

Chapter 2 Makeup of Organic Compounds

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Problems

Answers

According to the CAS registry number, by 2017, more than two hundred million of compounds have been known and more than 75 % of them are expected to be organic compounds. It is impossible to learn all of them and such is not necessary at all. If you master the makeup of organic compounds, you can organize your knowledge on organic compounds.

In this book, you will learn the basics of the makeup of organic compounds, which describes that organic compounds consist in the carbon framework and functional groups. The latter is responsible for the chemical reactivity of organic compounds. Then you will learn the principles of naming organic compounds based on their structure, *i.e.*, the **nomenclature** of organic compounds. Though the rule is rather complicated, the system of nomenclature will gradually become clear to you as your understanding on chemical structure is deepened. In this regard, study of chemical structure and that of nomenclature may be regarded complementary.

2.1 Structural unit of organic compounds

(a) Hydrocarbons and functional groups

(1) Linkage of carbon atoms

Organic chemistry is the chemistry of carbon compounds, and today organic compounds and carbon compounds are regarded essentially equivalent. The valence of a carbon atom is four, and it can combine with other carbon atoms and with another types of atoms. There are three patterns of C-C bonding; *i.e.*, **single bond**, **double bond**, and **triple bond**.

Compounds solely composed of single bonds are called **saturated compounds**, and compounds containing double and/or triple bonds are called **unsaturated compounds**. Since double and triple bonds are reactive and readily suffer from such reactions as addition reactions, these two bonds are named **unsaturated bonds**. Organic compounds are classified into two groups; **chain compounds** in which carbon atoms are linked to form a chain, and **cyclic compounds** containing ring structures.

The almost unlimited world of organic chemistry is developing, starting from a compound with one carbon atom. A carbon atom will make a variety of bonds (single, double, and triple bonds) with other carbon atoms and/or another kind of atoms.

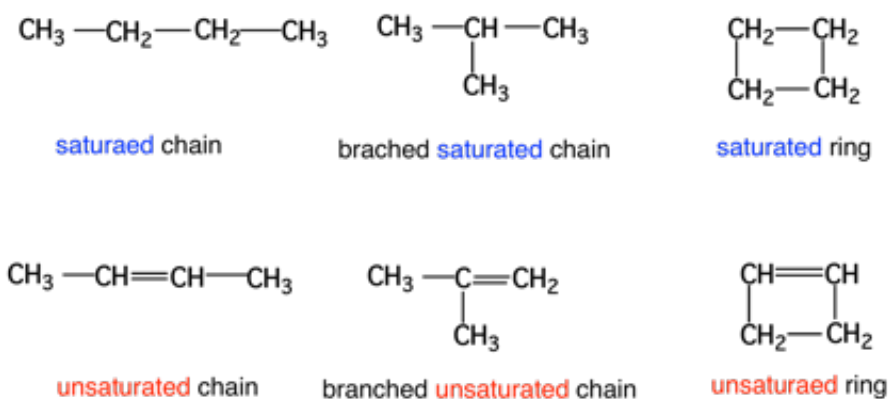


Figure 2.1 Some example of carbon compounds with four carbon atoms

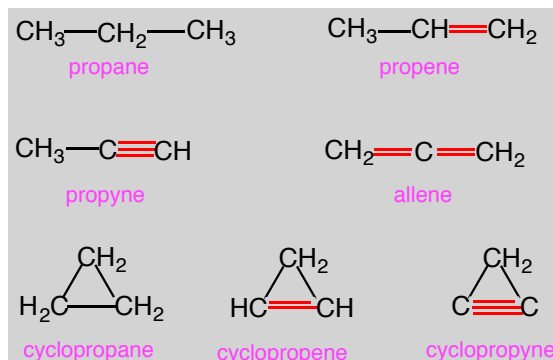
A carbon atom will combine with other atoms forming a chain or sometimes forming a ring. By these processes, the variety of carbon compounds will further be enhanced (Figure 2.1).

Exercise 2.1 Connecting carbon atoms

Find out carbon compounds composed of three carbon atoms (in any hybridization state) as many as possible.

Answer

Four chain compounds and cyclopropane are well documented. However, three-membered compounds with double and triple bonds are difficult to prepare or very unstable even if successfully prepared, because of their high strain. Formally a three membered ring with two double bonds (cyclic version of allene) are conceivable.

**(2) Groups, substituents, and functional groups**

Compounds quoted in the previous section are all composed of carbon and hydrogen atoms. Such compounds are named as **hydrocarbons**. Hydrocarbons form the most important group of organic compounds. In addition, hydrocarbons will form a variety of compound by replacing their hydrogen atoms with other atoms or groups of atoms that include not only carbon atoms but also other kinds of atoms. Such atoms or group of atoms are called **groups**. Sometimes the term **substituent** is used when the fact that hydrogen atoms are substituted is to be emphasized.

Methane CH_4 discussed in Ch. 1 is, for example, a typical hydrocarbon. When one of its hydrogen atom is substituted by a hydroxy group ($-\text{OH}$), methanol CH_3OH is obtained. Substitution with a carboxy group ($-\text{COOH}$) gives acetic acid CH_3COOH .

In this way, a variety of compounds is derived from a hydrocarbon, methane. Here the term substitution does not necessarily imply that the direct substitution of a hydrogen atom by such groups takes place. Rather, this is a formal explanation.

Formally, hydroxy or carboxy groups can be regarded as chemical entities obtained by removing one hydrogen atom from water H_2O or from formic acid HCOOH , respectively. Thus, groups can be defined as an atom or a group of atoms obtained by removing a hydrogen atom from a molecule. Except some special cases, groups cannot exist as such. These will form stable compounds by combining with atom(s) or other group(s).

The hydrocarbon part of methanol or acetic acid is also a kind of group that is obtained by removing one hydrogen atom from methane. Groups obtained by removing a hydrogen atom from hydrocarbons are named as a **hydrocarbon group**. The group obtained by removing one hydrogen atom from alkane is named an **alkyl group** and a general expression $-\text{C}_n\text{H}_{2n+1}$ is used. You can use $-\text{R}$ for simplicity. The hydrocarbon group contained in methanol and acetic acid is called a **methyl group** $-\text{CH}_3$.

A group obtained by removing a hydrogen atom from aromatic hydrocarbon is named an **aryl group**. You can use an abbreviation –Ar for simplicity. A phenyl group –C₆H₅ (-Ph) obtained by removing one hydrogen atom from benzene is a typical aryl group.

There are many compounds which contain hydroxy or carboxy groups. Compounds containing the same substituents tend to have similar chemical properties. For instance, compounds with a carboxy group are in common weakly acidic. Such a group is often referred to as a **functional group**. A series of compounds with a common functional group and differ only by the number of CH₂ unit in their molecular formula is called a **homogenous series**.

A double bond contained in ethylene and benzene is a mode of bonding and is not a group as defined before. However, it is generally treated as a functional group since it determines the chemical property of a homogenous series containing a double bond.

The three terms, a group, a substituent and a functional group, indicate much the same entities. There is, however, a small difference as to what each term emphasizes.

Point: Group, substituent and functional group

Group: An atom or a group of atoms obtained by removing a hydrogen atom (or atoms) from a molecule

Substituent: A group which replaces a hydrogen atom of a molecule. By substituting hydrogen atoms of a hydrocarbon, a variety of organic compounds will be derived.

Functional group: An atom or a group of atoms which determines the chemical property of compounds. Double and triple bonds are also included.

Homologous series: A series of compounds with the same functional group and differ only in the number of CH₂ unit.

Hydrocarbon group: A group obtained by removing hydrogen atom(s) from a hydrocarbon.

Exercise 2.2 The makeup of organic compounds

Examine the makeup of the following compounds.

- (a) ethanol
- (b) nitrobenzene

Answer

(a) A compound obtained by substituting one hydrogen atom of ethane CH₃CH₃ with a hydroxy group.

Alternatively, this compound is formed by combining an ethyl group –CH₂CH₃, an alkyl group, and a hydroxy group.

(b) A similar explanation is possible. Nitrobenzene is obtained by substituting one hydrogen atom of benzene by a nitro group.

The alternative explanation is that it is a compound formed by combining a phenyl group formed by removing one hydrogen atom from benzene, and a nitro group.

To summarize, there is no unique way of the makeup of a molecule. There may be several alternative ways as shown in the point below.

Point: Makeup of organic compounds

- (1) An organic compound is obtained by combining several groups.
- (2) An organic compound is obtained by substituting hydrogen atom(s) of a hydrocarbon with substituent(s) (functional group(s)).
- (3) An organic compound is obtained by combining a hydrocarbon group and a substituent(s) (a functional group(s)).

The three ways described above have essentially identical content. This will be reflected also in the nomenclature of organic compounds as you will learn later. A compound sometimes has two or more than two names.

You may accept that an organic compound is composed of the parent hydrocarbon, or a hydrocarbon group derived from it, and substituent(s) or functional group(s).

It is rather difficult to define how much you should know about hydrocarbons and substituents when you start learning organic chemistry. In principle, "The more, the better". However, unorganized knowledge is not dependable. In this book, the author tried to minimize the material to be discussed. However, you must notice that the author minimized the material under the assumption that you would study hard so that you would try to memorize all the material in this book.

(b) Classification of hydrocarbons

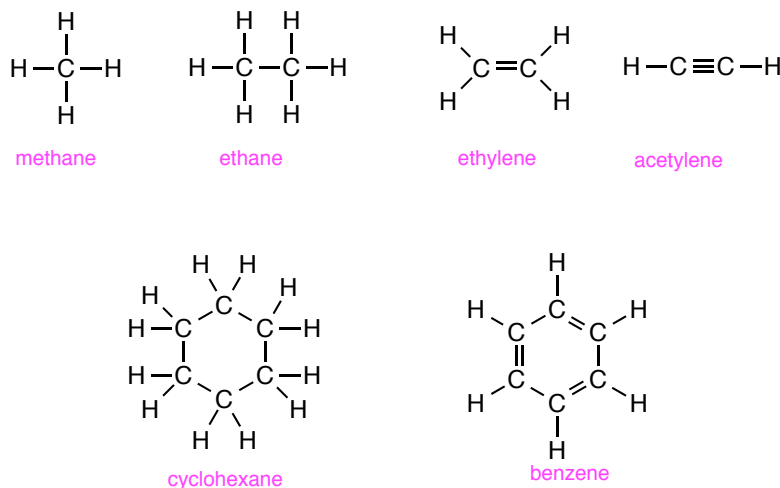
In this section hydrocarbons will be summarized. Hydrocarbons are the generic name for the compounds composed solely of carbon and hydrogen atoms. Hydrocarbons are very important, and they become the skeleton of many other organic compounds.

Hydrocarbons are classified according to the pattern of C-C bonds included. **Saturated hydrocarbons** do not contain unsaturated bonds but **unsaturated compounds** contain unsaturated bonds. **Aliphatic hydrocarbons** do not contain benzene rings and related systems. **Aromatic hydrocarbons** contain benzene rings and like. Among aliphatic compounds, those containing cyclic structure(s) are named as **alicyclic hydrocarbons**.

In Table 2.1, fundamental hydrocarbons are classified based on the type of C-C bonds. Methane, ethylene (ethene), and acetylene (ethyne) are the representative of respective homologues which consist in a series of compounds with a common basic structure but with a different number of the CH₂ unit.

Table 2.1 Representative hydrocarbons and their structures

name	simplified structure	hybridized state	C-C bond length (nm)	shape of molecule
methane	CH ₄	sp ³	-	tetrahedral
ethane	CH ₃ -CH ₃	sp ³	0.15351	-
ethylene	CH ₂ =CH ₂	sp ²	0.1339	planar
acetylene	CH≡CH	sp	0.1203	linear
cyclohexane	C ₆ H ₁₂	sp ³	0.1536	cyclic
benzene	C ₆ H ₆	sp ²	0.1399	hexagon



Methane CH₄ is the simplest member of the homologue **alkanes** which have a generic formula C_nH_{2n+2}. Ethane C₂H₆, the next simplest member of the homologue, is larger than methane by CH₂, and it is composed of two sp³ hybridized carbon atoms and six hydrogen atoms bonded to these. Alkanes in which all C-C bonds are single bonds, and all constituting carbon atoms are sp³ hybridized, are saturated hydrocarbons.

Ethylene CH₂=CH₂ is the simplest member of the homologue **alkenes**, C_nH_{2n}, which contain one double bond composed of two sp² hybridized carbon atoms.

Acetylene CH≡CH is the simplest member of the homologue **alkynes**, C_nH_{2n-2}, which contains one triple bond, composed of two sp hybridized carbon atoms.

The representative cycloalkane is cyclohexane C₆H₁₂ which is composed of six sp³ hybridized carbon atoms.

Benzene has a structure quite different from that of aliphatic hydrocarbons. Its skeleton is a hexagon in which double and single bonds are alternatively connected. Hydrocarbons having a benzene ring is named as aromatic hydrocarbons or **arenes**. As their names suggest, aromatic compounds have characteristic aroma, but some of these have disagreeable odor.

Point: Classification of hydrocarbons

Chain hydrocarbons (aliphatic hydrocarbons): Hydrocarbons in which carbon atoms are bonded in chain

Cyclic hydrocarbons: Hydrocarbons in which carbon atoms are connected in cycle

Alicyclic hydrocarbons: Cyclic hydrocarbons which do not contain unsaturated bonds

Aromatic hydrocarbons: Hydrocarbons containing benzene and related ring(s)

Saturated hydrocarbons: Hydrocarbons which do not contain unsaturated bonds (alkane)

Unsaturated hydrocarbons: Hydrocarbons which contain unsaturated bonds (alkene, alkyne)

2.2 Functional groups

(a) Important functional groups

As was discussed in Ch. 2.1(a), organic compounds are either hydrocarbons or their derivatives obtained by substituting their one or more than one hydrogen atoms by substituents. It is more practical to classify organic compounds based on functional groups, which include multiple bonds. The reason is as follows. It is appropriate to classify organic compounds depending on their reactivity

or property. Hence the presence of reactive multiple bonds is an important key for classification. Representative functional groups are tabulated in Table 2.2.

Table 2.2 Representative functional groups

type of compounds	functional group	name of functional group	simple example
alkene	$>C=C<$	(vinyl)	$CH_2=CHCH_3$ propene
alkyne	$-C\equiv C-$		$HC\equiv CH$ acetylene
arene	$-C_6H_5$, etc	phenyl	$C_6H_5CH_3$ toluene
halide	$-Cl$, etc	halogen	C_2H_5Cl ethyl chloride
alcohol	$-OH$	hydroxy	C_2H_5OH ethanol
phenol	$-OH$	hydroxy	C_6H_5OH phenol
ether	$-O-$	ether*	$C_2H_5OC_2H_5$ diethyl ether
aldehyde	$-CHO$	aldehyde	CH_3CHO acetaldehyde
ketone	$>C=O$	keto**	$(CH_3)_2CO$ acetone
carboxylic acid	$-COOH$	carboxy	CH_3COOH acetic acid
ester	$-COO-$	ester*	$CH_3COOC_2H_5$ ethyl acetate
acid anhydride	$-COOCO-$		$(CH_3CO)_2O$ acetic anhydride
acid halide	$-COCl$, etc		CH_3COCl acetyl chloride
amine	$-NH_2$, etc	amino	CH_3NH_2 methylamine
amide	$-NHCO-$	amido	CH_3CONH_2 acetamide
nitrile	$-C\equiv N$	cyano	CH_3CN acetonitrile
nitro compounds	$-NO_2$	nitro	$C_6H_5NO_2$ nitrobenzene
thiol	$-SH$	mercapto	CH_3SH methanethiol
sulfonic acid	$-SO_3H$	sulfo	$C_6H_5SO_3H$ benzenesulfonic acid

* sometimes referred to as an ether bond or an ester bond.

** sometimes $>C=O$ group is named as a carbonyl group. Compounds containing carbonyl group(s) are called carbonyl compounds.

Why functional groups take an important role to determine the reactivity or property of organic compounds? Functional groups listed in Table 2.2 have one of the features shown in the point below.

Point: The feature of functional groups

Either (1) the atom bonded to a hydrocarbon group (*e.g.*, the bonding atom) is not a carbon atom or (2) unsaturated bonds are included among functional groups.

For instance, a hydroxy group corresponds to case (1) and a carboxy and a nitro groups to both case (1) and case (2).

(b) Functional groups and electronegativity

Consider what will happen if the bonding atom is not a carbon atom. It is convenient to consider the property of hydrocarbons without any unsaturated bonds. As you will learn in Ch. 5, the reactivity of alkanes and cycloalkanes is very low, and some reactions will take place only when excessive heat or light is applied. This is because of the property of the C-C and C-H bonds.

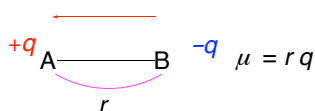
The extent that an atom holds electron is defined by a physical parameter **electronegativity** (*rf.*

“*Fundamental Chemistry*, Ch. 5) which is characteristic for each type of atoms. Table 2.3 gives the electronegativity scale proposed by Pauling which is most widely used.

Table 2.3 Electronegativity defined by Pauling

H 2.1						
Li 0.97	Be 1.5	B 2.0	C 2.5	N 3.1	O 3.5	F 4.1
Na 1.0	Mg 1.2	Al 1.5	Si 1.7	P 2.1	S 2.4	Cl 2.8
K 0.90	Ca 1.0	Ga 1.8	Ge 2.0	As 2.2	Se 2.5	Br 2.7
Rb 0.80	Sr 1.0	In 1.5	Sn 1.72	Sb 1.82	Te 2.0	I 2.2
Cs 0.86	Ba 0.97	Tl 1.4	Pb 1.5	Bi 1.7	Po 1.8	At 1.9

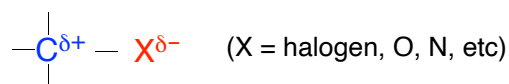
A bond A-B composed of two different atoms A and B (assume the electronegativity of A is larger than that of B) is associated with a biased distribution of electrons, *i.e.*, **polarization**. This polarization is indicated by an arrow (A) \leftarrow (B) in which the electronegativity of A is larger than that of B. A pair of positive and negative electron charge $\pm q$ (with the same magnitude), forms an **electric dipole**. The direction of the dipole is indicated by an arrow \leftarrow which starts from the atom (B) with smaller electronegativity to the atom (A) with larger electronegativity. In this case, the product $r q$, where r is the distance between the two charges $+q$ and $-q$, is called **dipole moment** (μ). The dipole moment is a vector with its magnitude μ (usually expressed by the unit D; Debye) and its direction. The magnitude of a dipole moment can be determined by experiments but its direction cannot be determined.



The dipole moment of a molecule (molecular moment) is defined as the vector sum of the dipole moment of each bond (bond moment) in the molecule. Even if each bond moment is large, their sum may be small or even null. A molecule with small or almost null dipole moment is named as a **nonpolar molecule**, and a molecule with a certain amount of dipole moment is named a **polar molecule**.

The polarization of a C-C bond in saturated hydrocarbons is almost null, and the polarization of a C-H bond is also very small and can be neglected in most cases. Thus, a hydrocarbon is accepted as nonpolar. Low reactivity of hydrocarbons is essentially due to this effect.

On the contrary, the C-O bond of methanol is largely polarized. If the polarization of methyl group is neglected, the molecular moment of methanol is essentially equal to the bond moment of C-O bond. Methanol is polar, and its property and reactivity are mostly due to this polarization.



(c) Substituent effect; inductive effect

Polarization of the C-O bond in methanol caused by a large electronegativity of oxygen in hydroxy group may be interpreted as an interchange of electrons between the hydrocarbon group and a substituent (a functional group). In methanol, the C-O bond connecting a hydroxy group and a methyl group is polarized, and the electron is drawn to the oxygen atom to some extent. We interpret this as an acquisition of electrons from the methyl group by the hydroxy group and introduce a new technical term **substituent effect** that explains this interchange of electrons.

The substituent effect originated from the electronegativity is referred to as **inductive effect (I effect)**. A hydroxy group exhibits an effect to attract electrons, *i.e.*, **electron-withdrawing effect**. An effect caused by some other substituents to give electrons to a hydrocarbon group is named as **electron-donating effect**. To distinguish two effects, the former is given an expression $+I$ effect and the latter $-I$ effect. The sign is chosen to indicate whether the hydrocarbon group loses (become positive) or gains (become negative) electrons.

Since organic compounds are composed of hydrocarbon groups and substituents, the movement of electrons is more conveniently explained by the substituent effect rather than by polarization of bonds.

(d) Resonance effect

A carboxy group has two electronegative oxygen atoms and is expected to exhibit $+I$ effect as a hydroxy group does. Surely a carboxy group exhibits not only $+I$ effect, but also a **resonance effect** because it contains a double bond. A carbonyl group $>\text{C}=\text{O}$ will act as a good example. As we have learned in connection with benzene, π electrons in the double bond are mobile; it is possible to write a resonance formula as shown in Figure 2.2. In this resonance formula, the carbon atom is positively charged, and affects a strong $+I$ effect to hydrocarbon groups R and R' bonded to the carbonyl group.

The substituent effect based on resonance is called **resonance effect**, or **R effect**. Sometimes resonance effect is called **mesomeric effect (M effect)**. Both a carbonyl and a carboxy groups exhibit $+R$ effect (Figure 2.2). Partial bias of electrons caused by inductive effect is represented by an arrow \rightarrow , and a curly arrow represents the movement of electron pair by resonance or during a reaction \curvearrowright .

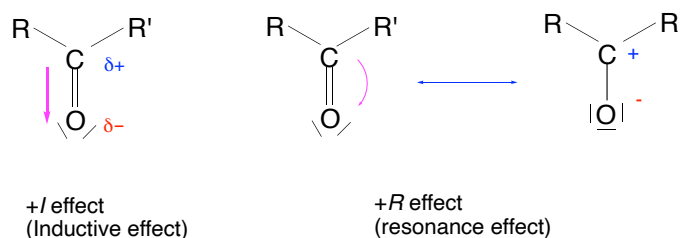


Figure 2.2 The substituent effect of a carbonyl group

You will learn inductive and resonance effects in detail in Ch. 4.

Point: Substituent effect

Effects of substituents upon hydrocarbon (electronic effect)

Inductive effect (*I* effect): Originated from electronegativity

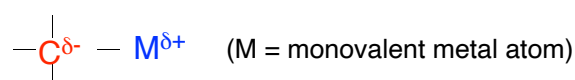
Resonance effect (*R* effect): Originated from resonance

Electron-withdrawing: Receiving electrons from hydrocarbon groups (+)

Electron-donating: Giving electrons to hydrocarbon groups (-)

(e) Organometallic compounds

Compounds in which such a metallic atom mostly belonging to either alkaline metal or alkaline earth metal is bonded to the carbon atom of hydrocarbons are named as **organometallic compounds**. As is clear from the electronegativity of two atoms, the direction of polarization is contrary to the direction of C-O and C-halogen bonds. The carbon atoms of C-alkali metal atom and C-alkaline earth metal bonds are negatively charged and the metal atoms are positively charged.



Organometallic compounds are generally highly reactive, tend to decompose in air and are difficult to isolate as such. Hence the metal atom of organometallic compounds is not classified as a functional group. However, the role of organometallic compounds is extremely large as is exemplified by the Grignard reaction which will be discussed in Ch. 11.

Atoms possessing the intermediate property between a metal and a nonmetal atom are called **metalloids**. In the periodic table, an oblique line connecting boron and astatine forms the borderline separating metals and nonmetals. Atoms around this line are mostly metalloids. As is shown in Table 2.2, the electronegativity of these metalloids are generally close to 2, indicating the polarization of C-metalloid bond is not so large, and devoid of ionic character associated with C-metal bonds.

2.3 Nomenclature of organic compounds**(a) Basic principle of nomenclature**

Though to learn and to teach the rule of naming organic compounds, *i.e.*, organic **nomenclature**, is one of the hard parts in organic chemistry, this is also an unavoidable part. In this book the essence of organic nomenclature is given at the early part of the book. From Ch. 5, the nomenclature of compounds treated in each chapter will be discussed.

Nomenclature of compounds and the way understanding them are two sides of the same coin. In fact, introduction of the modern nomenclature and the construction of the modern chemistry were established at one time by one chemist, Antoine Laurent Lavoisier (1743-1794). After he established a theory of combustion based on oxygen, he proposed a system of nomenclature for compounds known at that time (mostly inorganic compounds). His system became the root of the modern inorganic nomenclature after some amendments.

A system of organic nomenclature was proposed only after the way of thinking on the makeup of organic compounds. When the role of functional groups was made clear, an idea to pull together compounds with the same functional group emerged. This was the beginning of modern organic nomenclature.

Before, or immediately after, the birth of organic chemistry, there was no systematic nomenclature such as the modern one. Since the number of known compounds was very much limited in those days,

one could do without any rule. Names based on the names of discoverers, on natural products from which the compound was isolated or on the properties of the compound (color or smell, *etc*) were enough (Table 2.4). Such names are called **common names** or **trivial names**. Many common names are still in use as is exemplified by urea.

Table 2.4 Some common names

common name	English name	deviation of the word
marsh gas	methane	evolved from the bottom of marsh
urea	urea	contained in urine
muratic acid	hydrochloric acid	muria (fr) = brine
lactic acid	lactic acid	lact (L, fr) = milk

As the number of known compounds rapidly increased at the end of the 19th century, the necessity of a systematic nomenclature was highly desired. Chemists who felt the necessity assembled and discussed to propose the prototype of the modern nomenclature that was completed to the modern one after many amendments. The meetings to discuss the nomenclature were developed into the International Union of Pure and Applied Chemistry (IUPAC) that may be regarded as the United Nations in the world of chemistry.



The symbol mark of IUPAC

The characteristic nature of names based on the systematic nomenclature is as follows: In principle, with the aid of a few rules, even a non-chemist can give a name to any compound even if he or she does not have much knowledge of chemistry. It should also be possible to draw the structural formula of any compound if its name should be given. Since the rules of nomenclature are rather loose, sometimes a compound may have names more than one. Even so, an identical structure can be drawn for different names.

There are several kinds of systematic nomenclature. IUPAC recommends most strongly use of the **substitutive nomenclature**. Another method, the **radicofunctional nomenclature**, is also widely used. Both systems are to be used for compounds with substituents. In this regard, knowledge on the nomenclature of hydrocarbons (Ch. 5.1) is prerequisite. The purpose of this section is to adapt yourself to the way of thinking on nomenclature.

(b) Substitutive nomenclature

In this nomenclature, any organic compound is treated as a compound obtained by replacing hydrogen atom(s) of the parent hydrocarbon by substituent(s) (functional group(s)). The name of substituents is added to the name of parent hydrocarbon as a prefix or suffix. When the compound has one substituent, its name is added as a suffix (Figure 2.3), with some exceptions.

Point: Substitutive nomenclature

- (1) A substituted compound is obtained by replacing hydrogen(s) of a hydrocarbon with substituent(s).
- (2) Substituents are expressed with corresponding prefix or suffix.
- (3) When a compound has two or more than two substituents, the principal group is expressed as a suffix, and the rest as prefix.

Some substituents must be named as a prefix.

(c) Radicofunctional nomenclature

The radicofunctional nomenclature has much the same feature as the substitutive nomenclature, but in the former no suffix is used. To indicate the compound type, the substitutive nomenclature uses the principal group as a suffix, but the radicofunctional nomenclature uses the functional type name.

If the substituent is monovalent, the rest of the molecule bonded to the substituent (*i.e.*, hydrocarbon moiety) is expressed by a group (in most cases the name of hydrocarbon group). For simple compounds, the naming by radicofunctional nomenclature is simply (name of hydrocarbon group + functional type name) (Figure 2.6)

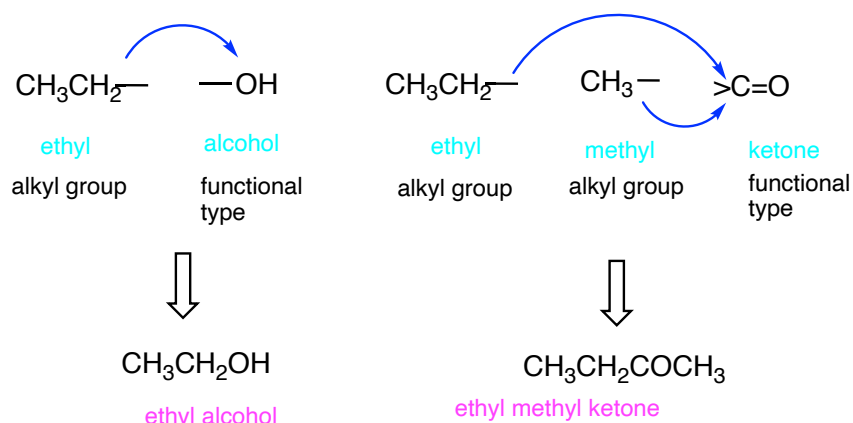


Figure 2.6 Radicofunctional nomenclature

Table 2.8 Functional type name

substituent	functional name
X of RCOX	fluoride, chloride, bromide, iodide
-CN	cyanide
>C=O	ketone
-OH	alcohol
-O-	ether, oxide
-S-, -SO-, -SO ₂ -	sulfide, sulfoxide, sulfone
-F, -Cl, -Br, -I	fluoride, chloride, bromide, iodide

When the substituent of functional type name is divalent, the names to combine this functional group are arranged either (a) alphabetical order or (b) in the order of simplicity (simpler one comes first). Method (a) is more widely used.

In Table 2.8, functional type names are summarized. Ketones, ethers, sulfides and others are names for divalent substituents and the rest are for monovalent ones. If a compound contains two

groups listed in Table 2.8, the one in the higher position of the Table will be the principal group, and the rest is expressed as prefix.

In this Table, some important groups of compounds are omitted. The reason is that the functional type names for carboxylic acids, esters, amides, aldehydes and ketones are identical with suffix used in the substitutive nomenclature.

Point: Radicofunctional nomenclature

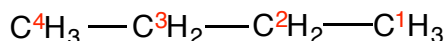
- (1) Parent body is expressed by the name of hydrocarbon group and substituents by functional type name.
- (2) For compounds with two or more than two substituents, the principal group is expressed by the functional type name and the rest by prefix.

(d) Locant

In nomenclature, the position at which the substituent is bonded to the hydrocarbon is indicated by a **locant**. In this book locants are given to the relevant atoms as superscripts like C^1 , C^2 , *etc.* Care should be taken so that the locant or the carbon atom to which the principal group is bonded is as small as possible.

(1) Chain compounds

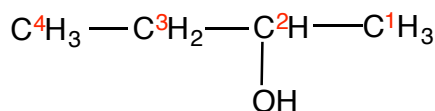
One end of the longest chain is assigned to C^1 , and locants are given in sequence, *i.e.*, C^2 , C^3 , *etc.* Care should be taken so that the locant at the carbon atom to which the principal group is bonded is as small as possible.



butane



1-butanol



2-butanol

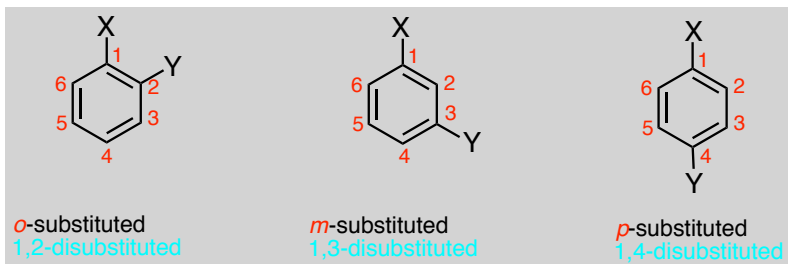
(2) Cyclic compounds

C^1 is assigned to the carbon atom to which the principal group is bonded. 1,2,4-trihydroxybenzene in Figure 2.4 is a good example. For disubstituted benzenes, however, a new notation describing the relation of two substituents is used instead of locants.

For such compounds as disubstituted xylene, there are **positional isomers (regioisomers)** in which the relation between two substituents is different. Positional isomers (regioisomers) are a kind of structural isomers. Compounds having two substituents at C^1 and C^2 are *ortho (o-)* isomers, those at C^1 and C^3 are *meta (m-)* isomers, and those at C^1 and C^4 are *para (p-)* isomers. This method is applied to all disubstituted benzene derivatives.

Details of the way how to give locants to aromatic hydrocarbons will be discussed in Ch 7

Point: *ortho*, *meta* and *para* isomers



Problems**2.1**

Draw all possible structures for saturated hydrocarbons composed of five carbon atoms and one ring.

2.2

Predict the direction of polarization of the bonds given below. Give your answer like X^+-Y^- .

(a) C-Br⁻ (b) Al-H (c) H-N (d) S-O

2.3

The substitutive names are given to the following compounds. Give radicofunctional names to them.

(a) CH₃OH; methanol (b) C₂H₅Br; bromoethane (c) C₆H₅Br; bromobenzene

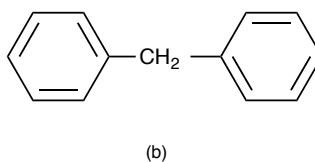
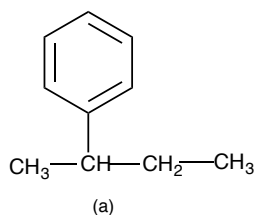
2.4

The radicofunctional names are given to the following compounds. Give substitutive names to them.

(a) CH₃Cl; methyl chloride (b) C₂H₅OC₂H₅; diethyl ether (c) C₆H₅I; phenyl iodide

2.5

Give names to the following compounds.

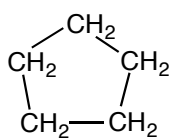
**2.6**

The following names are somewhat inadequate. Point out the problem if any, and give correct names.

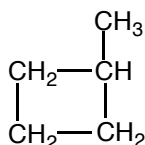
(a) 1-methylbutane, (2) 3-ethylbutane, (3) 3-methyl-3-butene.

Answers**2.1**

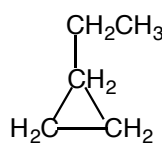
It is an effective method to decompose the molecule into its parts, (a) a five-membered ring, (b) a four-membered ring and a methyl group, (c) a three-membered ring and an ethyl group, (d) a three-membered ring and two methyl groups. In order to obtain the perfect answer for the case (d), you have to use what you have not learned yet. Names of possible structures are given for reference.



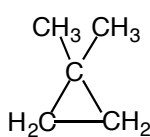
cyclopentane



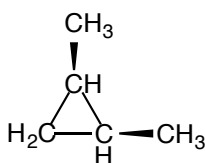
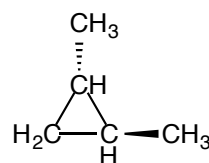
methylcyclobutane



ethylcyclopropane



1,1-dimethylcyclopropane

*cis*-1,2-dimethylcyclopropane*trans*-1,2-dimethylcyclopropane

* See Ch. 5 concerning *cis* and *trans* isomers for cyclopropanes.

2.2

(a) C^+-Br^- (b) Al^+-H^- (c) H^+-N^- (d) S^+-O^-

2.3

(a) methyl alcohol (b) ethyl bromide (c) phenyl bromide

2.4

(a) chloromethane (b) ethoxyethane (c) iodobenzene

2.5

(a) 2-phenylbutane, (b) diphenylmethane

2.6

(a) pentane. The longest chain should be the main chain.

(b) 3-methylpentane. The same mistake.

(c) 2-methyl-1-butene. The locant of double bond should be the smallest.