BASICS OF ORGANIC CHEMISTRY: A TEXTBOOK FOR UNDERGRADUATE STUDENTS

Anshul Bansal

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Basics of Organic Chemistry: A Textbook for Undergraduate Students

Authored by

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for Undergraduate Students

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PREFACE

Organic Chemistry is a challenging subject for a lot of students. Students are also confused about where to start organic chemistry because organic chemistry is very vast. Keeping these views in mind, I tried to write a very general book for students who face difficulties in understanding organic chemistry. In this book, I covered only the general topics that are extremely helpful in dealing with organic chemistry. The first chapter is about general concepts in organic chemistry like hybridization, inductive effect, electromeric effect, resonance, hyperconjugation, *etc.* The second chapter covers the introduction to the organic reaction mechanism: an important aspect of organic chemistry. The third chapter is about the reactive intermediates and the last two chapters are about the stereochemistry of organic compounds which I think is the backbone of organic chemistry.

A serious effort has been made to present the book in a very simple manner. No pains are spared to make the book free from errors. I am very grateful to The Almighty for giving me the energy to write this book. Finally, I express my sincere thanks to all those who helped and inspired me in writing this book. Last, but not least, it is a pleasure to acknowledge the silent contribution of my parents, Mr. Rakesh Bansal and Mrs. Urmil Bansal, my beloved wife Dr. Sumita Gulati and my little flowers Ajitesh and Ayansh in the completion of this book.

I will appreciate all those who read this and give their valuable suggestions or comments for further improvement in this book.

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INTRODUCTION

Organic chemistry, often considered both an art and a science, is a discipline that explores the properties, structure, composition, reactions, and synthesis of carboncontaining compounds. This textbook is designed not just to teach facts but to cultivate a deep understanding of the principles that govern this branch of chemistry. It is a beacon for those navigating the complexities of molecular structures and the dynamic processes that govern chemical transformations. Authored with clarity and pedagogical insight, this book aims to demystify the essential concepts of organic chemistry, making it accessible and engaging for learners at the foundational level.

Chapter 1: Structure and Bonding

In the opening chapter, we delve into the fundamental principles governing the structure and bonding of organic compounds. Readers will explore the intricacies of molecular architecture, the nature of chemical bonds, and the significance of molecular geometry, laying the groundwork for a profound understanding of organic chemistry.

Chapter 2: General Principles of Organic Reaction Mechanism

Moving beyond static structures, Chapter 2 introduces the dynamic realm of organic reaction mechanisms. Students will uncover the principles governing how organic compounds transform through chemical reactions, gaining insights into the driving forces behind these transformations and the factors influencing reaction pathways.

Chapter 3: Reaction Intermediates

This chapter takes a closer look at the transient species that emerge during chemical reactions intermediates. Understanding these fleeting entities is crucial for comprehending the intricacies of organic transformations, providing students with a deeper insight into the mechanisms underlying various reactions.

Chapter 4: Stereochemistry of Organic Compounds-I

Stereochemistry, the study of three-dimensional arrangements of atoms in molecules, takes the center stage in Chapter 4. Through a systematic exploration

of stereoisomerism, chirality, and conformational analysis, students will grasp the spatial relationships critical to the behaviour and reactivity of organic compounds.

Chapter 5: Stereochemistry of Organic Compounds-II

This chapter equips students with a comprehensive understanding of the stereochemical intricacies of organic compounds.

With its structured approach and emphasis on conceptual clarity, "Basics of Organic Chemistry: A Textbook for Undergraduate Students" is not just a textbook but a guided journey into the heart of organic chemistry. Whether you are a budding chemist or a student exploring the wonders of molecular science, this book serves as an invaluable resource, laying the groundwork for a lifelong appreciation of organic chemistry.

Structure and Bonding

Abstract: This chapter delves into the foundational concepts of chemical structure and bonding, essential for understanding molecular interactions and properties. The chapter begins with hybridization, exploring how atomic orbitals combine to form hybrid orbitals, influencing molecular geometry and bonding properties. Bond length and bond angles are analyzed, providing insight into the spatial arrangements and distances between atoms in molecules, which are crucial for predicting molecular shape and reactivity. The concept of bond energy is introduced, highlighting the energy changes associated with bond formation and dissociation, essential for thermodynamic and kinetic considerations.

The chapter then focuses on localized bonds and their impact on molecular stability and reactivity, contrasting them with delocalized electrons in various bonding scenarios. Van der Waals forces are examined as weak intermolecular forces that play significant roles in physical properties such as boiling and melting points. The chapter proceeds with an analysis of the inductive effect and the electromeric effect, both of which describe electron shifts within molecules under the influence of electronegativity and external fields, respectively.

Resonance and hyperconjugation are covered as mechanisms for electron delocalization, contributing to molecular stability and influencing chemical reactivity. Hydrogen bonding, a critical intermolecular force, is discussed in terms of its formation, significance in biological systems, and effects on physical properties. Lastly, the concept of aromaticity is introduced, explaining the unique stability and reactivity of aromatic compounds due to delocalized π -electrons in cyclic structures.

This comprehensive exploration of structure and bonding provides a detailed understanding of the intricate forces and interactions that determine the behavior of molecules, laying the groundwork for advanced studies in chemistry and related fields.

Keywords: Aromaticity, Bond angles, Bond energy, Bond length, Electromeric effect, Hyperconjugation, Hydrogen bonding, Hybridization, Inductive effect, Localized bonds, Resonance, Van der waals forces.

Molecules are created through the combination of atoms, enabling them to achieve the electronic configuration of an inert gas. The constitution of a chemical bond occurs when the combining atoms are attracted to one another. G.N. Lewis initially proposed that diatomic molecules like H₂, O₂, N₂, and Cl₂ achieve noble gas electronic configuration by contributing electron pairs, with every atom sharing electrons. The shared pair(s) of electrons hold the atoms together, constructing a covalent bond. The structure of a compound refers to how individual atoms within a molecule are interconnected and organised in 3-dimensional space. The characteristics of compounds are influenced by their structures. Understanding the skeletal postulation of organic compounds involves considering the type and toughness of bonds in a molecule. So, why do atoms unite to form molecules? The reason is that during formation of bonds, atoms attain a state of lower energy, resulting in the release of a specific quantity of energy known as "bond dissociation energy." Breaking the molecule back into its component atoms requires the same amount of energy. In the present chapter, we will explore about hybridization, discuss the framework of molecular structure, and examine several kinds of bonds and their properties.

HYBRIDIZATION

The ground state electronic configuration of carbon atom, which is the main component of all organic compounds, is



Since carbon has got four electrons in the outermost shell, in order to achieve a stable noble gas configuration, carbon should either loss or gain four electrons or alternatively share four electrons. But the loss or gain of four electrons would require the supply of a very large amount of energy which is not available under normal conditions. Thus, carbon only forms covalent bonds in its compounds. Hence, we may say that *covalent bond is the bond of immense significance in the study of organic compounds*.

According to orbital concept, a covalent bond is obtained when a half-filled atomic orbital of an atom combines with a half-filled atomic orbital of another atom. Now, it is evident from the electronic configuration of carbon that it has got only two half-filled atomic orbitals, therefore, it should be divalent. But in all its compounds such as CH₄, CCl₄, C₂H₆ *etc*. carbon forms four bonds and hence is tetravalent. Now the question arises, *why carbon shows tetracovalency*. To answer this question, let us compare the quantity of energy liberated during the formation of CH₂ and CH₄.

Organic Chemistry

We know that the energy of a normal C—H bond is about 418 KJ mol⁻¹. The reaction of carbon with two hydrogen atoms to form CH₂ should liberate approximately 836 KJ mol⁻¹ of energy.

• $C \bullet + 2H \bullet \longrightarrow H^{\bullet}C \bullet H$ $\Delta H = -836 \text{ KJ mol}^{-1}$

Alternatively for the formation of four bonds, carbon must have four half-filled atomic orbitals. This is possible if we assume that one of the 2s electrons gets unpaired and is promoted to the empty $2p_z$ orbital. Therefore, the electronic configuration of carbon in the first excited state is $1s^2$, $2s^1$, $2p_x^1$, $2p_y^1$, $2p_z^1$ as shown below:



This promotion requires 401 KJ mol⁻¹ of energy but this energy is more than compensated by the formation of two additional C—H bonds.

• C • 401 KJ • C • $+4H^{\bullet}$ H^{\bullet} $\Delta H = 418 \text{ x} 4 - 401 = 1271 \text{ KJ mol}^{-1}$

Thus there is net release of 836 KJ mol⁻¹ of energy in the formation of CH_2 in comparison to 1271 KJ mol⁻¹ in case of formation of CH₄. It is because of this reason that *carbon always shows tetracovalency*.

Furthermore, it is known that the s orbital of carbon has a spherical shape, while the p orbitals have a dumbbell shape and are perpendicular to one another. Based on this information, we would predict that three out of the four carbon bonds would be perpendicular to one other, while the fourth bond would lack a specific orientation. However, it is observed that all the bonds made by carbon in molecules such as methane are similar in all aspects. They have a bond strength of 434 KJ mol⁻¹, a bond length of 110 pm, and are aligned along the corners of a regular tetrahedron, with an H—C—H angle of 109.5°. To explain these observations, the concept of hybridization was developed.

CHAPTER 2

General Principles of Organic Reaction Mechanism

Abstract: This chapter presents an in-depth examination of the fundamental principles underlying organic reaction mechanisms, a critical area for understanding and predicting chemical behavior in organic chemistry. The chapter begins with arrow notations, the symbolic representation of electron movement in chemical reactions, which provides a visual and conceptual framework for tracking changes during reactions. The roles of various reagents are explored, differentiating between electrophiles and nucleophiles based on their electronaccepting and electron-donating characteristics. This distinction is crucial for understanding how these species interact in different reaction contexts. We categorize and describe the major types of organic reactions, including substitution, addition, and elimination reactions, each with unique pathways and outcomes.

Energy considerations are discussed to elucidate the energetic profile of reactions, including activation energy and reaction intermediates, providing insight into reaction feasibility and rates. The reaction mechanism section systematically dissects the step-by-step processes by which reactants transform into products, highlighting the importance of understanding detailed mechanistic pathways for predicting reaction behavior. Addition reactions are explored, focusing on how reagents add to unsaturated molecules such as alkenes and alkynes, influencing the formation of new chemical bonds. Elimination reactions, where elements are removed from a molecule to form double or triple bonds, are detailed, including mechanisms like E1 and E2.

Hammond's postulate is introduced as a principle that correlates the structure of transition states to the intermediates, aiding in the visualization and prediction of reaction dynamics. Substitution reactions are analyzed, distinguishing between nucleophilic and electrophilic substitutions, and their respective mechanisms (*e.g.*, SN^1 and SN^2).

This comprehensive chapter equips readers with a thorough understanding of the principles and mechanisms that govern organic reactions, serving as a foundational guide for advanced studies and practical applications in organic chemistry.

Keywords: Arrow notations; reagents; electrophiles, nucleophiles; types of reactions; energy considerations, reaction mechanism; Hammond's postulate; substitution reactions; addition reactions; elimination reactions.

Chemical reactions can convert one molecule into another, resulting in a different arrangement of atoms and a redistribution of electrons. Organic reactions, in particular, follow specific steps for the transformation of reactants into products. These steps are elucidated in the organic reaction mechanism, which provides a detailed account of the process. *The reaction mechanism not only outlines the number of steps involved but also reveals the sequence of bond breaking and formation.* Understanding reaction mechanisms is crucial in organic chemistry because numerous seemingly distinct reactions occur through a limited set of

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common steps. Therefore, studying reaction mechanisms is of great significance for comprehending and predicting organic reactions.

ARROW NOTATIONS IN ORGANIC CHEMISTRY

1. Curved arrow (\checkmark) : It signifies the transfer of a pair of electrons from the atom at the tail of the arrow to the atom at the head of the arrow. For example



2. *Fish hook arrow or half headed arrow (*): The movement of a single electron is denoted by a fish hook arrow. It represents the transfer of one electron, either in a reaction or during the formation of a radical. For example,



3. Double Headed arrow (\checkmark): A double head arrow (\checkmark) is used to separate two or more resonance structures (and not real structures). In other words, it is written between two imaginary species. For example,



4. Double Arrow (\iff , Reversible arrow): Double arrow is used to represent equilibrium between the reactants and the products of a reaction in a reversible reaction. For example,

- 1) $2H_2O \implies H_3O + OH$
- 2) $CH_3COCH_2 COOEt \Longrightarrow CH_3 C \Longrightarrow CH COOEt$ Acetoacetic ester (Keto form) OH (Enol form)

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5. *Middle Headed Arrow* (\rightarrow) : A half headed arrow (\rightarrow) is used to show the inductive effect symbolized by I. It points in the direction of electron drift.

C → X	$C \rightarrow Y$
+ I-effect	- I-effect

Fission of Covalent Bonds

In organic reactions, the breaking and formation of covalent bonds are commonly observed. Covalent bonds are typically depicted using a dash (—), while the movement of a pair of electrons is represented by a curved arrow (\frown), whereas the movement of a single electron is shown by *fish hook arrow* (\frown). There are two ways in which a covalent bond may be broken.

(*i*) Homolytic fission: Suppose the atoms X and Y are bonded through a covalent bond. This bond may break in such a way that each fragment carries one unpaired electron. The species formed by this fission are known as *free radical intermediates* and this manner of cleavage is known as *homolytic fission*. Homolytic fission is also called as **homolysis**. Generally non-polar bonds undergo homolytic fission which is favoured by high temperature, UV-irradiation or by the presence of radical initiators such as peroxides.

$$X \xrightarrow{Y} Y$$
 Homolytic $X + Y$

(*ii*) *Heterolytic fission*: When the covalent bond joining the atoms X and Y breaks in such a way that the pair of electrons stays on any one of the atoms, such fission is called as *heterolytic fission*. This type of fission gives *ionic intermediates*. Heterolytic fission is also called **heterolysis**, which occurs in polar bonds and is favoured by polar solvents.

or
$$X \xrightarrow{Y} Heterolytic Fission X^{+} + Y^{-}$$
 (When Y is more electronegative than X)
 $X \xrightarrow{Y} Y \xrightarrow{Heterolytic Fission X^{-}} + Y^{+}$ (When X is more electronegative than Y)

Reactive Intermediates

Abstract: This chapter explores the diverse and crucial world of reactive intermediates, which play pivotal roles in the mechanisms and outcomes of organic reactions. Beginning with an overview of reaction intermediates, we establish their importance as transient species that facilitate the transformation of reactants to products.

Carbocations, positively charged species with significant implications for reactivity and stability, are examined in detail, highlighting their formation, stabilization factors, and roles in various organic reactions. Carbanions, their negatively charged counterparts, are discussed with a focus on their nucleophilic nature, stabilization mechanisms, and involvement in organic synthesis. After that, the chapter delves into carbenes, neutral species with a divalent carbon atom, emphasizing their unique reactivity and applications in cyclopropanation and insertion reactions. Free radicals, species with unpaired electrons, are analyzed for their formation, stability, and participation in radical reactions, which are crucial in polymerization and halogenation processes.

The chapter continues with an examination of nitrenes, and nitrogen analogs of carbenes, noting their reactivity and applications in aziridination and insertion reactions. Arynes and benzynes, highly reactive intermediates derived from aromatic compounds, are explored, focusing on their formation and role in nucleophilic aromatic substitution reactions.

Enamines, intermediates formed from aldehydes or ketones and secondary amines, are discussed in the context of their stability and utility in organic synthesis, particularly in the Stork enamine reaction. The concept of formal charge is introduced to aid in understanding the electronic structure and reactivity of intermediates, providing a foundational tool for predicting the behavior of these species.

Through a comprehensive analysis of these reactive intermediates, this chapter equips readers with the knowledge to understand and predict the behavior of complex organic reactions, laying the groundwork for advanced studies and practical applications in organic chemistry.

Keywords: Reaction intermediates; carbocations; carbanions; carbenes; free radicals; nitrenes; arynes; benzyne; enamines; formal charge.

A majority of organic reactions involve multiple steps and the formation of *short-lived, highly reactive chemical species known as reactive intermediates or reaction*

Anshul Bansal All rights reserved-© 2024 Bentham Science Publishers *intermediates*. These intermediates can be covalent compounds, ions, or radicals and play a crucial role in organic reaction mechanisms. Understanding their structures and properties is essential for comprehending these mechanisms. While intermediates have energetically favorable levels to form under reaction conditions, they are often too unstable to be isolated. This is particularly true for intermediates where carbon has less than four covalent bonds. Reactive intermediates are highly transient species involved in organic reactions. The reactive intermediates are:

1. Carbocations, 2. Carbanions, 3. Free radicals, 4. Carbenes, 5. Nitrenes, 6. Arynes, 7. Enamines.

CARBOCATIONS

Chemical species carrying positive charge on a carbon which has only six electrons in its valence shell are called carbocations or carbonium ions. They are short lived and highly reactive species. Since the carbon atom carrying the positive charge is electron deficient and thus has a strong tendency to complete its octet by accepting a pair of electrons.

Classification of carbocations: Carbocations are classified into three categories *i.e.*, primary (1°), secondary (2°) and tertiary (3°) depending upon whether the cationic carbon is primary, secondary or tertiary. Methyl carbocation with one carbon is regarded as a special case.



Structure: The positively charged carbon atom of the carbocation is sp^2 hybridized. It uses its three hybrid orbitals for the formation of three covalent bonds with three monovalent atoms or groups; the remaining unhybridized p-orbital remains vacant. The carbocation adopts a planar structure in which all three covalent R bonds lie in the same plane, forming bond angles of 120 degrees between them. The empty p-orbital is at right angle to the plane of sp^2 -hybridised orbitals.

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Orbital picture of a carbocation

Carbocations have a strong tendency to complete the octet of carbon and consequently they are highly reactive species and participate in many chemical reactions i.e. in unimolecular substitution and elimination reactions, in the decomposition of diazonium salts and in various rearrangements.

Methods of Generation of Carbocations

Carbocations can be generated in a many ways. Some of the reactions in which carbocations are formed are given below:

i) By solvolysis of C—X bond (X = halogens) *i.e.* ionization of alkyl halides in polar solvents.

$$R \xrightarrow{\qquad } X \xrightarrow{\qquad \text{polar} \qquad } R \xrightarrow{\bigoplus} R + : X^{\bigoplus}$$

ii) Deamination of aliphatic amines by nitrous acid.

$$R \longrightarrow NH_2 \xrightarrow{HNO_2} RN_2 \longrightarrow R + N_2$$

iii) By action of superacids on alkyl fluorides.

$$R - F + SbF_5 \longrightarrow \overset{\textcircled{}}{R} + SbF_6^{\ominus}$$

iv) Protonation of alcohols followed by dehydration.

Stereochemistry of Organic Compounds-I

Abstract: This chapter provides a thorough exploration of the stereochemistry of organic compounds, a fundamental aspect of organic chemistry that influences the physical and chemical properties of molecules. The chapter begins with isomerism, distinguishing between the different types of isomers and setting the stage for a deeper investigation into structural isomerism and stereoisomerism.

Structural isomerism is examined, focusing on isomers that differ in the connectivity of their atoms, affecting their chemical behavior and properties. Stereoisomerism, which includes isomers with the same connectivity but different spatial arrangements, is introduced as a key concept in understanding molecular diversity.

Optical isomerism is detailed, highlighting the role of chirality and the ability of certain molecules to rotate plane-polarized light. The concept of chirality is expanded upon, discussing chiral centers and the absence of elements of symmetry, which leads to the existence of non-superimposable mirror images.

Enantiomerism, the relationship between pairs of chiral molecules that are mirror images of each other, is explored, emphasizing its significance in biological systems and pharmaceuticals. Projection formulas, including Fischer and Newman projections, are introduced as tools to represent three-dimensional structures in two dimensions, aiding in the visualization and differentiation of isomers. Diastereomers, stereoisomers that are not mirror images, are discussed with a focus on their different physical and chemical properties compared to enantiomers. The concept of prochirality is introduced, explaining how certain molecules can become chiral through specific chemical modifications.

Resolution techniques for separating racemic mixtures into individual enantiomers are covered, highlighting methods such as chiral chromatography and enzymatic resolution. Racemic mixtures, equimolar mixtures of enantiomers, are examined in terms of their formation and the challenges they present in synthesis and analysis.

This chapter equips readers with a comprehensive understanding of stereochemistry, providing the knowledge necessary to predict and explain the behavior of organic compounds based on their threedimensional structures, essential for advanced studies and practical applications in organic chemistry.

Keywords: Chirality; Diastereomers; Elements of symmetry; Enantiomerism; Isomerism; Optical isomerism; Projection formulas; Prochirality; Resolution; Racemic mixtures; Structural isomerism; Stereoisomerism.

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CONCEPT OF ISOMERISM

Isomers, derived from the Greek words "*isos*" meaning *equal* and "*meros*" meaning *part*, refer to *compounds with identical molecular formulas but distinct physical and chemical characteristics*. This phenomenon is known as isomerism. The varying properties of isomers arise from differences in the relative arrangements of atoms within their molecules.

Isomerism is of the following two types:

1. Structural or Constitutional Isomerism 2. Stereoisomerism

1. Structural or Constitutional Isomerism: Compounds that possess the same molecular formula but exhibit distinct structures as a result of different arrangements of atoms within their molecules. This phenomenon is referred to as structural or constitutional isomerism. It can be further categorized into six different types:

i) Chain or Skeletal or Nuclear Isomerism: This type of isomerism arises due to difference in the arrangement of carbon chain within the molecule.

For example, molecular formula $C_{4}H_{10}$ represents two chain isomers — *n*-butane (having straight chain) and *iso*butane (having branched chain).

<i>n-Butane</i> (straight chain)	Same molecular	2-Methylpropane (<i>Iso</i> butane)
$\mathrm{H}_{3}\mathrm{C}-\mathrm{C}\mathrm{H}_{2}-\mathrm{C}\mathrm{H}_{2}-\mathrm{C}\mathrm{H}_{3}$	$= C_4 H_{10} =$	$ \begin{array}{c} CH_3 \\ \\ H_3C - CH - CH_3 \end{array} $

Similarly, molecular formula C_5H_{12} represents three isomers, one straight chain and two branched chain isomers, *e.g.*, *n*-pentane (straight chain), *iso*pentane and *neo*-pentane (both branched chain).

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ii) Position isomerism: Position isomers, also known as positional isomers, are compounds that share the same molecular formula and carbon skeleton but vary in the placement of an attached atom, group, or multiple bond. This phenomenon is referred to as position isomerism. For instance, propan-1-ol and propan-2-ol are position isomers since they differ in the position of the -OH group.



Likewise but-1-yne and but-2-yne are position isomers.

4 3 2 1	4	3	2	1	
CH ₃ CH ₂ C ≕ CH	CH3 ·	— C =	=C-	-CH3	
But-1-yne (Triple bond at C_1)	But-2-y	vne (Tr	iple bo	ond at C	C ₂)

iii) Functional isomerism: Functional isomers are compounds that have the same molecular formula but possess different functional groups. In functional isomers, the arrangement of atoms within the molecule remains the same, but the functional groups attached to the carbon skeleton differ. For example, the molecular formula C_2H_6O represents ethanol (an alcohol) and dimethyl ether (an ether) which have different functional groups.

CH3CH2OH	СН3 — О — СН3
Ethanol	Dimethyl ether

Some more examples of functional isomerism are:

CHAPTER 5

Stereochemistry of Organic Compounds-II

Abstract: This chapter continues the exploration of stereochemistry in organic compounds, focusing on detailed methods for describing and differentiating the spatial arrangement of atoms within molecules. It begins with absolute configuration, which provides a precise description of the spatial arrangement of atoms around a chiral center, independent of other molecules.

Relative configuration is then discussed, explaining how the arrangement of atoms in one chiral molecule relates to another, often determined through chemical interconversion. The D-L system, a traditional method for denoting configurations based on the molecule's relationship to glyceraldehyde, is introduced for historical context and specific applications.

The R-S system, the modern and widely used method for assigning absolute configuration based on the Cahn-Ingold-Prelog priority rules, is detailed, providing a systematic approach for designating chiral centers. Geometrical isomerism is explored next, focusing on compounds with restricted rotation around double bonds or ring structures, resulting in distinct cis-trans configurations.

The E-Z system, an advanced method for designating geometrical isomers based on the Cahn-Ingold-Prelog priority rules, is introduced, offering a more precise description for complex molecules. Conformational isomerism, which arises from the rotation around single bonds, is then examined, highlighting its significance in the dynamic behavior of molecules.

Various conformations, particularly those of cycloalkanes and acyclic compounds, are analyzed, discussing the energy differences and interconversions between different conformers. Special attention is given to the impact of conformational isomerism on chemical reactivity and physical properties.

This chapter provides a deep understanding of the nomenclature and principles used to describe the three-dimensional arrangements of atoms in organic molecules, building on the foundations laid in the previous chapter. Mastery of these concepts prepares readers to analyze and predict the behavior of complex organic systems, essential for advanced studies and practical applications in organic chemistry.

Keywords: Absolute configuration; relative configuration; D-L system; R-S system; geometrical isomerism; E-Z system; conformational isomerism; conformations.

ABSOLUTE AND RELATIVE CONFIGURATIONS

For describing the configurations of different stereoisomers the following two terms are used:

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I. Absolute configuration II. Relative configuration

I. Absolute configuration: Absolute configuration refers to the precise spatial arrangement of atoms or groups within a specific stereoisomer of a compound. X-ray studies are commonly used to determine the absolute configuration.

II. Relative configuration: Relative configuration refers to the spatial arrangement of atoms or groups within a particular stereoisomer, relative to the atoms or groups of another compound chosen as a reference or standard. It provides information about the positional relationships between different atoms or groups within the molecule, but does not provide specific information about their absolute spatial orientation.

Consider, for example, the configurations of two enantiomers of lactic acid, one of these configurations represents dextro or (+) lactic acid while other represents laevo or (-) lactic acid.



Here it is not indicated which one of the two enantiomers has configuration I and which has configuration II. To solve this problem, two different conventions have been used as discussed below:

1. D-L system or D-L nomenclature: This system, known as the D-L system, is one of the oldest and most widely used methods for assigning configuration to a given enantiomer. In this method, the relative configuration of various optically active compounds was established by comparison of their projection formula with that of a standard substance arbitrarily chosen as proposed by Emil Fischer. The compound chosen as standard was glyceraldehydes and its two enantiomers were designated symbols D and L. The (+)-enantiomer was given the symbol D and was assigned the configuration in which OH group attached to chiral carbon is towards right and the H-atom towards the left, the CHO group lies at the top and CH₂OH lies at the bottom of Fischer projection. On the other hand, (-)-enantiomer was given the symbol L and assigned the configuration in which OH group is towards left and H-atom towards right.

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The relative configurations of numerous compounds were established by comparing them with D-(+)-glyceraldehyde or L-(–)-glyceraldehyde. If a compound can be derived from or transformed into D-(+)-glyceraldehyde, it belongs to the D-series. Conversely, if it can be derived from or transformed into L-(–)-glyceraldehyde, it belongs to the L-series. The general principle involved in correlating the configurations of two compounds is that *if a reaction does not involve the breaking of a bond about a chiral centre, the configuration about that chiral centre remains unchanged*. For example,

1. D-(+)-Glyceraldehyde can be converted into (-)-glyceric acid by simple oxidation reaction. Since this reaction does not involve breaking of bonds about the chiral centre, the configuration of (-)-glyceric acid must be same as that of D-(+)-Glyceraldehyde *i.e.* D-configuration.



2. By the following reactions, (+)-lactic acid can be obtained from L-(-)-glyceraldehyde, and therefore it is assigned the L-configuration.



Although the configurations assigned by Fischer to D- and L-glyceraldehyde were purely arbitrary at that time but subsequently in 1951, X-ray diffraction studies on

CONCLUSION

As we conclude our exploration of "Basics of Organic Chemistry: A Textbook for Undergraduate Students", it is our sincere hope that this journey has not only equipped you with the essential knowledge of organic chemistry but has also ignited a lasting passion for the subject. This textbook was crafted with the belief that understanding the fundamental principles of organic chemistry is not just a requirement for academic success but a key to unlocking the boundless possibilities within the molecular world.

Throughout these pages, you have delved into the intricacies of molecular structures, deciphered the language of chemical reactions, and navigated the threedimensional landscapes of stereochemistry. Beyond the theoretical framework, we trust that the practical insights provided, coupled with problem-solving exercises, have fortified your ability to apply these concepts in real-world scenarios.

Organic chemistry is a dynamic field, with its principles serving as the foundation for advancements in medicine, materials science, and countless other disciplines. As you move forward in your academic and professional pursuits, we encourage you to view the challenges of organic chemistry not as obstacles but as opportunities to engage with the captivating intricacies of the molecular world.

Remember that organic chemistry is not confined to the pages of this textbook; it is alive in the laboratory, in the synthesis of new compounds, and in the innovations that shape our world. The skills you've honed in critical thinking, problem-solving, and understanding molecular structures will undoubtedly serve you well, whether you continue your journey in academia, research, or any field that draws upon the principles of organic chemistry.

"Basics of Organic Chemistry: A Textbook for Undergraduate Students" is more than a textbook; it is a stepping stone in your academic and intellectual growth. We wish you continued success in your exploration of the sciences and a lifelong appreciation for the wonders of organic chemistry.

As we bid farewell to this textbook, our aspiration is that you depart with not just a comprehensive understanding of organic chemistry but also with the skills to critically analyse, solve problems, and appreciate the intricate beauty inherent in

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molecular structures. Remember, this book is not the end of your exploration but a catalyst for a lifelong journey into the ever-evolving world of organic chemistry.

May the knowledge gained within these pages empower you in your academic pursuits and beyond. Whether you embark on further studies, enter the realm of research, or apply these principles in a professional setting, we are confident that the insights gained here will serve as a solid foundation for your continued success. Happy exploring!

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