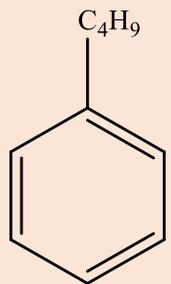


Anthracene

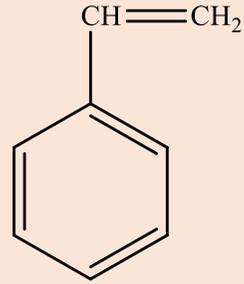
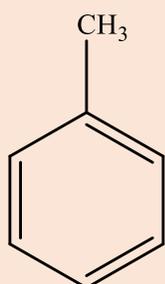


Benzo[a]pyrene

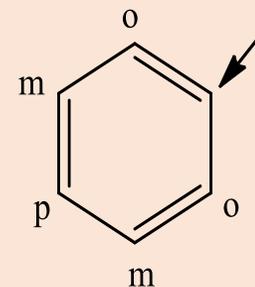
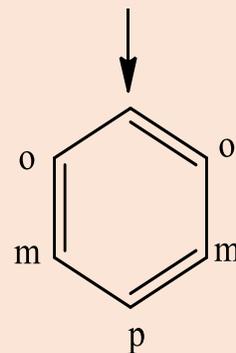
Monosubstituted mononuclear arenes are named from the name of the alkyl group (for example butyl-benzene), but are often better known by trivial names (methyl-benzene is known as toluene; vinyl-benzene as styrene, etc.)



butyl-benzene methyl-benzene
(toluene)



vinyl-benzene
(styrene)

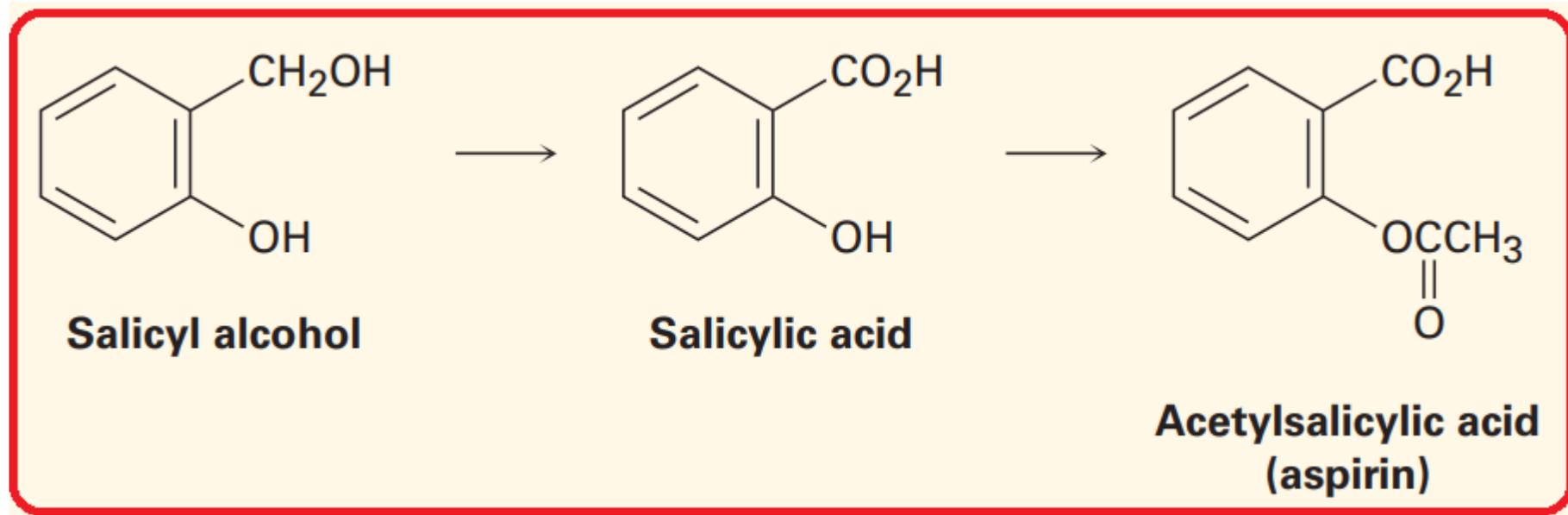


the position of the second substituent

C_6H_5- phenyl group

$C_6H_5CH_2-$ phenyl methyl group (benzyl group)

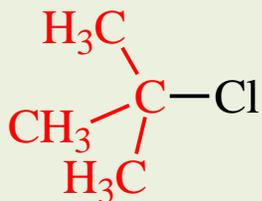
Derivatives of aromatic compounds



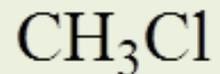


Alkyl halides (haloalkanes)

The general formula is $C_nH_{2n+1}X$ or $R-X$ where R is an alkyl group and X is a halogen element. If the halogen is attached to the aromatic ring, then it is an aryl halide.

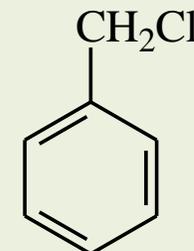
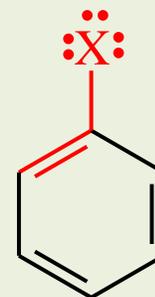


Tert-butyl chloride



Vinyl chloride

Aryl halides are unreactive.



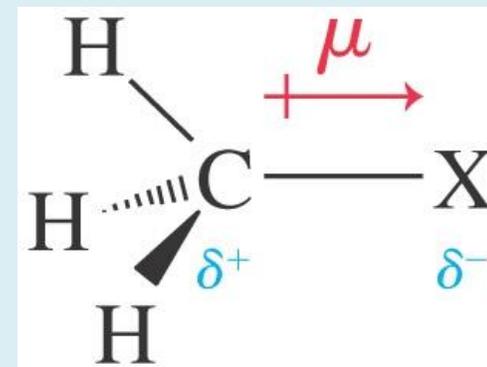
Benzyl chloride



Physical characteristics

- Alkyl halides have significantly **higher melting points** than alkanes with the same number of carbon atoms (due to higher molecular weight).
- They are polar but insoluble in water.
- They are soluble in common organic solvents and are themselves good solvents for many organic compounds.
- Volatility decreases with:
 - by increasing the molecular mass along the halogen series
 - by increasing the atomic number of halogens

They have a higher density than hydrocarbons.





Halogenated solvents:

CH_2Cl_2 methylene chloride

CHCl_3 chloroform

CCl_4 carbon tetrachloride

Physiological effect:

- Volatile alkyl halides have an **anesthetic effect** when inhaled
- **Trichloromethane** (chloroform) is a solvent that has an anesthetic effect.
- The acute toxicity of **carbon tetrachloride** appears to be the same as that of H_2S and HCN
- **Triiodomethane** (iodoform) is a pale yellow solid substance that is used as an antiseptic (disinfectant).



Preparation of alkyl halides

1. From alcohol:



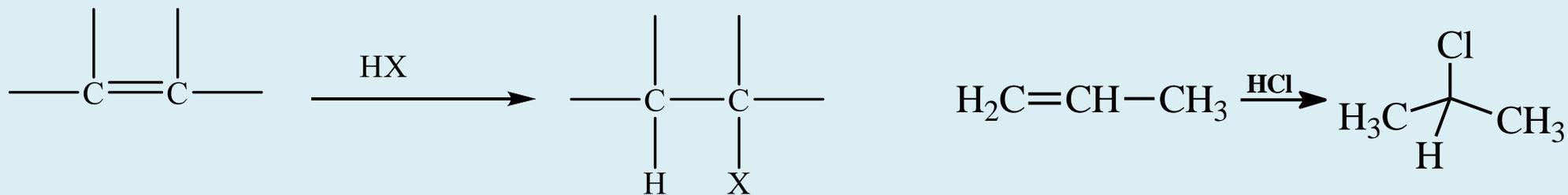
2. Halogenation of hydrocarbons

Free-radical halogenation of alkanes

Allyl substitution of alkenes

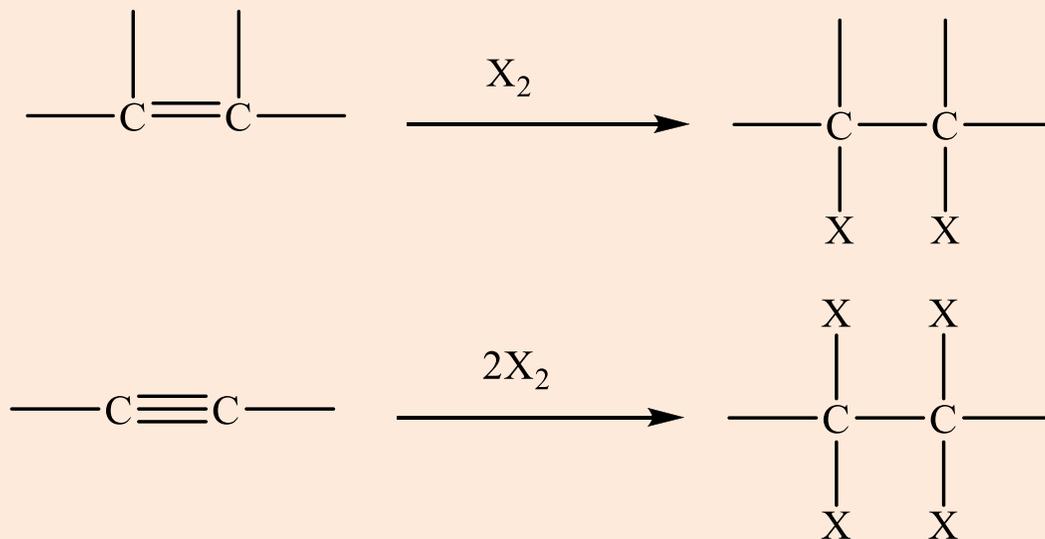
Benzyl substitution

3. Addition of hydrogen halides to alkenes (Markovnikov's and anti-Markovnikov's rule)





4. Addition of halogens to alkenes and alkynes

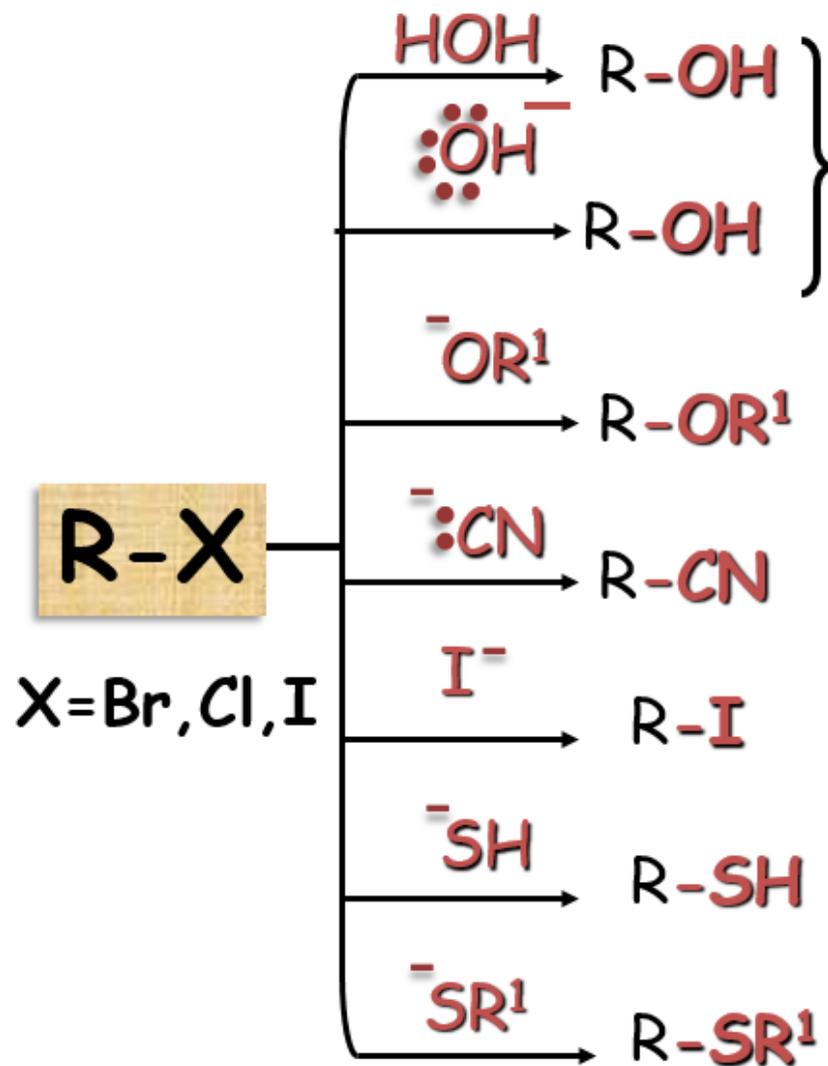


5. Halogen change



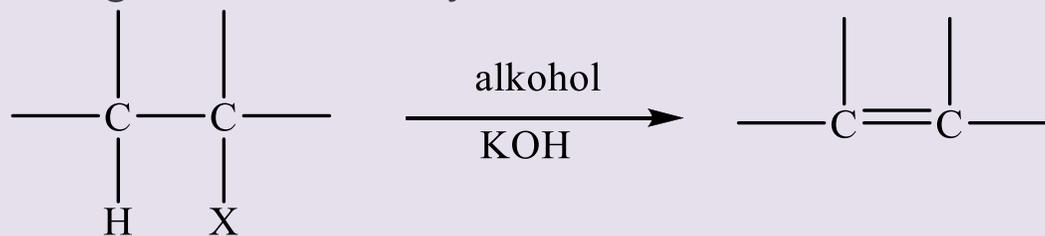


Reactions of alkyl halides

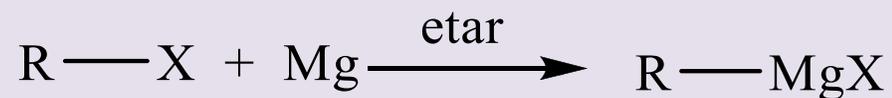




1. Dehydrohalogenation of alkyl halides



2. Grignard's reagent



3. Reduction





Nucleophilic substitution

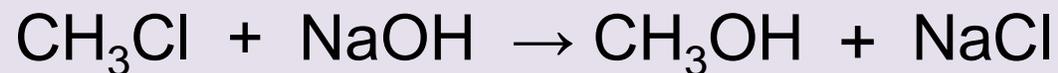


Z is a nucleophile and it can be: OH^- , H_2O , $\text{R}-\text{O}^-$, $\text{R}-\text{C}\equiv\text{C}^-$, I^- , NH_3 ,
 HS^- , RS^- , CN^-

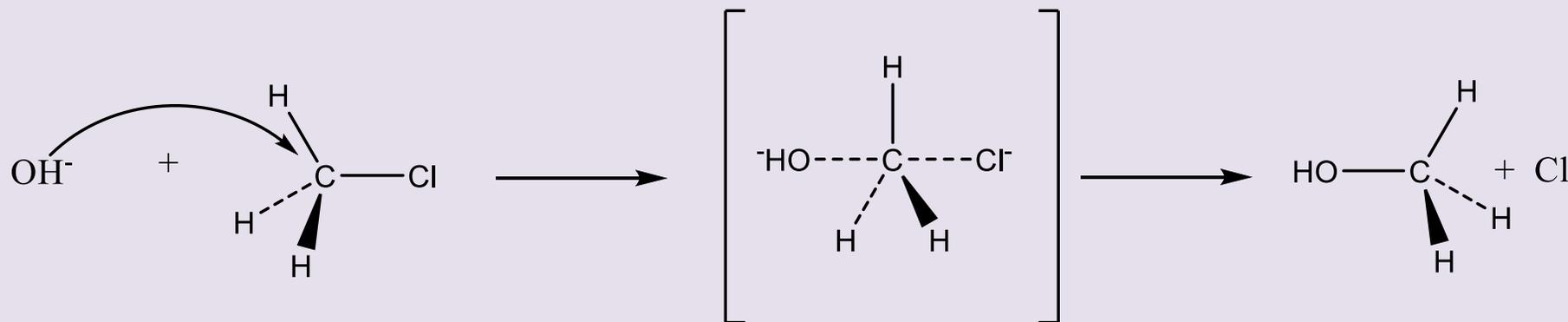


The S_N2 Reaction

- By heating methyl chloride and sodium hydroxide in water, methanol and sodium chloride are obtained in high yield



- This reaction has second-order kinetics, that is, it belongs to 2 S_N2 type
- during these reactions there is a change in configuration

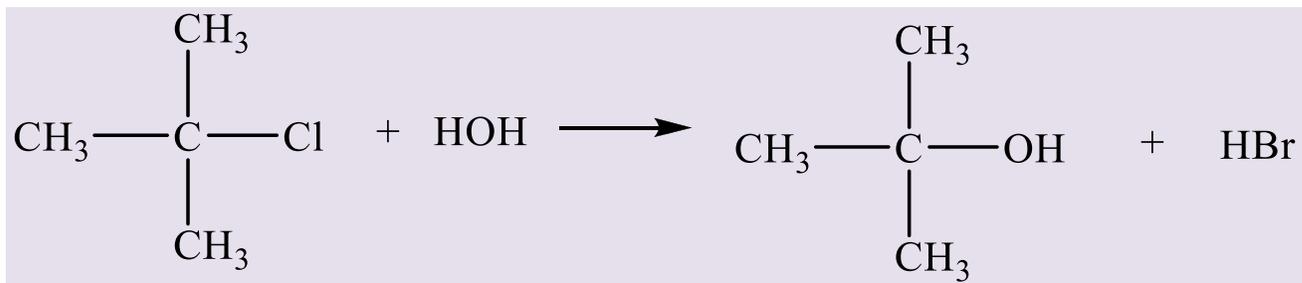




- Simultaneous building of a new and breaking of an old connection
- **Walden inversions** - configuration change
- The reactivity in these reactions depends on the ease of replacement of the leaving group
- group departure ability: $I^- > Br^- > Cl^- > F^-$
- Order of reactivity of alkyl halides:
- methyl halides > primary > secondary > tertiary

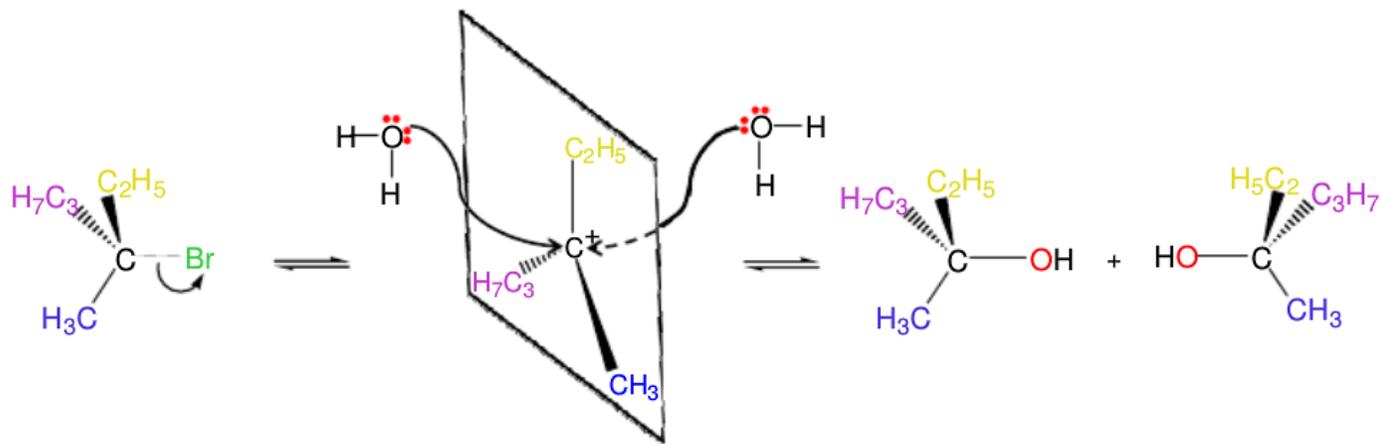
The nucleophile OH-
approaches methyl chloride
from the opposite side of the
leaving group (Cl-)

The S_N1 Reaction



2-chloro-2-methyl-propane

2-methyl-2-propanol

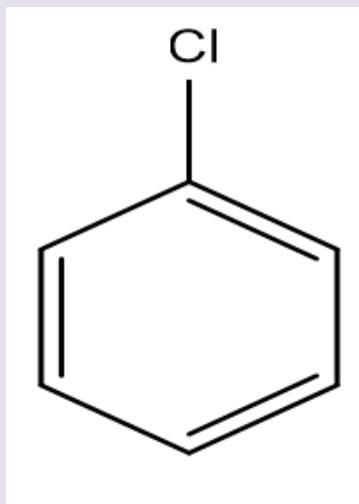


- Reactions in which the substrate molecule is replaced by molecules that are part of the solvent are called solvolysis. In this particular case, it is about hydrolysis, because the solvent is water.



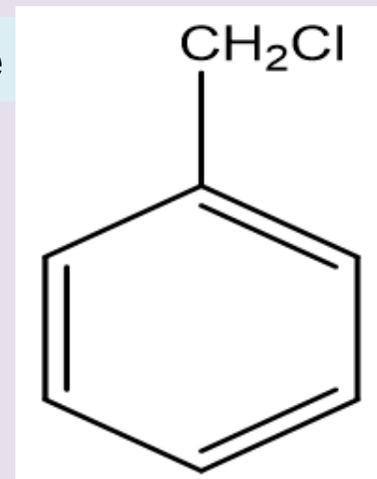
Aryl halides

- these are compounds where the halide is directly attached to the aromatic ring
- The general formula is **Ar-X**
- Aryl halide is not every compound that contains a halide and an aromatic ring



Chlorobenzene

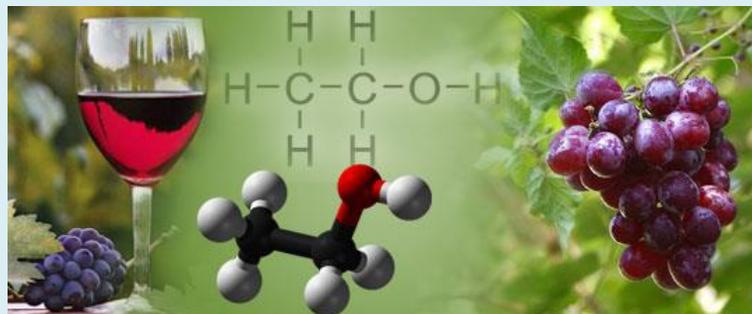
Not an aryl halide



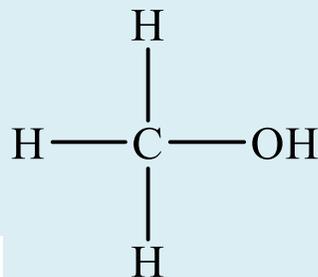
benzyl chloride

Alcohols

Alcohols are compounds that have a hydroxyl (-OH) group attached to a hydrocarbon chain (R-OH)

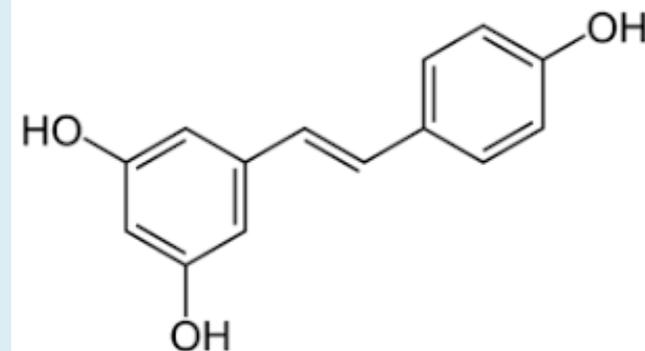


- The general formula of open-chain saturated monohydroxyl alcohols is $C_nH_{2n+2}O$
- The first member of the homologous series has the molecular formula CH_4O



or

CH_3-OH
Methanol (toxic)



resveratrol,
found in the skin of
red grapes



Alcohols are classified into:

Primary ($R-CH_2-OH$)

Secondary ($R_2-CH-OH$)

Tertiary (R_3-C-OH)

Methyl alcohol is usually classified in the group of primary alcohols

According to the number of hydroxyl groups, alcohol is divided into:

monohydroxyl

dihydroxyl

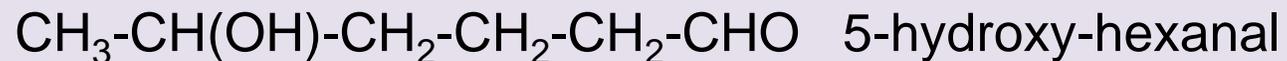
trihydroxyl

polyhydroxyl

Depending on the structure of the hydrocarbon chain, they can be **aliphatic** (unsaturated or saturated), **cyclic** or **aromatic** (phenols).



- As a substituent, the OH group is called a “hydroxyl group”
- It is indicated by the prefix “hydroxy-” when another group is present, which takes priority in listing, or when the hydroxyl group is in the side chain.



Physical features

When compared to alkanes, **they have abnormally high boiling points.**

The reason for high boiling points is the same as for water: **the association of molecules through hydrogen bonding**



Ethanol

- Ethanol is widely used in industry as a **solvent for paints, varnishes, fragrances and spices**, and is also used as a solvent for many reactions.
- alcoholic drinks contain ethanol. For this purpose, it is obtained by fermentation of sugar.

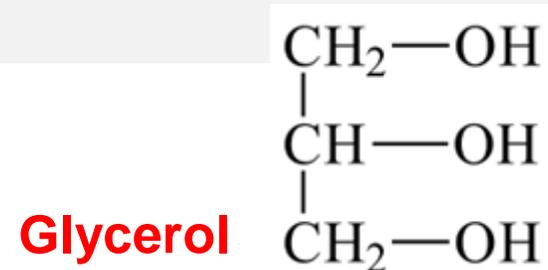


glucose

- It is also sold as 95% alcohol.
- Pure ethyl alcohol is called **absolute alcohol**.
- **Ethanol metabolism** occurs mainly in the liver and proceeds by oxidation in two steps, first to acetaldehyde (CH_3CHO) and then to acetic acid (CH_3COOH)



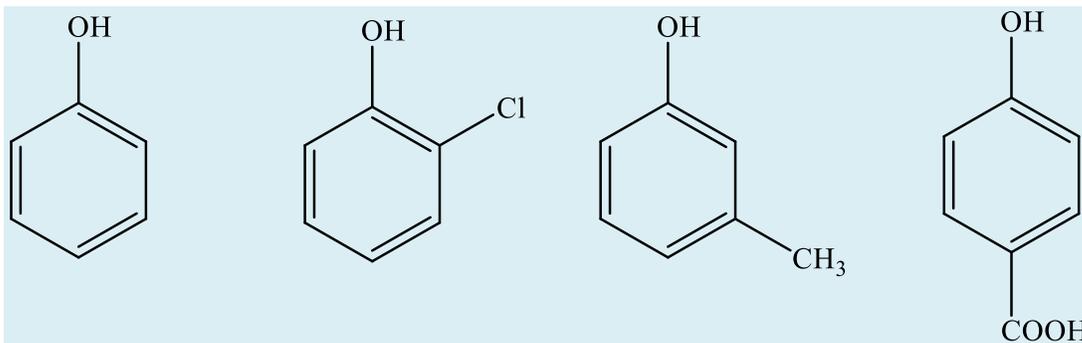
- A diluted solution of ethanol in water (60-70%) is used as an **antiseptic**.
- It destroys microorganisms by denaturing proteins and dissolving lipids. It is effective against most bacteria, fungi and some viruses. **Medical ethyl alcohol is classified as a hypnotic**. It is less toxic than other alcohols.
- **Methanol** is an easily volatile liquid with a characteristic smell.
- It is toxic (lethal dose is about 120 ml).
- **Glycerol (1,2,3-propanetriol)** is a colorless viscous liquid with a sweet taste. It is used in medical, pharmaceutical and cosmetic preparations to improve softness, lubricity and moisture. It is found in cough syrups, toothpastes, mouthwashes, skin and hair care products, shaving creams, soaps and the like.



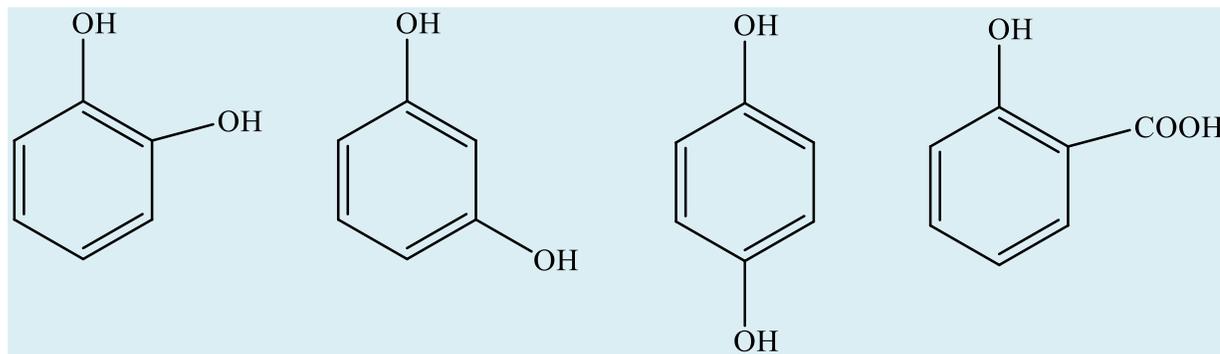


Phenols

General formula Ar-OH



phenol o-chloro-phenol m-cresol p-hydroxy-benzoic acid



catechol resorcinol hydroquinone salicylic acid

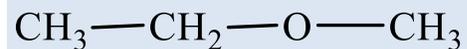


Ether

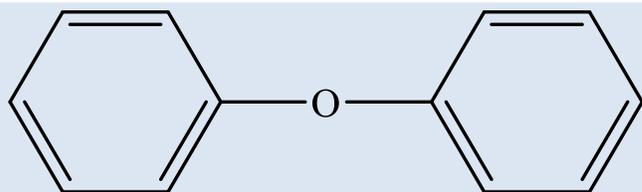
The simplest ethers have the general formula $C_nH_{2n+2}O$ and are therefore isomeric with alcohols.

General formula of an ether can be shown as **R-O-R**, **R-O-Ar**, **Ar-O-Ar**

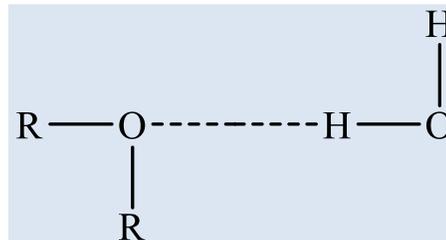
The first member of the series has the molecular formula CH_3-O-CH_3



ethyl methyl ether



diphenyl ether



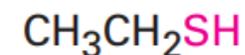
hydrogen bond

Physical features

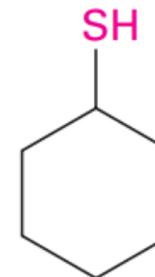
They are almost as soluble in water as alcohols.

Thiols and Sulfides

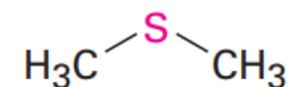
SH group - mercapto group



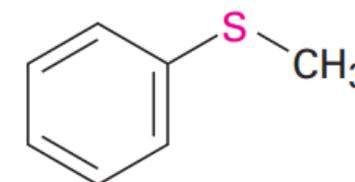
Ethanethiol



Cyclohexanethiol



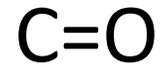
Dimethyl sulfide



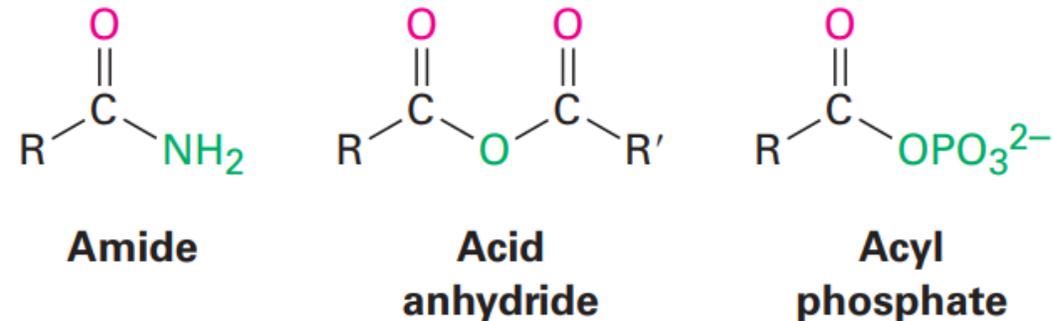
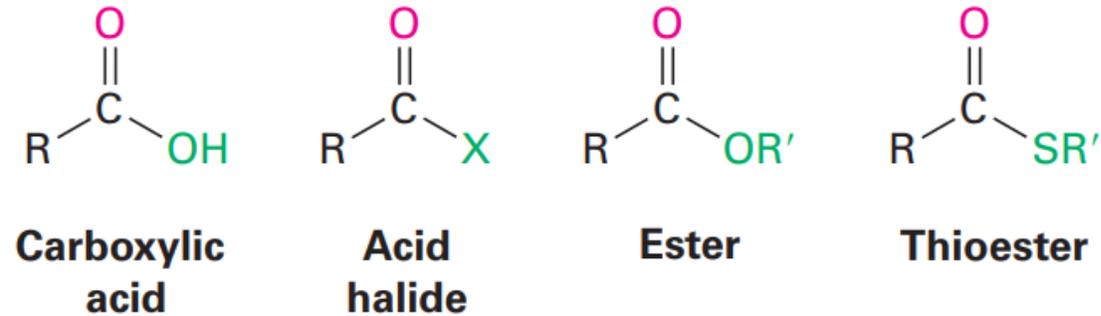
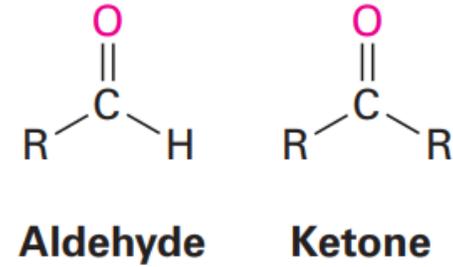
Methyl phenyl sulfide



Carbonyl compounds



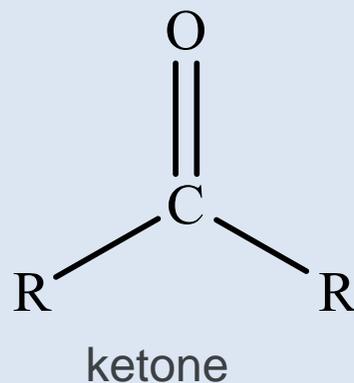
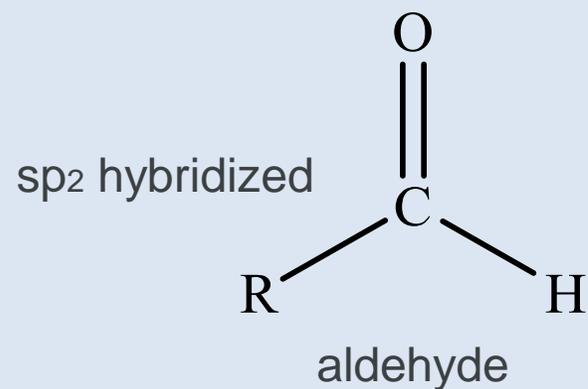
Classification of compounds
with carbonil group





Aldehydes and ketones

- General formula of aldehyde: $RCHO$
- General formula of ketones: $RCOR'$
- The groups R and R' can be aliphatic or aromatic.





Aldehydes and ketones

- (1) easier oxidation of aldehydes compared to ketones, where oxidation is very difficult
- (2) higher reactivity of aldehydes compared to ketones towards the nucleophilic addition reaction, which is characteristic of carbonyl compounds

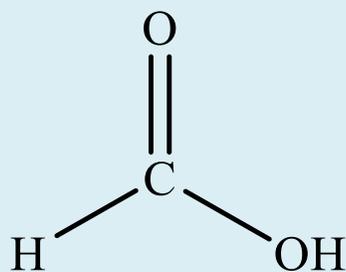


Nomenclature

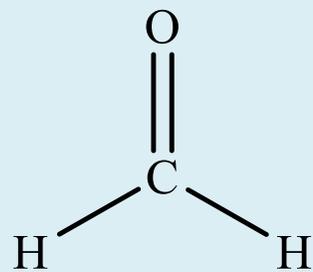
Aldehydes

The trivial names are derived from the trivial names of the corresponding carboxyl acid with the same number of C-atoms. The word aldehyde is added to the root of the Latin name of the acid.

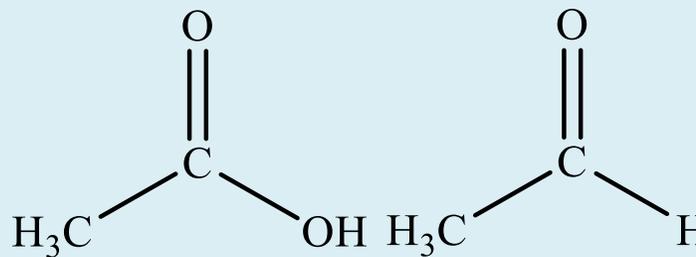
Example: **Formaldehyde and acetaldehyde** - corresponding acids are "formic" (acidum formicum) and acetic (acidum aceticum)



formic acid



formaldehyde



acetic acid

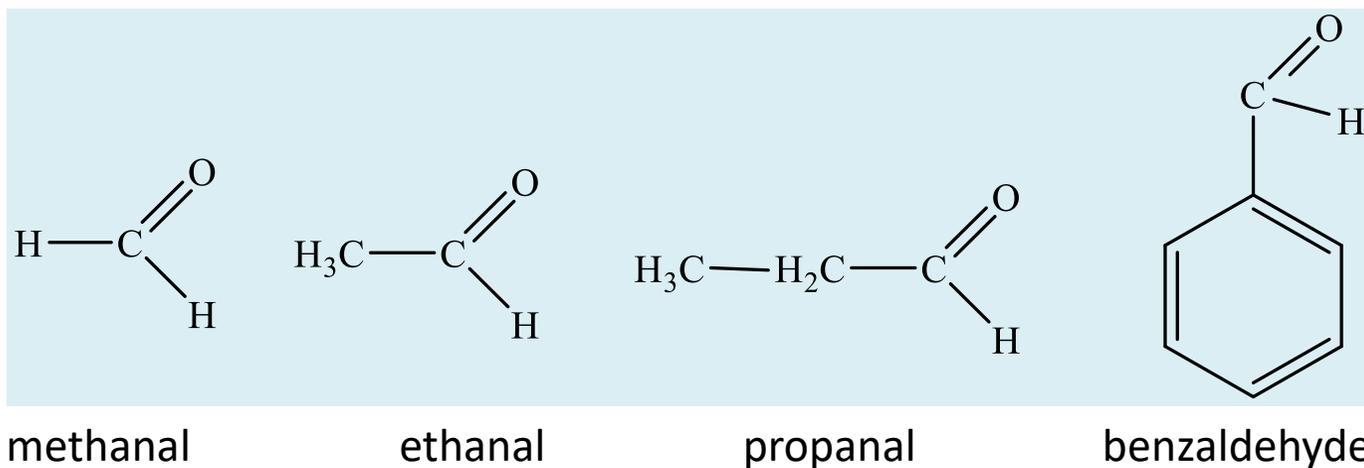
acetaldehyde



IUPAC nomenclatura

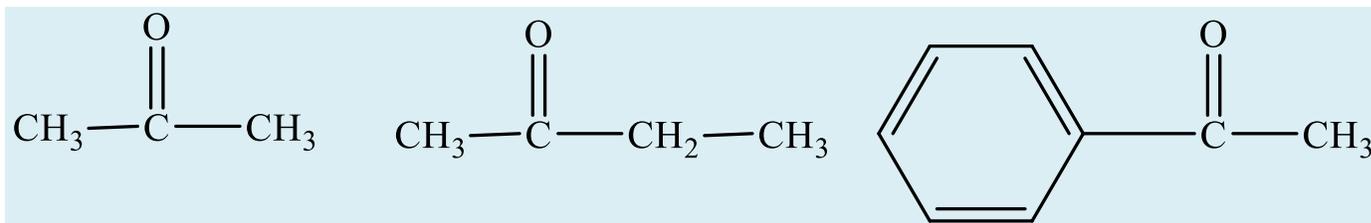
Aldehydes are named by adding the suffix **-al** to the name of the hydrocarbon with the longest chain. The first two aldehydes are methanal and ethanal.

The base sequence is numbered starting from the carbonyl group

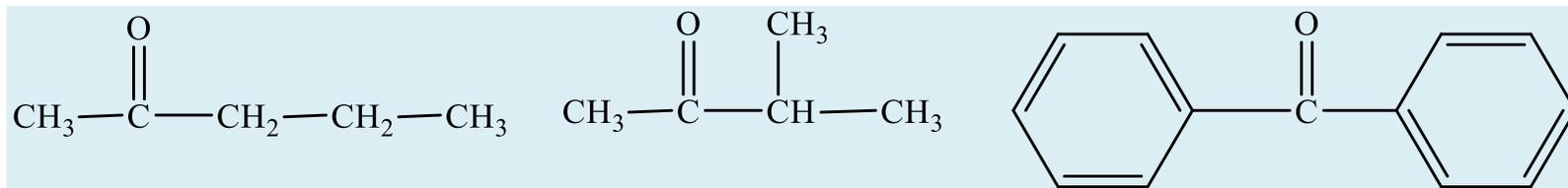




According to the IUPAC nomenclature, ketones are named by adding the suffix **-on** to the name of the longest hydrocarbon chain. The position of the carbonyl group is marked with the smallest possible number.



ethyl-methyl-ketone acetophenone



methyl-propyl-ketone

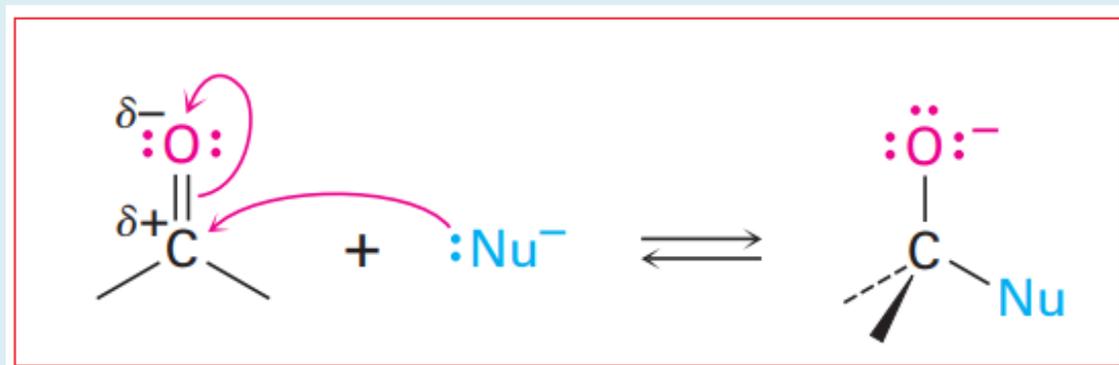
methyl-isopropyl-ketone

benzophenone



The carbonyl group determines the **reactions of aldehydes and ketones**, namely:

- The **nucleophilic addition reaction** is the most common general reaction type for aldehydes and ketones.

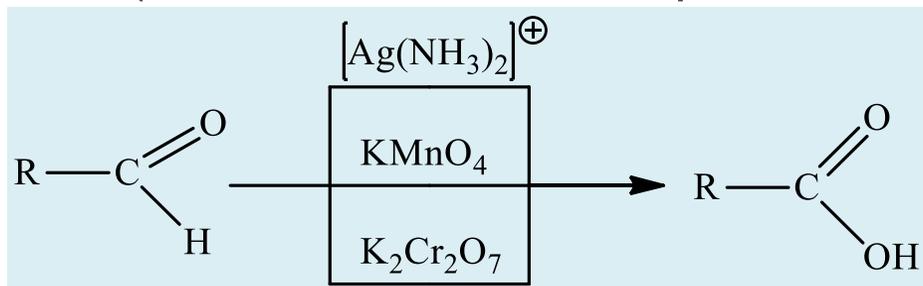


- Aldehydes undergo nucleophilic addition reactions more easily than ketones.

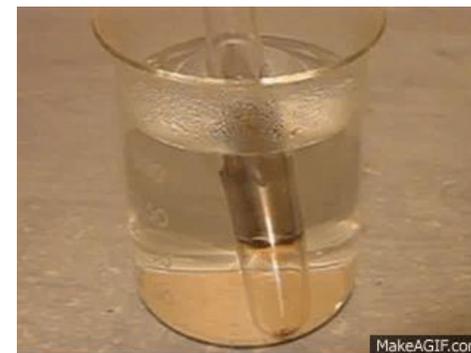
Reactions of aldehydes and ketones

1. Oxidation Aldehyde

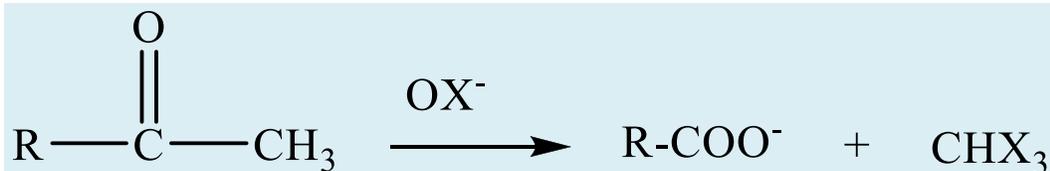
(this reaction serves to prove aldehyde)



Tollens test (silver mirror reaction)



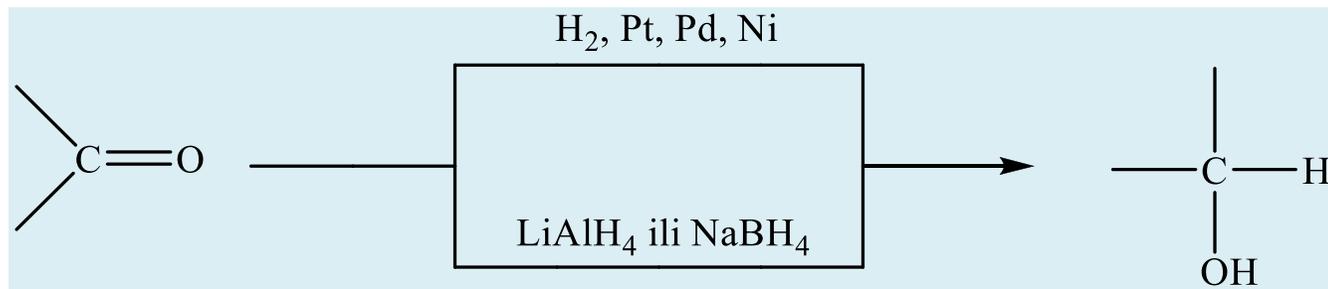
– Methyl ketones (proof reaction-haloform reaction)





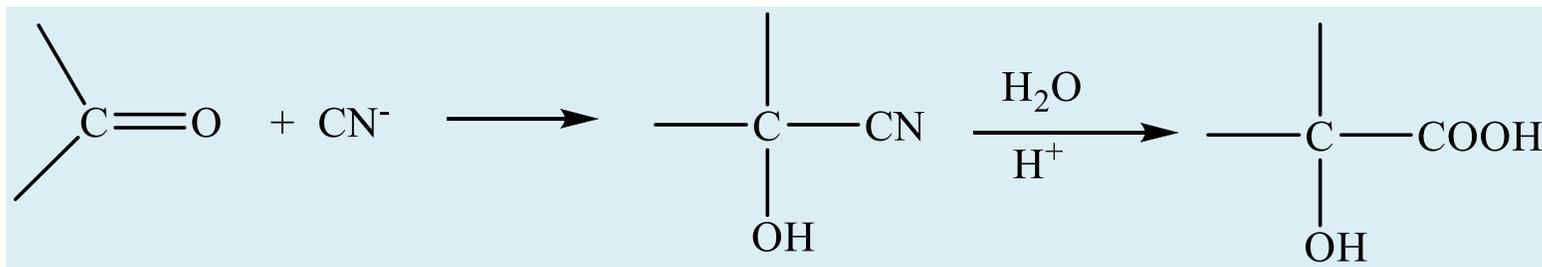
2. Reduction

Reduction to alcohol



3. Addition of cyanide

This reaction produces cyanohydrins. By further hydrolysis of the resulting molecule, α -hydroxy carboxylic acid will be formed.





4. Addition of alcohol

