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Chapter 1

CLASSIFICATION AND NOMENCLATURE OF ORGANIC COMPOUNDS

The problems of classification and nomenclature are especially relevant to organic chemistry, as its objects of study are millions of compounds. The nomenclature must be systematic and international, so that professionals from all over the world could unambiguously represent the structure of any compound, and, vice versa, write the structure by the name. In addition, the nomenclature must be suitable for computer processing.

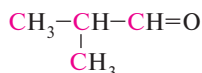
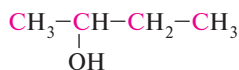
1.1. Classification

The classification of organic compounds is based on two capital features:

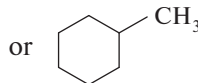
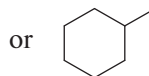
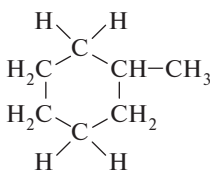
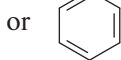
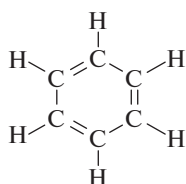
- a structure of molecular carbon skeleton;
- the presence of functional groups in a molecule.

Regarding the structure of carbon skeleton organic compounds are subdivided into the following groups.

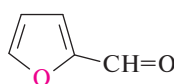
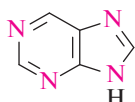
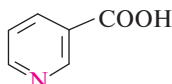
Acyclic (aliphatic) compounds. They may have unbranched or branched carbon chains.



Carbocyclic compounds. Their carbon chain forms a cycle (ring). When describing cyclic structures, it is more convenient to use so-called skeletal formulas. In such formulas the end of a skeletal line and its every angle imply a carbon atom with enough hydrogens (taking into account the tetravalency of the carbon atom). Extracyclic groups are often written in full.



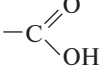
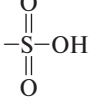


Heterocyclic compounds. They contain a cyclic skeleton, which in addition to carbon atoms contains at least one different atom (heteroatom) — most often nitrogen, oxygen, or sulfur.



Most organic molecules contain *functional* groups. That is a part of the molecule that determines its chemical properties and belonging to a certain class (Table 1.1). Such groups necessarily contain a heteroatom. A compressed notation in a line is commonly used to refer to functional groups with multiple bonds: $-\text{CO}-$ or $-\text{C}(\text{O})-$, $-\text{COOH}$, $-\text{NO}_2$, $-\text{SO}_3\text{H}$, as is shown in general formulas of the classes (Table 1.1).

Table 1.1. Some of the functional groups and classes of organic compounds

Functional group		Name of class	General formula of the class*
formula	name		
—	—	Hydrocarbons	R—H
—F, —Cl, —Br, —I (—Hal)	Halogens	Halogeno hydrocarbons	R—Hal
—OH	Hydroxy	Alcohols, phenols	R—OH Ar—OH
—O—	Oxy	Ethers	R—O—R'
—SH	Sulfanyl**	Thiols	R—SH
—S—	Sulfanyl***	Sulfides	R—S—R'
—NH ₂	Amino	Amines (primary)	R—NH ₂
	Nitro	Nitro compounds	R—NO ₂
	Carbonyl	Aldehydes, ketones	R—CH=O R—CO—R'
	Carboxy	Carboxylic acids	R—COOH
	Sulfo	Sulfonic acids	R—SO ₃ H

* The symbol R is usually used for any hydrocarbon group, the symbol Ar — for an aromatic group. It should be noted that the term “radical”, previously used for R group, is not recommended as the “radical” is used to denote a particle with an unpaired electron.

** Until recently it was called “mercapto”.

*** Formerly known as “thio”.

Molecules with one functional group are called *monofunctional*, those with several identical functional groups — *polyfunctional*. Compounds with different functional groups are called *heterofunctional*.

Examples of polyfunctional compounds are chloroform, glycerol. Heterofunctional compounds are simultaneously related to several classes. For example, lactic acid may be considered both as a carboxylic acid and as an alcohol, and taurine — as a sulfonic acid and an amine.

POLYFUNCTIONAL COMPOUNDS



chloroform

glycerol

HETEROFUNCTIONAL COMPOUNDS



lactic acid

taurine

The considered classification forms a foundation of the nomenclature of organic compounds.

1.2. Nomenclature

Nomenclature of organic compounds is a system of rules fully describing the structure of a molecule.

Historically, the first names of compounds were their *trivial* (or common) names that were given either based on their source of isolation (caffeine, urea) or their evident properties (glycerol and glucose from Greek *glykys*, sweet). Nowadays, trade names are widely used, in which, for example, a drug substance is named according to some pharmacological effect (analgin, sarcolysin) or by some structural element (bromural, phenazepam). Such names are convenient because of their brevity, but they give no information about the structure of the compound and cannot be systematized. Some of such names go out of use in the course of time. Nevertheless, many trivial names have become well-established and even formed the basis for systematic names.

Applying systematic nomenclature to drug substances is essential in pharmacy, as many medicines are produced under different trade names, but if we look at their systematic names, it may be often seen that the effective agent of these medicinal products may be the same compound (see Section 1.3).

The history of organic chemistry development saw various nomenclature systems (Geneva Rules, 1892; Liege Rules, 1930) which after a number of improvements formed the basis for the systematic chemical nomenclature of International Union of Pure and Applied Chemistry (IUPAC).

1.2.1. General principles of IUPAC nomenclature

Before studying the principles of IUPAC nomenclature, it is necessary to agree on the meaning of some basic terms.

Systematic name is a name that is fully comprised of specially created or chosen syllables, for example, pentane, thiazole.

Parent name is a part of the name used for the formation of a full name according to certain rules. For example, the name *ethanol* is derived from **ethane**. The parent name may be both systematic (for example, **hexane** from which *hexanal* is derived) and trivial (for example, **benzene** and *nitrobenzene* derived from it).

Substituent means any atom or a group of atoms replacing a hydrogen atom in the parent compound.

Functional (characteristic) group means any non-hydrocarbon atom or a group of atoms determining chemical properties of a compound and its belonging to some class.

Senior (principal) group means the functional group whose name is expressed as a suffix (also called an ending). This group has no other advantages.

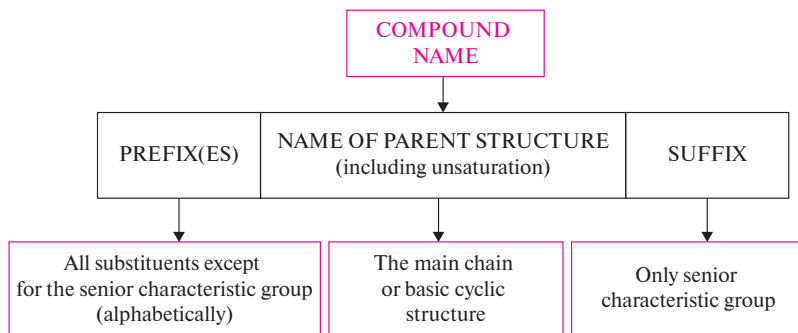
Multiplying prefixes means syllables **di-**, **tri-**, **tetra-**, etc., which are used to indicate the number of identical substituents or multiple bonds.

Locant (from the Latin *locus* for place) means a numeral or a letter (**N-**, **O-**, **o-**, **m-**, **p-**, **α-**, **β-**), showing the position of a substituent or a multiple bond in the parent structure.

Among several types of nomenclature systems applied in IUPAC rules, the substitutive nomenclature is the most versatile and therefore common. The radicofunctional nomenclature is used less often.

1.2.2. Substitutive nomenclature

The name of a compound is a complex word that consists of a root (parent structure name), prefix(es) and a suffix which describe the number and character of substituents (Scheme 1.1).



Scheme 1.1. General construction of a compound name by substitutive nomenclature

Functional groups are divided into two types: some of them are designated only as prefixes (Table 1.2), others are designated as suffixes or prefixes depending on a conventional order of priority (Table 1.3). If a compound contains more than one type of functional groups, the one that is placed higher than the others in Table 1.3 is considered as the senior group. All other functional groups are designated as prefixes. Multiplying affixes and locants are added as necessary.

Table 1.2. Functional groups designated in substitutive nomenclature only as prefixes

Class of compound	Functional group	Prefix
Halo hydrocarbons	-Br, -Cl, -F, -I	bromo-, chloro-, fluoro-, iodo-
Ethers	-O-	R-oxy-*
Sulfides	-S-	R-sulfanyl-*
Nitro compounds	-NO ₂	nitro-
Nitroso compounds	-NO	nitroso-

* Divalent groups -O- and -S- may be only a part of a substituent RO- (or RS-) and designated as a composite prefix, for example, alkyl + oxy- = alkoxy-.

1.2.3. Principles of forming a substitutive name

The formation of a name involves the following steps (in the order given below).

1. Identify the senior functional group that determines the choice of a parent structure and its numbering.
2. Identify the parent structure: the principal carbon chain or cyclic system which must include the maximum number of senior groups. The principal chain is chosen using the criteria below, provided that each subsequent criterion is used only if the preceding criterion does not allow an explicit choice:
 - a) maximum number of senior groups;
 - b) maximum number of multiple bonds (double and triple);
 - c) maximum length of the chain;
 - d) maximum number of substituents.

Table 1.3. Suffixes and prefixes for most important functional groups (in order of decreasing priority)

Class of compound	Functional group		
	formula*	name	
		prefix	suffix
Carboxylic acids	$-\overset{\color{red}{\text{C}}}\text{OOH}$	—	-oic acid
	$-\text{COOH}$	carboxy-	-carboxylic acid
Sulfonic acids	$-\text{SO}_3\text{H}$	sulfo-	-sulfonic acid
Salts of carboxylic acids	$-\overset{\color{red}{\text{C}}}\text{OOM}$	—	cation $\text{M}^+\dots$ -oate
	$-\text{COOM}$	—	cation $\text{M}^+\dots$ -carboxylate
Acid anhydrides	$-\overset{\color{red}{\text{C}}}\text{O}-\overset{\color{red}{\text{O}}}-\overset{\color{red}{\text{C}}}\text{O}-$	—	-oic anhydride
Esters	$-\overset{\color{red}{\text{C}}}\text{OO}(\text{R})^{**}$	—	(R)...-oate
	$-\text{COO}(\text{R})$	(R)-oxycarbonyl-	(R)...-carboxylate
Acid halides (on example of chloride)	$-\overset{\color{red}{\text{C}}}\text{(O)Cl}$	—	-oyl chloride
Amides	$-\overset{\color{red}{\text{C}}}\text{(O)NH}_2$	chlorocarbonyl-	-carbonyl chloride
	$-\text{C}(\text{O})\text{NH}_2$	—	-amide
	$-\text{C}(\text{O})\text{NH}_2$	carbamoyl-	-carboxamide
Nitriles	$-\text{C}\equiv\text{N}$	—	-nitrile
	$-\overset{\color{red}{\text{C}}}\equiv\text{N}$	cyano-	-carbonitrile
Aldehydes	$-\overset{\color{red}{\text{C}}}\text{H}=\text{O}$	oxo-	-al
	$-\text{CH}=\text{O}$	formyl-	-carbaldehyde
Ketones	$\begin{array}{l} \diagdown \\ \text{C}=\text{O} \\ \diagup \end{array}$	oxo-	-one
Alcohols, phenols	$-\text{OH}$	hydroxy-	-ol***
Thiols	$-\text{SH}$	sulfanyl-	-thiol
Amines	$-\text{NH}_2$	amino-	-amine
Imines	$=\text{NH}$	imino-	-imine

* Carbon atoms in the groups marked with color are included in the name of a parent structure.

** Hereinafter (R) indicates a substituting hydrocarbon group.

*** Most phenols have trivial names.

- Name the parent structure and the senior functional group.
- Identify and name the substituents.
- Number the atoms within the parent structure so as to give the lowest possible number to the senior group. If the choice of number is ambiguous, the rule of the lowest locants is used: a chain or cycle is numbered so as to give the lowest numbers to substituents. Out of two possible sequences of locants the lowest sequence is the one in which the lower is first met than in the other sequence, for example, 1,2,7- is “lower” than 1,3,4-.
- Combine individual parts of the name together (steps 3 and 4), following the alphabetical order of prefixes (multiplying prefixes are not included into the alphabetical order). Locants are placed *before* prefixes and suffixes¹, separated from a letter with a hyphen.

For a long time, IUPAC rules did not regulate the place of the locant in a systematic name. Thus, one could see such names as 1-butanol (in the USA), butan-1-ol (in Great Britain), butanol-1 (in Russia). The text provides the last (1993) version of IUPAC rules.

¹ For a long time, IUPAC rules did not regulate the place of the locant in a systematic name. Thus, one could see such names as 1-butanol (in the USA), butan-1-ol (in Great Britain), butanol-1 (in Russia). The text provides the last (1993) version of the IUPAC rules.

A key problem in that substitutive nomenclature consists in a choice of parent structure and naming it: a carbon chain or a cyclic skeleton; therefore, the principle of hydrocarbon nomenclature should be considered first.

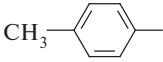
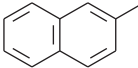
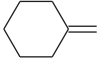



Acyclic hydrocarbons. The first four saturated acyclic hydrocarbons have semi-systematic names: methane, ethane, propane, and butane. Names of the succeeding members of this series consist of a root (mainly, names of Greek numerals) and the suffix **-ane** (Table 1.4).

Table 1.4. Names of unbranched saturated hydrocarbons

Formula	Name	Formula	Name
CH ₄	Methane	C ₉ H ₂₀	Nonane
C ₂ H ₆	Ethane	C ₁₀ H ₂₂	Decane
C ₃ H ₈	Propane	C ₁₁ H ₂₄	Undecane
C ₄ H ₁₀	Butane	C ₁₂ H ₂₆	Dodecane
C ₅ H ₁₂	Pentane	C ₁₄ H ₃₀	Tetradecane
C ₆ H ₁₄	Hexane	C ₁₆ H ₃₄	Hexadecane
C ₇ H ₁₆	Heptane	C ₁₈ H ₃₈	Octadecane
C ₈ H ₁₈	Octane	C ₂₀ H ₄₂	Eicosane

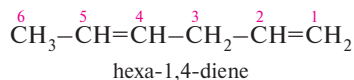
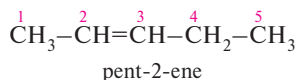
Univalent groups derived from these hydrocarbons by removing a hydrogen atom from a terminal carbon are named by replacing the suffix **-ane** in the name of the initial hydrocarbon by **-yl**, for example, methyl CH₃-. The following names are used for rather simple groups: isopropyl, isobutyl, *sec*-butyl, *tert*-butyl (Table 1.5).

Table 1.5. Names of the most important hydrocarbon groups

Group	Name	Group	Name
<i>Univalent</i>			
CH ₃ -	Methyl		Tolyl (<i>para</i> isomer shown)
CH ₃ CH ₂ -	Ethyl	C ₆ H ₅ CH ₂ -	Benzyl
CH ₃ CH ₂ CH ₂ -	Propyl	(C ₆ H ₅) ₃ C-	Trityl (short for triphenylmethyl)
(CH ₃) ₂ CH-	Isopropyl		Naphthyl (2-isomer shown)
CH ₃ CH ₂ CH ₂ CH ₂ -	Butyl		
(CH ₃) ₂ CHCH ₂ -	Isobutyl	<i>Divalent</i>	
CH ₃ CH ₂ CH(CH ₃)	<i>sec</i> -Butyl	-CH ₂ -	Methylene
(CH ₃) ₃ C-	<i>tert</i> -Butyl	-CH ₂ CH ₂ -	Ethylene
CH ₃ [CH ₂] ₄ -	Pentyl	CH ₃ CH=	Ethylidene
(CH ₃) ₂ CHCH ₂ CH ₂ -	Isopentyl	-CH ₂ CH ₂ CH ₂ -	Trimethylene
(CH ₃) ₃ CCH ₂ -	Neopentyl	CH ₃ CH ₂ CH=	Propylidene
CH ₂ =CH-	Vinyl	(CH ₃) ₂ C=	Isopropylidene
CH ₂ =CHCH ₂ -	Allyl		Cyclohexylidene
CH≡C-	Ethynyl	C ₆ H ₅ CH=	Benzylidene
	Cyclohexyl		Phenylene (<i>ortho</i> isomer shown)
	Phenyl*		

* Hereinafter designated as C₆H₅.

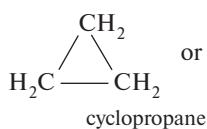
Unsaturated hydrocarbons with one double or triple bond are named by replacing the suffix **-ane** in the name of the corresponding alkane by the suffix **-ene** or **-ine**, respectively. If there are two or more double bonds, the suffix will be **-adiene**, **-atriene**, and so on. The chain is numbered so as the double bond (bonds in dienes) is designated with the lowest locant.



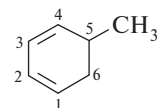
The following trivial names of unsaturated hydrocarbons are accepted: acetylene $\text{CH}\equiv\text{CH}$, isoprene $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$. The trivial name “ethylene” that was used for many years for the simplest alkene $\text{CH}_2=\text{CH}_2$ has been abolished in accordance with the latest IUPAC recommendations and is now used only for the divalent group (see Table 1.5).

Univalent groups derived from unsaturated compounds are named using the same principle as applicable to saturated compounds. If necessary, the location of multiple bonds is indicated, and the numbering always starts from the carbon atom with free valence, for example, but-3-enyl $\text{CH}_2=\text{CHCH}_2\text{CH}_2-$.

Cyclic hydrocarbons. Names of saturated monocyclic hydrocarbons are formed by adding the prefix **cyclo-** to the name of saturated unbranched acyclic hydrocarbons with the same number of carbon atoms. Unsaturation is expressed similar to acyclic hydrocarbons. The locants of multiple bonds must be the lowest possible.

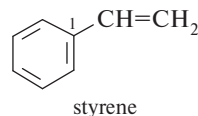
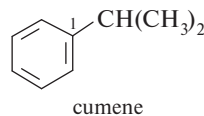
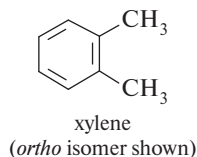
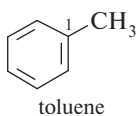


or

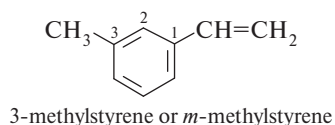
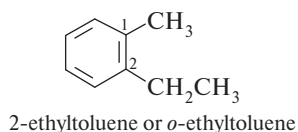


The substituent groups derived from cyclic hydrocarbons are named similarly to the groups of acyclic hydrocarbons (see Table 1.5). Their numbering starts from the carbon with free valence.

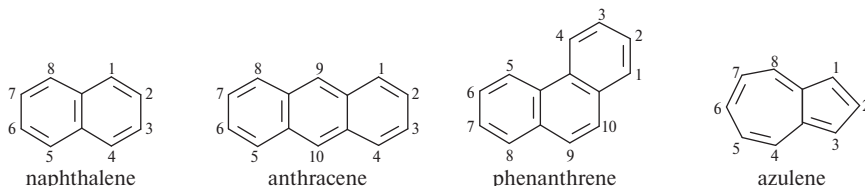
The series of aromatic monocyclic hydrocarbons (arenes) have trivial names, for example:



Other substituted monocyclic arenes are named as benzene derivatives or one of the hydrocarbons presented above, provided that the introduced substituent is not identical to the existing one. Traditional locants *o-* (*ortho-*), *m-* (*meta-*) and *p-* (*para-*) may be used, respectively, in place of 1,2; 1,3 and 1,4 in disubstituted compounds.



The most common fused¹ arenes have the following trivial names:

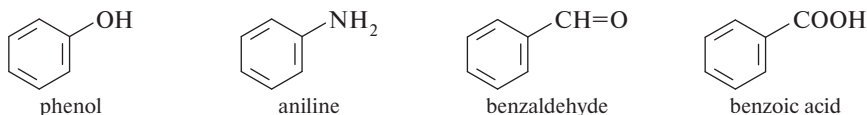


The numbering principle in fused systems is rather complicated, it is not considered here. In some cases, the historically developed numbering is retained (for example, in anthracene and phenanthrene).

Names of substituted monocyclic aryl groups are formed from the name **phenyl**. The numbering always starts from the carbon with free valence, and in the groups of fused arenes taking into account the initial numbering and, as far as possible, with the lowest locant at the atom with free valence.



Some functional compounds in the aromatic series have trivial and semisystematic names which are considered as parent, i.e., they may be used to construct the names of other substituted compounds (provided that the substituent is as inferior as the functional group of this compound). Examples are the following:



Attention should be paid to the use of trivial names in accordance with the latest IUPAC recommendations (1993). They show a tendency to a lower number of admissible trivial names, which can be considered a positive change as it eliminates unnecessary memorization. For example, the so familiar salicylic acid, malic acid or even ethylene are absent from the list of trivial names. In addition, not all of the trivial names are allowed for the use as parent ones, i.e., for making substitution in them.

The community of chemists must accept these innovations, but it is unlikely to happen quickly. Nevertheless, the authors of this book make an attempt at doing this.

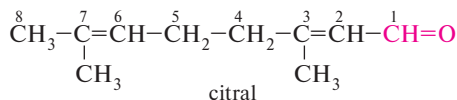
1.2.4. Examples of Using Substitutive Nomenclature

Building a name. Examples given below illustrate how the previously proposed Scheme 1.1 is applied to giving systematic names to compounds known in pharmacy and having well-established trivial or trade names.

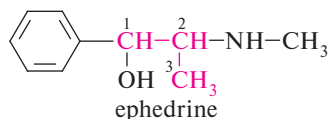
1. In the molecule of *citral* the locant is never used for the suffix **-al**, as the aldehyde group is always at the beginning of the chain. Double bonds are shown by the

¹ Fused, more specifically *ortho*-fused, are polycyclic compounds, in which any two rings have only two common atoms.

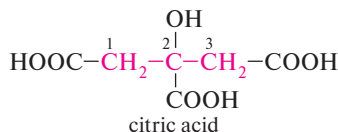
suffix **-dien(e)** with the corresponding locants in the name of parent structure. After designating two CH_3 substituents by the prefix **methyl-** with the multiplying prefix **di-** we have the systematic name: 3,7-dimethylocta-2,6-dienal.



2. In the *ephedrine* molecule, the senior functional group is the hydroxy one, so the parent structure is the chain of three carbon atoms — **propane**. Inferior substituents are shown by the prefixes **phenyl-** and **methylamino-** (amino group substituted by a methyl group) with locants 1 and 2, respectively. Having sorted the prefixes alphabetically, we get the full name: 2-methylamino-1-phenylpropan-1-ol.

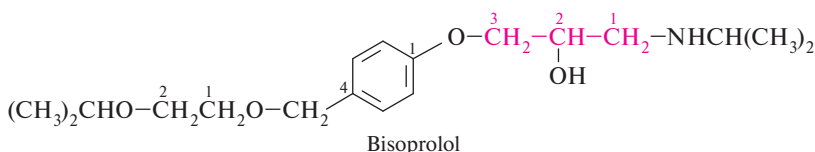


3. The molecule of *citric acid* contains three senior functional groups; all of them are carboxy groups. The parent structure, which contains all these groups, will be **propane** (but not pentane, since despite of a longer chain it involves only two senior groups).

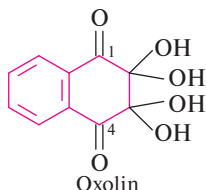


For the COOH group whose carbon atom is not a part of the parent structure, the combination **-carboxylic acid** is used as the suffix (ending), and the numbering of the parent structure does not include the carbons of these two COOH groups. Taking into account the substituent (the hydroxy group), the full name is 2-hydroxypropane-1,2,3-tricarboxylic acid.

4. In the molecule of β -adrenoceptor-blocking agent *Bisoprolol* (same as Concor or Coronal), the parent structure is **propane**, as this chain includes the senior functional group — hydroxy group, which will be cited with the suffix **-ol**. The atom C-1 contains the substituent **amino-**, which bears another substitution — the **isopropyl** group, and the full name of the substituent at C-1 is **isopropylamino-**. The substitution at C-3 in the structure of propane starts from the group **phenoxy-** ($\text{C}_6\text{H}_5\text{O}-$), in which the 4th position is substituted with the methyl group with its substituent **ethoxy-** ($\text{C}_2\text{H}_5\text{O}-$), where, in its turn, there is the **isopropoxy-** group [$(\text{CH}_3)_2\text{CHO}-$] at the 2nd position. As a whole, the composite substituent at C-3 will be named 4-[2-(isopropoxy)ethoxymethyl]phenoxy-.



These composite substituents should be ordered alphabetically: “isopropoxy” before “isopropylamino”. Taking into account all substituents, the systematic name of Bisoprolol is 3-[4-[2-(isopropoxy)ethoxymethyl]phenoxy]-1-(isopropylamino)propan-2-ol. It should be noted that the use of brackets in the name allows determining clearly the belonging of locants to one or another prefix.



5. In the molecule of antiviral drug *Oxolin* the choice of the parent structure is evident: all functional groups belong to the bicyclic system. It is more convenient to name it from the parent hydrocarbon, naphthalene. In its unsubstituted form, a bicyclic structure contains four more hydrogens than naphthalene. The so-called *additive* nomenclature is used in such cases, and the parent structure will be named **1,2,3,4-tetrahydronaphthalene**.

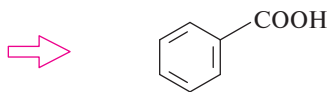
Further, it is necessary to add a suffix for senior groups (=O) and a prefix to substituents (OH groups) with necessary multiplications. As a result, the systematic name of Oxolin is 2,2,3,3-tetrahydroxy-1,2,3,4-tetrahydronaphthalene-1,4-dione.

Building the structure. A reverse problem — drawing the structure according to the systematic name — is usually simpler. The skeleton of the parent structure — an open chain or cycle — is drawn first, then carbon atoms are numbered and substituents are placed. Finally, hydrogen atoms are added, provided that each carbon is tetravalent.

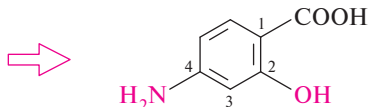
The structures of two known medicinal agents are given as an illustration.

1. *para*-Aminosalicylic acid (PASA), the systematic name 4-amino-2-hydroxybenzoic acid:

a) parent structure: the trivial name of the cycle with the senior functional group (COOH);



b) arrangement of substituents: the NH₂ group at C-4 atom and the OH group at C-2 atom.

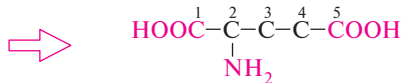


2. Glutamic acid, the systematic name 2-aminopentanedioic acid:

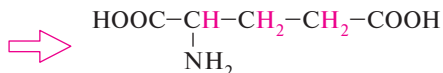
a) principal carbon chain and numbering;



b) ordering of substituents: two COOH groups (-dioic acid) and the NH₂ group at C-2 atom;



c) adding hydrogen atoms.



1.2.5. Radicofunctional nomenclature

The names in this nomenclature are comprised of two elements: the name of the hydrocarbon group (or groups in case there are several groups) and the name of the functional class of compounds (Table 1.6).