LECTURE 1

THEME: Introduction of bioorganic chemistry. Classification, structure, chemical properties of organic compounds. Properties of alcohols, aldehydes, ketons.

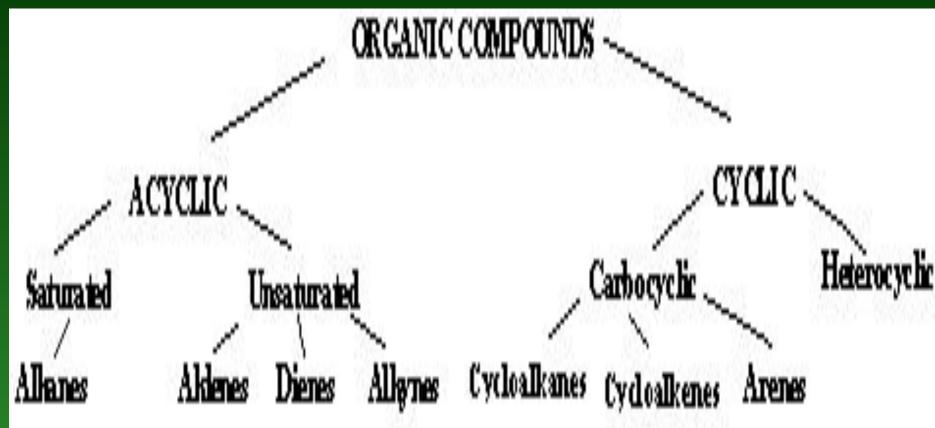
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• Organic Chemistry – the chemistry of the hydrocarbons and their derivatives; the chemistry of carbon compounds.

• **Bioorganic Chemistry** was study structure and properties of biomolecule. Such as: proteins, lipids, hormones, carbohydrates, vitamins, enzyme, fats, at el.

CLASSIFICATION

• By structure of carbon chain:



• By functional groups: alkanes, alkenes, alkynes, alcohols, aldehydes, ketones, carboxylic acids.

- Acyclic compounds, that don't contain any cycle in their molecules.
- Saturated compounds that contain only σ -bonds and no π bonds (simple C C bonds).
- Alkanes saturated hydrocarbons that contain only $-C - C - and - C - H - \sigma$ bonds. Unsaturated — compounds that contain σ -bonds and π - bonds (double bonds (-C = C-) or triple ($-C \cong C -$) bonds, and simple -C-C - bonds).

Alkenes — unsaturated hydrocarbons that contain only one -C - C – double bond (-C = C - C).

Diene — unsaturated compounds that contain two double -C - C – bonds.

Alkynes — unsaturated hydrocarbons that contain -C - C - triple bond ($-C \cong C -$). Cyclic — organic compounds that contain any cycle in its molecules.

Carbocyclic - hydrocarbons containing a cycle that consists of only Carbon atoms. Cycloalkanes — saturated hydrocarbons containing a Carbon cycle. Cycloalkenes — ansaturated hydrocarbons containing a Carbon cycle. Arenes — aromatic compounds that contain benzoic kernel Heterocyclic - organic compounds that contain cycle between atoms of Carbon and other elements (S, O, N).

Functional group classification

Name of class of organic compounds	Functional group	General formula of class of organic compounds
Halogen carbonhydrates	—F, —Cl, —Br, —I	R—Hal
Alcohols, phenols	—OH	R—OH
Thioalcohols, thiophenols	—SH	R— SH
Ethers	—OR	R—0—R
Aldehydes		R-C
Ketones	0 C	0 RCR
Carbon acids	с	R-CO OH
Sulfoacids	—SO ₃ —H	R—SO ₃ —H
Esters	o	0 RCR
Amides	О СNH2	0 R
Nitryles	—C ≅ N	R—C ≅ N
Nitrocompounds	-NO ₂	R—NO ₂
Amines	NH ₂	R—NH ₂

Functional Group is any part of an organic compound, which is not a carbon-hydrogen or carbon-carbon single bon.

All organic compounds concerning to the same class form homological row - it is the row of organic compounds in which each next matter differ —CH₂— group from previous one. Alkanes Methane CH₄ Ethane C₂H₆ Propane C₃H₈ Butane $C_4 H_{10}$ Pentane $C_5 H_{12}$ Hexane C₆H₁₄ Heptane C₇H₁₆ Octane C₈H₁₈ Nonane C₉H₂₀ Decane $C_{10}H_{22}$ Undecane $\overline{C}_{11}\overline{H}_{24}$ **Dodecane** C₁₂H₂₆

NOMENCLATURE

Nomenclature of organic compounds had been formed during last centuries. There are:

- Common (trivial)
- International. In order to systematize the nomenclature of organic compounds, IUPAC (International Union of Pure and Applied Chemistry) system of nomenclature was first introduced in 1947.

<u>Trivial nomenclature.</u> At first organic compounds were named by chance, for example, because the natural sources of its receiving or their properties (citric acid, formic acid). Many trivial names of organic compounds are used nowadays.

Nomenclature of organic compounds had been formed during last centuries. There are:

 CH_4 CH_3 — CH_3 CH_3 — CH_2 — CH_3 methanemethylmethanedimethylmethane

IUPAC nomenclature: The IUPAC system is the most rational and widely used system of nomenclature in organic chemistry. The most important feature of this system is that any molecular structure has only one name. The **IUPAC** name of any organic compound

essentially consists of three parts:

1.word root;

2.suffix;

3.prefix.

1. Word root. It is the basic unit of the name. It denotes the number of carbon atoms present in the **principal chain** (the longest possible continuous chain of carbon atoms including the functional group and the multiple bonds) of the organic molecule. For chains from one to four carbon atoms, special word roots (based upon the common names of alkanes) are used but for chains of five or more carbon atoms, Greek number roots are used as given below:

Word	Chain	Word	Chain
root	length	root	length
Meth-	C ₁	Hept(a)-	C ₇
Eth-	C_2	Oct(a)-	C ₈
Prop-	C_3	Non(a)-	C ₉
But(a)-	C4	Dec(a)-	C ₁₀
Pent(a)-	Cs	Undec(a)-	C ₁₁
Hex(a)-	C ₆	Dodec(a)-	C ₁₂

2. Suffix. There are two types of suffixes:
a) Primary suffix. A primary suffix is always added to the word root to indicate whether the carbon chain is saturated or unsaturated.

Type of carbon chain	Primary suffix	General name
Saturated	ane	Alkane
Unsaturated with one double bond	ene	Alkene
Unsaturated with one triple bond	yne	Alkyne
Unsaturated with two double bonds	diene	Alkadiene
Unsaturated with two triple bonds	diyne	Allcadiyne

The following examples illustrate the usage of word roots and primary suffixes in naming of organic compounds:

Organic compound	Word root	Primary suffix	IUPAC name
CH ₃ CH ₂ CH ₂ CH ₃	But	ane	Butane
CH ₂ =CHCH ₃	Prop	ene	Propene
CH≡CH	Eth	yne	Ethyne
CH ₂ =CH-CH=CH ₂	Buta	diene	Butadiene
CH≡CH–CH≡CH	Buta	diyne	Butadiyne

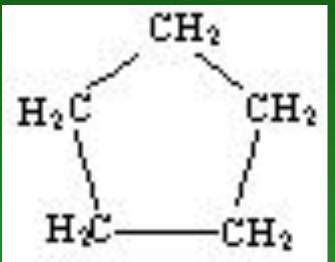
b) Secondary suffix. A secondary suffix is added to the primary suffix to indicate the nature of the functional groups are present in the organic compound. Secondary suffixes of some important functional groups are given below:

Class of organic compounds	Functional group	Secondary suffix
Alcohols	OH	ol
Aidehydes	CHO	ഖ
Ketones	C=O	one
Carboxylic acids	COOH	oic acid
Acid amides	CONH2	amide
Acid chlorides	COCI	oyl chloride
Esters	COOR	alky1oate
Nitriles	CN	nitrile
Thioalcohols	SH	thiol
Amines	NH ₂	amine

The following examples illustrate the use of word root, primary suffix and secondary suffix in naming organic compounds:

Organic compound	Word root	Primary suffix	Secondary suffix	IUPAC name
CH ₃ CH ₂ OH	Eth	ane	ol	Ethanol
CH ₃ CH ₂ CH ₂ NH ₂	Prop	ane	amine	Propanamine
CH ₃ CH ₂ CH ₂ COOH	But	ane	oic acid	Butanoic acid
CH ₃ CH ₂ CN	Prop	ane	nitrile	Propanenitrile
CH ₂ =CHCHO	Prop	ene	al	Propenol
CH≡CHCOOH	Prop	yne	oic acid	Propynoic acid

3. Prefix. There are two types of prefixes:
a) Primary prefix. A primary prefix is used simply to distinguish cyclic from acyclic compounds.
For example, in case of carbocyclic compounds, (cyclic compounds containing only carbon atoms in the ring), a primary prefix, *cyclo-* is used immediately before the word root.



CyclopentaneCyclopentanePrimary prefixWord rootPrimary suffixIUPAC name

If the prefix *cyclo*- is not used, it simply indicates that the compound is acyclic or with open chain.

b) Secondary prefix. In IUPAC system of nomenclature certain groups are not considered as functional groups but instead are treated as substituents, these groups are called secondary prefixes and are added order to denote the side chains or substituent groups. The secondary prefixes for some groups which are always treated as substituent groups:

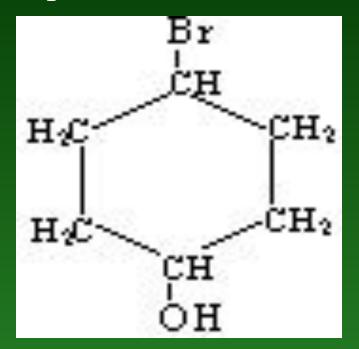
Sub stituent group	Secondary prefix	Substituen group	Secondary prefix
F	Fluoro	OCH ₃ (OMe)	Methoxy
Cl	Chloro	OC ₂ H ₃ (OEt)	Ethoxy
Br	Bromo	R	Alkyl
Ι	Iodo	CH3	Methyl
NO2	Nitro	C ₂ H ₅	Ethyl
NO	Nitroso	CH2CH2CH3 (n-Pr)	n-Propyl
*N≡N	Diazo	CH(CH ₃) ₂ (i-Pr)	Isopropyl
OR	Alkoxy	CH(CH ₃) ₃ (t-But)	t-Butyl

- Reactivity of functional group
- Sulphonic acids > carboxylic acids > anhydrides > esters
 > acid chlorides > acid amides > nitriles > aldehydes > ketones > alcohols > amines > ethers > alkenes > alkenes > alkynes.
- All the remaining functional groups such as halo (fluoro, chloro, bromo, iodo), nitroso (–NO), nitro (– NO₂), and alkoxy (–OR) are always treated as substituent groups.

The following examples illustrate the usage of word root, primary and secondary prefixes and suffixes in naming of organic compounds:

Organic compound	Secondary prefix	Word root	Primary suffix	IUPAC name
CH ₃ CH ₂ –Br	Bromo	eth	ane	Bromoethane
CH ₃ -NO ₂	Nitro	meth	ane	itromethane
C ₂ H ₅ -O-C ₂ H ₅	Ethoxy	eth	ane	Ethoxyethane

In the case of carbocyclic compounds primary prefixes are also used. For example,



hex

1-0l

an (e)

4-Bromocyclo4-Bromocyclohexan-1-ol

SecondaryPrimaryWordPrimarySecondaryprefixprefixrootsuffixsuffix

Complete IUPAC name of organic compound consists of the following parts:

SECONDARY PREFIX + PRIMARY PREFIX + WORD ROOT + PRIMARY SUFFIX + SECONDARY SUFFIX

Rules for IUPAC names of complex aliphatic organic compounds.

I. Rules for IUPAC nomenclature of complex saturated hydrocarbons (Alkanes)

Alkanes which contain a number of branched chains are called complex alkanes. These alkanes are usually named by the IUPAC system according to the following rules: **1. Longest chain rule.** Find the longest continuous chain of Carbon atoms in the molecule. This is called the parent chain. For example:

$$CH_3$$

 $CH_3 - CH_2 - CH - CH_2 - CH_2 - CH_3$

Longest chain contains 6 Carbon atoms. Named as hexane Longest chain contains 7 Carbon atoms Named as heptane **2. Rule for larger number of side chains.** If two different chains of equal lengths are possible, select the one with larger number of side chains or alkyl groups. For example,

 $\begin{array}{c} CH_3 - CH - CH_2 - CH_2 - CH_3 \\ CH_3 \quad CH_2 - CH_3 \end{array}$

Named as hexane with two alkyl substituents (correct)

Named as hexane with one alkyl substituent (wrong)

 $CH_3 - CH + CH - CH_2 - CH_2 - CH_3$

CH3 CH2 - CH3

3. Lowest number rule or lowest locant rule. Number the Carbon atoms of the parent chain as 1, 2, 3, 4, ... etc. starts from that end which gives the lowest possible number to the Carbon atom carrying the substituents.

$$\begin{array}{ccccccc} 1 & 2 & 3_{1} & 4 & 5 & 6 \\ CH_{3} - CH_{2} - CH - CH_{2} - CH_{2} - CH_{3} \end{array}$$

$$\begin{array}{ccccc}
6 & 5 & CH_3 \\
6 & 5 & 4_1 & 3 & 2 & 1 \\
CH_3 - CH_2 - CH - CH_2 - CH_2 - CH_3
\end{array}$$

The number that indicates the position of the substituent in the parent chain is called the positional number or the locant. The correct locant for the methyl is 3.

4. Lowest sum rule and lowest set of locants rule. When two or more substituents are present, two rules are generally mentioned. These are:

a) Lowest sum rule. When two or more substituents are present, the numbering of the Carbon atoms of the parent chain is done in such way that the sum of locants is the lowest. This is called the lowest sum rule.
b) Lowest set of locants rule. When two or more substituents are present in the parent Carbon atom chain the lowest set of locants are numbered from all the possible directions.

$$\begin{array}{c}2 & 1\\ CH_2 - CH_3\\ 3! & 4\\ CH_3 - CH - CH - CH_2 - CH_2\\ 5! & 6\\ CH_2 - CH_2 - CH_3\end{array}$$

correct Sum of the locants = 3 + 4 = 7Set of locants = 3, 4 wrong Sum of the locants = 4 + 5 = 9Set of locants = 4,5

$$\begin{array}{cccccc} CH_3 & CH_3 & CH_3 & CH_3 \\ 1 & 2I & 3 & I4 & 5 \\ CH_3 - C - CH_2 - CH - CH_3 & CH_3 & I2 & 1 \\ - CH_3 - C - CH_2 - CH - CH_3 & CH_3 - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 & CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_2 - CH - CH_3 \\ - CH_3 & - C - CH_3 \\ - CH_3 & - CH_3 \\ -$$

correctwrongSum of the locants = 2+2+4=8Sum of the locants = 2+4+4=10Set of locants = 2,2,4Set of locants = 2,4,4

But when the length of the carbon chain is long, the two rules often give different results. For example,

Correct numbering Sum of locants = 2 + 7 + 8 = 17 Set of locants = 2, 7, 8 (correct)

$$\begin{array}{ccccccc} & & & & & CH_3 & CH_3 \\ 10 & 19 & 8 & 7 & 6 & 5 & 14 & 13 & 2 & 1 \\ CH_3 - CH - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH & - CH & - CH_2 - CH_3 \end{array}$$

Wrong numbering Sum of locants = 3 + 4 + 9 = 16 Set of locants = 3, 4, 9 (wrong) **5. Name of the complex alkane.** We use prefix to indicate the position of substituent on the parent chain writing the number of the Carbon atom carrying the substituent.

6. Alphabetical order of the simple substituents. When two or more simple substituents are present on the parent chain, each prefixes is arranged in alphabetical order before the name of the parent alkane. 7. Numbering of the different substituents in equivalent positions. When two different substituents are present in equivalent positions, the numbering of the parent chain is done in such a way that the subtituent which comes first in the alphabetical order gets the lower number.

8. Naming of the same substituents in different positions. When the same substituents occur more than once on the parent chain at different positions, the positional number of each substituent is separated by commas and suitable numerical prefixes such as di (for two), tri (for three), tetra (for four) etc. are attached to the name of the substituents. However, the prefixes di, tri etc. are not considered while deciding the alphabetical order of the alkyl groups. In case the same substituent occurs twice on the same Carbon atom, its positional number is also repeated twice.

9. Naming of the complex substituent (or substituted substituent).

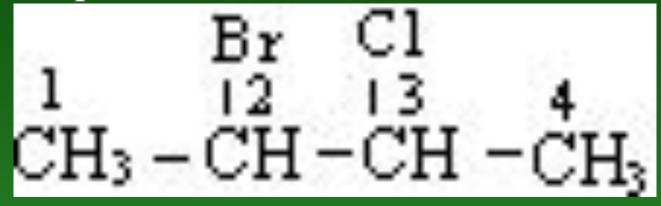
a) In the case the substituent on the parent chain is complex (i. e., it has branched chain), it is named as a substituted group by separately numering the Carbon atom of this group attached to the parent chain as 1. The name of such a substituent is always enclosed in brackets to avoid confusion with the numbers of the parent chain.

- **b**) While deciding the alphabetical order of the various substituents, the name of the complex substituent is considered to begin with the first letter of complete name.
- c) When the names of two or more substituents are composed of identical words, priority of citation is given to that substituent which has lowest locant at the cited point of difference within the complex substituent.

II. Rules for IUPAC nomenclature of unsaturated hydrocarbons (Alkenes and Alkynes). When naming compounds containing multiple (double and triple) bonds, the following additional rules are followed: 1. The parent chain must contain the multiple bond regardless of the fact whether it also denotes the longest continuous chain of Carbon atoms or not. 2. If both double and triple bonds are present, the numbering of the parent chain should always be done from that end which is nearer to the double or the triple bond.

3. If, however, there is a choice in numbering the double bond is always given preference over the triple bond.

III. Rules for IUPAC nomenclature of complex haloalkanes. Some important rules according to 1993 recommendations are discussed below:
1. When where are two different substituents: For example,



2 - Bromo - 3 - chlorobutane(Not 2 - Chloro - 3 - bromobutane) Lowest set of locants. In principle, when two or more different sets of locants are possible, that set of locants is preferred, which has the lowest term at the first point of difference even if it violates the lowest sum rule. For example: the locant set 2, 7, 8 (sum 17) is preferred over 3, 4, 9 (sum 16).

2 - Bromo - 8 - ethyl - 7 - methyldecane(Not 9 - Bromo - 3 - ethyl - 4 - methyldecane) 3. Name of a prefix for a substituted substituent is considered to begin with the first letter of its

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$$\begin{array}{c} 4 & 12 & 11 \\ CH_3 - CH_2 - CH & -CH & CH_2 - CH_3 \\ CH_3 - [CH_2]_4 - CH_2 - CH - CH_2 - CH_2 - CH_3 \\ 13 & -[CH_2]_4 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 \\ 13 & -[CH_2]_4 - CH_2 - CH_2 - CH_3 \\ 13 & -[CH_2]_4 - CH_2 - CH_2 - CH_3 \\ 13 & -[CH_2]_4 - CH_2 - CH_2 - CH_3 \\ 14 & -[CH_2]_4 - CH_3 - CH_3 \\ 14 & -[CH_2]_4 - CH_2 - CH_3 \\ 14 & -[CH_2]_4 - CH_3 - CH_3 - CH_3 \\ 14 & -[CH_2]_4 - CH_3 - CH_3 - CH_3 - CH_3 \\ 14 & -[CH_2]_4 - CH_3 - CH_3 - CH_3 - CH_3 - CH_3 - CH_3 \\ 14 & -[CH_2]_4 - CH_3 \\ 14 & -[CH_2]_4 - CH_3 - CH_$$

7 - (1, 2 - Difluorobutyl) - 5 - ethyltridecane

4 - (1 - Chloroethyl) - 5 - (2 - chloroethyl) nonane

IV. Rules for IUPAC nomenclature of compounds containing one functional group, multiple bonds and substituents. While naming organic compounds containing one functional group, double and triple bonds, and substituents, the following additional rules are observed.

1. Parent chain. Select the longest possible chain of Carbon atoms containing the functional group and the maximum number of multiple bonds as **parent chain.**

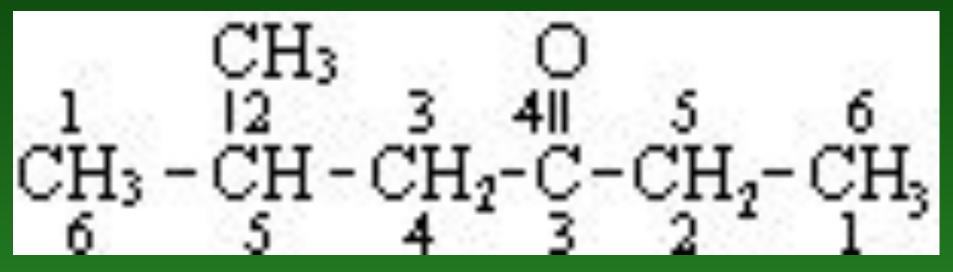
CH₂-OH $H - CH_2$ $-CH_3$

Parent chain contains four rather than five Carbon atoms.

 $CH = CH_{2}$ $C - CH_2 - CH - CH_2 - CH - C$

Parent chain contains six rather than seven Carbon atoms.

2. Lowest number for the functional group. Number the parent chain in such a way that the functional group gets the lowest possible number followed by double and triple bonds even if it violates the **lowest sumrule**.



(Wrong) (> C = 0 group gets number 4 which is not lowest)

(Conect) (> C = O group gets lowest number 3)

3. Numbering of the chain terminating functional groups. When a chain terminating functional group such as - CHO, - COOH, - COOR, - CONH2, - COCl, - C \equiv N etc. is present, it is always given **number 1.** The locant 1 (unity) for the principal functional group is omitted when there is no ambiguity. But in this chapter, this numerical locant is always included when another numerical locant appears in the same name. For example,

$$\begin{array}{c}
 1COOH \\
 - CH_3 - CH_7 - CH - CH_2 - CH_3 \\
 - CH_3 - 2 \\
 - CH - CH_2 \\
 - CH_2 - CH_2 \\
 - CH_2 \\
 - CH_2 \\
 - CH_2 \\
 - CH_2
\end{array}$$
Propa

2-ethylbutan-loic acid

Propane-1, 2, 3-triol

If the organic molecule contains more than one similar complex substituents, then the numerical prefixes such as di, tri, tetra etc. are replaced by bis, tris, tetrakis, etc. For example,

$$HO - \frac{1}{CH_{2}} - \frac{2}{CH_{2}} - O - \frac{2}{CH_{2}} - \frac{1}{COOH}$$
$$HO - \frac{1}{CH_{2}} - \frac{2}{CH_{2}} - O - \frac{2}{CH_{2}} - \frac{1}{COOH}$$

2,2-Bis(2-hydroxyethoxy)ethanoic acid

5. Types of chemical bonds and their description

In the molecule all atoms have influence on each other. The result of this influence is called electronic bonds. It compels neighboring atoms to be side by side.

There are 4 types of chemical bonds:

<u>**Covalent bond.</u>** This is the main type of bond in organic chemistry. It formed is between atoms with similar electronegativity. In this case common electronic cloud is formed.</u>

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Polar bond. This is a covalent bond between 2 atoms with different electronegativity in which electron pair is not shared equally. But the difference of electronegativity is not big.

 $CH_3 \cdot Cl \longrightarrow CH_3 \rightarrow Cl$

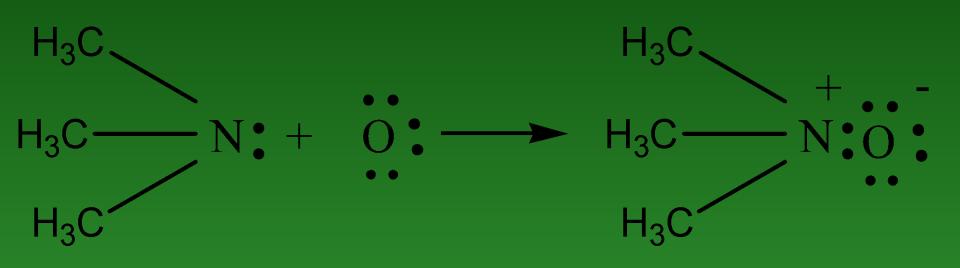
Ion bond. This is a bond between 2 atoms with different electronegativity (difference of electronegativity is very big).

$$NaCl \rightarrow Na^{+} + Cl^{-}$$

Donor-acceptor bond. This is a type of covalent bond, but it has different origin. In covalent bond a pair of electrons consists of 2 electrons from 2 atoms. But in donor-acceptor bond only one atom gives 2 electrons, but another atom accepts one electron.

acceptor

<u>Semipolar bond.</u> This is a type of donor-acceptor bond, then one atom has 2 free electrons, and another atom has 6 electrons.

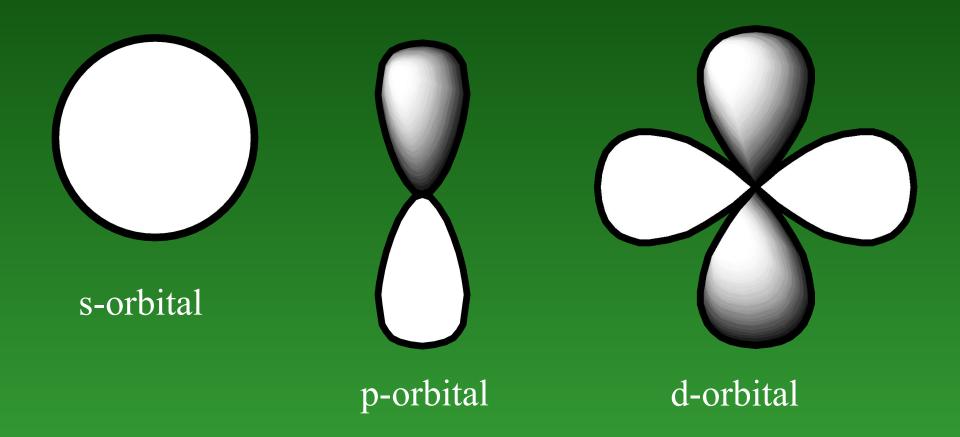


Hydrogen bond. This bond is formed between atom of H+ and negative atom. This bond is designated as 3 points (...).

i i 0,176 nm 0,099 nm

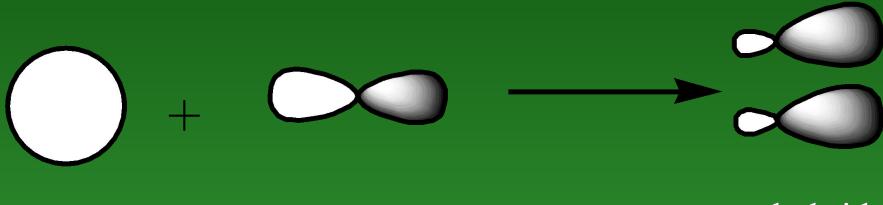


Hybridization of atom orbitals: sp-, sp2-, sp3-Atom orbital is the space where the atom can be. There are s-, p- and d-atom orbitals.



In organic compounds the atom of Carbon has hybrid orbitals. There are 3 main types of them:

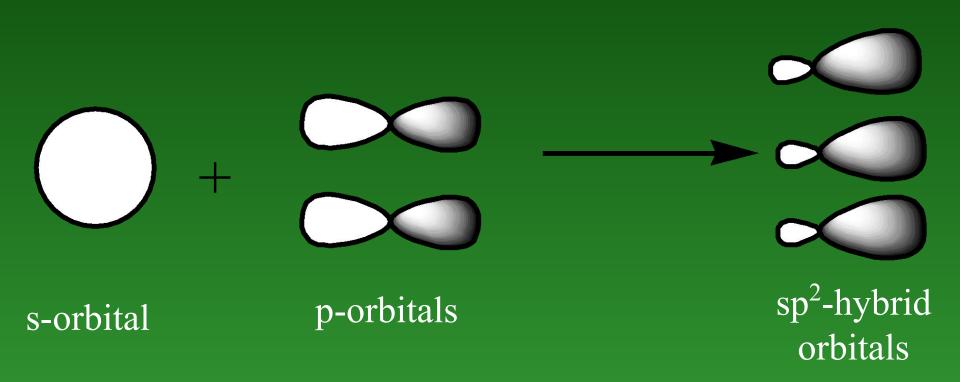
• sp-hybridization of atom orbitals. This hybridization is formed when s-orbital joined to p-orbital.



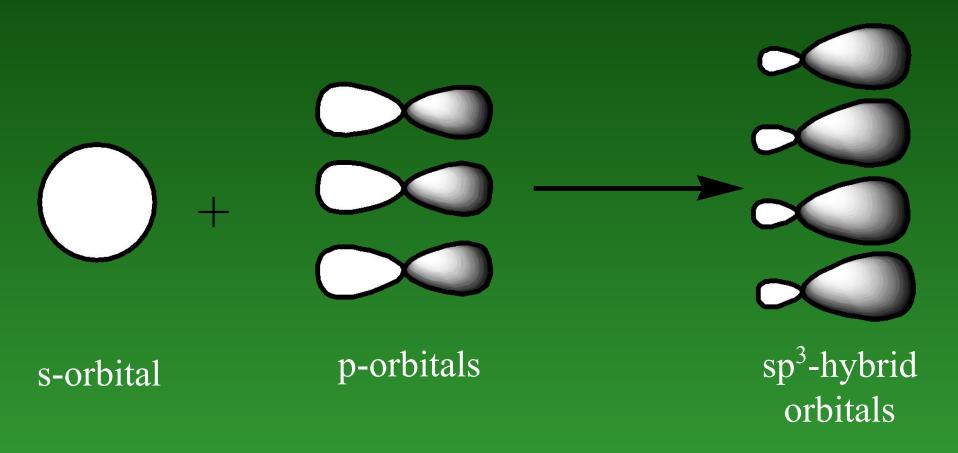
s-orbital

p-orbital

sp-hybrid orbitals sp²-hybridization of atom orbitals. This hybridization is formed when s-orbital joined to 2 p-orbitals.

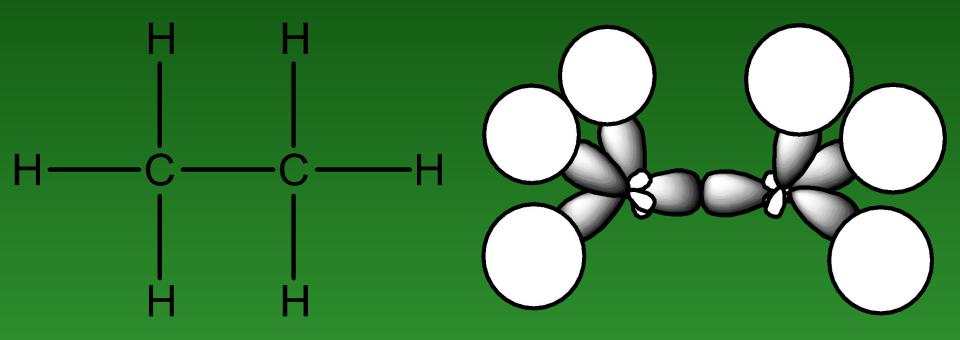


 sp³-hybridization of atom orbitals. This hybridization is formed when s-orbital joined to 3 p-orbitals.

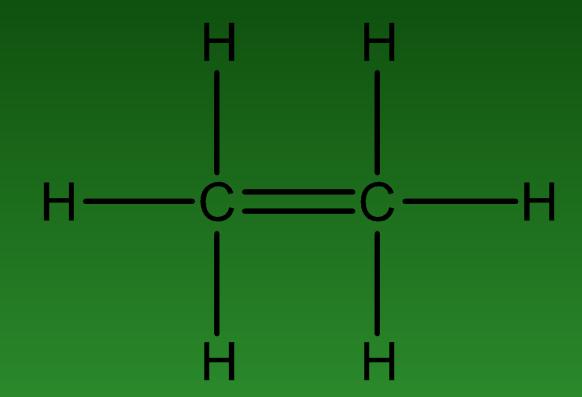


The Carbon atom forms covalent bonds in the molecule of organic compounds. There are 2 types of covalent bonds: σ - and π -bonds.

 σ -bond is formed after joining of two different atomic orbitals (s- and p-orbitals) or two hybrid orbitals (sp³-hybrid orbitals):

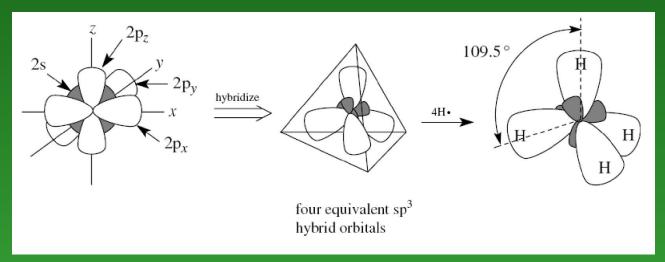


π -bond is formed after joining of two identical s- or p-orbitals.

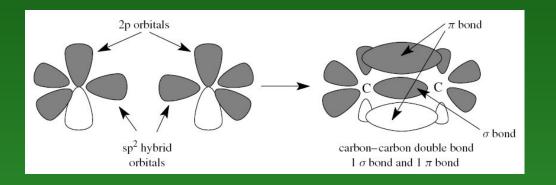


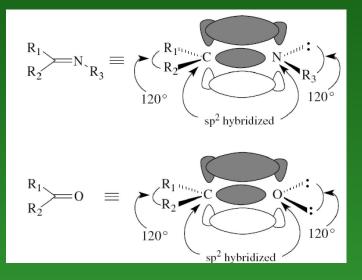
Hybrid Atomic Orbitals

- Orbitals formed by mixing the wave functions of pure s and p orbitals of an atom. There are three major types of hybrid atomic orbital :
- sp^3 formed by combining the wave function of one s orbital with the wave functions of three p orbitals. Four hybrid orbitals oriented towards the vertices a tetrahedron are formed.

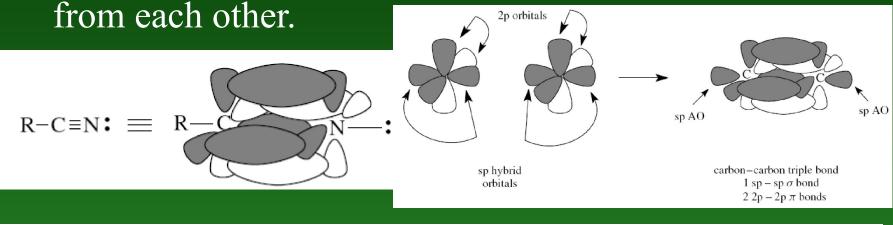


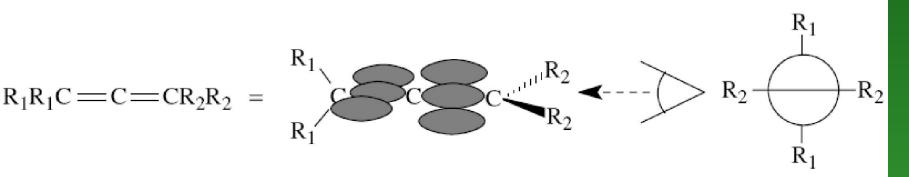
sp² – formed by combining the wave function of one s orbital with the wave functions two p orbitals. Three coplanar hybrid orbitals oriented towards the vertices of an equilateral triangle are formed. Each of the three sp² hybrids has a shape that is much like that of an sp hybrid orbital, but the three are oriital, at 120⁰ from each other.





sp – obtained by combining the wave function of one s orbital with the wave function of one p orbital. Two colinear hybrid orbitals oriented in opposite directions are formed. The hybrid orbitals are oriented at 180^o from each other.





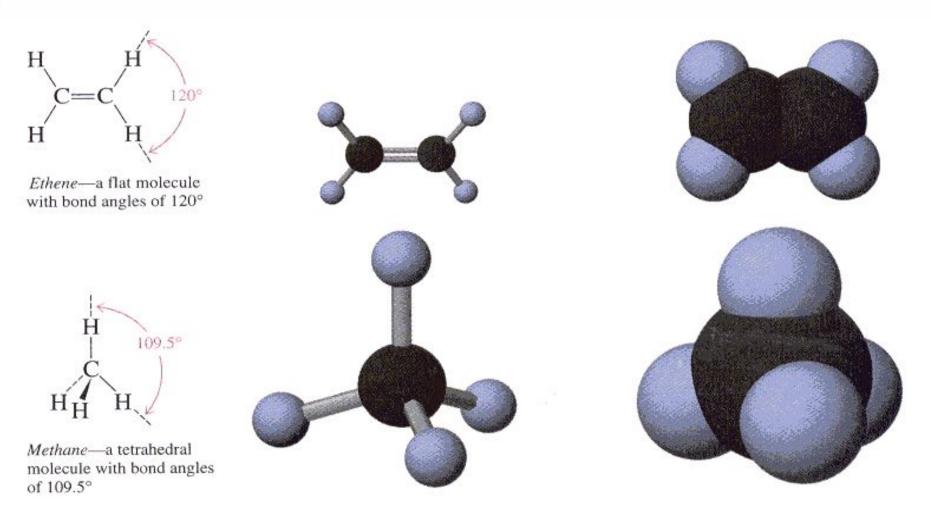
80°. Н−С≡С−Н

Ethyne—a linear molecule with bond angles of 180°

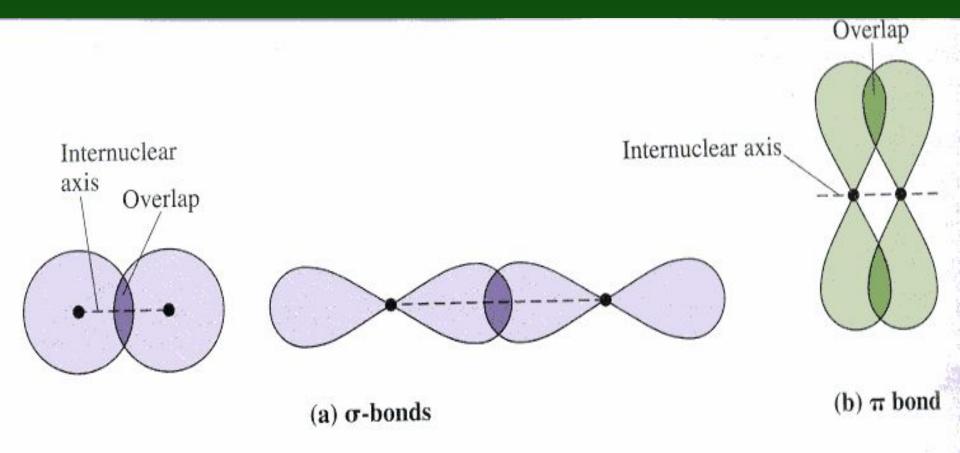
n

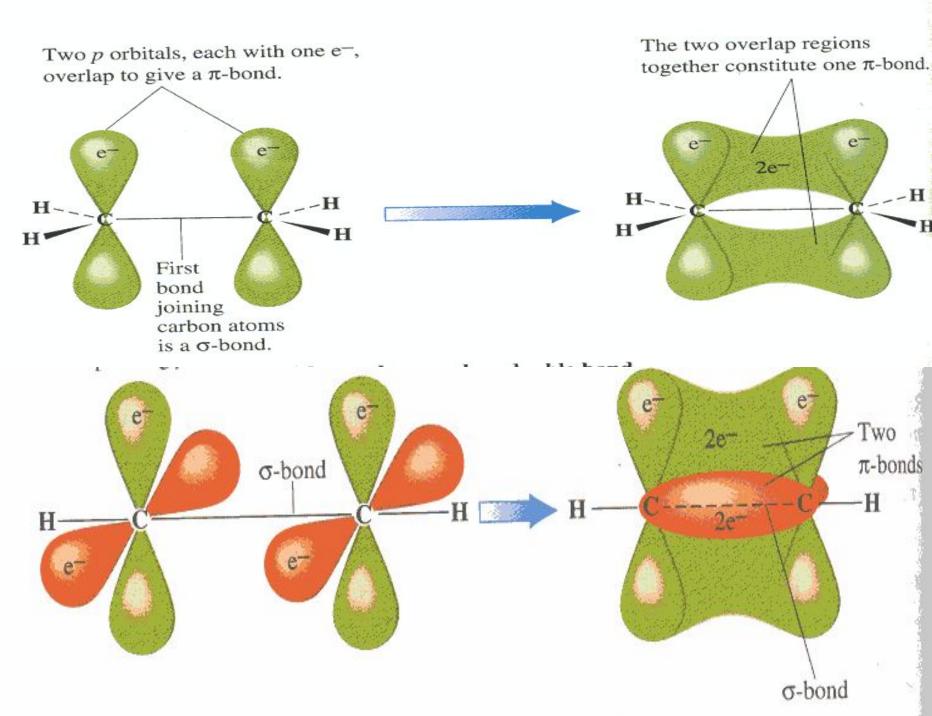


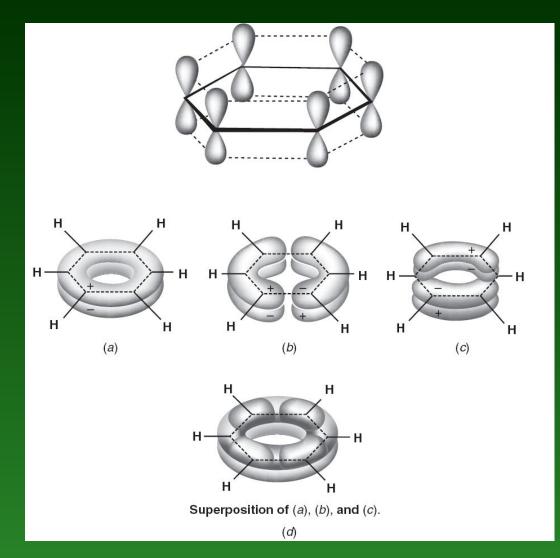




Formation bond in molecules of organic compounds







The six p orbitals of benzene overlap to form three bonding orbitals, (a), (b), and (c). The three orbitals superimposed are shown in (d). Types of bond fission or cleavage (breaking of a covalent bond).
Homolytic (symmetrical) fission. If a covalent bond breaks in such a way that each atom takes away one electron of the shared pair, it is called homolytic or symmetrical fission.

 $\mathrm{H}-\mathrm{H} \to \mathrm{H} \cdot + \mathrm{H} \cdot$

Heterolytic (unsymmetrical) fission. When a covalent bond joining two atoms A and B breaks in such a way that both the electrons of the covalent bond are taken away one of the bonded atoms, the mode of bond cleavage is called heterolitic fission. H – C1 → H⁺ + Cl⁻

- **Electrophilic** are electron loving chemical species. Their attraction for electrons is due to the presence of an electron-deficient atom in them.
- Electrophilic may be either positively charged or electrically neutral chemical species.
- Positive electrophiles: H^+ , $H_3^-O^+$, $C1^+$, Br^+ , I^+ , NO_2^+ , NO^+ , R^+ (carbocation) etc.
- Neutral electrophiles: R[·] (free radicals),:CR₂ (carbenes),:NR (nitrenes), BP₃, A1C₃, FeC1₃² SnC1₄.

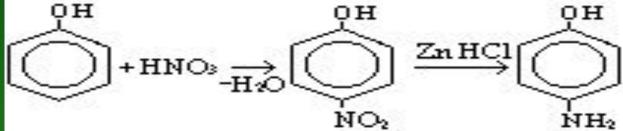
- Nucleophiles are nucleus loving chemical species. Since the nucleus of any atom is positively charged, therefore, nucleophiles must be electron rich chemical species containing at least one lone pair of electrons. They may be either negatively charged or neutral chemical species:
- Negative nucleophiles: H⁻ (hydride ion), CR⁻, Br⁻, I⁻, R⁻ (carbanion), OH⁻, OR⁻, SR⁻, NH₂⁻, CN⁻, RCOO⁻.
- Neutral nucleophiles: H₂O, NH₃, RNH₂, ROH, RSH, ROR etc.

Types of organic reactions.

- All the organic reactions can be broadly classified into the following four types:
- (a) substitution reactions,
- (b) addition reactions,
- (c) elimination reactions,
- (d) rearrangement reactions.

(i) Substitution reactions which are brought about by nucleophiles are called nucleophilic substitution reactions:

CH₃OH + CH₃COOH \rightarrow CH₃COOCH₃ + H₂O (ii) Substitution reactions which are brought about by electropholes are called electrophilic substitution reactions:



(iii) Substitution reactions brought about by free radicals are called free radical substitution reactions:

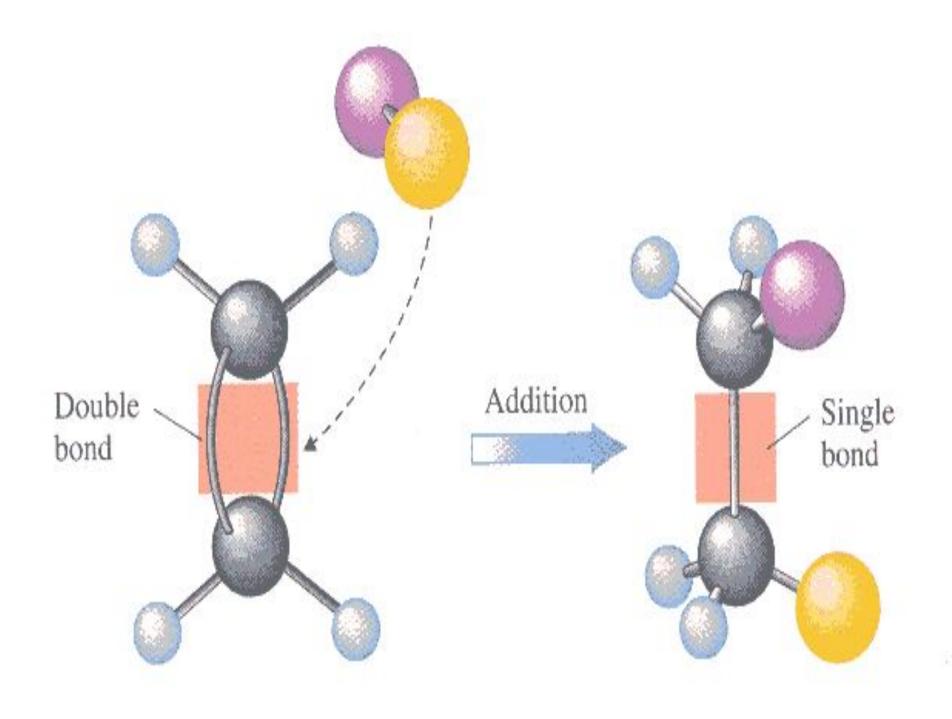
$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

Addition reactions

- Reactions, which involve combination between two reacting molecules to give a single molecule of the product are called addition reactions. Such reactions are typical of compounds containing multiple (double or triple) bonds.
- Addition reactions are of the following three types:
- (i) Addition reactions brought about by nucleophiles are called **nucleophilic addition reactions:**

$$\begin{array}{ccc} OH & NOH \\ R - C - R' + NHOH \rightarrow R - C - R' \rightarrow R - C - R' + HOO \\ NHOH \end{array}$$

- ii) Addition reactions brought about by electrophiles are called **electrophilic addition reactions.**
- i) Addition reactions brought about by free radicals are called **free radical addition reactions.**



• Elimination reactions. An elimination reaction is one that involves the loss of two atoms orgroups of atoms form the same or adjacent atoms of a substance leading the formation of a multiple (double or triple) bond:

$$\begin{array}{cc} \mathbf{CH}_2 - \mathbf{CH}_2 \rightarrow \mathbf{CH}_2 = \mathbf{CH}_2 + \mathbf{H}_2\mathbf{O} \\ \mathbf{H} & \mathbf{OH} \end{array}$$

- These are of two types:
- β-Elimination reactions.
- α-Elimination reactions.

Reactions involving the migration of an atom or a group from one atom to another within the same molecule are called **rearrangement reactions.**

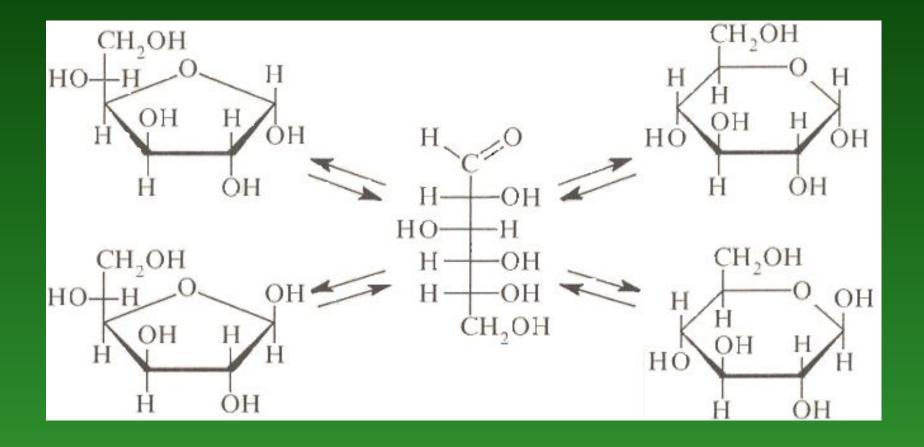
Oxidation — a net decrease in the number of π bonds to hydrogen or electropositive element, or a net increase in the number of bonds to electronegative elements. A net loss of electrons.

$$\begin{array}{c} O \\ R - C - H + Ag^{+} \xrightarrow{NHb} H O \\ A \end{array} R - C - OH$$

Reduction — a net increase in the number of σ bonds to hydrogen or electropositive element, or a net decrease in the number of bonds to electronegative elements. A net gains electrons.

$$\begin{array}{c} O \\ R - C - H + H_2 \xrightarrow{Ni} R - C - O - H \\ H \end{array}$$

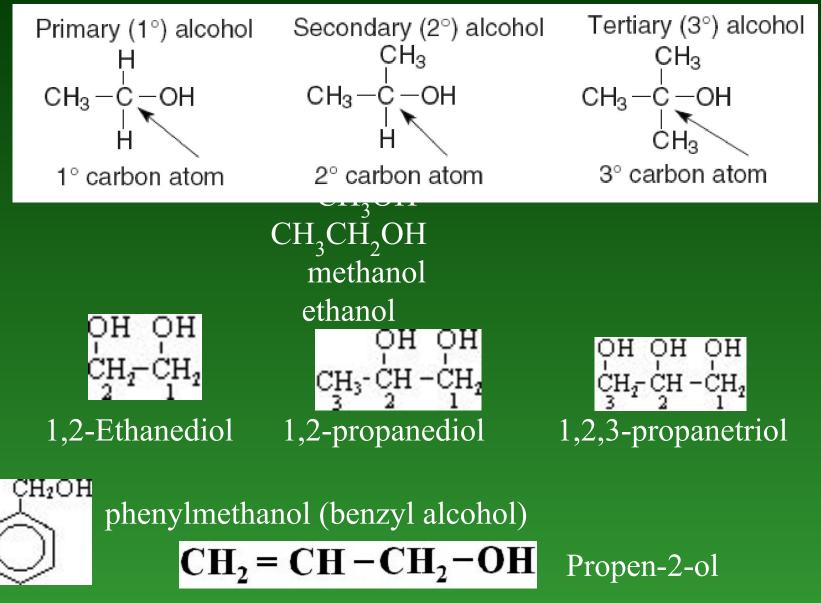
Rearrangement reactions



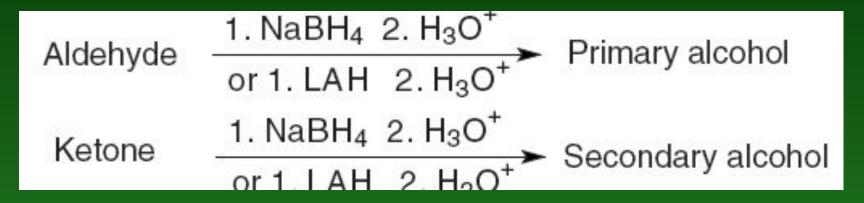
Alcohols

• Alcohols are a family of compounds containing a hydroxyl (OH) group bonded to an sp3 hybridized carbon atom. The most widely known alcohol is ethanol (ethyl alcohol, CH₃CH₂OH).

classification



Preparation of Alcohols



Reaction

Alcohols react with active metals such as sodium and potassium,

CH₃CH₂OH + [−] NH₂ → CH₃CH₂O p <i>K</i> a = 15.9) [–] + NH ₃ p <i>K</i> a = 36 Much weaker acid
$CH_3CH_2OH + OH CH_3CH_2O$ $pK_a = 15.9$ Slightly weaker acid	- + H ₂ O p <i>K</i> _a = 15.7
$2 \text{ ROH} + 2 \text{ Na} \rightarrow 2 \text{ RO}^- + 2 \text{ Na}^+ + \text{H}_2$	
$C_2H_5OH + Na^{\bigoplus}NH_2^{\bigoplus} \rightleftharpoons C_2H_5O^{(1)}$ sodium amide sodium e (sodamide)	
$2C_2H_5OH + 2Na \longrightarrow 2C_2H_5OH$	$O^{\bigcirc}Na^{\oplus} + H_2$
$C_2H_5OH + Na^{\oplus}H^{\ominus} \longrightarrow C_2H_5O^{\oplus}$	$\Theta_{Na} \oplus H_2$

Basic Properties

Nucleophilic Properties

$$CH_{3}I + C_{2}H_{5}OH \xleftarrow{slow} CH_{3}OC_{2}H_{5} + HI$$

$$CH_{3}I + C_{2}H_{5}O^{\textcircled{}}Na^{\textcircled{}} \xrightarrow{fast} CH_{3}OC_{2}H_{5} + NaI$$

$$\xrightarrow{(\textcircled{})} \stackrel{\textcircled{}}{\ominus} \stackrel{\textcircled{}}{\ominus}$$

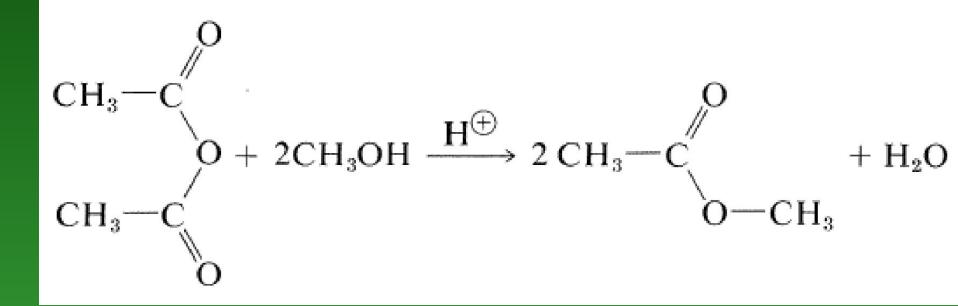
$$CH_{3}I + (CH_{3})_{2}CHO^{\textcircled{}} \xrightarrow{S_{N}2} (CH_{3})_{2}CHOCH_{3} + I^{\textcircled{}}{\ominus}$$

$$(CH_{3})_{2}CHI + CH_{3}O^{\textcircled{}} \xrightarrow{E2} CH_{3}CH = CH_{2} + CH_{3}OH + I^{\textcircled{}}{\ominus}$$

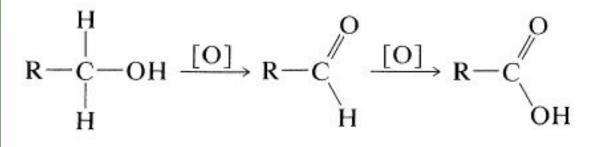
$$CH_{3} - C \xrightarrow{(\textcircled{})} + CH_{3}OH \xleftarrow{H^{\textcircled{}}{\oplus}} CH_{3} - C \xrightarrow{(\textcircled{})} + H_{2}O$$

$$CH_3 - C + CH_3OH \longrightarrow CH_3 - C + HCl$$

Cl + HCl - CH₃ - C + HCl



primary alcohols



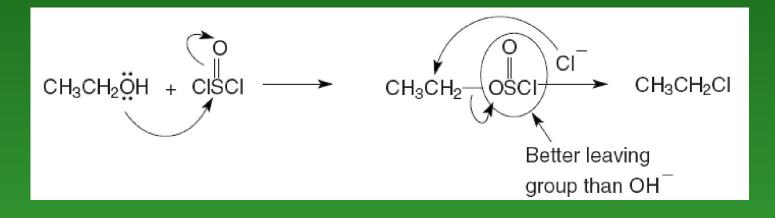
secondary alcohols

tertiary alcohols

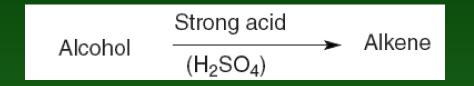
$$\begin{array}{c} R \\ | \\ R \longrightarrow C \longrightarrow C \\ | \\ R \end{array}$$
 fragmentation



 Conversion of Alcohols to Alkyl Halides



Dehydration Reactions



 $\overline{\mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{OH}} === \overline{\mathrm{CH}_{2}} = \overline{\mathrm{CH}_{2}} + \mathrm{H}_{2}\mathrm{O}$

Carbonyl campounds

- compounds which contain a *carbonyl group* a carbon-oxygen double $b \ge C = 0$
- Adehyde a carbonyl compound containing two hydrogen atoms or hydrogen and alkyl group.

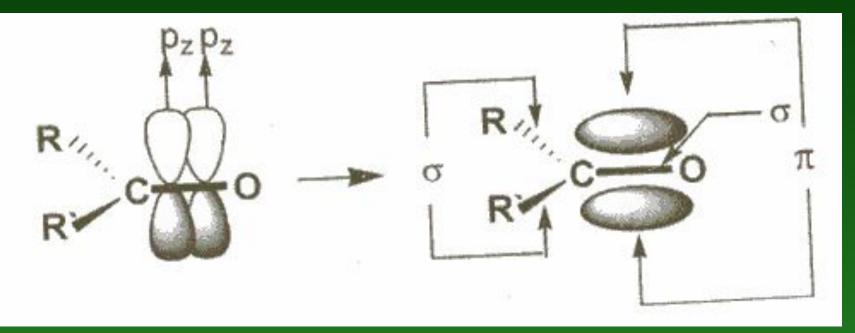


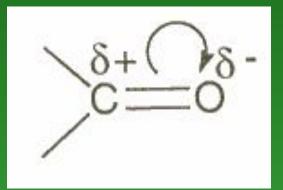
• Ketene - a carbonyl compound containing a pair of cumulative double bonds of which one is the carbonyl group, or ketone is a carbonyl compound containing two alkyl groups. R - C - R R - C - R CH_3 CH_3 $CH_$

pro panone

butanone

Structure of carbonyl group





REACTION OF ALDEHYDES AND KETONES

Acids and electrophilic reagents attack the basic oxygen.

> Some reactions of aldehydes involve the aldehyde hydrogen

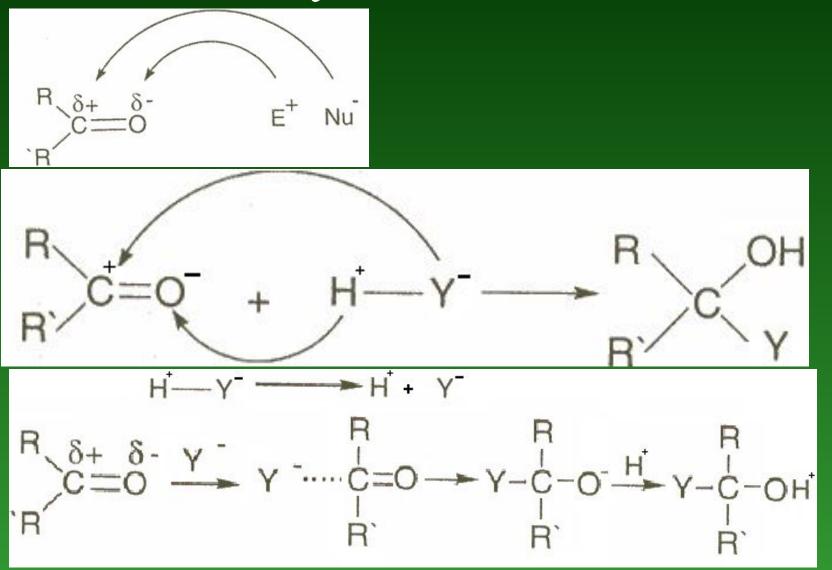
The ^{CL}-hydrogen is reactive and yields intermediate enols and enolate ions. Bases and nucleophilic reagents attackthe electron deficient carbonyl carbon

Keto – enol equilibrium.

• Aldehydes and ketones exist in solution as an equilibrium mixture of two isomeric forms, the keto form and the enol (from -ene + -ol, unsaturated alcohol) form.

$$\begin{array}{cccc} OH & OH & OH \\ H_3C - C - CH_3 \rightarrow H_3C - C = CH_2 & H_3C - C - CH_2 - CH_3 \rightarrow & H_3C - C = CH - CH_3 \end{array}$$

Nucleophilic addition reaction of Aldehydes and Ketones.



Hemiacetals and Hemiketals.

• The product of the addition of one molecule of an alcohol to an aldehyde is called a hemiacetal. Similarly, the addition of one molecule of alcohol to a ketone produces a hemiketal.

$$\begin{array}{cccc} \delta^{*} O & H^{\delta^{+}} & O^{-H} \\ \delta^{+} C & + O^{-} R_{2} \rightleftarrows R_{1}^{-} C^{-} O^{-} R_{2} \\ K_{1} & H^{\delta^{-}} & H \end{array}$$

aldehyde alcohol hemiacetal

nemiketai

Acetals and Ketals.

• If a small amount of acid catalyst is added to a hemiacetal reaction mixture, then the hemiacetal reacts with a second alcohol molecule to form an **acetal**.

etal
$$R-C \xrightarrow{O}_{H} + 2HO-R \rightarrow R - C \xrightarrow{I}_{H} + 2HO - R \rightarrow R - C - OR$$

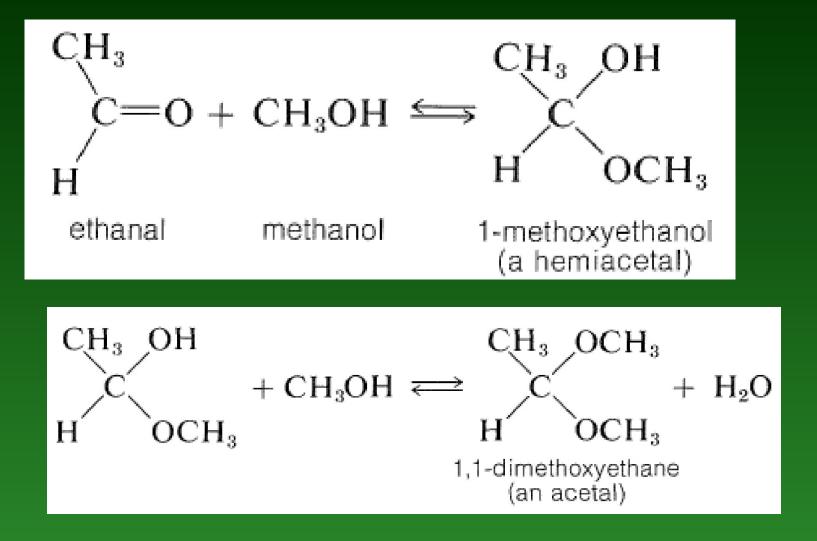
Similarly, ш the presence of an acid catalyst, the reaction of a second alcohol molecule with a hemiketal produces a *ketal*.

$$\begin{array}{ccc} O-H & H & O-R_4 \\ R_1 - C - O-R_3 + O-R_4 \rightleftharpoons R_1 - C - O-R_3 \\ R_2 & R_2 \end{array}$$

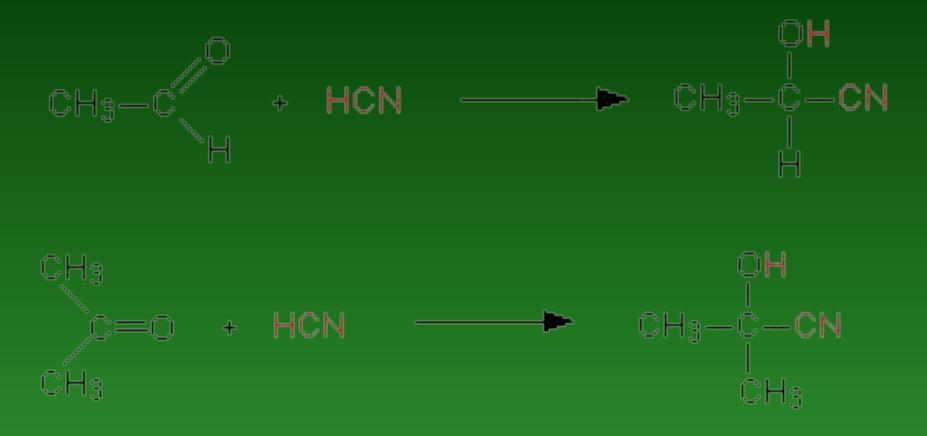
$$\begin{array}{c} O & OCH_3 \\ CH_3 - C - CH_3 + 2CH_3OH \rightarrow CH_3 - C - CH_3 + H_2O \\ OCH_3 \end{array}$$

ketal

ac



Addition of hydrogen cyanide to aldehydes and ketones



Reaction with the ammonia and its derivatives (addition-elimination reactions) Ammonia $\begin{array}{ccc} O & OH & NH \\ R-C-R' + NH_3 \rightarrow R-C-R' \rightarrow R-C-R' \end{array}$ NH₂ Amines imine NR" $R = \overset{I}{C} = R' + NH_2R'' \rightarrow R = \overset{I}{C} = R' \rightarrow R = \overset{I}{C} = R' + H_2O$ NHR" $Hydroxylamine_{R-C-R'+NH_{2}OH} \xrightarrow{OH}_{P} \xrightarrow{NOH}_{R-C-R'+H_{2}OH}$ oxyme NHOH $\begin{array}{c} \bigcirc & & \bigcirc & & & & \\ \square & & & & \\ R - \square & - R' + H_2 N - N H_2 \rightarrow R - \square & - R' \rightarrow R - \square & - R' + H_2 \bigcirc \\ \end{array}$ Hydrazine hydrazone $NH - NH_2$ $\begin{array}{ccc} O & OH & N-NHC {}_{6}H {}_{5}\\ R-C-R'+H_{2}N-NHC {}_{6}H {}_{5} \rightarrow R-C-R' \rightarrow R-C-R'+H_{2}O\end{array}$ **Derivative of hydrazine** NH-NHC4Hs alkyl- or arylhydrazone. \bullet

Oxidation of Aldehydes and Ketones. a) Using Tollens' reagent (the silver mirror test) Tollens' reagent contains the diamminesilver(I) ion, $[Ag(NH_3)_2]^+$. 2Ag(NH3)2+ + RCHO + 30H- ----- > 2Ag + RCOO + 4NH3 + 2H2O • Using Fehling's solution or Benedict's solution: • Fehling's solution contains copper (II) ions complexed with tartrate ions in sodium hydroxide solution. • Benedict's solution contains copper (II) ions complexed with citrate ions in sodium carbonate solution.

RCHO + 2Cu²⁺(incomplex) + 5OH⁻ ------ RCOO⁻ + Cu₂O + 3H₂O

The reduction of an aldehyde and a ketone

• In general terms, reduction of an aldehyde leads to a *primary alcohol*.



• Reduction of a ketone leads to a *secondary alcohol*.



Thanks you for attention!