

THE ESSENTIALS OF ORGANIC CHEMISTRY



GEORGE ▲ FIELD ▲ HAMBLEY

The Essentials of Organic Chemistry

by

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A supplementary text on fundamental
aspects of organic chemistry

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Preface

We have written *The Essentials of Organic Chemistry* as there is insufficient coverage of organic chemistry currently provided in all of the widely used first-year university general chemistry textbooks. This deficiency is usually covered by recommending a comprehensive organic text for first-year students, many of whom do not proceed to chemistry majors. *The Essentials of Organic Chemistry* is designed to supplement general chemistry texts and to provide a coverage of organic chemistry to meet the needs of most first-year university courses in chemistry. This book is not designed to stand alone as a chemistry text and relies on the coverage of such areas as bonding and hybridisation provided in most of the general chemistry texts. *The Essentials of Organic Chemistry* has been written in the style of *Chemistry, The Central Science* by Brown, LeMay and Bursten but might also be used with other widely used texts.

We wish to thank the staff at Prentice Hall Australia for their assistance and motivation. Without their support the project would not have proceeded. In particular we wish to acknowledge Andrew Binnie and David Weston who initiated the project and Kaylie Smith who shepherded it through to completion.

The authors invite comment from students and staff about this text.

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Organic Hydrocarbons

1

Organic chemistry deals with compounds in which carbon is the principal element. Carbon forms a vast number of compounds; many millions of organic compounds are known, and about 90% of all new compounds prepared each year contain carbon. Consequently, the study of carbon compounds has come to constitute a separate branch of chemistry.

The terms *organic chemistry* and *organic compounds* are historical. They arose in the eighteenth century from the 'vitalist theory,' which held that organic compounds could be formed only by living organisms. In 1828, Friedrich Wöhler, a German chemist, reacted two non-organic compounds which had never been part of a living system, potassium cyanate (KOCN) and ammonium chloride (NH_4Cl), and obtained urea (H_2NCONH_2). Urea was a well-known organic substance that had been isolated from the urine of mammals. This was the first-documented instance in which an organic compound had been produced from inorganic materials. Today, although there is a vast number of organic compounds obtained from natural sources, the majority of organic compounds are synthetic and chemists prepare many organic compounds from inorganic and organic starting materials.

Because the compounds of carbon are so numerous, it is convenient to organise them into families that exhibit structural similarities. The simplest class of organic compounds is the **hydrocarbons**, those composed only of carbon and hydrogen. Organic compounds containing other elements can be considered to be derivatives of hydrocarbons.

The key structural feature of hydrocarbons, and most other organic substances, is the presence of stable carbon-carbon C—C bonds. The ability of carbon to form stable, extended chains of atoms bonded through single, double, or triple bonds is almost unique among the non-metallic elements. Hydrocarbons are divided into four classes on the basis of the kinds of C—C bonds in their molecules. Figure 1.1 shows an example of each of the four types of hydrocarbons: alkanes, alkenes, alkynes, and aromatic hydrocarbons.

Alkanes are hydrocarbons that contain only single bonds, as in ethane, C_2H_6 . Because alkanes contain the largest possible number of atoms bonded to each carbon atom, they are called *saturated hydrocarbons*. Notice that each carbon atom in an alkane has four single bonds, whereas each hydrogen atom forms one single bond. **Alkenes**, also known as *olefins*, are hydrocarbons with one or more C—C double bonds. **Alkynes** contain at least one C—C triple bond. In **aromatic hydrocarbons**, the carbon atoms are connected in a planar ring structure, joined by a combination of double and single bonds between carbon atoms. Benzene, C_6H_6 , is the best-known example of an aromatic hydrocarbon. Alkenes, alkynes, and aromatic hydrocarbons are called *unsaturated hydrocarbons* because they contain fewer attached atoms than an alkane having the same number of carbon atoms.

The members of the different series of hydrocarbons exhibit different chemical

Alkanes

methane	CH_4	CH_4
butane	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$	C_4H_{10}

Alkenes

ethylene	$\text{CH}_2=\text{CH}_2$	C_2H_4
propene	$\text{CH}_3-\text{CH}=\text{CH}_2$	C_3H_6

Alkynes

acetylene	$\text{H}-\text{C}\equiv\text{C}-\text{H}$	C_2H_2
2-butyne	$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$	C_4H_6

Aromatic hydrocarbons

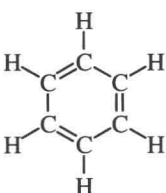
benzene		C_6H_6
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Figure 1.1 Names, geometrical structures, and molecular formulas for examples of alkanes, alkenes, alkynes, and aromatic hydrocarbons

properties; however, they are alike in many ways. Because carbon and hydrogen do not differ greatly in electronegativity (2.5 for carbon, 2.2 for hydrogen), the carbon—hydrogen bond is relatively non-polar and consequently hydrocarbon molecules are relatively non-polar. Hydrocarbons are almost insoluble in water, but they dissolve readily in non-polar solvents. Furthermore, hydrocarbons become less volatile with increasing molar mass because of an increase in the London dispersion forces.

1.1 ALKANES

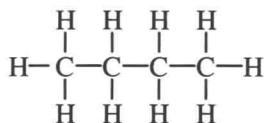
Table 1.1 lists examples of the simplest alkanes. We are familiar with many of these substances because of their widespread use. Methane is the major component of natural gas which is used for cooking on gas stoves and for water heaters. Propane is the major component of bottled gas and is used as an automotive fuel (LPG), for heating and for cooking in areas where natural gas is not available. Butane is used in disposable lighters

Table 1.1 Several members of the series of straight-chain alkanes

<i>Molecular formula</i>	<i>Condensed structural formula</i>	<i>Name</i>	<i>Boiling point (°C)</i>
CH ₄	CH ₄	Methane	-161
C ₂ H ₆	CH ₃ CH ₃	Ethane	-89
C ₃ H ₈	CH ₃ CH ₂ CH ₃	Propane	-44
C ₄ H ₁₀	CH ₃ CH ₂ CH ₂ CH ₃	Butane	-0.5
C ₅ H ₁₂	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃	Pentane	36
C ₆ H ₁₄	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	Hexane	68
C ₇ H ₁₆	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	Heptane	98
C ₈ H ₁₈	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	Octane	125
C ₉ H ₂₀	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	Nonane	151
C ₁₀ H ₂₂	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	Decane	174
C ₁₅ H ₃₂	CH ₃ (CH ₂) ₁₃ CH ₃	Pentadecane	270
C ₂₀ H ₄₂	CH ₃ (CH ₂) ₁₈ CH ₃	Eicosane	343

and in fuel canisters for camping stoves and lanterns which operate on gas. Alkanes with 5 to 12 carbon atoms per molecule are liquids and are commonly found in petrol (gasoline). Those with more than 20 carbon atoms are waxy solids.

The formulas for the alkanes given in Table 1.1 are written in a notation called a *condensed structural formula*. This notation reveals the way in which atoms are bonded to one another, but it does not require all of the bonds to be drawn. For example, the structural formula and condensed structural formula for butane, C₄H₁₀, are:



structural formula



condensed structural formula

Either the structural formulas or condensed structural formulas are common ways to represent organic compounds.

Each succeeding compound in the series listed in Table 1.1 has an additional CH₂ unit. A group of compounds, such as that shown in Table 1.1, is known as a **homologous series** because the same general formula can be used to describe all members of the group. The general formula for all the compounds listed in Table 1.1 is C_nH_{2n+2}, where n is the number of carbon atoms. Ethane, for example, contains two carbon atoms (n = 2) and six hydrogen atoms (2n + 2 = 2 × 2 + 2 = 6).

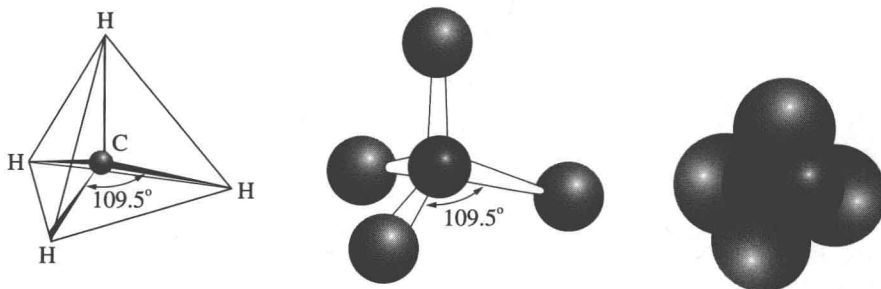


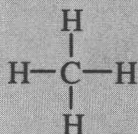
Figure 1.2 Representations of the three-dimensional arrangement of bonds about carbon in methane.

Structures of alkanes

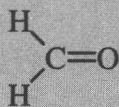
The structural formulas and condensed structural formulas for alkanes do not indicate anything about the three-dimensional structures of these substances. The geometry about each carbon atom in an alkane is tetrahedral; that is, the four groups attached to each carbon are located at the corners of a tetrahedron. However, the three-dimensional structures are often represented as shown for methane in Figure 1.2. The bonding involves sp^3 -hybridised orbitals on the carbon atom.

A CLOSER LOOK: Bonding in carbon compounds

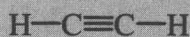
An isolated, neutral carbon atom has four valence electrons and it needs to form four covalent bonds in order to achieve a closed shell (8-electron) configuration. These four bonds can be four single bonds, one double bond and two single bonds, one triple bond and one single bond, or two double bonds.



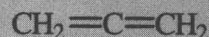
four single bonds



two single bonds
one double bond



one single bond
one triple bond



two double bonds

According to valence bond theory the hybridisation of the atomic orbitals of the carbon atoms in these four cases, will be sp^3 , sp^2 , sp , and sp respectively.



sp^3

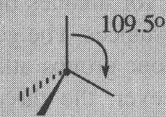


sp^2

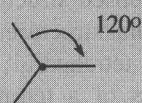


sp

Valence shell electron pair repulsion theory (VSEPR) allows the prediction of the geometry that the hybridised orbitals will adopt. The basis of VSEPR theory is simply that the orbitals, since they are occupied by electrons, will arrange themselves as far away from each other as they can. If there are four orbitals, then they will adopt a tetrahedral geometry, three orbitals will adopt a trigonal planar geometry and two a linear geometry. A carbon atom that is sp^3 hybridised will have a tetrahedral geometry, one that is sp^2 hybridised will have trigonal planar geometry and one that is sp hybridised will have a linear geometry.



Tetrahedral



Trigonal Planar



Linear

Rotation about the C—C single bond is a relatively facile process. You might imagine grasping the top left methyl group in Figure 1.3, which shows the structure of propane, and twisting it relative to the rest of the structure. Motion of this sort occurs very rapidly in alkanes at room temperature and a long-chain alkane is constantly undergoing motions that cause it to change its shape.

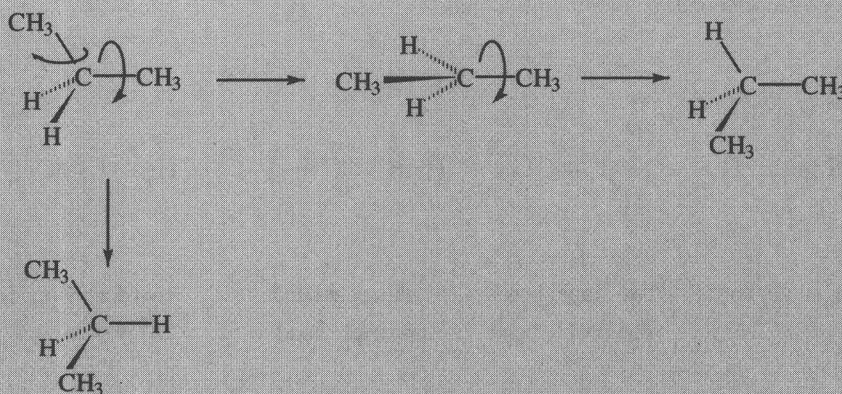


Figure 1.3 Three-dimensional models for propane, C_3H_8 , showing rotations about the C—C single bonds

The rotation about any C—C single bond in an alkane can be examined in detail. When the carbon atom at one end of the C—C bond in ethane is rotated with respect to the other, the energy of the molecule changes as a function of the rotation angle because the hydrogen atoms occupy space and repel each other. The isomers generated simply by rotation about single bonds are called **conformational isomers**. If the carbon atoms of ethane are arranged so that the hydrogen atoms are as far apart as possible, then looking along the C—C bond the hydrogen atoms on one carbon atom appear to lie between those on the other carbon atom. This is the lowest energy arrangement for the ethane molecule and it is called the **staggered conformation**. If the carbon atoms are rotated with respect to each other such that the hydrogen atoms are as close as possible, this is the highest energy arrangement for the ethane molecule and it is called the **eclipsed conformation**.

The conformation of a molecule about any particular bond is best visualised as a *Newman projection*. This is a schematic view down the length of the bond, with the atoms at either end of the bond depicted as a point for the atom nearest the observer, and a circle for the atom away from the observer. Groups attached to the near atom radiate from the point and groups attached to the remote atom radiate from the periphery of the circle. Figure 1.4 shows Newman projections of the staggered and eclipsed conformations of ethane.

For the ethane molecule, the energy of the molecule is a function of the rotation angle with an energy maximum every 120° of rotation. The energy difference between the maxima and minima is small (only about 12 kJ mole^{-1}) and at room temperature the ends of the ethane molecule are rapidly rotating with respect to each other. If the hydrogen atoms are replaced by larger groups, the energy barrier can be significantly higher and the free rotation can be restricted or stopped. The larger the groups the larger the barrier, and the interaction of bulky groups with each other is called *steric hindrance*.

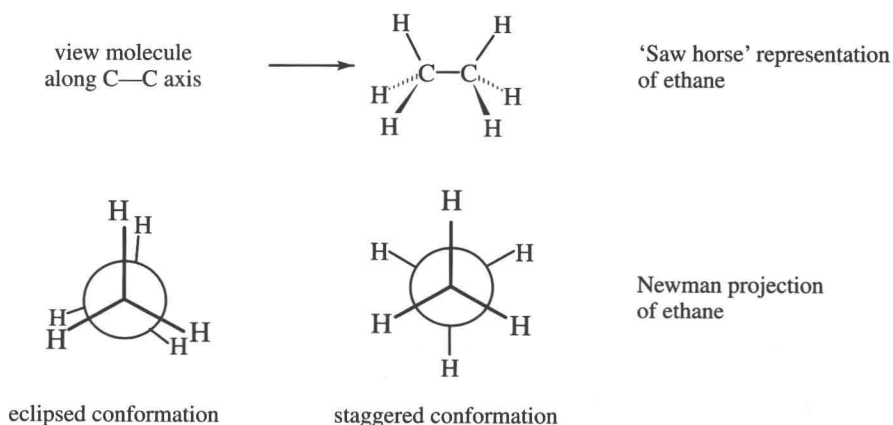
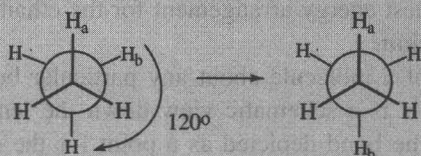


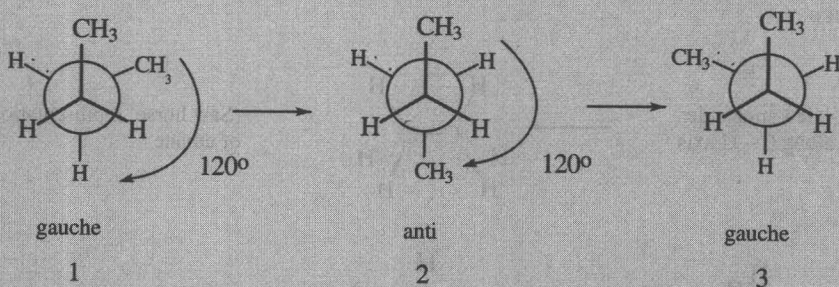
Figure 1.4 Newman projections of the eclipsed and staggered conformations of ethane

A CLOSER LOOK: The conformational isomers of butane

Conformational isomers (conformers) are those isomers that can be interconverted by rotation about single bonds. There is only a low energy barrier to rotation about a C—C single bond and the eclipsed and staggered conformers of ethane are known to rapidly interconvert in the gas phase. Each CH_3 group of the ethane molecule has three-fold symmetry so rotation about the C—C bond by 120° from one staggered conformation produces another (identical) staggered conformation.

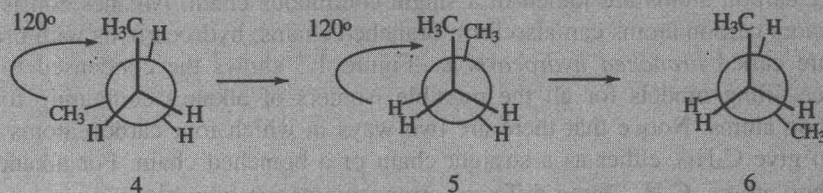


Butane can be considered as being derived from ethane by the replacement of one H atom on each C atom with a CH_3 group. This substitution destroys the three-fold symmetry that is present in ethane and, as a consequence, each rotation by 120° about the central C—C bond produces a different conformational isomer. The resulting conformations of butane are shown in the Newman projections below.



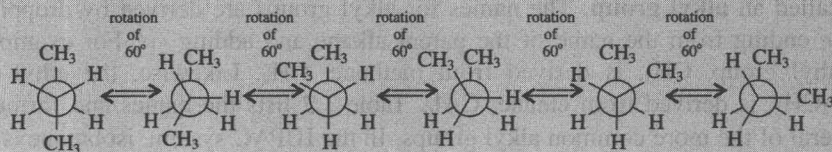
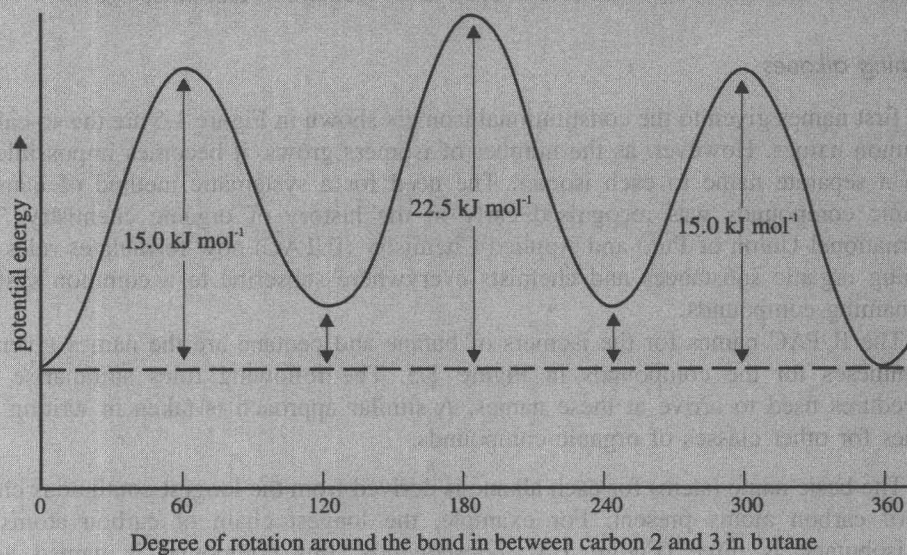
The conformations 1 and 3 are labelled **gauche** and conformation 2 is labelled **anti**. The two gauche conformations, 1 and 3, are mirror images of each other and have the same energy. Conformation 2 (anti) has lower energy than the others because it has the relatively bulky CH_3 groups located as far apart from each other as is possible in the butane molecule.

There are also three eclipsed conformations:



Conformations 4 and 6 are mirror images but in this case they have lower energy than conformation 5 because in 5 the bulky CH_3 groups are forced together. All of the eclipsed conformations have higher energy than the staggered conformations.

The energy of the butane molecules as a function of the 'torsion' angle about the central C—C bond is plotted below.



Constitutional isomers

The alkanes listed in Table 1.1 are termed *straight-chain* or *linear hydrocarbons* because all of the carbon atoms are joined in a single continuous chain. Alkanes consisting of four or more carbon atoms can also form branched chains; hydrocarbons with branched chains are called *branched hydrocarbons*. Figure 1.5 shows the condensed formulas and space-filling models for all the possible isomers of alkanes containing four and five carbon atoms. Notice that there are two ways in which four carbon atoms can be joined to give C_4H_{10} , either as a straight chain or a branched chain. For alkanes with five carbon atoms, C_5H_{12} , three different arrangements are possible.

Compounds with the same molecular formula, but with a different atom connectivity, are called **constitutional isomers**. The constitutional isomers of a given alkane have different physical properties to one another. Note that the melting point and boiling point of the isomers of butane, given in Figure 1.5, differ from those of the isomers of pentane. The number of possible isomers increases rapidly with the number of carbon atoms in the alkane. For example, there are 18 possible isomers of octane, C_8H_{18} , 75 possible isomers of decane, $C_{10}H_{22}$, and more than 366,000 isomers of eicosane, $C_{20}H_{42}$.

Naming alkanes

The first names given to the constitutional isomers shown in Figure 1.5 are the so-called common names. However, as the number of isomers grows, it becomes impossible to give a separate name to each isomer. The need for a systematic method of naming organic compounds was recognised early in the history of organic chemistry. The International Union of Pure and Applied Chemistry (IUPAC) now formulates rules for naming organic substances and chemists everywhere subscribe to a common system for naming compounds.

The IUPAC names for the isomers of butane and pentane are the names given in parentheses for the compounds in Figure 1.5. The following rules summarise the procedures used to arrive at these names. A similar approach is taken in writing the names for other classes of organic compounds.

1. The basic name (stem) for each alkane is derived from the longest continuous chain of carbon atoms present. For example, the longest chain of carbon atoms in isobutane is three (Figure 1.5); consequently, this compound is named as a derivative of propane, which has three carbon atoms.
2. In general, a group that is formed by removing a hydrogen atom from an alkane is called an **alkyl group**. The names for alkyl groups are derived by dropping the *-ane* ending from the name of the parent alkane and adding *-yl*. For example, the methyl group, CH_3 , is derived from methane, CH_4 . Likewise, the ethyl group, CH_3CH_2 , is derived from ethane, C_2H_6 . Table 1.2 lists the names and formulas of several of the more common alkyl groups. In the IUPAC system, isobutane is called methylpropane.
3. The location of an alkyl group along a chain of carbon atoms is indicated by numbering the carbon atoms along the chain. For example, the name 2-methylpentane indicates the presence of a methyl group, CH_3 , on the second carbon atom of