## AL-FARABI KAZAKH NATIONAL UNIVERSITY

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# Study Guide and Practice Tests for Organic Chemistry

(Organic Compounds of Aliphatic Series)

Educational-Methodical Handbook

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This tutorial handbook provides a brief theoretical course on the chemistry of organic compounds of aliphatic series and exercise as a guide material for the examination which taken at the end of each section of the theoretical course.

The manual is intended for students of al Farabi Kazakh National University, studying in the field 5B060600 – «Chemistry» and 5B072100 – «Chemical Technology of Organic Substances», studying practical courses «Organic Chemistry» and «Chemistry of Organic Compounds of Aliphatic Series».

В настоящем учебном пособии представлен краткий теоретический курс по химии органических соединений алифатического ряда и задания для закрепления материала в виде тестов в конце каждого раздела теоретического курса.

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## FOREWORD

Main purpose of this book is giving knowledge on the fundamentals of organic chemistry and organic science, and show its significance and role as a theoretical framework the most important branches of chemical industry.

The future specialists in study of course "Organic Chemistry" have to know about concepts of organic chemistry, know the general laws relating the structure and properties of organic compounds, methods for major classes of compounds, the mechanism of the basic reaction types, environmental problems technology of organic substances, be able to solve problems associated with the technology of organic substances, synthesize, and identify the compound, to learn skills chemical calculations to substantiate technical solutions, methods of separation, isolation, purification, identification, and synthesis of organic compounds; in addition, treatment of liquid, solid, combustible, volatile and toxic substances, with instruments and laboratory equipment of organic synthesis.

This tutorial manual provides a brief theoretical course on the chemistry of organic compounds of aliphatic series and exercise as a guide material for the examination which taken at the end of each section of the theoretical course.

#### THE CONCEPT OF FUNCTIONAL GROUPS

In organic chemistry, **functional groups** are specific groups of atoms within molecules that are responsible for the characteristic chemical reactions of those molecules. The same functional group will undergo the same or similar chemical reaction regardless of the size of the molecule.

In organic molecules, the atoms are linked by covalent bonds. Organic molecules are generally large and may be complex, involving many such bonds. Inorganic compounds have considerably simpler structure in terms of number, but not necessarily type, of bonds. In organic molecules, to a first approximation, we may say that one bond does not affect another. Thus an atom such as a chlorine atom, -Cl, or a group of atoms such as the alcohol group, -OH, on one end of a molecule will behave chemically in the same way almost without regard to the molecule to which it is covalently attached. The idea of different independent or semi-independent atoms or groups of atoms on the same molecule is central to our modern understanding of organic chemistry. It is called the concept of **functional groups**. The nomenclature of organic compounds, like most of the rest of our understanding of reactions of organic compounds, is based upon the concept of functional groups.

Functional groups consist of one or more atoms, and they can be atoms of identical or different elements. The simplest organic molecule is one carbon bonded covalently to four hydrogens, CH<sub>4</sub>. This compound, a gas, is called methane and is a major component of natural gas. For any other functional group to attach itself to methane, one hydrogen must be removed and the other functional group must be attached in its place. This process is called **substitution** of the functional group.

The principle used is that organic compounds are named and generally understood as substituted compounds of carbon and hydrogen, the substitution being that of a functional group for one or more hydrogens. The simplest compounds of carbon and hydrogen are the Alkanes, followed by the Alkenes and Alkynes.



If a chlorine atom is substituted onto methane, the compound produced is chloromethane:  $CH_3Cl$ .

Combining the names of functional groups with the names of the parent alkanes generates a powerful systematic nomenclature for naming organic compounds. The non-hydrogen atoms of functional groups are always associated with each other and with the rest of the molecule by covalent bonds. When the group of atoms is associated with the rest of the molecule primarily by ionic forces, the group is referred to more properly as a polyatomic ion or complex ion. And all of these are called radicals, by a meaning of the term radical that predates the free radical.

The first carbon after the carbon that attaches to the functional group is called the alpha carbon.

Functional groups are attached to the carbon backbone of organic molecules. They determine the characteristics and chemical reactivity of molecules. Functional groups are far less stable than the carbon backbone and are likely to participate in chemical reactions. Six common biological functional groups are hydrogen, hydroxyl, carboxyl, amino, phosphate, and methyl.

-H	-OH	-COOH	NH <sub>2</sub> COOH	$OP(OR)_3$	-CH <sub>3</sub>
Hydrogen	Hydroxyl	Carboxyl	Amino	Phosphate	Methyl

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#### **Test – The Concept of Functional Groups**

## № 1. Indicate properties characteristic to the free radicals

- A. Presence of a pair of electrons
- B. The presence of an unpaired electron
- C. The presence of a positive charge
- D. The presence of a negative charge
- E. Absence of electrons

#### № 2. How is the name of this substituent CH<sub>2</sub>=CH-

- A. Isopropyl
- B. Vinyl
- C. Ethyl
- D. Propyl
- E. Ethinyl

## $\texttt{N} {\ensuremath{\underline{2}}}$ 3. Among the following compounds indicate an inorganic compound

- A. Naphthalene
- B. Carbonic acid
- C. Saccharose
- D. Acetic acid
- E. Ethanol

#### SHAPES OF ATOMIC ORBITALS

The quantum-mechanical treatment of electrons in atoms gives a clear picture of the energy levels associated with every atomic orbital which can be defined by a set of four quantum numbers. The question of **where** in space the electron may be is a somewhat more ambiguous question and receives a somewhat more ambiguous answer. Solutions of the Schroedinger equation correspond to waves rather than to particles, and at least in principle all electromagnetic waves extend throughout all space! This interesting result is not helpful in locating the physical electron on a given atom.

The location of an electron can be described in either of two equivalent ways using the quantum-mechanical results. If the electron is visualized as a real very small object moving very rapidly, then the space it occupies can be described in terms of the probability of finding the electron at a given point or within a given space at any instant. If the desired probability is set at 99%, or 95%, a physical space occupied by the electron can be calculated on this time-average basis. If, on the other hand, the electron is visualized as an electromagnetic wave, then the amplitude of that wave, or the wave function, will be greater at some locations than at others. The space the electron occupies can be considered to be the space within which the amplitude of its wave function is greater than 1%, or 5%, of its maximum amplitude. Again, a three-dimensional space «containing» the electron will be defined.

The electron can be described equally well in either way or the three-dimensional spaces defined as «containing» the electron as a wave and as a particle are the same. Chemists find it convenient to describe the location of electrons in atoms and molecules in terms of this type of shape. These representations of orbital shapes are those which are said to contain 99% or 95% of the electron density of the orbital.

In a previous section, the shapes of the orbitals were assumed to be spherical and atomic and ionic radii could be calculated on that basis. In the quantum-mechanical treatment of atoms, ions, and molecules, many of the orbitals are not found to be spherical in shape. Moreover, the different orbitals on the same atom do interpenetrate each other and the electronic structure of the outer atom is to some extent a composite of several orbitals. For these reasons the atomic radius and ionic radius are now viewed as useful empirical measurements of the sizes of atoms and ions rather than as properties with fundamental significance. Even so, practicing chemists still learn much about the structures of compounds using molecular models made up of scale models of spherical atoms.

The values of all four quantum numbers influence the location of an electron, or in the terminology just introduced the distribution of electron density in space or the shape of an orbital, but the effects of the four different numbers are not the same. The **principal** quantum number n affects primarily the size of the orbital and has a lesser influence on its shape. The **subshell** quantum number l affects primarily the shape of the orbital. The **magnetic** quantum number m affects primarily the orientation of the orbital in three-dimensional space. The **spin** quantum number s has little effect upon the location of the orbitals of an isolated atom, but does have an influence on orbital interactions when the orbitals of different atoms impinge upon each other.

## s-Orbitals

Orbitals with subshell quantum number l = 0 are called s orbitals. All s orbitals are spherical in shape and have spherical symmetry. This means that the wave function will depend only on the distance from the nucleus and not on the direction.

In any atom, the size of the s orbital increases as the principal quantum number of the orbital increases but the geometry remains spherical. The electron density also tends to extend further. Other orbitals behave in the same way as the principal quantum numbers of the orbitals increase.

## **p-Orbitals**

Orbitals with subshell quantum number l = 1 are called p orbitals. Since the magnetic quantum number m can be -1, 0, or +1 when the value of the subshell quantum number l is one, p orbitals come in sets of three. In each set, one of the orbitals is aligned along each of the three mutually perpendicular axes of the atom; these axes are tradetionally designated x, y, and z. The three 2p orbitals are correspondingly designated  $2p_x$ ,  $2p_y$ , and  $2p_z$ . The p orbitals either as a set or individually do not have spherical symmetry and so a simple plot of radial probability density cannot be made for them. If, however, the distance from the nucleus is taken along any one of the three axes and the orbital is that along the same axis, then a suitable plot can be made.

## d-Orbitals

Orbitals with subshell quantum number l = 2 are called d orbitals; since m can be -2, -1, 0, +1, or +2 when l is two, d orbitals come in sets of five. The d orbitals, and the more complex f orbitals, are usually visualized in three-dimensional representations, even if these have to be shown on a two-dimensional page.

## **f-Orbitals**

Orbitals with subshell quantum number l = 3 are called f orbitals. These orbitals are found only in the lanthanide and actinide elements. Since m can be -3, -2, -1, 0, +1, +2, or +3 when l has the value 3, f orbitals come in sets of seven. The f orbitals are rarely of direct chemical interest because they tend to be buried deep within the electronic cloud of an atom, but they do play a major role in the spectroscopy of the lanthanides and actinides. The f orbitals are the most complex orbitals with which most chemists are concerned, even though 5g orbitals, with quantum number l = 4, are known to exist.

## **Electrons Shared: Covalent Bonding**

When John Dalton developed the atomic-molecular theory of matter in the last century, he visualized the atoms as hard, massive particles much like billiard balls. The billiard ball analogy was very useful in the development of the kinetic-molecular theory of gases. In order to account for the attachment of atoms to each other when compounds were formed, Dalton and others visualized atoms as having hooks or fasteners attached so that they could react with other atoms. It became clear almost immediately that the nature of these points of attachment varied considerably from one element to another and were characteristic of the atoms of the elements themselves. Hydrogen seemed to have only one point of attachment, oxygen usually two, and carbon usually four. Most other elements had a quite variable capacity for attachment; their number of attachment points depended upon what other elements they were combining with to form a particular molecule or ion. A point of attachment of an atom came to be called a **valence**.

## **Stoichiometry and Structure**

The atomic-molecular theory led chemists to make ever more accurate determinations of the atomic mass of atoms (atomic weights) and the molar mass of molecules. From molar masses and atomic masses the stoichiometry of many compounds was determined. Stoichiometry alone, however, does not determine the actual threedimensional arrangement of the atoms of a molecule in space which is the molecular structure. Moreover, it became clear that the bonding between different atoms in the same molecule was not identical. For example, if the salt NaClO<sub>4</sub> is dissolved in water and the equally soluble salt KBr is added, a precipitate of KClO<sub>4</sub> will form. Removal of the water will then leave the salt NaBr. The atoms of K and of Na can be interchanged in this way, but the oxygen atoms will remain attached to the chlorine. Perbromate salts are known to exist, but they cannot be formed in this way. The bonding between Na or K and perchlorate must be different in kind from the bonding within perchlorate between Cl and O.

Chemists now recognize three qualitatively different types of chemical bonding which are differentiated on the basis of the type of interaction of the electrons with other atoms. In ionic bonding, electrons are transferred from one originally neutral atom to another. This produces a negative ion or anion and a positive ion or cation. Anions and cations, having opposite charge, are attracted to each other electrostatically; ionic bonds as such do not exist. In the salt NaClO<sub>4</sub>, the sodium ions and perchlorate ions are associated with each other in the lattice structure of an ionic crystal. This type of «bonding» is discussed in another section.

The most common type of chemical bonding is **covalent bonding**. Covalent bonding arises when two, or less often a different number of, electrons are shared between two or more atoms. For example, in the molecule of water ( $H_2O$ ), each hydrogen atom originally has one

electron; in the molecule, it shares one pair of electrons with the oxygen atom. The second electron of each pair originally belonged to the oxygen. The remaining four electrons in the outer orbitals of the oxygen, as well as the two electrons in the inner 1s subshell of the oxygen, are not directly involved in the covalent bonding. In most normal covalent bonding, each atom contributes one electron per bond of the two electrons required per bond. In the salt NaClO<sub>4</sub>, the chlorine atoms and the oxygen atoms are attached to each other by covalent bonds which do not dissociate in aqueous solutions. Covalent bonding is the subject of this section and those following it.

When covalent bonding occurs in which both of the electrons of a bond are contributed by the same atom, the covalent bond is called a **coordinate covalent bond**. Coordinate covalent bonding is usually found in complex ions or molecules in which the central atom is a transition metal ion. The coordinating groups or molecules, called **ligands**, contribute both of the electrons involved in the coordinate covalent bond to the central metal atom. Coordinate covalent bonding is the subject of other sections.

Many atoms which cannot react by transfer of electrons form stable compounds. Hydrogen atoms, reacting with each other to form the quite stable diatomic gas, cannot have electron affinities greater than their own ionization potentials. The stability of the diatomic hydrogen molecule is the simplest example of the sharing of electrons between two or more atoms that is called covalent bonding. Covalent bonding is so much more common in chemistry than is ionic bonding that the term chemical bonding is sometimes used in place of the term covalent bonding.

# Test — Stoichiometry and Structure, Electrons Shared: Covalent Bonding, Shapes of Atomic Orbitals

#### № 1. What is the chemical structure of the molecule?

A. The thermal stability of the molecule.

B. The order of atom bonds in a molecule.

C. The total number of atoms in the molecule.

D. Dependence of the properties of the molecule from value of the relative molecular mass.

E. Chemical nature of the atoms in the molecule.

№ 2. What is the structure of majority of organic compounds?

A. Nonmolecular

B. MolecularC. IonicD. CrystalE. Disorderly

#### № 3. What is the inductive effect?

A. The displacement of the electron density in the communications, accompanied by the transition of electrons to the atom.

B. The displacement of the electron density to the electronegative part of the molecule by s-bonds

C. The displacement of the electron density by the p- bonds.

D. The uneven distribution of electrons between atoms.

E. The displacement of the electron density to the electronegative part of the molecule by p-bonds.

#### № 4. What bond is called s- bond?

A. Bond, carried out due to the overlap of the electron orbitals located outside the bonding line between the centers of the nuclei of atoms.

B. The bond, carried out due to the overlap of the electron orbitals located on the bonding line between the centers of the nuclei of atoms

C. Bond, carried out due to the electrostatic interaction of oppositely charged particles.

D. Bond, carried out due to the overlap of unhybridized orbitals of carbon atoms. E. Bond, carried out by the interaction of the substituents.

#### № 5. What bond is called p- bond?

A. Bond, carried out due to the electrostatic interaction of oppositely charged particles by centers of the atomic nuclei.

B. The bond, carried out due to of the lateral (side) the overlap of p-electron orbitals

C. Bond, carried out due to the overlapping non-hybridized carbon atom orbitals.

D. Bond, carried out due to the overlap of the electron orbitals located on the the bonding line between the centers of the nuclei of atoms.

E. Bond, carried out due to of the lateral (side) overlapping s-electron orbitals.

# $N_{2}$ 6. What bond has the greatest influence on the physical properties of organic substances?

A. Polar covalent

B. Hydrogen

C. Covalent nonpolar

D. Van der Waals

E. Ionic

#### LEWIS STRUCTURES OF ATOMS

When the stoichiometry of molecules was first understood in the nineteenth century, and came to be used to discuss their structure, the concept of valence or combining capacity was employed. A valence was generally indicated by a short line joining the atoms in a molecule. For example, the structure of water was written H-O-H which indicated two one-valence hydrogen atoms attached to a two-valence oxygen atom. The number of valences was generally characteristic of the type of atom; thus hydrogen had one valence, oxygen two, and chlorine one. Nitrogen had either three or four valences depending upon the particular compound in which it was found.

A more quantitative picture of bonding was introduced by the American physical chemist G. N. Lewis. Lewis suggested that the valences should be replaced by the valence (outer) electrons. The valence electrons are the electrons used by an atom in chemical bond formation. Valence electrons include the electrons in the outermost shell of the atom, which is often called the **valence shell**. When electrons in inner shells of the atom are also used in bonding, as occasionally happens, then these electrons are considered valence electrons also even though they are not in the valence shell.

The **Lewis structure of an atom** is written as the element symbol, which represents the nucleus of the atom and its surrounding inner electrons which are not used in chemical bonding, and a surrounding group of dots which represent the valence electrons. Since two electrons, or more correctly one **pair** of electrons, are used in the formation of a single covalent bond, the surrounding group of electrons is usually written in pairs.

- 1. What can be predicted by the chemical properties of substance?
- A. Relative molecular mass
- B. The structure of the molecule
- C. Absolute molecular mass
- D. Number of isomers
- E. Qualitative structure of the molecule

## **Unequal Sharing of Electrons Produces Polar Bonds**

Most chemical bonds are covalent in that electrons are shared, but this sharing need not be equal. The sharing is exactly equal only if the two atoms are identical, as they are in the diatomic elements such as oxygen,  $O_2$ . When the two atoms are not identical and the sharing is noticeably unequal, the covalent bond is said to have ionic character or to be polar. In the water molecule, the electrons are closer to the oxygen; in the HF molecule, the electrons are closer to the fluorine. An atom which has a greater tendency to pull the electrons in a covalent bond toward itself is called **electronegative**, while an atom which has a lesser tendency to pull the electrons in a covalent bond toward itself is called electropositive.

The concept of electronegativity was made quantitative by Linus Pauling, an American chemist who has won two Nobel prizes (one for chemistry, one for peace). Pauling compared the bond enthalpies of the known homopolar (two identical atoms) and heteropolar (two different atoms) bonds of various elements, and from them calculated the values we now call the **Pauling scale** of electronegativities. Similar scales have been calculated by others from ionization potentials and electron affinities, but the Pauling scale has remained as the scale most chemists use.

Any homopolar bond has an electronegativity difference of zero and is purely covalent with equal sharing of electrons. As the difference in electronegativity of the two atoms in a heteropolar bond increases, the bonding electrons are found to lie closer to the more electronegative atom. In HF, with an electronegativity difference of 1.9, one would expect the bond to be polar and the electrons (and therefore also the net negative charge) to lie more toward fluorine than toward hydrogen.

## The Basic Shapes of Molecules

Although the prediction of molecular geometry is most correctly done by quantum-mechanical calculations involving the orbitals on the different atoms which make up the compound, this approach is beyond the scope of the present section. However, it is quite possible to predict the geometrical structures of many compounds without calculations by using what has come to be called valence shell electron-pair repulsion, abbreviated as V.S.E.P.R.

The fundamental principle of valence shell electron-pair repulsion is that when a molecule consists of a central atom which is surrounded by other atoms, the geometry of the molecule will be such that all of the electron pairs in the valence shell of the central atom will be as far from each other as possible. This will be true whether the electron pairs in the valence shell are used for bonding or not. Thus if a central atom has two electron pairs in its valence shell, the basic structure of the molecule is linear; if there are three, it is triangular; if there are four, it is tetrahedral; if there are five, it is a trigonal bipyramid; and if there are six, it is an octahedron.

Once the basic shape of a molecule has been established, and in this regard the simple V.S.E.P.R. approach gives the same geometric pattern as does the more sophisticated hybridization of atomic orbitals approach, the substituents can be arranged in the basic shape. For the two larger basic shapes, five and six electron pairs in the valence shell, the possible arrangements of substituents (noncentral atoms) and nonbonding electron pairs is not unique. In arranging the substituents and electron pairs about the central atom of a trigonal bipyramid, the unshared electron pairs should be placed in equatorial positions. In an octahedron, the unshared electron pairs should be placed as far from one another as possible. For example, if an octahedral basic structure contains four substituents and two unshared electron pairs, the two unshared pairs should not be placed adjacent to each other.

The electron pairs take up positions as far from each other as possible. The repulsion can easily be observed in a physical model simply by tying balloons together tightly in the appropriate numbers. Four identical balloons will form a tetrahedron while six identical balloons will form an octahedron.

The number of electron pairs in the valence shell establishes the basic shape of a molecule. Since the number of electron pairs used in the valence shell of the central atom is shown in the Lewis structure of a molecule as discussed earlier in a preceding section, the basic shape of many molecules can be deduced directly from their Lewis structures. Test — Lewis Structures of Atoms, The Basic Shapes of Molecule, Unequal Sharing of Electrons Produces Polar Bonds

№ 1. What is the valence of carbon in ethylene?

A. 1

B. 4 C. 3

D. 2

E. 5

#### № 2. What is valence sulfur in sulfonic acids?

A. 2

**B**. 4

C. 6

D. 3

E. 5

F. 8

## $\mathbb{N}_{2}$ 3. What valence exhibits a nitrogen atom in amines, and nitro compounds?

A. 5

B. 4

C. 3

D. 2

E. 6

## № 4. Lewis acids include

A. boron trifluoride

B. nitrogen fluoride

C. carbon tetrafluoride

D. sulfur difluoride

E. aluminum trichloride

## DISTORTIONS DUE TO ELECTRON PAIR REPULSION

Once the substituents on the central atom of the molecule are arranged in one of the basic shapes, a qualitative picture of the actual molecular geometry can be obtained by considering the distortions of the basic structure which will be introduced by the repulsion which exists between the unshared electron pairs and the electron pairs used in bonding to the substituents. **The effect of this repulsion will be to move the substituents closer to each other, and farther away from any unshared electron pairs, than they would be found in the basic structure.** 

In a perfectly tetrahedral molecule, such as methane, the bond angle between any two adjacent atoms must be, and is,  $109.5^{\circ}$ . In ammonia, NH<sub>3</sub>, there is one orbital occupied by a lone pair of nonbonding electrons; this repels the three bonding electron pairs so that the H-N-H angle is  $107.3^{\circ}$ . In water, H<sub>2</sub>O, there are two unshared electron pairs or lone pairs; the repulsion is greater and the H-O-H angle is  $104^{\circ}$ .

It is possible for a single atom, particularly an atom of oxygen or sulfur, to share two of the electron pairs on a neutral atom rather than one. The compounds  $SOCl_2$  and  $POCl_3$  are examples of compounds in which this happens. The two electron pairs shared must occupy roughly the same space, the space between the two atoms to which they are bound, and so the two bonding pairs act as if they were a single electron pair in establishing the basic molecular geometry. For this reason  $SOCl_2$  is a planar triangular molecule while  $POCl_3$  is tetrahedral.

## The Linear Combination of Atomic Orbitals

When atoms are brought together to form compounds, their atomic orbitals approach each other sufficiently closely to interact. In the formation of covalent bonds, the electrons in the atomic orbitals on one atom interact with the electrons in the atomic orbitals on another atom to accomplish the sharing of electrons between the atoms. The interaction involves primarily, but not entirely, the interaction of one orbital on one atom with one orbital on another atom. In order to understand molecular geometry, however, it is often necessary to consider the effect of many (ideally all) of the other orbitals on the interacting atoms. One approach which does this is called the «hybridization» of atomic orbitals.

In another section, an extension of the ideas of Lewis structures of molecules called the **valence shell electron pair repulsion**, or V.S.E.P.R., approach was used to rationalize the observed geometries of many of the simpler inorganic molecules. In this section we shall show that the approach of valence shell electron pair repulsion is an approximation to a more fundamental understanding of the covalent bonding in molecules which is usually called the **valence bond theory**.

The basic idea of valence bond theory is that a covalent bond is formed by the overlap of atomic orbitals. The two electrons of paired spin which are shared by two bonded atoms lie in an atomic orbital of each of the two atoms. The greater the degree of overlap of the atomic orbitals, the greater will be the degree of sharing and the stronger will be the covalent bond between them. The atomic orbitals can be the original atomic orbitals of the atoms, but often the geometry of these orbitals is such that effective overlap cannot occur in the known geometry of the molecule. Under these circumstances, the atomic orbitals on an atom can reconfigure themselves into a different configuration, and the reconfigured orbitals are said to be **hybridized**.

The hybridization of atomic orbitals approach, when used in this qualitative and descriptive way, gives little information on energy levels within molecules. It is most easily used with molecules consisting of some arrangement about a single atom, i.e. where a single atom is at the center of symmetry of the molecule. The primary reason for qualitative use of this approach is because it gives information on the molecular geometry. This method of linearly combining atomic orbitals is particularly useful when the bonding in a molecule is essentially determined by one of the atoms in it, unlike the case of molecular oxygen where both of the atoms are significantly involved and no atom is located at the center of symmetry of the molecule. (Such molecules are more easily treated using the molecular orbital approach.)

In 1931, the American physical chemist Linus Pauling demonstrated that the wave functions of the electrons in the orbitals of an atom could be combined mathematically (essentially, by adding together the amplitudes of their waveforms in three-dimensional space – which by mutual constructive and destructive interference will give a different three-dimensional configuration), using the equations of waves, to give sets of equivalent Schroedinger wave functions that we now call hybridized atomic orbitals. For many molecules, hybridization gives a set of atomic orbitals that can overlap more effectively with the atomic orbitals on other atoms in the molecule, thus providing an overall molecular structure which has stronger bonds and is lower in energy. While the mathematical treatment of Pauling is beyond our scope, the results of it are most useful in furthering our understanding of the bonding in molecules.

The principles of the **valence bond theory** derived from Pauling's analysis can be stated as follows:

- Not all of the full, half-full, or empty orbitals on any atom need be used in a hybridization. (Those which are not used in hybridization can be used in bonding as if the hybridization had not taken place).
- Orbitals that are full, half-full, or empty do not hybridize with each other. The hybridizing orbitals are all half-full in normal covalent bonding. (Orbitals which are all full or all empty are used in coordinate covalent bonding).
- The hybridized atomic orbitals on one atom overlap with either normal or hybridized orbitals on another atom, or with both, depending on the molecular geometry.
- The number of orbitals **produced** in any hybridization is equal to the number of original atomic orbitals **used** in that hybridization.

In using the hybridization of atomic orbitals approach in this way, we need look only at the empty or half-full orbitals on the central atom. We can look at either the empty or half-full orbitals, not both at the same time. There are only a limited number of types of hybridization commonly found in molecules, and a list is given below. More details of each of them are given in another section.

## sp Hybridization

The hybridization of one s orbital and one p orbital on a central atom gives rise to two sp orbitals. Hybridization as sp gives two orbitals, which are in a **linear** arrangement, that is,  $180^{\circ}$  apart. An example of sp hybridization is found in HgCl<sub>2</sub> (mercury (II) chloride).

## sp<sup>2</sup> Hybridization

The hybridization of one s orbital and two p orbitals on a central atom gives rise to three  $sp^2$  orbitals. Hybridization as  $sp^2$  gives three orbitals, which are planar and  $120^\circ$  apart. An example of  $sp^2$  hybridization is BCl<sub>3</sub>.

## sp<sup>3</sup> Hybridization

The hybridization of one s and all three p orbitals on a central atom gives rise to four sp<sup>3</sup> orbitals. Hybridization as sp<sup>3</sup> gives four identical orbitals, which are aligned in a tetrahedral configuration and so are 109.5° apart. This very common structure is found in CH<sub>4</sub>, NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, and CCl<sub>4</sub>; it is the usual hybridization form of singly-bonded carbon atoms in organic compounds.

In its ground state, the carbon atom has the electronic structure  $1s^22s^22p^2$ . The hybridization requires four half-full orbitals, so the electronic structure of the carbon atom must reach the **excited state** structure of  $1s^22s^12p^3$ , with one electron in each of the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals, before hybridization can occur. This requires energy--an energy which is more than recovered in the lower-energy more-overlap structures of molecules which are possible with  $sp^3$  hybridization.

## dsp<sup>2</sup> Hybridization

Atoms of the transition metals and of other elements which have d atomic orbitals available to them can use these d orbitals in hybridization. The hybridization of one s, two p, and one d orbital on a central metal atom gives rise to four hybrid dsp<sup>2</sup> orbitals. They are square planar in alignment and 90° apart, because the hybrid uses the  $d_{xy}$ , s,  $p_x$  and  $p_y$  orbitals, all of which are in the xyplane. An example of a square planar complex ion is Ni(CN)<sub>4</sub><sup>2-</sup>.

# dsp<sup>3</sup> Hybridization

Atoms which have d orbitals available to them can also use them to form other types of hybrid orbitals. The hybridization of one s, one d, and three p orbitals on a central atom gives rise to five  $dsp^3$  orbitals. Hybridization as  $dsp^3$  gives five orbitals, three equatorial and two axial, because this hybridization uses the  $d_z2$ , the s, and all three of the p orbitals; one of the p orbitals ,  $p_z$ , is perpendicular to the xy plane. In effect, the trigonal bipyramidal geometry of this hybridization is the trigonal plane of  $sp^2$  hybridization with the addition of the z axis component due to the  $p_z$  and  $d_z 2$  orbitals. An example of  $dsp^3$  hybridization is PCl<sub>5</sub>, whose geometry is that of a trigonal bipyramid.

# d<sup>2</sup>sp<sup>3</sup> Hybridization

Atoms which have two or more d orbitals available to them can use more than one d orbital in a hybridization. The hybridization of two d orbitals, one s orbital, and three p orbitals on a central atom gives rise to six hybrid  $d^2sp^3$  orbitals. Hybridization as  $d^2sp^3$  gives six orbitals which are equivalent in energy and geometry. All adjacent orbitals are 90° apart, and all nonadjacent orbitals are 180° apart. This form of hybridization has the geometric structure of an octahedron, with six vertices and eight sides. The orbitals which contribute to the square planar geometry of the equatorial plane of the octahedron are the s, p<sub>x</sub>, p<sub>y</sub>, and d<sub>xy</sub> atomic orbitals; the z axis component is again due to the p<sub>z</sub> and the d<sub>z</sub>2 atomic orbitals. Molecules or ions which have this structure are said to have octahedral structures or symmetry; sulfur hexafluoride and uranium hexafluoride are examples of such molecules.

#### INTRODUCTION TO THE ALKANES

**Hydrocarbons** are simple organic compounds which contain only carbon and hydrogen. If the carbon atoms are linked in chains, the compounds are called aliphatic compounds; if the atoms are linked in rings, the compounds are called alicyclic.

The chain compounds, or aliphatic compounds, may be further classified on the basis of the individual carbon-to-carbon bonds. Every carbon atom can form four bonds to other atoms thus the noble gas configuration is reached (8 outer electrons). Every hydrogen atom forms one bond producing 2 outer electrons, the most stable state for hydrogen.

Chain compounds in which all carbon-to-carbon bonds are only simple single bonds are called **alkanes**. These compounds are also called saturated hydrocarbons, because each carbon-to-carbon bond is a single bond, and the valence of the carbon atom is, therefore, saturated. No more atoms can be bonded to the atoms in the compound, without breaking the compound into two or more fragments. If it contains one or more bonds which can react with hydrogen it is called an **unsaturated** hydrocarbon. Almost all other organic compounds can be named as derivatives of these simple hydrocarbons. Alkanes which have long carbon chains are often called paraffins in chemical industry. The most simple alkane is methane with the formula CH<sub>4</sub>. The second alkane is chane with the formula C<sub>2</sub>H<sub>6</sub>. The general formula of alkanes is  $C_nH_{2n+2}$ .

The first four alkanes are methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), propane (C<sub>3</sub>H<sub>8</sub>) and butane (C<sub>4</sub>H<sub>10</sub>).

The simplest alkane is the gas **methane**, whose molecular formula is CH<sub>4</sub>. Methane exists as a tetrahedral shape, but it is often represented by a flattened structure as are most organic compounds. Flattened structures for the three simplest alkanes are given in the Figure below. In many cases the structures can be further simplified without loss of information by omitting all single bonds and writing the letter symbol of the element close to the letter symbol of the element to which it is attached. Thus the representation of methane as CH<sub>4</sub>, ethane as H<sub>3</sub>CCH<sub>3</sub> (rather than as C<sub>2</sub>H<sub>6</sub>), and propane as H<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub> (rather than as C<sub>3</sub>H<sub>8</sub>) is a representation of structure as well as of molecular composition.

Chemical formula	Structural formula	Half structural formula
$ m CH_4$	H H-C-H H	$CH_4$
$C_2H_6$	н н н-с-с-н н н	$H_3C - CH_3$
$C_3H_8$	H H H H-C-C-C-H H H H	$H_3C - CH_2 - CH_3$
C <sub>4</sub> H <sub>10</sub>	H H H H H-C-C-C-C-H H H H H H H H H	$\begin{array}{c} H_3C-CH_2-CH_2-\\ CH_3 \end{array}$

For many simple organic compounds representations like this are adequate for discussion and identification purposes. When they are not adequate, all organic chemists resort to more elaborately drawn structures which convey the necessary information.

The structure of ethane can be derived from that of methane by substitution of a  $-CH_3$  group, called a **methyl group**, for one of the hydrogens of methane. The structure of propane can be derived either by substitution of a methyl group upon ethane or by substitution of an ethyl group upon methane; either method yields the same product, **propane**. Likewise, the structure of the next member of the series, **butane**, can be derived by the substitution of a methyl group upon propane. The alkane series of compounds can be extended indefinitely by this method. The names of the compounds and their substituent groups are given in the Table below. For even longer chains, the name is simply the number (given as a Greek prefix).

The alkanes above propane are named by giving the number of carbons (in Greek) with the ending **-ane** added. If an alkane is not a straight chain, then the longest straight chain in it is used as the basis of the name and the shorter side chains are considered to be substituents; thus names such as methylpropane and methylbutane are derived.

## **Positional Isomers of Alkanes**

Two four-carbon alkanes are known, and they have measurably different chemical and physical properties. Their structures are  $H_3CCH_2CH_2CH_3$  and  $H_3CCH(CH_3)_2$ . Therefore they were named **normal butane**, often abbreviated as n-butane, and **isobutane**. The straight-chain form is considered the «normal» form. Alternatively, they could be named using the systematic IUPAC method as 1-methyl-propane and 2-methylpropane, or even as butane and 2-methylpropane. The IUPAC method names the longest straight carbon chain in the usual way and then numbers the carbons; the location of a substituent group is given by the number of its carbon. The IUPAC method is always used for more complicated molecules, but many of the simpler ones still use non-systematic names, called **trivial names**, because these are less cumbersome to use.

The two forms of butane are described as two **positional isomers** of butane because they differ only in the position of the substituent group. The pentanes have three positional isomers:  $H_3CCH_2CH_2$   $CH_2CH_3$ , **normal pentane** or **n-pentane**;  $H_3CCH_2CH_2(CH_3)_2$ , **isopentane**; and  $H_3CC(CH_3)_3$ , **neopentane**. This older nomenclature is still used to distinguish normal or n-compounds, which have straight chains, from iso-compounds, which branch at the carbon next to the end carbon, but neo-compounds are now named using the IUPAC system. The IUPAC systematic names for the three positional isomers of pentane would be pentane, 2-methylbutane, and 2, 2-dimethylpropane. Note that the appearance of two substituents on the same carbon causes no problem; the same location is simply given twice.

Table 1

Name	Molecular Formula	Structural Formula	Boiling Point (oC)
Methane	CH <sub>4</sub>	CH <sub>4</sub>	-161.0
Ethane	$C_2H_6$	CH <sub>3</sub> CH <sub>3</sub>	-88.5
Propane	$C_3H_8$	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	-42.0
Butane	$C_4H_{10}$	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	0.5
Pentane	C5H12	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	36.0
Hexane	$C_6H_{14}$	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	68.7
Heptane	$C_7 H_{16}$	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	98.5
Octane	$C_8H_{18}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	125.6
Nonane	$C_9H_{20}$	$CH_3(CH_2)_7CH_3$	150.7
Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	174.1

## Structural Formulas of the First Ten Continuous-chain Alkanes

**Note:** In the table above octane, nonane, and decane have  $(CH_2)$  groups followed by a subscript designating the number of  $(CH_2)$  groups attached to the carbons between the end  $CH_3$ 's of each chain.

Names of the higher members of this series consist of a numerical term, followed by «-ane». Examples of these names are shown in the table below. The generic name of saturated aliphatic (acyclic) hydro-carbons (branched or unbranched) is «alkane».

Each compound differs from the next by a multiple of the  $-CH_2$ -(methylene group). Essentially we are building the series of compounds by removing a hydrogen atom from one of the carbon atoms and adding  $-CH_2$ - to the chain and then replacing the hydrogen.

A series of compounds whose structures differ from each other by a specific structural unit (such as  $-CH_2$ - in the case of alkanes) is called a **homologous series**. A general formula can be written for all of the members of a homologous series such as the alkanes. For the alkanes, the formula  $C_nH_{2n+2}$ , where n is the number of carbon atoms in the compound.

There are general trends in physical and chemical properties within homologous families which can be used to study these families as a whole. For instance, as the molecular weight of the compounds in a family increases, the boiling point increases. This can be seen from the table listing the first ten members of the alkane family above.

It is interesting to note that the first four alkanes, which all exist in the vapor state under normal atmospheric conditions, are the principle ingredients in natural gas. The members of the alkane family use the Greek (sometimes Latin) prefix for the number of carbon atoms, and the characteristic ending -ane to identify and describe their position and structure within their respective family.

If one hydrogen atom, with its associated electron, is removed from a hydrocarbon molecule, a **Radical** is left:

CH <sub>4</sub>	CH <sub>3</sub> -CH <sub>3</sub>	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>
Methane	Ethane	Propane
CH <sub>3</sub> -	CH <sub>3</sub> -CH <sub>2</sub> -	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -
Methyl	Ethyl	Propyl

Radicals are named by substituting the ending -yl for the normal -ane ending of the parent compound.

For convenience in naming organic compounds, carbon atoms in a structural formula are given position numbers. In an unbranched chain molecule, the numbering of carbon atoms can begin at either end of the chain:

#### CH3-CH2-CH2-CH3 CH3-CH2-CH2-CH2-CH3 Butane Pentane

Not all alkanes have unbranched chains of carbon atoms. Complex alkanes are named by using the longest chain of carbon atoms as the basis of the compound name. The parent chain does not necessarily occur in a straight line. This compound CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)  $CH_2CH_3$  – 3-methylpentane has pentane ( $C_5H_{12}$ ) as the parent chain since the longest chain contains five carbon atoms. The carbon atoms of the longest chain are given position numbers beginning at one end of the parent chain. The CH<sub>3</sub>- group which is attached to the main chain is called a side chain or substituent. The side chain is named as a radical. We indicate, by number, the position of the carbon atom of the parent chain to which the side chain (radical) is attached. Thus, the name 3-methylpentane for the above saturated alkane. The parent compound is pentane, the radical is methyl which attached to the number-3 carbon atom of the parent chain. The name is written with a hyphen between the substituent (radical) position number and name. The radical and parent are written as one word. Numbering of the carbon atoms of the parent chain begins at the end which will give the lowest position numbers to the radical.

**Note:** Be aware that 3-methylpentane is written with a methyl radical  $(CH_3)$  in parenthesis immediately to the right of the carbon to which it is attached. It is not part of the parent chain but rather attached as a side branch.

#### CH<sub>3</sub>CH<sub>2</sub>C(CH<sub>3</sub>CH<sub>2</sub>)(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub> 3-ethyl-3-methylhexane

It is relatively easy to see that if one does not follow the established rules the previous structure may have been mistakenly named 4-ethyl-4-methylhexane. **One must begin numbering the carbons of**  **the parent chain from that end closest to the attached radical**. You may have wondered why the structure was not named 3-methyl-3-ethylhexane. The fact of the matter is that both 3-ethyl-3-methylhexane and 3-methyl-3-ethylhexane are correct. It is permissible to choose one of two rules:

1. When there is more than one radical attached, and the number is not a factor, list them in alphabetical order.

2. When there is more than one radical attached, and the number is not a factor, list them in order of their mass (smaller to larger).

The first rule listed is generally the accepted method of representing the attached radicals and functional groups. Whatever method is chosen it is important to be consistent.

If there are two or more radicals attached which are alike, it is convenient to use prefixes (di-, tri-, tetra-, penta-, etc.) instead of writing each group separately. A comma is placed between the position numbers of the substituents which are alike.

#### CH<sub>3</sub>CH(CH<sub>3</sub>)CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub> 2,3-dimethylpentane

The parent chain is the five carbon chain-pentane. The carbons of the parent chain must be numbered starting from the left because the radicals (methyl) are located closest to that end. The two similar radicals are positioned on the second and third carbons of the parent chain, thus, the 2,3- designation. Because there are two radicals of the same kind the prefix di- is utilized to indicate the number present. Again, note the presence of the **comma** and **hyphen**. For structures such as methane (CH<sub>4</sub>), ethane (CH<sub>3</sub>-CH<sub>3</sub>), and propane (CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>3</sub>) only one structural diagram needs to be drawn. There is, however, an alternative structure for butane.

CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	CH <sub>3</sub> CH(CH <sub>3</sub> )CH <sub>3</sub>	
Butane (C <sub>4</sub> H <sub>10</sub> )	Methylpropane (C <sub>4</sub> H <sub>10</sub> )	

As noted in section 10.1, the existence of two or more substances with the same molecular formula ( $C_4H_{10}$  in this instance), but different arrangements of atoms and bonds, is called **isomerism**. The two structures of butane diagrammed above are called isomers of butane. Most

organic compounds have isomers but there is no known way of predicting exactly how many isomers most compounds can form. Pentane  $(C_5H_{12})$ , the next member of the alkane family, has three isomers:

> CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> CH<sub>3</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub> CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>3</sub> Pentane Methylbutane Dimethylpropane

Because there is only one form of methylpropane, methylbutane, and dimethylpropane it is not necessary to include the position numbers when writing their name.

Hexane ( $C_6H_{14}$ ), the next member of the alkane family, has five isomers, and heptane ( $C_7H_{16}$ ) has nine. Isomers are named according to the longest chain, and not according to the total number of carbon atoms in the molecule. Thus, the isomers of heptane are:

1. heptane

- 2. 2-methylhexane
- 3. 3-methylhexane
- 4. 2,2-dimethylpentane
- 5. 3,3-dimethylpentane
- 6. 2,3-dimethylpentane
- 7. 2,4-dimethylpentane
- 8. Ethylpentane
- 9. trimethylbutane

The number of isomers increases dramatically with the number of carbons in the parent chain as indicated by octane with eighteen (18), nonane with thirty-five (35), and decane with seventy-five (75).

Table 2

Fraction	Composition of carbon chains	Boiling range (°C)	Percent of crude oil
Natural Gas	$C_1$ to $C_4$	Below 20	10%
Petroleum ether (solvent)	C <sub>5</sub> to C <sub>6</sub>	30 to 60	10%
Naphtha (solvent)	C <sub>7</sub> to C <sub>8</sub>	60 to 90	10%
Gasoline	C <sub>6</sub> to C <sub>12</sub>	75 to 200	40%
Kerosene	C <sub>12</sub> to C <sub>15</sub>	200 to 300	10%
Fuel oils, mineral oil	C <sub>15</sub> to C <sub>18</sub>	300 to 400	30%
Lubricating oil, petroleum jelly,	C <sub>16</sub> to C <sub>24</sub>	Over 400	10%
greases, paraffin wax, asphalt			

### **Fractions Obtained from Crude Oils**

All alkanes are inflammable, the product of the burning being carbon dioxide ( $CO_2$ ) and water ( $H_2O$ ). Methane, ethane, propane and butane are gaseous at room temperature and are collectively referred to as natural gas. Hydrocarbons are nonpolar allowing van der Waals forces to act between them. Short alkanes have weak van der Walls forces. With an increase of carbon atoms the van der Waals forces increase. As the molecular chains become longer the molecules become liquid and eventually solid.

#### Test – Alkanes

#### № 1. Which group of atoms is called homologous difference?

A. CH
 B. CH<sub>4</sub>
 C. CH<sub>3</sub>

D. CH<sub>2</sub>

D. CH<sub>2</sub>

E.  $C_2H$ 

#### № 2. Give a full definition to the concept «isomers»

A. Isomers – are substances which have the same qualitative composition, and differ from each other by different melting or boiling point.

B. Isomers – are substances which have the same qualitative and quantitative composition and differ from each other by chemical and physical properties

C. Isomers – substances that consist of atoms of the same elements.

D. Isomers – substances which have a different qualitative and quantitative composition and different chemical structure of the molecules.

E. Isomers – a structural unit of the polymers.

## № 3. Indicate properties characteristic to the free radicals

A. presence of a pair of electrons

B. absence of electrons

## C. the presence of a positive charge

D. the presence of a negative charge

E. the presence of an unpaired electron

## № 4. What hydrocarbon is the bulk of natural gas?

- A. Methane
- B. Ethane

C. Propane

D. Acetylene

E. Ethylene

## $\ensuremath{\mathbb{N}\!\!_{2}}$ 5. Indicate formula the neighboring homolog of ethane

A. C<sub>3</sub>H<sub>6</sub>

B. C<sub>3</sub>H<sub>8</sub>

C. C<sub>3</sub>H<sub>4</sub> D. C<sub>2</sub>H<sub>5</sub> E.  $C_2H_3$ 

№ 6. Which compound is preferably formed by carrying out the following

reactions?  $\begin{array}{c} CH_{3} \\ I \\ CH_{3}-CH-CH_{2}-CH_{3} \\ \hline \\ H_{3} \\ A. \\ CH2-CH-CH_{2}-CH_{3} \\ I \\ CI \\ B. \\ CH_{3}-C-CH_{2}-CH_{3} \\ CH \\ CH \\ \end{array}$ C.  $CH_{3}$ C.  $CH_{3}$ -CH-CH<sub>2</sub>-CH<sub>2</sub> CI D.  $CH_{3}$ -CH-CH-CH-CH<sub>3</sub> CI CH<sub>2</sub>-CI CH<sub>2</sub>-CI CH<sub>2</sub>-CI CH<sub>3</sub>-CH-CH<sub>2</sub>-CH<sub>3</sub> № 7. Indicate scheme of butane isomerization reaction: A)  $CH_3-CH_2-CH_2-CH_3+Br_2 \xrightarrow{hv} CH_3-CH_2-CH_2-CH_2-Br + HBr$ B)  $CH_3-CH_2-CH_2-CH_3 \xrightarrow{t, AlCl_3} CH_3-CH_2-CH_3$   $\downarrow \\ CH_3$   $CH_3-CH_2-CH_2-CH_3 \xrightarrow{t, Ni} CH_3-CH_2-CH_2-CH_2+H_2$ 

- D)  $CH_3$ - $CH_2$ - $CH_2$ - $CH_3 \xrightarrow{t, kat} CH_3$ - $CH_3 + CH_2$ = $CH_2$
- A.A
- B.C
- C. B
- D. D
- E. The isomerization reaction is not specified.

#### № 8. Indicate general formula of alkanes:

- A.  $C_nH_{2n+2}$
- B. CnH2n
- C. C<sub>n</sub>H<sub>2n-1</sub>
- D. CnH<sub>2n-2</sub>

E. CnH2n-3

# $N_{2}$ 9. Which gas is obtained by heating sodium acetate CH3COONa with solid sodium hydroxide?

- A. Carbon monoxide (IV)
- B. Ethane
- C. Carbon monoxide (II)
- D. Hydrogen
- E. Methane

# $\mathcal{N}_{2}$ 10. Indicate mechanism of the reaction of methane with chlorine under illumination:

A. Ionic

- B. Heterolytic
- C. Covalent nonpolar
- D. Free radical
- E. Covalently-polar

#### № 11. Name the compound according to the nomenclature IUPAC:

CH<sub>3</sub>

H<sub>3</sub>C-H<sub>2</sub>C - HC - CH<sub>3</sub>

- A. 1,1-dimethylpropane
- B. 2-methylbutane
- C. Isopentane
- D. 3-methylbutane
- E. 3,3-dimethylpropane

# № 12. How many possible isomers of monobrom derivatives of alkane having in its structure 4 carbon atoms

A. 2

- B. 4
- C. 3
- D. 0
- E. 1
- F. 5

#### № 13. How many isomers have tetrafluorodihloretane?

- A. 1
- B. 2
- C. 3
- D. 4 E. 0
- E. 0
- F. 5

№ 14. What formed by reaction between 1-phenyl-2-chloropropane and an alcoholic solution of sodium ethylate?

A.  $C_6H_5CH_2CH(OC_2H_5)CH_3$ B.  $C_6H_5CH_2CH(ONa)CH_3$ C.  $C_6H_5CH_2CH=CH_2$ D.  $C_6H_5CH=CHCH_3$ E.  $C_6H_5CH=CHCH_3$ F.  $C_6H_5CH_2CH(OH)CH_3$ F.  $C_6H_5CH_2CH_2(OH)$ 

## Ne 15. By Tishchenko reaction (heating hydrazones with alkali) is formed

- A. Alkenes
- B. Alcohols
- C. Alkynes
- D. Dienes
- E. Aromatic hydrocarbons
- F. Alkanes

## № 16. Specify the tautomeric forms of nitroethane

F. A, E.

#### № 17. Indicate a compound that is formed by the following reaction:

CH<sub>3</sub> -C=CH<sub>2</sub> + HBr 
$$\xrightarrow{H_2O_2}$$
?  
CH<sub>3</sub>  $\stackrel{P}{\longrightarrow}$ ?  
A.  $\stackrel{I}{\underset{H_3C-H_2C - HC - CH_3}{\overset{I}{\longrightarrow}}$   
B.  $\stackrel{CH_3 - CH - CH_2Br}{\underset{CH_3}{\overset{P}{\longrightarrow}}}$   
C. CH<sub>3</sub>  $\stackrel{C}{\xrightarrow{-C}}$  - CH<sub>3</sub>  
D. Butyle bromide

E. Isobutyle bromide

#### № 18. In nature, methane acid found?

A. in potatoes and cereals
B. in ants
C. in the morning dew
D. Sunflower oil
E. in grapes
F. nettles, needles
G. A, E.

#### № 19. Specify the conditions for the nitration of alkanes:

A. crashed. HNO<sub>3</sub> B. conc. HNO<sub>3</sub>, hn, t °C C. nitrogen oxides, H<sub>2</sub>SO<sub>4</sub>, t °C D. crashed. HNO<sub>3</sub>, NO<sub>2</sub>, P E. HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>, t °C, P F. t °C, P G. crashed. HNO<sub>3</sub>, hn, t °C

## № 20. What particles are formed by nitration of alkanes in the gas phase?

- A. Anions
- B. Ions
- C. Radicals
- D. Cations
- E. molecular ions
- F. anions and cations
- G. Particles containing an unpaired electron

## № 21. Specify the reaction mechanism of nitration of alkanes:

- $A. S_{\rm E}$
- B. Sr
- C.  $S_N 1$
- $D. S_N 2$
- $E.\;A_N$
- F. radical
- G. ion

#### № 22. To monovalent residues include alkanes

- A. Methyl
- B. Propylene
- C. Ethyl
- D. Ethylene
- E. Ethyne
- F. Propyl

#### № 23. Which material does not react with methane?

- A. Chloro
- B. Iodine

- C. Bromine
- D. Fluorine
- E. Oxygen
- F. Nitrogen
- G. Argon

#### № 24. The reaction of haloalkanes with lithium metal called

- A. Butlerov Reaction
- B. Shorygin Reaction
- C. Grignard Reaction
- D. Markovnikov Reaction
- E. Zaitsev Reaction
- F. Organolithium synthesis
- G. A method of producing organolithium compounds

#### № 25. The reaction of haloalkanes with magnesium metal called

- A. Shorygin Reaction
- B. Grignard reaction
- C. Butlerov Reaction
- D. Markovnikov Reaction
- E. Zaitsev Reaction
- F. Organomagnesium synthesis
- G. A method for producing one organomagnesium

## № 26. The reaction of haloalkanes with metallic zinc is called

- A. Shorygin Reaction
- **B.** Zaitsev Reaction
- C. Butlerov Reaction
- D. Markovnikov Reaction
- E. Koch Reaction
- F. Organozinc synthesis
- G. A method for producing one organozinc compounds

## № 27. The reaction of haloalkanes with metallic sodium is called

- A. Shorygin Reaction
- B. Wurtz reaction
- C. Butlerov Reaction
- D. Markovnikov Reaction
- E. Koch Reaction
- F. Sodium organic synthesis
- G. A method for producing sodium organic compounds

# $N_{2}$ 28. Reacting secondary and tertiary haloalkanes with an alcoholic solution of sodium hydroxide is the reaction

- A. Wurtz
- B. Zaitseva
- C. Dumas

D. Lvov'sE. ButlerovaF. Preparation of alkenesG. Dehydrohalogenation

# № 30. Specify final product of following conversion:

 $CaO \xrightarrow{C} ? \xrightarrow{2H_2O} ? \xrightarrow{Br_2} ? \xrightarrow{Cl_2} ?$ 

A. There are no right answers. B. CHBrCl-CHBrCl C. CH<sub>2</sub>Br-CH<sub>2</sub>Cl D. CHBr<sub>2</sub>-CHCl<sub>2</sub> E. CH<sub>2</sub>=CH<sub>2</sub> F. CH<sub>2</sub>Br-CH<sub>2</sub>Br
#### INTRODUCTION TO THE ALKENES

Alkenes are is the simplest of the **unsaturated hydrocarbons**, hydrocarbons which will react with hydrogen. Alkenes contain one or more reactive **double bonds** between carbon atoms, and are easily indicated by the symbol =. Since a double bond requires two carbon atoms, the simplest alkene is  $C_2H_4$  or  $H_2C=CH_2$ , ethene. The presence of a double bond is indicated by the change of ending from **-ane** to **-ene**. An older form of the name, ethylene, is used in chemical industry. The general formula is  $C_nH_{2n}$ . All alkenes have at least one double bond.

Name	Chemical formula	Structures
Ethene (ethylene)	C <sub>2</sub> H <sub>4</sub>	H_C=C_H HH
Propene	C <sub>3</sub> H <sub>6</sub>	H H H H-C=C-C-H H
Butene	$C_4H_8$	H H H H-C-C-C=C-H H H H
Pentene	C5H10	H H H H H-C-C-C=C-C-H H H H H

Alkenes and Cycloalkanes have the same general formula,  $C_nH_{2n}$ . Therefore, the general formula does not identify the structure as an alkene nor cycloalkane. To further become problematic there are alkenes which contain more than one double bond. Those with two double bonds have the formula,  $C_nH_{2n-2}$ .

Cycloalkenes have the general formula  $C_nH_{2(n-m)}$ . The letter m represents the number of double bonds. Thus, cyclopropene has the formula  $C_3H_4$  while that of cyclobutene is  $C_4H_6$ . The properties of alkanes and alkenes are very similiar.

Organic compounds which have a more complex structure than simple alkanes are named as compounds which have been substituted. By substituted is meant replacement of a hydrogen by some other atom or group of atoms, or the insertion of a different type of chemical bond in the molecule. Each of the different types of carbon-carbon bonds is designated by a change in the ending of the name of the compound. For a carbon-carbon single bond, no ending change takes place because this is the normal structure of alkanes; the ending remains -ane. Replacement of a single bond with a double bond, which requires loss of a molecule of hydrogen, is indicated by changing the ending to -ene. Thus ethane, H<sub>3</sub>C-CH<sub>3</sub>, can be converted to ethene, H<sub>2</sub>C=CH<sub>2</sub>. Replacement of a single bond with a triple bond is less common. It is indicated by changing the ending to -yne. Thus ethane, H<sub>3</sub>C-CH<sub>3</sub>, can be converted to ethyne, HCCH, upon the loss of two molecules of hydrogen.

Substitution can occur in whichever direction gives a useful name. Thus the compound  $CH_3Cl$  can be named either as a methane which has had a chlorine substituted upon it (name: chloromethane) or as a chlorine which has had a methane substituted upon it (name: methyl chloride). Both forms are correct, and both directions of substitution may be used in naming organic compounds.

If and only if there is more than one possible location for the substitution, its location is specified by the number of the carbon at which the substitution takes place. This numbering is arbitrarily from one upwards. For simple compounds it begins at one end of the longest carbon chain, but for more complex or ring structures the numbering is not necessarily obvious. International standardizing groups establish an agreed appropriate numbering pattern for more complex structures. This agreed numbering is given in reference works such as the Ring Index.

## **Simple Substitution**

Simple substitution occurs when the substituent group replaces one hydrogen, or forms a single bond to the carbon chain (an equivalent statement). Some of the simple substituent groups and their effect on the name are shown in the following Table. The examples are all for methyl but any **alkyl** (alkyl = substituent alkane) compound is named in the analogous way; R denotes any alkyl group. Both directions of substitution can be used. The forms indicated by asterisks in the Table are less common forms.

Table 3

COMPOUNDS	NAMES		
RCL	Chloromethane	Methyl Chloride	
RBR	Bromomethane	Methyl Bromide	
RI	Iodomethane	Methyl Iodide	
ROH	Hydroxymethane	Methyl Alchohol (Methanol)	
RNH <sub>2</sub>	Aminomethane	Methyl Amine	

Simple Organic Substitution and Nomenclature

When two or more different substituents appear on the same chain, they are named in alphabetical order.

When two or more of the same substituent appear in the same chain, the number of substituents is indicated by a numerical prefix (di, tri, tetra, so on ...). For example, butene has one double bond while butadiene has two.

#### Test – Alkenes

№ 1. How is the name of this substituent CH <sub>2</sub> =CH-
A. Isopropyl
B. Vinyl
C. Ethyl
D. Propyl
E. Ethinyl
-

 $N\!\!\!_{2}$  2. Indicate a reaction in which hydrogen bromide HBr joins the double bond against Markovnikov's rule

A.  $CHF_2 - CH = CH_2 + HBr$ 

 $B. \ CH_3CH_2\text{-}CH = CH_2 + HBr$ 

C. CH<sub>3</sub>-CH=CH-CH<sub>3</sub> + HBr

D. CH<sub>3</sub>-CH=CH<sub>2</sub> + HBr

E. All reactions of unsaturated compounds are carried out by the Markovnikov's rule.

 $N_{2}$  3. Identify to which a carbon atom will be join hydrogen atom in the following reaction:

$$\begin{array}{c} 1 & 2 & 3 & 4 \\ \mathrm{CH}_2\text{-}\mathrm{CH}_2\text{-}\mathrm{CH}_3\text{-}\mathrm{CH}_3 + \mathrm{HBr} & \longrightarrow ? \\ & 5^{\mathrm{I}} \\ \mathrm{CH}_3 \end{array}$$

A. To the first

- B. To the fifth
- C. To the third
- D. To the fourth
- E. To the second

## № 4. Indicate qualitative reaction to alkenes

- A. hydrogenation reaction
- B. accession of HBr
- C. combustion reaction
- D. interaction with bromine water
- E. reaction with halogens at 500C

# $N_{2}$ 5. Name the the reaction product of propene with bromine in carbon tetrachloride solution:

- A. 1-bromo propane.
- B. 1,3-dibromo propane
- C. 1,2-dibromo propane
- D. 2-bromo propane
- E. 3-bromo propene

#### № 6. Name the compound according to the systematic nomenclature:

- A. 2,5,5-hexene, dimethyl-3
- B. 2,2,5-trimethyl hexane
- C. 1-isopropyl-2-t-butyl ethylene
- D. 2,5,5-trimethyl hexane
- E. 2,2,5-trimethyl-3-hexene

#### № 7. What alkene is preferably formed from 2-methyl-2-chlorobutane?

- A. 2-methyl butene -1
- B. butene-2
- C. 3- methy butene l-1
- D. 3-methyl butene -2
- E. 2-methyl butene -2

#### № 8. Indicate product of following reaction:

$$CH_3-C=CH_2 + HBr \longrightarrow ?$$

A. 
$$\downarrow_{Br}^{CH_2-CH_2-CH_2-CH_3}$$
  
B.  $CH_3 - C - CH_3$   
 $\downarrow_{CH_3}^{Br}$ 

$$E. \begin{array}{c} CH_3 & CH_3 \\ CH_3 - C-CH_2 - C-CH_3 \\ CH_3 - Br \end{array}$$

## № 9. Indicate product of following reaction:

$$\begin{array}{c} CH_{3}-C=CH-CH_{3}+H_{2}O \longrightarrow ?\\ CH_{3}\\ CH_{3}-CH_{1}-CH_{3}\\ CH_{3}-CH_{2}-CH_{3}\\ CH_{3}-CH_{3}-CH_{3}\\ CH_{3}-CH_{3}-CH_{3}-CH_{3}\\ CH_{3}-CH_{3}-CH_{3}\\ CH_{3}-CH_{3}-CH_{3}-CH_{3}\\ CH_{3}-CH_{3}-CH_{3}-CH_{3}\\ CH_{3}-CH_{3}-CH_{3}-CH_{3}\\ CH_{3}-CH_{3}-CH_{3}-CH_{3}\\ CH_{3}-CH_{3}-CH_{3}-CH_{3}-CH_{3}\\ CH_{3}-CH_{3}-CH_{3}-CH_{3}-CH_{3}-CH_{3}-CH_{3}-CH_{3}\\ CH_{3}-C$$

# $\mathcal{N}_{2}$ 10. What is the structure of the molecule, formed by complete hydrogenation of acetylene

A. LinearB. TetrahedralC. TrigonalD. FlatE. Cylindrical

## № 11. How many geometrical isomers has hexadiene-2,4?

A. 2 B. 9 C. 6 D. 8 E. 10

F. 4

 $\mathcal{N}\!\!\!\!\!\!\!\!\!$  12. Reaction's large speed of electrophilic addition of alkadienes 1.3 based

A. high activation energy by linking

B. presence of acid catalysts

C. to form an intermediate complex -s.

D. low activation energy by mating

E. base catalysis

F. A,C

#### № 13. The addition reaction of hydrogen chloride by reacting propylene is

A. radical addition

B. electrophilic addition

C. radical substitution

D. electrophilic substitution

E. nucleophilic substitution

F. is an addition reaction where, in a chemical compound, a  $\pi$  bond is broken and two new  $\sigma$  bonds are formed.

#### № 14. Call final product of following conversion:

$$CH_3I \xrightarrow{HI} A \xrightarrow{Cl_2} B \xrightarrow{2Na} C \xrightarrow{Pd} D$$

- A. Ethylene
- B. Ethane
- C. Acetylene
- D. Propane
- E. Propylene
- F. Ethene

#### № 15. Name the following compound according IUPAC nomenclature

CH<sub>3</sub>-CH-CH=CH-NO<sub>2</sub>

 $CH_3$ 

- A. 2-methyl-4-3 nitrobuten
- B. 1-nitro-2-methyl-2
- C. 3-methyl-1-nitrobuten-1

D. 3,3-dimethyl-1-nitropropene-1

E. 3-methyl-2-nitrobuten-1

F. Izopropilnitroetilen

G. 2-methyl-1-nitrobuten-1

## № 16. The reaction of conjugated dienes with alkenes called reaction A. Wurtz

- B. Diels-Alder
- C. Dumas
- D. Zaitseva
- E. Butlerova
- F. Diene synthesis
- G. Cyclization

#### № 17. By the diene synthesis reaction formed

- A. Unsaturated cyclic compound
- B. Alkynes
- C. Alkenes
- D. Alkanes
- E. Derivatives of cyclohexene
- F. Alcohols
- G. Six-membered ring

Multiple answers could be selected, for example - B, F, G

# № 18. The interaction of molecules of acetylene with each other in an aqueous solution of copper monochloride and ammonium chloride formed

- A. Acetone
- B. Vinyl acetylene
- C. Dimerization products Diacetylene
- D. Enin
- E. Allen
- F. Diacetylene
- G. Diene

## № 19. While irolize of methane is formed:

- A. Ethylene
- B. Acetylene
- C. Propylene
- D. Ethane
- E. Propane
- F. Ethyne
- G. C<sub>2</sub>H<sub>2</sub>

# $\mathcal{N}\!\!_{2}$ 20. When reacting acetylene with hydrogen chloride in the presence of mercuric salts formed

- A. Ethyl chloride
- B. Vinyl chloride
- C. 1,1-dihloetan
- D. 1,1,1-trichloroethane
- E. 1,2- dichloroetane
- F. Unsaturated chloride
- G.  $CH_2 = CH-Cl$

#### INTRODUCTION TO THE ALKYNES

**Alkynes** are hydrocarbons which contain a triple carbon-carbon bond. As with alkenes, the simplest member of the series is the twocarbon molecule. The triple bond is indicated by changing the ending of the name to -yne, in the same manner as the double bonds in alkenes are indicated by the ending -ene. Alkynes, like alkenes are unsaturated hydrocarbons with the general formula  $C_nH_{2n-2}$ . They are very unstable and quite reactive. For example, ethyne the simplest alkyne,

Structure of Ethyne, which is more commonly known by its common name **acetylene**, is a gas often used as a fuel for cutting and welding torches because it burns with a very hot flame.

The alkynes follow much the same pattern of reactivity and nomenclature as do the alkenes. However, the alkynes which have the triple bond at the end of the molecule often have the terminal hydrogen relatively acidic, while no other hydrogen on the alkyne or on the corresponding alkene is even slightly acidic. This acidity arises because the bonding electrons of the terminal hydrogen tend to associate themselves with the electrons in the triple bond, lending a considerable ionic character to the bond to hydrogen.

Alkynes Name	Chemical formula	Structures
Ethyne	$C_2H_2$	H-CEC-H
Propyne	$C_3H_4$	H H−C≡C−C−H H
Butyne	C <sub>4</sub> H <sub>6</sub>	H H H−C≡C−C−C−H H H
Pentyne	$C_5H_8$	CH₃

## **Halogens as Functional Groups**

If atoms other than carbon and hydrogen are substituted for part of a hydrocarbon molecule, the chemical reactivity of the hydrocarbon is generally increased. The nonhydrocarbon part of the molecule is called a **functional group**. Most of the chemical reactivity of the substituted hydrocarbon is due to the functional group attached to it.

One family of substituted hydrocarbon molecules has a halogen atom substituted for a hydrogen atom. For example, if we substitute a bromine atom for a hydrogen atom on methane, we obtain  $CH_3Br$ **Bromomethane** (methylbromide)

In subsequent discussions of compounds, we will represent any hydrocarbon radical by R- and any halogen atom by -X. The general formula for the halogen-substituted hydrocarbon compounds is R-X. As one might expect, it is possible to have more than one hydrogen atom replaced by a halogen atom. In the compound  $CCl_4$  — Tetrachloromethane (carbon tetrachloride), more commonly called carbon tetrachloride, four chlorine atoms are substituted for the four hydrogen atoms in a methane molecule. Trichloromethane (CHCl<sub>3</sub>), or chloroform, which is used extensively as a solvent and formerly was employed as an anesthetic, is another example of a multisubstituted hydrocarbon.

Organic halides are organic compounds in which one or more hydrogen atoms have been substituted by a halogen atom. The IUPAC name for halides is the same as branched chain hydrocarbons. The branch is named by shortening the halogen name to fluoro-, chloro-, bromo-, or iodo-. The halide(s) are treated as branched groups and are located on the continuous chain of carbons as you would locate and name any alkyl branch:

Fluorine	Fluoro-
Chlorine	Chloro-
Bromine	Bromo-
Iodine	Iodo-

Prefixes for the first four members of the halogen family.We number the carbon atoms to avoid any ambiguity in naming the compounds. Thus,

Test -Alkynes

№ 1. Name the the end product of the following reactions:

$$CH_3$$
- $CH_2$ - $CH=CH_2$   $\xrightarrow{Br_2}$  ?  $\xrightarrow{2KOH}_{ROH, t}$  ?

- A. Butene-2 B. Butyn-2
- C. Butene-1
- D. Butyn-1
- E. 1-Butanol

№ 2. Name the compound according to the systematic nomenclature:

$$\begin{array}{c} {}_{I}^{CH_{3}} \\ {}_{I}^{CH_{2}-CH-C} \equiv C\text{-}CH_{2}\text{-}CH_{3} \end{array}$$

A. 1-isopropyl-2-sec-butyl acetylene

B. 2,5-dimethyl-3-heptyn

C. 3,6-dimethyl-4 heptyn

D. 5-ethyl-2-methyl-5-ethyl

E. 3-hexyne2-methyl-3-hexyne

 $\mathcal{N}_{2}$  3. With the help of what he reagents can be carried following transformation:

$$CH_3$$
- $CBr_2$ - $CBr_3$   $\xrightarrow{?}$   $CH_3$ - $C\equiv CH_3$ 

A. zinc dust under heating.

B. alcoholic potassium hydroxide solution under heating

C. aqueous sodium hydroxide solution under heating.

- D. alcoholic potassium hydroxide solution at room temperature.
- E. Grignard reagent in absolute ether.

#### № 4. With the help of what reagents can be carried following transforma-

## tion: $CH_3$ -CHBr-CH<sub>2</sub>Br $\xrightarrow{?}$ CH<sub>3</sub>-C≡CH

A. zinc dust under heating.

B. Grignard reagent in absolute ether.

C. aqueous sodium hydroxide solution under heating.

D. alcoholic potassium hydroxide solution at room temperature.

E. alcoholic potassium hydroxide solution under heating

#### № 5. Call final product of following conversion:

 $HC \equiv CH \xrightarrow{NaNH_2} ? \xrightarrow{CH_3I} ? \xrightarrow{NaNH_2} ? \xrightarrow{C_2H_5Br} ?$ A. pentene-1 B. pentyn-2 C. pentene-2 D. pentyn-1 E. pentane

№ 6. Specify a compound that reacts with an ammoniacal solution of silver hydroxide:

A)  $CH_3-C\equiv C-CH_3$ B)  $C_2H_5-C\equiv C-C_2H_5$ C)  $CH_3-CH_2-C\equiv C-CH_3$ D)  $CH_3-CH_2-C\equiv CH$ A. A B. B C. C D. ABC E. D

 $N_{2}$  7. What main product formed when heating methylallene in the presence of the catalyst?

A) $CH_3$ -C $\equiv$ C-CH <sub>3</sub>	D) $CH_2 = C - CH - CH_3$
B) $HC \equiv C - C_2 H_5$	CH <sub>3</sub> -C-CH=CH <sub>2</sub>
C) CH <sub>2</sub> =C-CH-CH <sub>3</sub>	E) Polymer formation
CH <sub>2</sub> =C-CH-CH <sub>3</sub>	
A. A	
B. C	
C. B	
D. D	
E. E	
F. A, D	

# $N_{\rm e}$ 8. Locate all isomeric chlorobutanes in order of increasing their reactivity ability to reaction $S_{\rm N}2$ .

A. tert-butyl chloride, izobutilhlorid, n-butyl chloride, sec-butyl chloride. B. tert-butyl chloride, sec-butyl chloride, izobutilhlorid, n-butyl chloride

C. sec-butyl chloride, tert-butyl chloride, izobutilhlorid, n-butyl chloride.

D. tert-butyl chloride, izobutilhlorid, sec-butyl chloride, n-butyl chloride.

E. n-butyl chloride, izobutilhlorid, sec-butyl chloride, tert-butyl chloride. F. C, D.

# $N_{2}$ 9. Locate in order of increasing reactivity ability in reactions of the type $S_{N1}$ isomeric chlorophenylpropane

A. 1-chloro-3-phenylpropane, 2-chloro-2-phenylpropane, 1-chloro-1-phenylpropane.

B. 1-chloro-3-phenylpropane, 1-chloro-1-phenylpropane, 2-chloro-2-phenylpropane

C. 2-chloro-2-phenylpropane, 1-chloro-1-phenylpropane, 1-chloro-3-phenylpropane.

D. 1-chloro-1-phenylpropane, 1-chloro-3-phenylpropane, 2-chloro-2-phenylpropane.

E. 2-chloro-2-phenylpropane, 1-chloro-3-phenylpropane, 1-chloro-1-phenylpropane.

F. A, E.

## № 10. Which group of atoms is called homologous difference?

A. CH

- $B. \ CH_2$
- C. CH<sub>3</sub>
- D. CH<sub>4</sub>
- E. C<sub>2</sub>H

#### OXYGEN FUNCTIONAL GROUPS: ALCOHOLS

Alcohols are the most simple organic oxygen compounds which contain one or more hydroxyl groups (-OH groups). They are named systematically from the corresponding alkanes by changing the ending -ane to -ol. Thus methane gives rise to methanol, CH<sub>3</sub>OH, and ethane to ethanol, CH<sub>3</sub>CH<sub>2</sub>OH. The alcohol hydrogen is ionizable but only very weakly so. Alcohols can be oxidized but cannot generally be reduced. A common reaction of alcohols is their reaction with carboxylic acids to form esters, which are discussed in later sections. Alcohols are used industrially as solvents, cleaning agents, and disinfectants. Ethanol, often given the trivial name grain alcohol, is the alcohol found in alcoholic beverages; most other alcohols are highly toxic if ingested.

Alkanes	Alcohols
Methane (CH <sub>4</sub> )	Methanol (CH <sub>3</sub> OH)
Ethane $(C_2H_6)$	Ethanol (C <sub>2</sub> H <sub>5</sub> OH)
Propane (C <sub>3</sub> H <sub>8</sub> )	Propanol (C <sub>3</sub> H <sub>7</sub> OH)
Butane (C <sub>4</sub> H <sub>10</sub> )	Butanol (C <sub>4</sub> H <sub>9</sub> OH)
Pentane (C <sub>5</sub> H <sub>12</sub> )	Pentanol (C <sub>5</sub> H <sub>11</sub> OH)

#### Ethanol (Ethyl Alcohol)

Methanol (Methyl alcohol): Also known as wood alchohol it can be produced by the fermentation of wood products. Methanol (CH<sub>3</sub>OH) has a strong flavour. Partially due to its small molecular weight and size it is easily absorbed by the body and is a dangerous poison. Five to ten milliliters can cause damage to the optic nerves resulting in blindness. It is known to damage other organs such as the liver, kidneys and heart. The symptoms of a methanol poisoning are stomach cramps, headache, nausea, weakness, visual disturbances, breathing problems and unconsciousness. Methanol is highly flammable.

Ethanol (Ethyl alcohol): Ethanol is also referred to as grain alchohol and can be produced by the fermentation of sugar. Because of its somewhat large molecular weight and size it is not absorbed by the body to the extent as is methanol. However, it still effects the nervous system and other bodily function. By means of fermentation ethanol ( $C_2H_5OH$ ) and carbon dioxide ( $CO_2$ ) is produced. The product has a relatively low alcohol content approximating 18%. With distillation the concentration can approach 95%. If a second distillation is conducted with the inclusion of a water extraction substance it is possible to achieve near 100% ethanol. The boiling point of ethanol is 78.5° celsius. Besides its use in alcoholic beverages it is also used as a solvent for oils, resins and many other industrial processes.

Molecules having two or more alcohol groups are called polyfunctional alcohols or polyols. Polyols with two and only two alcohol groups are called diols although the older term glycols is still used. Industrially, HOCH<sub>2</sub>CH<sub>2</sub>OH is called ethylene glycol rather than ethanediol. One of the most biologically important alcohols is 1,2,3propanetriol, which is usually called glycerol or glycerin. Glycerol, HOCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH, forms the storage fats for plant and animal cells. The chemistry of polyols is significant both industrially and biochemically.

#### 1, 2, 3-Propanitriol (Glycerol or Glycerin)

The ending -triol identifies a triple alcohol while the numbers indicate on which carbon atoms the OH groups are located. The formula for 1,2,3-propanitriol is  $C_3H_5(OH)_3$ . This alcohol is produced from the alkene known as propene. Propene is an unsaturated hydrocarbon with the formula  $C_3H_6$ . Due to the presence of the hydroxyl groups glycerin dissolves in water very well. Glycerin tastes sweet, has high viscosity and is water soluable. High doses may lead to an intoxicated condition resulting in headache and kidney pain. It is used in plastics, antifreeze, ointments, ink, brake fluid and coloring substances. Nitroglycerin is produced by the nitration glycerin. The correct

name of nitroglycerin is glycerin trinitrate. It has the formula  $C_3H_5(NO_3)_3$ .

Phenol: With the replacement of a hydrogen atom on a benzene molecule with a hydroxyl group (OH group) phenol is produced. It has the chemical formula  $C_6H_5OH$  with a melting point of 43 degrees and a boiling point of 182 degrees.



Phenol (Methyl-1,3,5-cyclohexatriene)

#### Test-Oxygen Functional Groups: Alcohols

№1. Dimethylacetylene restored to olefin (Na / NH3), and then the product is oxidized by Wagner. What alcohol to get?

- A. 1, 2-butanediol
- B. 2, 3-butanediol
- C. 1, 3-butanediol.
- D. 3, 3-butanediol
- E. 2, 2-butanediol
- F. 1, 4 butanediol

## №2. Boiling point alcohols with increasing relative molecular mass

- A. naturally decrease
- B. naturally increase
- C. regularity are not observed
- D. the boiling point of all alcohols approximately equal
- E. changes with dramatically jumps
- F. all answers correct

#### № 3. Between alcohol molecules formed

- A. ionic bond
- B. intermolecular hydrogen bonds
- C. covalent bond
- D. polar covalent bond
- E. bridging bond
- F. polar bond

#### № 4. Qualitative reaction to primary alcohols is the reaction with

A. with anhydrous nickel chloride.

- B. with the anhydrous zinc chloride
- C. with the anhydrous cupric chloride
- D. with the anhydrous sodium chloride
- E. with the anhydrous magnesium chloride
- F. with the anhydrous ferrum chloride

# $N_{2}$ 5. In the projection formulas Haworth for D- sugars CH<sub>2</sub>OH-group depicted in the cycle

A. Below

- B. Above
- C. Laterally
- D. No difference
- E. Diagonally
- F. Parallel

#### № 6. In the interaction of methanol with isobutene formed

- A. Metilizobutilen
- B. Methyl isobutyl ether
- C. Isobutanol
- D. Butanol
- E. Methylbutyl ether
- F. 1-Methoxy-2-methylpropane

#### № 7. The interaction of ethanol with phosphorus pentachloride forms

- A. Chloroacetate
- B. Chloroethane
- C. acetic acid
- D. ethyl phosphate
- E. Ethylfosfin
- F. ethyl chloride

# № 8. Which of these reactions lead to the preparation of a secondary alcohol (after hydrolysis required):

A.  $LiAlH_4 + ketone$ 

- B. All reactions are correct
- C. 2-Butene + Hg(OAc)<sub>2</sub>, then NaBH<sub>4</sub>
- D. Butene +  $H_2O(H^+)$

#### № 9. The strongest acidic properties shows

A. (CH<sub>3</sub>)<sub>2</sub>C-OH B. CH<sub>3</sub>OH C. C<sub>2</sub>H<sub>5</sub>OH D. iso-C<sub>3</sub>H<sub>7</sub>OH E. CH<sub>3</sub>-CH (OH)-CH<sub>3</sub> F. A, C.

#### № 10. The interaction of ethanol with thionyl chloride forms

- A. Chloroacetate
- B. Chloroethane
- C. Ethanesulfonic
- D. Ethylsulphate
- E. Ethylmercaptan
- F. Ethylsulfonic

## № 11. The interaction of ethanol with the heated cupper oxide is formed

- A. acetic acid
- B. acetaldehyde
- C. cupper ethylate
- D. cupper acetate
- E. ethanal

# № 12. What is formed by heating the ethanol in the presence of concentrated sulfuric acid at 180 °C?

- A. Ethane
- B. Ethylsulphate
- C. Ethanesulfonic
- D. Diethyl
- E. Ethylene

## № 13. Specify the qualitative reaction to the polyhydric alcohols

A. Reacting of metallic sodium with hydrogen formation.

B. Interaction with a freshly prepared copper hydroxide (II) with formation of a solution with bright blue color

C. Burning of an oxygen in atmosphere with the formation of carbon dioxide and water.

D. All answers are correct

E. Reaction with Cu(OH)<sub>2</sub> – qualitative test for polyhydric alcohol

#### № 14. Ethylene glycol is formed by oxidation with potassium permanganate and:

- A. Ethylene
- B. Acetylene
- C. Benzene
- D. Butane
- E. Ethane

## № 15. Physical properties of ethylene glycol and glycerin

- A. colorless syrupy liquid
- B. moving liquid of light yellow color
- C. colorless gaseous substance, readily soluble in water
- D. resinous substance
- E. readily soluble in water, liquid sweetish taste

№ 16. What compound should be taken as the carbonyl component for condensing with 2-nitro ethanol as methylene component in the result of subsequent reactions to obtain 2-1,3-aminopropanediol

A. Methanol

- B. Methanol
- C. Ethanol
- D. Aminoethanol
- E. Formaldehyde
- F. benzaldehyde
- G. acetic acid

№ 17. What compound will form at catalytic dehydrogenation of the next OH

CH3-CH-CH-C6H5 CH3 ? alcohol CH3-C=CH-C6H5 A. Ċŀk B. CH3-CH-C-C6H5 ĊHŁ CH3-CH-CH-C6H5 C. ĆНр—р CH3-C-CH-C6H5 D. CH<sub>2</sub> CH3-CH-CH-C6H5 E. CH2-C6H4

F. phenyl izopropylketone

G. methylbenzylketon

#### INTRODUCTION TO CARBOXYLIC ACIDS

A **carboxylic acid** is an organic compound that contains a **carboxyl group** (-COOH). The general formula of a carboxylic acid is R–COOH, with R referring to the rest of the (possibly quite large) molecule. Carboxylic acids occur widely and include the amino acids (which make up proteins) and acetic acid (which is part of vinegar and occurs in metabolism).

O R-C-OH Carboxylic acid

Salts and esters of carboxylic acids are called carboxylates. When a carboxyl group is deprotonated, its conjugate base forms a carboxylate anion. Carboxylate ions are resonance-stabilized, and this increased stability makes carboxylic acids more acidic than alcohols. Carboxylic acids can be seen as reduced or alkylated forms of the Lewis acid carbon dioxide; under some circumstances they can be decarboxylated to yield carbon dioxide.

## Example of carboxylic acids and nomenclature

Carboxylic acids are commonly named as indicated in the table below. Although rarely used, IUPAC-recommended names also exist. For example, butyric acid ( $C_3H_7CO_2H$ ) is, according to IUPAC guidelines, also known as butanoic acid.

To more easily understand much of the below discussion of reactions involving carboxylic acids it can be helpful to notice that the carboxyl group itself is a «hydroxylated carbonyl group» meaning that two of the carbon atom's four bonds are to an oxygen atom, the carbon atom's third bond is to a second oxygen atom (whose other bond is to a hydrogen atom), and the carbon atom's fourth bond attaches to R. (A carbon atom double bonded to an oxygen atom is a carbonyl group and two of the carbon atom's bonds remain available for bonding. A hydrogen atom bonded to an oxygen atom is a hydroxyl group with the oxygen atom's second bond available for bonding.) The carboxylate anion R–COO<sup>-</sup> is usually named with the suffix -ate, so acetic acid, for example, becomes acetate ion. In IUPAC nomenclature, carboxylic acids have an -oic acid suffix (e.g., octadecanoic acid). For trivial names, the suffix is usually -ic acid (e.g., stearic acid).

Carboxylic acids are named systematically from their corresponding alkanes by changing the ending -**ane** to **-oic** acid. Methane thus gives rise to methanoic acid, HCOOH, which is more widely known by its trivial name formic acid, while ethane gives rise to ethanoic acid, which is much more commonly called acetic acid. Carboxylic acids have an easily ionizable acidic hydrogen.

Many carboxylic acids are known by both systematic and trivial names. Those of some of the simplest carboxylic acids are given in the Table below. Trivial names followed by an asterisk in the Table below are considered obsolete and their use is discouraged.

Table

#### Names of the Simplest Carboxylic Acids

Alkane	Compound	Systematic Name	Trivial (Common) Name
Methane (CH <sub>4</sub> )	HCOOH	Methanoic Acid	Formic Acid
Ethane (C <sub>2</sub> H <sub>6</sub> )	CH <sub>3</sub> COOH	Ethanoic Acid	Acetic Acid
Propane (C <sub>3</sub> H <sub>8</sub> )	C <sub>2</sub> H <sub>5</sub> COOH	Propanoic Acid	Propionic Acid*
Butane (C <sub>4</sub> H <sub>10</sub> )	C <sub>3</sub> H <sub>7</sub> COOH	Butanoic Acid	Butyric Acid*
Pentane (C <sub>5</sub> H <sub>12</sub> )	C4H9COOH	Pentanoic Acid	Valeric Acid*
Hexane (C <sub>6</sub> H <sub>14</sub> )	C5H11COOH	Hexanoic Acid	Caproic Acid*
Heptane (C7H16)	C <sub>6</sub> H <sub>13</sub> COOH	Heptanoic Acid	Enanthic Acid*

The -COOH group is characteristic of carboxylic acids and is called a carboxyl group. Below is the structural formula of ethanoic acid. These diagrams identify the location of the double bond.



Carboxylic acids containing long unbranched carbon chains are called **fatty acids**. Fatty acids are major components of the fats or lipids found in living organisms. Although over 70 different fatty acids are known, most have an even number of between 12 and 24 carbon atoms. Of these, the most common and most important have either 16 or 18 carbon atoms and may contain a few double bonds. Fatty acids are usually known by their trivial names, which are given in the Table below.

Table

Systematic Name	Trivial (Common) Name	Carbon Atoms
n-dodecanoic acid	Lauric Acid	12
n-tetradecanoic acid	Myristic Acid	14
n-hexadecanoic acid	Palmitic Acid	16
n-hexadecan-9-enoic acid	Palmitoleic Acid	16
n-octadecanoic acid	Stearic Acid	18
n-octadecan-9-enoic acid	Oleic Acid	18
n-octadecan-9,12-dienoic acid	Linoleic Acid	18
n-octadecan-9,12,15-trienoic acid	Linolenic Acid	18
n-eicosanoic acid	Arachidic Acid	20
n-eicosan-5,8,11,14-tetraenoic acid	Arachidonic Acid	20
n-tetracosanoic acid	Lignoceric Acid	22

#### Systematic and Trivial Names of Simple Fatty Acids

The organic acids with double acid groups or containing other substituents are usually known by their trivial names, which are given in the Table below.

Table

Compound	Systematic Name	Trivial (Common)
		Name
1	2	3
НООССООН	2-Ethanedioic Acid	Oxalic Acid
HOOCC <sub>2</sub> COOH	3-Propanedioic Acid	Malonic Acid
HOOC(CH <sub>2</sub> ) <sub>2</sub> COOH	4-Butanedioic Acid	Succinic Acid
HOOC(CH <sub>2</sub> ) <sub>3</sub> COOH	5-Pentanedioic Acid	Glutamic Acid
HOOC(CH <sub>2</sub> ) <sub>4</sub> COOH	6-Hexanedioic Acid	Adipic Acid
HOOCCH=CHCOOH	cis-butenedioic Acid	Maleic Acid
HOOCCH=CHCOOH	trans-butenedioic Acid	Fumaric Acid
HOOCCH(OH)CH(OH)COOH	2,3-Dihydroxybutanedioic	Tartaric Acid
	Acid	

#### Names of Other Selected Organic Acids

HOC(CH <sub>2</sub> COOH) <sub>2</sub> COOH	3-Hydroxy-3- carboxylpentanedioic Acid	Citric Acid
1	2	3
HOCH <sub>2</sub> CH <sub>2</sub> COOH	1-Hydroxypropanoic Acid	Lactic Acid
C <sub>6</sub> H <sub>5</sub> CH=CHCOOH	3-Benzyl-2-propanoic Acid	Cinnamic Acid
C <sub>6</sub> H <sub>5</sub> COOH	1-Carboxyl-1,3,5-	Benzoic Acid
	cyclohexatriene	
H <sub>3</sub> CCOCOOH	2-Ketopropanoic Acid	Pyruvic Acid

It is neither necessary nor practical to remember all of these trivial names, although practicing organic chemists remember many of them. Trivial names, these and others, are very widely used in both organic and biological chemistry.

The melting and boiling points are higher for carboxylic acids than the melting and boiling points of alkanes due to the polarity of the carboxyl group. As with alcohols short carboxylic acids dissolve in water, but long carboxylic acids do not dissolve well. When etanoic acid is dissolved in water the hydrogen atom of the carboxyl group becomes the cation  $H^+$  and  $H_3CCOO$  becomes an anion. Carboxylic acids (organic acids) are weaker than inorganic acids due to the the low degree of dissociation.

H<sub>3</sub>CCOOH + NaOH → H<sub>3</sub>CCOONa + H<sub>2</sub>O

When ethanoic acid (H<sub>3</sub>CCOOH) reacts with caustic soda (NaOH) sodium acetate (H<sub>3</sub>CCOONa) and water are produced. Sodium acetate is a salt of the ethanoic acid and can be used as a soap. Often salts of the carboxylic acids with long chains are used as soaps.

**Methanoic acid (Formic acid):** It smells very strong and is corrosive. The melting point is 8 degrees with a boiling point of 100 degrees. The name formic acid is comes from the Latin, formica which means ant. This acid was discovered by the distillation of ants. A bite of an ant can be painful due to the presence of this acid. It is the most simple and strongest carboxylic acid.

**Ethanoic acid (Acetic acid):** This acid also smells strong and is corrosive, but less so than methanoic acid. As shown above ethanoic acid is commonly called acetic acid. Vinegar (Fr. Vin, wine + Egar, sour) means sour wine. A 5% solution of ethanoic acid (acetic acid) and water is known as vinegar. The melting point of ethanoic acid is

16 degrees with a boiling point of 118 degrees. Ethanoic acid originates when ethanol (grain alcohol) is oxidized (reacts with oxygen).

> $CH_{3}CH_{2}OH + O_{2} \longrightarrow CH_{3}COOH + H_{2}O$ Ethanol + Oxygen  $\longrightarrow$  Ethanoic Acid + Water

Ethanoic acid often originates in wine by means of the above reaction causing the wine to become sour. Acetic acid in the form of vinega is used as a preserving agent and in the textile industry.

Mulitple cation carboxylic acids, hydroxycarboxylic acids, aromatic carboxylic acids, amino acids: There are carboxylic acids such as oxalic acid (COOH)<sub>2</sub> which have more than one carboxyl group. There are also hydroxycarboxylic acids which not only have a carboxyl group but also possess a hydroxy group.

Tartaric acid or dihydroxylbutanidioic acid has two carboxyl groups and two hydroxyyl groups. Citric acid and lactic acid are also hydroxycarboxylic acids. There are also acids produced from benzene known as aromatic acids.





#### **Glutamic Acid**

The simplest is benzoic acid. One of the hydrogen atoms from benzene is replaced by a carboxyl group. Benzoic acid has the formula  $C_6H_5COOH$ . Replacing the next hydrogen atom with a hydroxyl group produces salicylic acid. An ester (to be discussed later) of ethanoic acid and the hydroxyl group of salicylic acid produces acetylsalicylic acid or aspirin. Certain amino acids possess carboxyl groups, hydroxyl groups and benzene rings in addition to the ever present amino group (NH<sub>2</sub> group). The amino acids are important genetic components. Proteins are made up of approximately twenty amino acids. Glutamic acid, sodium glutamate and potassium glutamate (both salts of the glutamic acid) are used in the food industry.

## Reactions

The most widely practiced reactions convert carboxylic acids into esters, amides, carboxylate salts, acid chlorides, and alcohols. Carboxylic acids react with bases to form carboxylate salts, in which the hydrogen of the hydroxyl (–OH) group is replaced with a metal cation. Thus, acetic acid found in vinegar reacts withsodium bicarbonate (baking soda) to form sodium acetate, carbon dioxide, and water:

$$CH_3COOH + NaHCO_3 \rightarrow CH_3COO^-Na^+ + CO_2 + H_2O$$

Carboxylic acids also react with alcohols to give esters. This process is heavily used in the production of polyesters. Likewise, carboxylic acids are converted into amides, but this conversion typically does not occur by direct reaction of the carboxylic acid and the amine. Instead esters are typical precursors to amides. The conversion of amino acids into peptides is a major biochemical process that requires ATP. The hydroxyl group on carboxylic acids may be replaced with a chlorine atom using thionyl chloride to giveacyl chlorides. In nature, carboxylic acids are converted to thioesters. Carboxylic acid can be reduced to the alcohol by hydrogenation or using stoichiometric hydride reducing agents such as lithium aluminium hydride.



Carboxylic acid organic reactions

N,N-Dimethyl (chloromethylene) ammonium chloride  $(CIHC=N^+(CH_3)_2Cl^-)$  is a highly chemoselective agent for carboxylic acid reduction. It selectively activate the carboxylic acid and is known to tolerate active functionalities such as ketone as well as the moderate ester, olefin, nitrile, and halide moieties.

## **Classes of Carboxylic Acids**

#### Saturated aliphatic acids

Formic acid, HCOOH, is found not only in ants but also in the droplets on the tiny hairs of the stinging nettle plant (in the family Urticaceae), and the acidity of this compound causes the stinging sensation felt when these hairs are touched.



The New Zealand tree nettle (Urtica ferox), showing secretory ... G.R. Roberts, Nelson, New Zealand

Acetic acid, CH<sub>3</sub>COOH, has been known to humankind for thousands of years (at least in water solution). It is the compound that gives the sourness to vinegar and is produced by the bacterial oxidation of ethanol in wine. Household vinegar contains about five percent acetic acid. Acetic acid is important in the metabolic processes of humans and, indeed, of all animals and plants.





In these processes, the CH<sub>3</sub>CO (acetyl) group of the acetic acid molecule is attached to a large biochemical molecule called coenzyme A; the entire compound is known as acetyl coenzyme A. In the metabolism of food materials (the body's conversion of food to energy), the carbon atoms of carbohydrates, fats, and, to some degree, proteins are converted to acetyl groups that are bonded to coenzyme A to form acetyl coenzyme A. The acetyl groups of acetyl coenzyme A are then converted, by means of the tricarboxylic acid cycle and oxidative phosphorylation, to energy (in the form of adenosine triphosphate, or ATP) and carbon dioxide (CO<sub>2</sub>), which is exhaled. Not all the acetyl groups of acetyl coenzyme A of an organism is converted to energy. Some is used to synthesize fatty acids, terpenes, steroids, and other needed molecules. The carboxylic acids that occur in fats have an even number of carbon atoms because they are synthesized entirely from the two-carbon acetyl units of acetyl coenzyme A.

In animals, molecules of acetic acid (acetate) serve as precursors in the biosynthesis of steroid.

The even-numbered fatty acids from 4 to 10 carbon atoms are mostly found in milk fats. Butanoic (butyric) acid, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub> COOH, is an important component of cow's milk. Goat's milk is rich in fats containing the 6-, 8-, and 10-carbon acids: hexanoic (caproic), octanoic (caprylic), and decanoic (capric) acids, respectively. Common names for these three acids are derived from the Latin caper, meaning «goat». Some hard cheeses (e.g., Swiss cheese) contain natural propanoic acid. The higher even-numbered saturated acids, from  $C_{12}$  to  $C_{18}$  (lauric, myristic, palmitic, and stearic), are present in the fats and oils of many animals and plants, with palmitic and stearic acids being the most prevalent. Lauric acid  $(C_{12})$  is the main acid in coconut oil (45-50 percent) and palm kernel oil (45-55 percent). Nutmeg butter is rich in myristic acid ( $C_{14}$ ), which constitutes 60–75 percent of the fatty-acid content. Palmitic acid (C16) constitutes between 20 and 30 percent of most animal fats and is also an important constituent of most vegetable fats (35-45 percent of palm oil). Stearic acid  $(C_{18})$  is also present in most fats but usually in smaller amounts than palmitic. Cocoa butter is unusually rich in stearic acid (35 percent).

Even-numbered saturated fatty acids higher than  $C_{18}$  are much less common in fats but do occur in some waxes. Waxes obtained from animal and plant sources typically consist of carboxylic esters derived from long-chain acids and long-chain alcohols. For example, beeswax contains, among other components, the ester made from cerotic acid ( $C_{26}$ ) and the unbranched-chain alcohol containing 30 carbons, triacontanol. Odd-numbered fatty acids have been found only in trace amounts in natural compounds, but many have been produced synthetically in the laboratory.

## Unsaturated aliphatic acids

A number of acids important in organic chemistry contain carboncarbon double bonds.

There exist  $\alpha$ ,  $\beta$ -unsaturated acids, in which the double bond is between the second and third carbons of the chain, as well as unsaturated acids, in which the double bond occurs in other positions. Although many of these latter acids occur in nature, they are less easy to synthesize than  $\alpha$ ,  $\beta$ -unsaturated acids. Esters of acrylic acid (ethyl and butyl acrylate) and methacrylic acid (methyl methacrylate) are important monomers for the synthesis of polymers. Methyl methacrylate polymerizes to yield a strong transparent solid that is used as a plastic under such proprietary names as Plexiglas and Lucite. The trans isomer of crotonic acid is found in croton oil. The cis isomer does not occur in nature but has been synthesized in the laboratory. Angelic and tiglic acids are a pair of cis-trans isomers. Angelic acid is found as an ester in angelica root, whereas tiglic acid occurs in croton oil and in several other natural products.

Ricinoleic acid, an unsaturated hydroxy acid (i.e., one containing an -OH group), occurs in castor oil. When this acid is pyrolyzed (heated in the absence of air), it breaks down to give undecylenic acid and n-heptaldehyde.

The zinc salt of undecylenic acid is used to treat fungal infections of the skin, especially tinea pedis (athlete's foot). Esters of this acid are used in perfumery. Sorbic acid, CH<sub>3</sub>CH=CHCH=CHCOOH, which has two double bonds in conjugation (that is, two double bonds separated only by one single bond), and its potassium salt (potassium sorbate) are used as preservatives in many food products as well as in their packaging materials, since they inhibit the growth of molds and other fungi.

Many unsaturated acids occur in fats.

CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH=CH(CH<sub>2</sub>)<sub>7</sub>COOH palmitoleic acid (C<sub>16</sub>) CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>CH=CH(CH<sub>2</sub>)<sub>7</sub>COOH oleic acid (C<sub>18</sub>) CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>(CH=CHCH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>COOH linoleic acid (C<sub>18</sub>) CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>(CH=CHCH<sub>2</sub>)<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>COOH linolenic acid (C<sub>18</sub>) CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>(CH=CHCH<sub>2</sub>)<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>COOH arachidonic acid (C<sub>20</sub>)

These naturally occurring unsaturated fatty acids have certain characteristics. (1) If there are two or more carbon-carbon double bonds, each double bond is separated from the next by a  $CH_2$  (called methylene) group. (2) Virtually all double bonds in these and other naturally occurring unsaturated fatty acids have the cis configuration. (3) Linoleic and linolenic acids are needed by the human body, but the body cannot synthesize them. They must be obtained in the diet and, therefore, are called essential fatty acids. (4) Many unsaturated fatty acids are liquids at room temperature, in contrast to the saturated stearic ( $C_{18}$ ) and arachidic ( $C_{20}$ ) acids, which are solids. The reason is that the regular nature of the saturated hydrocarbon chains allows the molecules in the solid to stack in a close parallel arrangement, while the presence of cis double bonds in the unsaturated hydrocarbon chains breaks up this arrangement and forces the molecules to remain farther apart. Since the molecules in the unsaturated fatty acids are not as close to each other, less energy is needed to separate them, and a lower melting-point results. This situation is paralleled in the fats themselves, which are esters of these long-chain carboxylic acids where the alcohol component is glycerol, (HOCH<sub>2</sub>)<sub>2</sub>CHOH. Solid fats, obtained mostly from animal sources, have a high percentage of saturated fatty acids. Liquid fats (often called oils), obtained mainly from plant or fish sources, have a high percentage of unsaturated fatty acids. An exception is coconut oil, which, though obtained from a plant, has only a low percentage of unsaturated acids. The liquidity in this case is because of the high percentage of lauric acid (C12), which has a low molecular weight. Polyunsaturated fats may be defined as those containing an average of more than one double bond per fatty acid molecule.

Arachidonic acid is important because the human body uses it as a starting material in the synthesis of two kinds of essential substances, the prostaglandins and the leukotrienes, both of which are also unsaturated carboxylic acids. Examples are PGE<sub>2</sub> (a prostaglandin) and LTB<sub>4</sub> (a leukotriene). The symbol PG represents prostaglandin, E indicates the presence of a keto group on the five-membered ring, and the subscript  $_2$  indicates two double bonds. Similarly, LT represents leukotriene, B is one form, and the subscript 4 indicates four double bonds.



Prostaglandins and leukotrienes are made in small amounts, but they are significant because they act as hormone mediators. Some prostaglandins raise blood pressure, whereas others lower it.  $PGE_2$ induces labour in pregnant women and is used medicinally for this purpose, as well as for therapeutic abortions. The PGEs, along with several other PGs, suppress gastric ulceration and appear to heal peptic ulcers. The PGE<sub>1</sub> analog, misoprostol, is currently used to prevent ulceration associated with the use of nonsteroidal anti-inflammatory drugs (NSAIDs).

#### Tests - Carboxylic acid

# $N_2$ 1. What compound (X) is formed by Reformatsky reaction of acetone and ethyl bromoacetate:

CH<sub>3</sub>COCH<sub>3</sub> + BrCH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub>  $\xrightarrow{Zn, \text{ ether}}$  A  $\xrightarrow{H_2O, H^+}$  X

- A. Ethyl ester of 3-methylbutanoic acid.
- B. Ethyl ester 3-hydroxy-3-methylbutanoic acid
- C. 3-hydroxy butyric acid
- D. Ethy ester of  $\beta$ -hydroxybutyric acid
- E. Ethyl 3-hydroxy butyric acid
- F. Ethyl ester 3-hydroxy-3-methylbutanoate

#### No 2. What compounds are formed when heated $\alpha$ -hydroxy acids? A. Lactides

- B. Lactones
- C. Dihydric alcohols
- D. Cyclic ketones
- E. Cyclic diester of lactic acid

#### № 3. Specify the final product of the following transformations:

$$\begin{array}{ccc} CH_3 \text{-}C-Cl & \overset{KCN}{\longrightarrow} & ? & \overset{H_2O, H^{T}}{\longrightarrow} & ? \\ & & & \\ O \\ A. & Pyruvic acid \\ B. & Acetone \end{array}$$

C. Oxalic acid

D. Glycolic acid

E. Acetyl carboxylic acid

#### № 4. How to obtain acetoacetic ester from ethyl acetate?

- A. Claisen ester condensation
- B. Friedel-Crafts reaction
- C. Wurtz reaction
- D. Condensation of Kannitsaro
- E. The action of sodium

#### № 5. Specify the final product of the following transformations:

 $CH_{3}CHO \xrightarrow{HCN} \dots \xrightarrow{H_{2}O H^{+}} ?$ 

- A. hydroxy ethanoic acid
- B. a- hydroxypropanoic acid
- C. 2- methyl propenoic acid
- D. 2- hydroxypropanoic acid
- E. b- hydroxypropanoic acid

#### № 6. Specify the strongest acid

- A. Br-CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-COOH.
- B. CH<sub>3</sub>-CH<sub>2</sub>-CHBr-COOH
- C. CH<sub>3</sub>-CHBr-CH<sub>2</sub>-COOH
- D. CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-COOH
- E. CH<sub>3</sub>-CH<sub>2</sub>- COOH
- F. 2-bromobutanoic acid
- G. 1-bromobutanoic acid

#### № 7. What types of salts can form oxalic acid

- A. Cannot form salts
- B. Forms acidic and medium salts
- C. Forms only medium salts
- D. Forms only acidic salts
- E. Forms basic salts
- F. Complete and incomplete Oxalates

G. Forms medium and basic salts

# $\mathcal{N}\!\!\!\!$ 8. Under the action of concentrated sulfuric acid to oxalic acid will be produced

- A. Carbon oxide (II), water
- B. Carbon oxide (II), carbon oxide (IV), water
- C. Carbon oxide (IV), water
- D. Carbon and water
- E. Carbon, hydrogen, water
- F. Carbonic acid and carbon monoxide
- G. A, C.

#### № 9. What a monobasic carboxylic acid is the strongest?

- A. Acetic acid.
- B. Methane acid
- C. Propane acid
- D. 2-methylpropane acid
- E. They are all equal
- F. Formic acid
- G. A, C.

#### № 10. In the esterification reaction as the catalyst used

- A. Water.
- B. Sulfuric acid
- C. Palladium
- D. Nickel
- E. Bromine
- F. Hydrogen chloride
- G. Zinc

# № 11. To shift the equilibrium of the esterification reaction towards the formation of the ester must

- A. increasing catalyst concentration.
- B. to remove the water from the reaction
- C. to increase the temperature of the reaction.
- D. to reduce the concentration of catalyst.
- E. all the answers are correct.
- F. to remove the ester from the reaction
- G. A, C.

#### № 12. Specify the name of the historically methane acid:

- A. acetic acid.
- B. formic acid
- C. valeric acid.
- D. caproic acid.
- E. tartaric acid.

F. hydro carboxylic acid
 G. methane acid
 Вопрос с множественным выбором, средний, Ответ – В, F

# $\mathbb{N}_{2}$ 13. With the increase of the relative molecular weight carboxylic acids, the solubility in water

- A. Increases
- B. Decreases
- C. all carboxylic acids are readily soluble in water
- D. all carboxylic acids are poorly soluble in water
- E. is not observed regularities
- F. Worsens
- G. Increases and worsens

#### № 14. In nature, methane acid found?

- A. in potatoes and cereals
- B. in ants
- C. in the morning dew
- D. Sunflower oil
- E. in grapes
- F. nettles, needles
- G. A, E.

#### № 15. The salts of acetic acid are called

- A. Sulfates
- B. Acetates
- C. Carbonates
- D. Anhydrides
- E. Ethoxide
- F. Ethanoic acid salts
- G. Nitrates

## № 16. From which groups is a carboxyl group?

- A. carbonyl and amino groups
- B. of carbonyl and hydroxyl
- C. aldehyde and hydroxyl
- D. amino group and a hydroxyl
- E. aldehyde and amino.
- F. acetate group and hydrogen
- G. carbonil and amino

## № 17. What is the chemical reaction is not characteristic of carboxylic acids:

- A. interaction with metals.
- B. interaction with acidic oxides
- C. interaction with alcohols.
- D. interaction with amphoteric oxides and hydroxides.

- E. interaction with basic oxides.
- F. interaction with nitrogen
- G. A, C.

#### № 18. When fused sodium salt of isobutyric acid with soda lime produced

A. 
$$\begin{array}{c} CH_3 & CH_3 \\ I & I \\ CH_3-CH-CH_2-CH_2-CH_2-CH-CH_3 \end{array}$$

- B. CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>3</sub>
- C. CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>

- CH<sub>3</sub>-CH-CH<sub>3</sub>
- F. Dimetilmetan
- G. Dimetiletan

#### № 19. Which of the following compounds are C-H acids:

## a) b-diketones, b) a malonic ester, c) acetoacetic ester, d) nitroalkanes?

- A. a, d
- B. a, b, c, d
- C. a, b, d
- D. b,c, d
- E. a, c, d
- F. All
- G. d, c, a.

## № 20. When reacting 3-nitro-butanoic acid with thionyl chloride SOCl<sub>2</sub> formed

- A. chloranhydride 3-nitrobutanoic acid
- B. chloranhydride 3-chlorbutanoic acid
- C. 3-nitro-2- chlorbutanoic acid
- D. chloranhydride 3- nitro -2- chlorbutanoic acid
- E. β- nitrobutanoic acid chloranhydride
- F. β- nitro butyric acid chloranhydride

## № 21. Arrange the compounds in order of their acidic properties:

a) CH<sub>3</sub>-CH<sub>2</sub>-COOH; b) CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>OH; c)H<sub>2</sub>O; d)CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-SH; f) CH<sub>3</sub>-CΞCH

- A. a>c>b>d>f
- B. a>d>c>b>f
- C. a>b>c>d>f
- D. a>f>b>c>d
- E. The strongest propionic

F. The weakest metilatsetiln

#### № 22. What caused the increased acidity of hydroxy acids?

- A. isomesomeric effect of the carboxyl group
- B. negative inductive effect of the OH group
- C. positive inductive effect of OH groups
- D. The presence of a hydroxyl group
- E. lesser strength OH bond in a carboxyl group

# № 23. What type of isomerism is possible for malic acid HOOC-CH (OH) - CH<sub>2</sub>-COOH?

- A. optical isomerism
- B. positional isomers of multiple bonds
- C. structural isomers
- D. chiral
- E. associated with an asymmetric carbon atom

# $N_{2}$ 24. Which compound is produced in the dehydration of 2-hydroxy-propanoic acid?

- A. propanoic acid
- B. propenoic acid
- C. Acetaldehyde
- D. vinylcarboxylic acid
- E. etilenkarbonic acid

#### № 25. Enter the product following reaction:

?

HO-CH<sub>2</sub>-C
$$\equiv$$
N  $\xrightarrow{\text{H}_2\text{O}, \text{H}^+}$ 

A. HO-CH<sub>2</sub>-COOH

- B. H<sub>2</sub>N-CH<sub>2</sub>-CONH<sub>2</sub>
- C. H<sub>2</sub>N-CH<sub>2</sub>-CH=N-OH
- D. hydroxyacetic acid
- E. carboxymetanol

#### № 26. Specify the final product the following transformations:

$$CH_{3} - CH-COOH \xrightarrow{NaOH} ? \xrightarrow{(CH_{3}CO)_{2}OH^{+}} ?$$

$$A. \xrightarrow{CH_{3}-CH-COONa}_{OCOCH_{3}}$$

$$B. \xrightarrow{CH_{3}-CH-CO-O-CO-CH_{3}}_{ONa}$$
- D. 2-acetoxypropionic acid
- E. The ester of lactic acid and acetic acid

#### № 27. In chemical reactions acetoacetic ester usually takes part

- A. and keto and enol forms
- B. only the enol form
- C. only the E, E configuration enol forms
- D. all forms
- E. for acetoacetic ester characterized by the reaction of the enol and keto forms

#### № 28. The interaction of acrylic acid with a hydrogen chloride formed

- A. 2-chloropropionic acid.
- B. 3-chloropropionic acid
- C. Acid chloride of acrylic acid
- D. Ethylene
- E. Acetylene
- F.  $\beta$ -chloropropionic acid
- G. Chloromethyl acetic acid

## $\mathcal{N}_{2}$ 29. Reacting the carboxylic acid with chlorine in the presence of phosphorus called

A. Tabor

- B. Gel-Folgarda-Zelinsky
- C. Zaitseva
- D. Lviv
- E. Butlerov
- F. Tishchenko

## $N_{2}$ 30. When reacting the carboxylic acid with phosphoric anhydride formed

- A. Complex esters
- B. Carboxylic anhydrides
- C. Carboxylic acid chlorides
- D. Carboxamides
- E. Nitriles of carboxylic acids
- F. Hydroxamic acid

#### № 31. Upon heating carboxylic acid amides with phosphorus pentoxide for-

#### med

- A. Hydroxamic acid
- B. Nitriles of carboxylic acids
- C. Complex esters
- D. Carboxylic anhydrides

- E. Carboxylic acid chlorides
- F. Carboxamides

### № 32. Isomers fumaric acid is

A. racemic acid B. oleic acid C. malonic acid D. succinic acid E. oxalic acid F. Carboxylic acid

## $N_{2}$ 33. What is the acid formed by the action of sodium acetate on CH<sub>3</sub>COONa sulfuric acid?

- A. Methane. B. Ethanoic
- C. Propanoic.
- D. Coal.
- E. Monofilament.
- F. Acetic
- G. Formic

### № 34. Specify the final product the following transformations:

CH<sub>3</sub>-CH(Br)-COOH  $\xrightarrow{H_2O, t}$  ..... NaOH ? A. CH<sub>3</sub>-CH(OH)-COONa B. CH<sub>3</sub>-CH(ONa)-COOH C. CH<sub>3</sub>-CH(ONa)-COONa D. 2 oksipropionat sodium E. The sodium salt of  $\beta$ -hydroxypropionic acid

# $\mathbb{N}_{2}$ 35. In a pyruvic acid compound is converted by heating with dilute sulfuric acid?

- A. Propanoic acid
- B. Ethanal
- C. Acetate
- D. Acetaldehyde
- E. CH<sub>3</sub>-CHO

## 

A. Acetic acidB. EthanolC. AcetateD. Ethanoic acidE. CH<sub>3</sub>COOH

№ 37. With what reagent pyruvic acid reacts by the ketone group:
A. NaHCO<sub>3</sub> (H<sub>2</sub>O)
B. C<sub>6</sub>H<sub>5</sub>NHNH<sub>2</sub>
C. C<sub>6</sub>H<sub>5</sub>ON (H +, t)
D. hydrazine
E. hydroxylamine

## $N_{2}$ 38. The electrolysis of aqueous solutions of sodium salts of carboxylic acids called reaction of:

- A. Wurtz
- B. Kolbe
- C. Dumas
- D. Zaitseva
- E. Butlerova
- F. A method for producing alkanes
- G. under the influence of electricity Decarboxylation

## № 39. The decomposition of sodium salts of carboxylic acids in the presence of sodium hydroxide by heating the reaction called

- A. Wurtz
- B. Dumas
- C. Kolbe
- D. Zaitsev
- E. Butlerov
- F. A method for producing alkanes
- G. Pyrolysis

#### INTRODUCTION TO ALDEHYDES

The common names of aldehydes are derived from the names of the corresponding carboxylic acids.



The systematic names for aldehydes are obtained by adding -al to the name of the parent alkane.



The presence of substituents is indicated by numbering the parent alkane chain from the end of the molecule that carries the - CHO functional group. For example,

Another method of arriving at the same systematic way of naming aldehydes is from the corresponding alkanes, by changing the ending -ane to -al or to the longer form -yl aldehyde. Methane thus gives rise to methanal, CH<sub>2</sub>O, which is more widely known by its trivial name formaldehyde, while ethane gives rise to ethanal, CH<sub>3</sub>CH<sub>2</sub>O, which is more widely known by its trivial name acetaldehyde. The remaining aldehydes are generally named systematically although some older forms still prevail; propanal is sometimes still referred to as propionaldehyde. Aldehydes can be reduced to alcohols or oxidized to carboxylic acids. The parent chain is the longest chain that includes the aldehyde group. It's name is made by replacing the ending -e of parent alkane name with -al. The numbering of the chain always starts with the carbon of the aldehyde group being 1. For example:

			CH <sub>3</sub>
Н	CH <sub>3</sub>	<b>CH<sub>2</sub>-C</b> H <sub>3</sub>	С <b>Н-С</b> Н3
C=O	C=O	C=O	C=O
H	H	Н	H
Methanal	Ethanal	Propanal	2-Methylpropanal

In all cases the aldehyde function has a higher status than either an alcohol, alkene or ketone and provides the nomenclature suffix. The other functional groups are treated as substituents. In other words, the -al ending takes precedence over -ol, -ene, or -one. In those events when the -CHO functional group is not part of the parent chain it is generally referred to as an aldo functional group.

## **Oxidation of Aldehydes**

Aldehydes are the most easily oxidized of all organic compounds, though ketones resist oxidation strongly. They can also be slowly oxidized by oxygen in the air. In this example, potassium dichromate, together with hydrogen sulfate (sulfuric acid), easily oxidizes ethanal to ethanoic acid, chromium sulfate, potassium sulfate and water.

# $3CH_3CHO + K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow 3CH_3COOH + Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O$

The addition of hydrogen across a C=O double bond raises several important points. First, and perhaps foremost, it shows the connection between the chemistry of primary alcohols and aldehydes. But it also helps us understand the origin of the term aldehyde. If a reduction reaction in which H<sub>2</sub> is added across a double bond is an example of a hydrogenation reaction, then an oxidation reaction in which an H<sub>2</sub> molecule is removed to form a double bond might be called dehydrogenation. Thus, using the symbol [O] to represent an oxidizing agent, we see that the product of the oxidation of a primary alcohol is literally an «al-dehyd» or **aldehyde.** It is an alcohol that has been dehydrogenated.

The choice of oxidizing agents to convert a primary alcohol to an aldehyde is much more limited. Most reagents that can oxidize the alcohol to an aldehyde carry the reaction one step further — they oxidize the aldehyde to the corresponding carboxylic acid.

$$CH_3CH_2OH \xrightarrow{H_2CrO_4} \begin{bmatrix} O \\ CH_3CH \end{bmatrix} \xrightarrow{O} CH_3COH$$

A weaker oxidizing agent, which is just strong enough to prepare the aldehyde from the primary alcohol, can be obtained by dissolving the complex that forms between  $CrO_3$  and pyridine,  $C_6H_5N$ , in a solvent such as dichloromethane that doesn't contain any water.

$$CH_3CH_2OH \xrightarrow{CrO_3/pyridine}{CH_2Cl_2} CH_3CH$$

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Another method of arriving at the same systematic way of naming aldehydes is from the corresponding alkanes, by changing the ending -ane to -al or to the longer form -yl aldehyde. Methane thus gives rise to methanal, CH<sub>2</sub>O, which is more widely known by its trivial name formaldehyde, while ethane gives rise to ethanal, CH<sub>3</sub>CH<sub>2</sub>O, which is more widely known by its trivial name acetaldehyde. The remaining aldehydes are generally named systematically although some older forms still prevail; propanal is sometimes still referred to as propionaldehyde. Aldehydes can be reduced to alcohols or oxidized to carboxylic acids. The parent chain is the longest chain that includes the aldehyde group. Its name is made by replacing the ending -e of parent alkane name with -al. The numbering of the chain always starts with the carbon of the aldehyde group being 1. For example:

			CH <sub>3</sub>
Н	$\mathbf{CH}_3$	CH <sub>3</sub> -CH <sub>2</sub>	С <b>Н</b> 3-СН
C=O	C=O	C=O	C=O
Н	Н	Н	Н
Methanal	Ethanal	Propanal	2-Methylpropanal

In all cases the aldehyde function has a higher status than either an alcohol, alkene or ketone and provides the nomenclature suffix. The other functional groups are treated as substituents. In other words, the -al ending takes precedence over -ol, -ene, or -one. In those events when the -CHO functional group is not part of the parent chain it is generally referred to as an aldo functional group.



Test - Introduction to Aldehydes, Oxidation of Aldehydes

 $\label{eq:hyperbolic} \begin{array}{l} \textbf{N}\underline{\bullet} \mbox{ 1. Specify a reaction as a result acetaldehyde is formed} \\ A. CH_3-C^oCH + H_2O (Hg^{2+},H^+) \\ B. CH^oCH + H_2O(Hg^{2+},H^+) \\ C. CH_3-CH=CH-CH_3 + H_2O (H^+) \\ D. CH_3-CH_2-Cl + H_2O(OH^-) \\ E. CH_4 + O_2 \end{array}$ 

 $N_{2}$  2. Aldehydes, which cannot react with itself in the aldol-crotonic condensation:

CH3-CH=O

A. a, b, c. B. a, e, f C. c, d, e. D. e, c, f. E. a, d, f. F. a, b, d.





 $N_{2}$  4. Which compound is formed in the result of aldol condensation of a mixture of the following substances?

$$C_{6}H_{5}C=O + CH_{3}C=O \xrightarrow{OH} ?$$

$$A. \xrightarrow{CH_{3}CC_{6}H_{4}C=O}_{OH} A. \xrightarrow{CH_{3}CC_{6}H_{4}C=O}_{OH} A. \xrightarrow{CG_{4}S_{C}CH_{2}CH=O}_{OH} A. \xrightarrow{C_{6}G_{5}CHCH_{2}CH=O}_{OH} A. \xrightarrow{C_{6}G_{5}CCH_{2}CH_{2}OH}_{OH} A. \xrightarrow{C_{6}G_{5}CH-C+C+D}_{OH} A. \xrightarrow{C_{6}G_{5}CH-C+C+D}_{OH} A. \xrightarrow{C_{6}G_{5}CH-C+C+D}_{OH} A. \xrightarrow{C_{6}G_{5}CH-C+C+D}_{OH} A. \xrightarrow{C_{6}G_{5}CH-C+D}_{OH} A. \xrightarrow{C_{6}G_$$

№ 5. Determine the carbonyl compound which is methylene component of aldol-crotonic condensation in the next pairs:

 $N_{2}$  6. Which compound is formed by treatment with a mixture of ethanol and sodium metal next aldehyde?

 $C_6H_5\text{-}CH_2\text{-}CH=CH\text{-}CH_2\text{-}HC=O?$ 

- A. C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-HC=O.
- B. C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-CH=CH-CH<sub>2</sub>-CH<sub>2</sub>OH
- C. C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>OH.
- D. C<sub>6</sub>H<sub>11</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>OH.
- E.  $C_6H_{11}$ -CH<sub>2</sub>-CH=CH-CH<sub>2</sub>-CH<sub>2</sub>OH.
- F. A, E.

#### № 7. Formaldehyde polymer called

- A. Paraldehyde.
- B. Paraformaldehyde
- C. Uniforms
- D. Formalin
- E. Methenamine
- F. Aniline

#### № 8. Polymer acetaldehyde called

- A. Paraformaldehyde
- B. Paraldehyde
- C. Uniforms
- D. Formalin
- E. Methenamine

### F. Aniline

#### № 9. When reacting acetaldehyde with phosphorus pentachloride forms

- A. Chloroethane
- B. 1, 1-dichloroethane
- C. 1, 2-dichloroethane
- D. 1, 1, 2-trichloroethan
- E. 1, 1, 2, 2-tetrachloroethane
- F. 1, 2, 2-dichloroethane

### $\underline{\texttt{N}}\underline{\texttt{9}}$ 10. When condensation of acetaldehyde in the presence of a base formed

- A. Crotonaldehyde
- B. Aldol
- C. Krotol
- D. Polymer
- E. Ethanol
- F. Methanol

## № 11. Condensation of carbonyl compounds with formaldehyde, and salts of secondary amines by reaction called

- A. Dieckmann
- B. Mannich
- C. Michael
- D. Ester condensation
- E. Aldol-crotonic condensation
- F. Tishchenko

### № 12. The reaction product of formaldehyde with ammonia called

- A. Paraformaldehyde
- B. Urotropin
- C. Formalin
- D. Paraldehyde
- E. Methenamin

### № 13. Oxygen atoms in the molecules of aldehydes has

- A. Positive charge
- B. Partial negative charge
- C. Partial positive charge
- D. This gives the oxygen partial positive charge and the carbon a partial negative charge.

E. This gives the oxygen partial negative charge and the carbon a partial positive charge.

### $\underline{\texttt{Ne}}$ 14. In the interaction of hydrazine with an excess of acetaldehyde formed

- A. Hyrdazones
- B. Azines
- C. Acetals

D. Azides,  $N^-=N^+=N^-$ E. RR'C=N-N=CRR' type compound

№ 15. Which of the carbonyl compounds are reacted in the reaction of Cannizzaro under the action of an alkali:

 $\begin{array}{cccc} CH_{3}C=O & C_{6}H_{5}\text{-}C=O & CH_{3}C=O \\ A) & \overset{H}{H} & B) & H_{2}C=O & C) & H & D) & \overset{C}{C}H_{3} & E) & CH_{3}\text{-}CH_{2}CH=O \\ A. & B, C & \\ B. & D, E & \\ C. & B, D & \\ D. & A, B & \\ E. & A, D, E & incorrect answers \end{array}$ 

#### № 16. Specify the final product of the following transformations:

$$CH_{3}CHO \xrightarrow{HCN} \xrightarrow{HCN} \dots \xrightarrow{H_{2}O, H^{+}} ?$$

- A. hydroxy ethanoic acid
- B. a- hydroxypropanoic acid
- C. 2- methyl propenoic acid
- D. 2- hydroxypropanoic acid
- E. b- hydroxypropanoic acid

#### № 17. Specify the qualitative reaction to aldehydes:

- A. Silver mirror reaction
- B. Catalyst hydration with the formation of primary alcohols
- C. Obtaining of hexamine (urotropine) from methanol
- D. Aldol-crotonic condensation.
- E. Oxidation withcopper hydroxide

## $N_{2}$ 18. What substances derived from formic aldehyde by Cannizzaro reaction?

- A. isomeric glycols
- B. methanol and formic acid
- C. formic acid salt
- D. oligomers paraformaldehyde
- E. there is no right answer
- F. methane acid and carbinol
- G. methane and propane acid

## № 19. Specify the conditions and reagents for the preparation of aldehydes by means of a Grignard reagent

- A. high temperatures
- B. Derivatives of formic acid
- C. Low temperature
- D. Alkaline condition
- E. Derivatives of methane acid

#### INTRODUCTION TO KETONES

Ketones are organic compounds which incorporate a **carbonyl functional group**, C=O. The carbon atom of this group has two remaining bonds that may be occupied by hydrogen or alkyl substituents. If at least one of these substituents is hydrogen, the compound is an **aldehyde**. If neither is hydrogen, the compound is a **ketone**. The general formula for ketones is  $R_2C=O$  where the R- group represents any alkyl. Examples:

 $\begin{array}{ccc} CH_{3}\text{-} & CH_3CH_{2}\text{-} & CH_3CH_2CH_{2}\text{-} & CH_3CH_2CH_2CH_2\text{-} \\ Methyl & Ethyl & Propyl & Butyl \end{array}$ 

The ketones can be named systematically from the corresponding alkanes by changing the ending of each alkane to  $-\mathbf{yl}$  followed by the word ketone after both alkyl groups are named, as in the form methyl ethyl ketone for CH<sub>3</sub>COCH<sub>2</sub>CH<sub>3</sub>.

The common name for a ketone may be listed by molecular weight. Methyl is chosen first because it has a lower molecular weight than ethyl.

Methyl ethyl ketone

The common name may also be listed in alphabetical order  $\bigcirc_{\parallel}$ 

 $CH_3 \ddot{C}CH_2CH_3$  Ethyl methyl ketone with respect to the two alkyl groups on the C=O double bond.

If both of the alkyl groups are the same the numerical prefix di- is used, as in the case of dimethylketone. Dimethyl ketone is more commonly known by the trivial name acetone, and finds significant use as a solvent.

CH <sub>3</sub>	CH <sub>3</sub>	$CH_2CH_3$	CH <sub>3</sub>	$CH_2CH_3$
C=O	 C=O		 C=O	C=O
	I	C=O	I	
$CH_3$	$CH_2CH_3$	CH <sub>2</sub> CH <sub>3</sub>	$CH_2CH_2CH_3$	$CH_2CH_2CH_3$
Dimethyl	Methyl Ethyl	Diethyl Ketone	Methyl Propyl	Ethyl Propyl
Ketone	Ketone	Dietity: Retolic	Ketone	Ketone

For all except the simplest ketones, this form is not used and the ketone group is indicated systematically by use of the IUPAC system of nomenclature which assigns the suffix **-one** to ketones. Further, the parent chain includes the carbonyl group and is numbered so that the carbonyl location is the lowest number. The number of the location must be part of the name whenever there would be an uncertainty.

Dimethyl ketone would be named 2-propanone, while methyl ethyl ketone would be named as a substituted butane, 2-butanone. However, in the case of both 2-propanone and 2-butanone the number is not necessary since these ketones cannot be arranged in any other order – There is no uncertainty.

CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>
	l j				CH <sub>3</sub> CH
C=O	C=O	C=O	C=O	C=O	с=0
1	I			1	C=O
$CH_3$	$CH_2CH_3$	$CH_2CH_2CH_3$	$CH_2CH_3$	$CH_2CH_2CH_3$	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
Propanone	Butanone	2-Pentanone	3-Pentanone	3-Hexanone	2-Methyl-3-
					Hexanone

Notice: Propanone, Dimethyl Ketone and Acetone are Identical

A ketone carbonyl function may be located anywhere within a chain or ring, and its position is given by a locator number. Chain numbering normally starts from the end nearest the carbonyl group. In cyclic ketones the carbonyl group is assigned position  $N_{2}1$ , and this number is not cited in the name, unless more than one carbonyl group is present.

When the suffix form cannot be used, perhaps because another suffix such as that of a carboxylic acid is required, the alternative designation -keto can be used for the ketone group. An example is 2ketopropanoic acid.

A variety of oxidizing agents can be used to transform a secondary alcohol to a ketone. A common reagent for this reaction is some form of chromium (VI) — chromium in the +6 oxidation state — in acidic solution. This reagent can be prepared by adding a salt of the chromate ( $CrO_4^{2-}$ ) or dichromate ( $Cr_2O_7^{2-}$ ) ions to sulfuric acid. Or it can be made by adding chromium trioxide ( $CrO_3$ ) to sulfuric acid. Regardless of how it is prepared, the oxidizing agent in these reactions is chromic acid, H<sub>2</sub>CrO<sub>4</sub>.



 $N\!\!_{2}$  1. When condensation of ethyl acetate with acetone in the presence of sodium ethylate formed

- A. acetoacetic ester
- B. Acetylacetone
- C. sodium acetate
- D. acetic acid
- E. acetic anhydride

№ 2. What product is formed by cleavage of ketones –ketopentanoic acid? CH<sub>3</sub>CH<sub>2</sub>CCH<sub>2</sub>COOH

\_ || O

A. Propanol

- B. Butanol
- C. Butana
- D. Ethanal
- E. Propanal
- F. Butyl alcohol

#### № 3. Call final product of following conversion:



- B. methyl ethyl ketone

- C. 2-butenol-2
- D. 1,2-butanediol
- E. Butanone

## $N_{2}$ 4. From which carbonyl compounds formed 4-hydroxygeptanone-2 under aldol condensation?

- A. Propionaldehyde
- B. Acethone
- C. Acetaldehyde
- D. Formaldehyde
- E. Formic aldehyde
- F. Dimethylketone
- G. Acetylene

## № 5. Specify the compound that forms by next reaction

$$C_{6}H_{5}-CH_{2}C \equiv CH \xrightarrow{H_{2}O(H^{+})} ?$$
A. C6H5-CH2CH=O  
B. 
$$C_{6}H_{5}-CH_{2}C-CH_{3}$$
C. C6H5CH2CH=CH-OH  
D. 
$$C_{6}H_{5}CH_{2}C=CH_{2}$$
CH  
E. 
$$C_{6}H_{5}-CH_{2}-CH-CH_{2}$$

- F. methylbenzylketone
- G. phenyl izopropylketone

## № 6. What compound will form by next reaction?

$$C_{6}H_{5}-C=O + CH_{3}MgBr \longrightarrow ?$$

$$C_{6}H_{5}-C=O$$

$$H$$

$$B. \qquad \begin{array}{c} C_{6}H_{5}-C=O\\ H\\ O\end{array}$$

$$C. \qquad \begin{array}{c} C_{6}H_{5}-C-CH_{3}\\ O\\ O\end{array}$$

$$C. \qquad \begin{array}{c} C_{6}H_{5}-C-OMgBr\\ O\\ O\end{array}$$

D. 
$$C_6H_5$$
-CH<sub>2</sub>-C-CH<sub>3</sub>  
 $O$   
E.  $C_6H_5$ -CH<sub>2</sub>-OMgBr

- F. methylphenylketone
- G. phenyl izopropylketone

#### № 7. How is the next process?

- A. keto-enol tautomerism
- B. imine-enamine tautomerism
- C. isomerization of b-ketoesters
- D. mutual transition enol and keto forms
- E. equilibrium of ketone and enol forms

## № 8. Specify the mechanism of the oxidation reaction a- keto acids:

D. Decarboxylation mechanism

E. The mechanism of oxidation with the release of carbon dioxide

### № 9. Specify the final product the following transformations

$$\begin{array}{c} \text{CH}_{3}\text{-}\text{C}\text{-}\text{CH}_{2}\text{-}\text{C}\text{-}\text{OC}_{2}\text{H}_{5} \xrightarrow{\text{C}_{2}\text{H}_{5}\text{ONa}} ? \xrightarrow{\text{C}_{2}\text{H}_{5}\text{Br}} ? \xrightarrow{\text{H}_{2}\text{O}, \text{H}^{+}, \text{t}} ?\\ \text{A. Ethanol}\\ \text{B. 2-pentanone}\\ \text{C. acetic acid}\\ \text{D. methyl propyl}\\ \text{E. propilmetilketon} \end{array}$$

#### № 10. Specify the final product the following transformations:

$$CH_3-C-CH_2-C-OC_2H_5 \xrightarrow{C_2H_5ONa} ? \xrightarrow{CH_3Br} ? \xrightarrow{H_2O, H^+, t} ?$$

- A. Butanone
- B. oksoetanic acid
- C. b- oxopropanoic acid
- D. methyl ethyl ketone
- E. ethyl methyl ketone

## $N_{2}$ 11. Reacting acetylene with ketones in the presence of technical potassium hydroxide called reacting

- A. Wurtz
- B. Tabor
- C. Dumas
- D. Dieckmann
- E. Butlerov
- F. Ethynylation
- G. Acetylation

## $N_{2}$ 12. When reacting acetylene with ketones in the presence of technical potassium hydroxide formed

- A. Alkynes
- B. Acetylene alcohols
- C. Vinyl alcohol
- D. Saturated alcohols
- E. Diene alcohols
- F. Acetylenic carbinols
- G. Ethynilated alcohols

#### 13. In chemical reactions acetoacetic ester usually takes part

- A. and keto and enol forms
- B. only the enol form
- C. only the E, E configuration enol forms
- D. all forms
- E. for acetoacetic ester characterized by the reaction of the enol and keto

forms

#### INTRODUCTION TO ESTERS

Esters have a very sweet fruity smell. Naturally occurring esters are found in fruits. An ester is a product of the reaction of an acid (usually organic) and an alcohol (the hydrogen of the acid R-COOH is replaced by an alkyl group R'). Esters mainly result from the condensation (a reaction that produces water) of a carboxylic acid and an alcohol. The process is called esterification. This reaction can be catalyzed by the presence of H<sup>+</sup> ions. Sulphuric acid, H<sub>2</sub>SO<sub>4</sub>, is often used as a catalyst for this reaction. The name ester is derived from the German **Es**sig-Ae**ther**, an old name for acetic acid ethyl ester (ethyl acetate). Esters have the general formula R-COOR',



Esters are named in the same manner as salts (although esters and salts have completely different properties): two-word names are used. Note that in the general formula, R-COOR' (the carbon is doublebonded to one oxygen atom and single-bonded to another), the alkyl group (R') is always attached to an oxygen atom. This alkyl group (R') is named as the first word of the two-word name. The second word is derived by adding the ending -oate to the stem of the acid name (-oic in the acid name is replaced by -oate).

A reversible reaction between an alcohol and a carboxylic acid causes loss of water and the formation of an ester:

Alcohol + Carboxylic Acid 
$$\leftrightarrows$$
 Ester + Water  
R'OH + RCOOH  $\leftrightarrows$  RCOOR' + H<sub>2</sub>O.

Esters are named as derivatives of the carboxylic acid from which they are formed. Condensation of ethanoic acid with methanol will produce methyl ethanoate. As stated above the ending of the acid -oic is changed to -oate, much as if the ester were a salt of the acid. The esterification reactions are generally easily reversible by addition of water; the reverse reaction is called the hydrolysis of the ester and proceeds in the presence of aqueous base.



 $CH_3OH + CH_3COOH \rightarrow CH_3COOCH_3 + H_2O$ methanol + ethanoic acid  $\rightarrow$  methyl ethanoate + water

The esterification process will proceed more nearly to completion if a substance which removes water without reacting with the acid or the alcohol is added to the reaction, such as sulfuric acid. For example, the reaction between ethanoic acid and ethanol produces the ester ethyl ethanoate.



 $CH_{3}COOH + CH_{3}CH_{2}OH \longleftarrow H_{2}SO_{4} \longrightarrow CH_{3}COOCH_{2}CH_{3} + H_{2}O$ ethanoic acid + ethanol  $\longleftarrow H_{2}SO_{4} \longrightarrow$  ethyl ethanoate + water

The concentrated  $H_2SO_4$  removes water from the products and is a dehydrating agent. Most esters have very pleasant odors (see below). Many flavoring and scenting agents are made from esters. Esters are volatile liquids which are not ionized and they are soluble in organic solvents but not in water.

The simplest ester is H-COO-CH<sub>3</sub> (methyl methanoate).





In the laboratory, methyl methanoate can be produced by the condensation reaction of methanol and methanoic acid, as follows:

 $HCOOH + CH_3OH \xrightarrow{\leftarrow} HCOOCH_3 + H_2O$ methanoic acid + methanol  $\xrightarrow{\leftarrow}$  methyl methanoate + water

Industrial methyl methanoate, however, is usually produced by the combination of methanol and carbon monoxide in the presence of a strong base:

 $\begin{array}{c} CH_{3}OH + CO & \xleftarrow{} HCOOCH_{3} \\ methanol + carbon monoxide & \xleftarrow{} methyl methanoate \end{array}$ 

As shown in the diagram above the hydrogen atom on the right can be replaced with a  $CH_3$  group or additional  $CH_2$  units, producing other methyl esters, such as:



For esters derived from the simplest carboxylic acids, the traditional names are recommended by IUPAC, such as, formate, acetate, propionate, butyrate, though out of these only acetate may carry further substituents. For esters from higher acids, the alkane name with an -oate ending is generally preferred, e.g., hexanoate. Common esters of aromatic acids include benzoates such as methyl benzoate, with substitution allowed in the name.

### **IUPAC** nomenclature

Ester names are derived from the parent alcohol and the parent acid, where the latter may be organic or inorganic. Esters derived from the simplest carboxylic acids are commonly named according to the more traditional, so-called «trivial names« e.g. as formate, acetate, propionate, and butyrate, as opposed to the IUPAC nomenclature methanoate, ethanoate, propanoate and butanoate. Esters derived from more complex carboxylic acids are, on the other hand, more frequently named using the systematic IUPAC name, based on the name for the acid followed by the suffix -oate. For example, the ester hexyl octanoate, also known under the trivial name hexyl caprylate, has the formula  $CH_3(CH_2)_6CO_2(CH_2)_5CH_3$ .

Ethyl acetate derived from an alcohol (blue) and an acyl group (yellow) derived from a carboxylic acid.

The chemical formulas of organic esters usually take the form  $RCO_2R'$ , where R and R' are the hydrocarbon parts of the carboxylic acid and the alcohol, respectively. For example, butyl acetate (systematically butyl ethanoate), derived from butanol and acetic acid (systematically ethanoic acid) would be written  $CH_3CO_2C_4H_9$ . Alternative presentations are common including BuOAc and  $CH_3COOC_4H_9$ .

Cyclic esters are called lactones, regardless of whether they are derived from an organic or an inorganic acid. One example of a (organic) lactone is  $\gamma$ -valerolactone.

## Orthoesters

An uncommon class of organic esters are the orthoesters, which have the formula  $RC(OR')_3$ . Triethylorthoformate  $(HC(OC_2H_5)_3)$  is derived, in terms of its name (but not its synthesis) from orthoformic acid  $(HC(OH)_3)$  and ethanol.

#### **Inorganic esters**

 $\begin{array}{c} O \\ R - O - \begin{array}{c} O \\ P \\ O \\ O \\ O \\ H \end{array}$ A phosphoric acid ester

Esters can also be derived from an inorganic acid and an alcohol. Thus, the nomenclature extends to inorganic oxo acids and their corresponding esters: phosphoric acid and phosphate esters/organophosphates, sulfuric acid and sulfate esters/organosulfates, nitric acid and nitrate, and boric acid and borates. For example, triphenyl phosphate is the ester derived from phosphoric acid and phenol. Organic carbonates are derived from carbonic acid; for example, ethylene carbonate is derived from carbonic acid and ethylene glycol.

So far an alcohol and inorganic acid are linked via oxygen atoms. The definition of inorganic acid ester that feature inorganic chemical elements links between alcohols and the inorganic acid – the phosphorus atom linking to three alkoxy functional groups in organophosphate – can be extended to the same elements in various combinations of covalent bonds between carbons and the central inorganic atom and carbon–oxygen bonds to central inorganic atoms. For example, phosphorus features **three** carbon–oxygen–phosphorus bondings and one phosphorus–oxygen double bond in **organophosphates**,



structure of a generic organophosphate

Three carbon–oxygen–phosphorus bondings and no phosphorus–oxygen double bonds in phosphite esters or organophosphites,

structure of generic phosphite ester showing the lone pairs on the P **Two** carbon–oxygen–phosphorus bondings, **no** phosphorus–oxygen **double bonds** but **one** phosphorus–carbon bond in **phosphonites**,



structure of generic phosphonite - ester of phosphonous acid

**One** carbon–oxygen–phosphorus bondings, **no** phosphorus–oxygen **double bonds** but **two** phosphorus–carbon bonds in **phosphinites**.



In corollary, boron features borinic esters (n = 2), boronic esters (n = 1), and borates (n = 0).

As oxygen is a group 16 chemical element, sulfur atoms can replace some oxygen atoms in carbon–oxygen–central inorganic atom covalent bonds of an ester. As a result, **thiosulfinates' and thiosulfonates**, with a central inorganic sulfur atom, demonstrate clearly the assortment of sulfur esters, that also includes **sulfates**, **sulfites**, **sulfonates**, **sulfinates**, **sulfenates** esters.

## Structure and bonding

Esters contain a carbonyl center, which gives rise to 120 ° C–C– O and O–C–O angles. Unlike amides, esters are structurally flexible functional groups because rotation about the C–O–C bonds has a low barrier. Their flexibility and low polarity is manifested in their physical properties; they tend to be less rigid (lower melting point) and more volatile (lower boiling point) than the corresponding amides. The pK<sub>a</sub> of the alpha-hydrogens on esters is around 25.

Many esters have the potential for conformational isomerism, but they tend to adopt an s-cis (or Z) conformation rather than the s-trans (or E) alternative, due to a combination of hyperconjugation and dipole minimization effects. The preference for the Z conformation is influenced by the nature of the substituents and solvent, if present. Lactones with small rings are restricted to the s-trans (i.e. E) conformation due to their cyclic structure.



Physical properties and characterization

Esters are more polar than ethers but less polar than alcohols. They participate in hydrogen bonds as hydrogen-bond acceptors, but cannot act as hydrogen-bond donors, unlike their parent alcohols. This ability to participate in hydrogen bonding confers some water-solubility. Because of their lack of hydrogen-bond-donating ability, esters do not self-associate. Consequently, esters are more volatile than carboxylic acids of similar molecular weight.

## **Characterization and analysis**

Esters are generally identified by gas chromatography, taking advantage of their volatility. IR spectra for esters feature an intense sharp band in the range 1730–1750 cm<sup>-1</sup> assigned to  $v_{C=0}$ . This peak changes depending on the functional groups attached to the carbonyl. For example, a benzene ring or double bond in conjugation with the carbonyl will bring the wavenumber down about 30 cm<sup>-1</sup>.

## Esterification of carboxylic acids

The classic synthesis is the Fischer esterification, which involves treating a carboxylic acid with an alcohol in the presence of a dehydrating agent:

$$RCO_2H + R'OH \rightleftharpoons RCO_2R' + H_2O$$

The equilibrium constant for such reactions is about 5 for typical esters, e.g., ethyl acetate. The reaction is slow in the absence of a catalyst. Sulfuric acid is a typical catalyst for this reaction. Many other acids are also used such as polymeric sulfonic acids. Since esterifycation is highly reversible, the yield of the ester can be improved using Le Chatelier's principle:

- Using the alcohol in large excess (i.e., as a solvent).
- Using a dehydrating agent: sulfuric acid not only catalyzes the reaction but sequesters water (a reaction product). Other drying agents such as molecular sieves are also effective.
- Removal of water by physical means such as distillation as a low-boiling azeotropes with toluene, in conjunction with a Dean-Stark apparatus.

Reagents are known that drive the dehydration of mixtures of alcohols and carboxylic acids. One example is the Steglich esterification, which is a method of forming esters under mild conditions. The method is popular in peptide synthesis, where the substrates are sensitive to harsh conditions like high heat. DCC (dicyclohexylcarbodiimide) is used to activate the carboxylic acid to further reaction. DMAP (4-dimethylaminopyridine) is used as an acyl-transfer catalyst.<sup>[11]</sup>



Another method for the dehydration of mixtures of alcohols and carboxylic acids is the Mitsunobu reaction:

 $RCO_2H + R'OH + P(C_6H_5)_3 + R_2N_2 \rightarrow RCO_2R' + OP(C_6H_5)_3 + R_2N_2H_2$ 

Carboxylic acids can be esterified using diazomethane:

$$RCO_2H + CH_2N_2 \rightarrow RCO_2CH_3 + N_2$$

Using this diazomethane, mixtures of carboxylic acids can be converted to their methyl esters in near quantitative yields, e.g., for analysis by gas chromatography. The method is useful in specialized organic synthetic operations but is considered too hazardous and expensive for large scale applications.

## Alcoholysis of acyl chlorides and acid anhydrides

Alcohols react with acyl chlorides and acid anhydrides to give esters:

 $RCOCl + R'OH \rightarrow RCO_2R' + HCl$  $(RCO)_2O + R'OH \rightarrow RCO_2R' + RCO_2H$ 

The reactions are irreversible simplifying work-up. Since acyl chlorides and acid anhydrides also react with water, anhydrous conditions are preferred. The analogous acylations of amines to give amides are less sensitive because amines are stronger nucleophiles and react more rapidly than does water. This method is employed only for laboratory-scale procedures, as it is expensive.

## Alkylation of carboxylate salts

Although not widely employed for esterifications, salts of carboxylate anions can be alkylating agent with alkyl halides to give esters. In the case that an alkyl chloride is used, an iodide salt can catalyze the reaction (Finkelstein reaction). The carboxylate salt is often generated in situ. In difficult cases, the silver carboxylate may be used, since the silver ion coordinates to the halide aiding its departure and improving the reaction rate. This reaction can suffer from anion availability problems and, therefore, can benefit from the addition of phase transfer catalysts or highly polar aprotic solvents such as DMF.

## Transesterification

Transesterification, which involves changing one ester into another one, is widely practiced:

$$RCO_2R' + CH_3OH \rightarrow RCO_2CH_3 + R'OH$$

Like the hydrolysation, transesterification is catalysed by acids and bases. The reaction is widely used for degrading triglycerides, e.g. in the production of fatty acid esters and alcohols. Poly(ethylene terephthalate) is produced by the transesterification of dimethyl terephthalate and ethylene glycol:

$$(C_{6}H_{4})(CO_{2}CH_{3})_{2} + 2 C_{2}H_{4}(OH)_{2} \rightarrow$$
  
 $\rightarrow \frac{1}{n} \{(C_{6}H_{4})(CO_{2})_{2}(C_{2}H_{4})\}_{n} + 2 CH_{3}OH$ 

## Carbonylation

Alkenes undergo «hydroesterification» in the presence of metal carbonyl catalysts. Esters of propionic acid are produced commercially by this method:

$$C_2H_4 + ROH + CO \rightarrow C_2H_5CO_2R$$

The carbonylation of methanol yields methyl formate, which is the main commercial source of formic acid. The reaction is catalyzed by sodium methoxide:

$$CH_3OH + CO \rightarrow CH_3O_2CH$$

## Addition of carboxylic acids to alkenes

In the presence of palladium-based catalysts, ethylene, acetic acid, and oxygen react to give vinyl acetate:

$$C_2H_4 + CH_3CO_2H + \frac{1}{2}O_2 \rightarrow C_2H_3O_2CCH_3 + H_2O_2$$

Direct routes to this same ester are not possible because vinyl alcohol is unstable.

### **Test-Introduction to Esters**

#### № 1. Isomers fumaric acid is

- A. racemic acid
- B. oleic acid
- C. malonic acid
- D. succinic acid
- E. oxalic acid
- F. Carboxylic acid

# INTRODUCTION TO NITROGEN FUNCTIONAL GROUPS

Nitrogen can be attached to carbon in many ways. The organic compounds which contain nitrogen are essential to life. The most important organic nitrogen compounds are the amines and their derivatives the amides.

Substitution of an ammonia for hydrogen or carbon produces an amine group on an organic compound. Amines are classified as primary, secondary, or tertiary depending on the number of carbons which form bonds to the nitrogen. Following the normal organic practice of designating a carbon chain by the symbol R, a primary amine would be an amine with the structure  $RNH_2$ ; a secondary amine would have the structure  $R_2NH$ ; and a tertiary amine would have the structure  $R_3N$ . The carbon chains on a secondary or tertiary amine need not be identical.

Amines, like ammonia, can be protonated giving rise to alkylammonium ions. An example is the ethylammonium ion,  $CH_3CH_2NH_3^+$ , which is the conjugate acid of ethylamine. Amines are basic and form the largest and most significant class of organic bases.

## Amides

A reversible reaction between an amine and a carboxylic acid causes loss of water and the formation of an amide; the reaction is:

$$RNH_2 + R'COOH \longleftrightarrow R'CONHR + H_2O.$$

The amide bond is reasonably stable. When it forms between amino acids, in which both an amine group and a carboxylic acid group are present in the same molecule, the polymeric chain produced is a polypeptide. If the polypeptide chain is long enough, it is called a protein.

### **Test-** Introduction to Nitrogen Functional Groups

#### № 1. Which of the following groups relates to the chromophore?

- A. -OH
- B. C=C-N=N
- C. -SH
- D. All groups are chromophores.
- E. -C-O-C-

#### № 2. The interaction between acetone and hydrazine forms

- A. Hydrazide.
- B. Hydrazone
- C. Azine.
- D. Azide
- E. Imine
- F. A, C.

#### № 3. The interaction between acetone and hydroxylamine formes

- A. Hydroxamic acid
- B. Oxime
- C. Hydroxyl
- D. Izopropenol
- E. Propane
- F. Propyne

#### № 3. The quaternary ammonium salt – methyl allyl ethyl-n-propylamine iodide

A. has no asymmetric center and optically inactive

- B. exists as a configuration of enantiomers due to the fact that the four orbitals used to form bonds
  - C. has an axis of symmetry and exhibits optical activity
  - D. has a plane of symmetry and exhibits optical activity
  - E. exist as diastereomers
  - F. C, D.

#### $N_{2}$ 4. Condensation of carbonyl compounds with formal dehyde, and salts of secondary amines by reaction called

- A. Dieckmann
- B. Mannich
- C. Michael
- D. Ester condensation
- E. Aldol-crotonic condensation
- F. Tishchenko

## $N_{2}$ 5. Reacting the carboxylic acid with chlorine in the presence of phosphorus called

A. Tabor

- B. Gel-Folgarda-Zelinsky
- C. Zaitseva
- D. Lviv
- E. Butlerov
- F. Tishchenko

## $\underline{\mathbb{N}}{}_{\underline{2}}$ 6. When reacting the carboxylic acid with phosphoric anhydride formed

- A. Complex esters
- B. Carboxylic anhydrides
- C. Carboxylic acid chlorides
- D. Carboxamides
- E. Nitriles of carboxylic acids
- F. Hydroxamic acid

## $\mathcal{N}_{2}$ 7. Upon heating carboxylic acid amides with phosphorus pentoxide formed

- A. Hydroxamic acid
- B. Nitriles of carboxylic acids
- C. Complex esters
- D. Carboxylic anhydrides
- E. Carboxylic acid chlorides
- F. Carboxamides

### № 8. When Beckmann rearrangement of cyclohexanone oxime forms

- A. Cyclohexane.
- B. Caprolactam
- C. Caprylic acid
- D. Heptanoic acid
- E. Cyclohexanol
- F. Carboxylic acid

### Ne 9. In rearrangement of hydroxamic acids in acidic medium formed

- A. Alcohols
- B. Amines
- C. Carboxylic acid
- D. Ketones
- E. Aldehydes
- F. Nitro acid

#### TEST KEYS

## **Test – The Concept of Functional Groups**

1	2	3
В	В	В

## Test – Stoichiometry and Structure

1	2	3	4	5	6
В	В	В	В	В	В

## Test - Lewis Structures of Atoms



## Test - The Basic Shapes of Molecules

1	2	3	4
В	В	B,C	A,E

#### Test – Alkanes

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
D	B	Е	Α	B	B	С	Α	Е	D	В	B	В	D	F
16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
B	BE	BF	AF	CF	BF	ACF	BFG	B						

#### Test – Alkenes

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
B	Α	Е	D	С	E	E	B	B	В	F	D	BF	AF	CF	BFG	AEG	BCD	BFG	BFG

### Test -Alkynes

1	2	3	4	5	6	7	8	9	10
D	В	Α	Е	В	Ε	С	В	B	В

### Test - Oxygen Functional Groups: Alcohols

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
B	B	B	В	BF	BF	BF	B	B	B	BE	BE	BE	AE	AE	A E	BF

## Test - Carboxylic acids

1	2	3	4	5	6	7	8	9	10	11	12	13	14
BF	AE	AE	AE	BD	BF								
15	16	17	18	19	20	21	22	23	24	25	26	27	28
BF	BF	BF	BF	BF	AEF	BEF	BDE	ADE	BDE	ADE	ADE	ADE	BFG
29	30	31	32	33	34	35	36	37	38	39			
B	B	B	B	BF	ADE	BDE	ADE	BDE	BFG	BFG			

Test - Introduction to Aldehydes, Oxidation of Aldehydes

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
В	B	B	В	В	В	B	B	В	В	В	B	BF	BF	AF	B D	AE	BF	BCE	

Test – Ketones:

1	2	3	4	5	6	7	8	9	10	11	12	13
BF	BF	BF	BF	BF	BF	ADE	BDE	BDE	ADE	BFG	BFG	ADE

Test – Esters



## Test - Introduction to Nitrogen Functional Groups

1	2	3	4	5	6	7	8	9
В	B	B	B	В	В	В	В	В

Educational issue

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