

FUNDAMENTALS OF THEORETICAL ORGANIC CHEMISTRY

by O. A. REUTOV Moscow State University

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PREFACE

This book, designed for a student familiar with basic organic chemistry, is really a second edition of the "Theoretical Problems of Organic Chemistry," which appeared in 1956 and was based on the author's lectures given at Moscow University. It is not primarily concerned with the structures of individual classes of compounds but with chemical dynamics, i.e., the mechanisms of the most important organic reactions.

The first, introductory chapter outlines the current theory of chemical structure and the electronic concepts of organic chemistry. Some physico-chemical methods for investigating organic structures are described, and data obtained via them are given in the appendices for reference. Chapters 2 to 9 discuss the relationship of the various reaction mechanisms to three factors: the chemical structure of the reactants, the solvent, and the reaction conditions (catalysts, temperature, etc.). The problems of tautomerism and the resulting ability of compounds to undergo reactions via two paths are discussed in Chapter 10 in the light of data obtained in the last two decades.

The immensity of the subject and the limitations of space have imposed certain restrictions on the coverage. Thus, for example, our discussion is centered around those homogeneous reactions which were historically important in the development of modern theoretical organic chemistry. Furthermore, in treating structures, we were forced to focus most of our attention on molecules in their ground states. In addition, many subjects which would properly fall in the area covered by the title of the book inevitably had to be omitted; we can justify this on the grounds that the work is intended primarily for graduate and post-graduate students.

Many fundamental discoveries in the seven years since the publication of the initial work have compelled a reconsideration of certain theoretical aspects of organic chemistry. Our ideas of the mechanism of substitution at a saturated carbon have been changed and amplified, and much new information has been obtained from studies of the mechanisms of molecular and free-radical rearrangements. New fields, such as the chemistry of carbenes and of benzyne, have been opened up; much new light has been shed on the problem of aromaticity of nonbenzenoid aromatics, etc.

In preparing this edition, we have tried to incorporate these changes in theory. We have also tried to make the material more accessible to average students of organic chemistry.

During preparation of the manuscript, the author had the benefit of some extremely valuable comments and suggestions which resulted from the use of his first book as a textbook in many Soviet universities. In particular, these suggestions prompted the writing of a separate section on the acid-base properties of organic compounds.

The author wishes to express his deep gratitude to all those who contributed their ideas, effort and time to the development of the present text, and wishes to assure his readers that all indications of shortcomings of the present edition will be received with equal gratitude.

O. A. Reutov

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CHAPTER 1

THEORY OF CHEMICAL STRUCTURE

Fundamentals

Historical Introduction

Toward the middle of the last century organic chemistry was a vast storehouse of largely unorganized factual material. Little attention was paid to theory, and the theoretical ideas which did exist at the time were incapable of explaining many of the known facts. They were even less suited for predicting new phenomena. This lag of theory behind practice had a seriously deleterious effect on the further development of the field.

The mood prevailing among chemists at that time was colorfully expressed by Wöhler: "The organic chemistry of our day can drive anyone mad. It seems to me to be a virgin forest full of wonderful things, a vast jungle with no way out, without an end, where one dares not penetrate."

In this situation there was an urgent need for answers to some fundamental problems. The most basic of these problems was this: "Are molecules random, disordered aggregates of atoms held together by (weak) attractive forces, or do they have a definite architecture which can be determined from their properties?" The prevailing theory of types, developed by Gerhardt and adhered to (although with some reservations) by the majority of chemists of the time, was of no help at all. It refused to tackle the problem of molecular structure on the ground that it is beyond cognition, a "thing in itself" (*Ding an sich*). But this contention flew in the teeth of available experience, because by the 1860's organic chemistry had already accumulated many facts and generalizations which could form a basis for solving the problem of molecular structure. For example, the theory of radicals had definitely shown, on the basis of experiment, that certain atomic groupings pass without any change from the starting material to the product during a chemical reaction. But chemists were loath to dispense with a theory which did make some real contributions. For example, the theory of types helped to study those parts of the molecule which undergo the greatest changes during the reaction and, to some extent, helped to understand the causes of these changes.

Then, in 1853, came Frankland's epochal discovery of valence of elements. Frankland (1825-1899) worked with organometallic compounds. During this work he found that in these compounds the metal was always associated with a strictly defined, integral number of organic groups (radicals), a number which defined the valence of the metal. Thus, Frank-

land obtained the following compounds:

CH_3Na	$(\text{CH}_3)_2\text{Hg}$	$(\text{CH}_3)_3\text{Al}$	$(\text{CH}_3)_4\text{Sn}$
methylsodium	dimethylmercury	trimethylaluminum	tetramethyltin

This discovery proved that atoms combine into molecules in well-defined ratios which are determined by the valences of the participating atoms. Following this, Kekulé (1829-1896) made another fundamental contribution by proving (in 1857) that carbon is tetravalent.

The concept of valence led directly to the idea that molecules have a definite structure, but it remained unclear how this structure could be determined.

Gerhardt (1816-1856), the founder of the theory of types, and his successors believed that the molecular structure of a substance could not be established by studying its reactions. They believed that the molecule changes fundamentally in the course of the reactions and becomes something different—a new entity. Therefore the chemical properties of a substance can reveal only its past and future, but never its present.*

Gerhardt's school was willing to concede that the problem of molecular structure could be solved by physical methods of investigation at some future date. But since the physical methods of their own time were in their infancy, their attitude was tantamount to a refusal to study the problem.

A new epoch in organic chemistry began with the advent of the theory of chemical structure, whose creation is largely due to the efforts of the Russian chemist A. M. Butlerov (1828-1886). Butlerov rejected the prevailing view on the indeterminacy of molecular structure. He showed that molecules exhibit a definite sequence of chemical bonds, i.e., a chemical structure, and demonstrated that this molecular structure could be established by studying the chemical properties of the substance. Conversely, Butlerov showed that knowledge of structure allowed the prediction of many properties of the compound. This postulate of chemical structure was substantiated by the already available data, and Butlerov used it to predict new substances which were later discovered by himself and other workers.

Butlerov's ideas on chemical structure were formulated in his paper "On the chemical structure of substances," published in 1861: "I start from the postulate that each chemical atom** which is part of a body participates in the formation of this body and acts in this process with a given amount of its characteristic chemical force (affinity). I designate by the name of "chemical structure" that distribution of the action of this force by virtue of which chemical atoms, influencing each other directly or indirectly, combine into a chemical particle" [1].

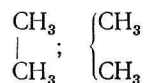
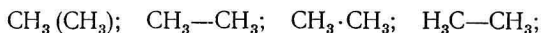
*For example, it was believed that the chemical properties of nitrobenzene will lead to only the following conclusions: nitrobenzene is a substance obtained by the action of a nitrating mixture on benzene (the "past" of nitrobenzene); its reduction gives aniline (the "future" of nitrobenzene). This, of course, means that many other definitions of nitrobenzene could be produced, for example, that of a substance obtained by the oxidation of nitrosobenzene and forming *m*-dinitrobenzene on nitration, etc. In this system, each substance thus had to be represented by many formulas describing its reactions, while its molecular structure was not considered at all.

**Butlerov refers to "chemical atoms" in the sense of the smallest quantities of elements present in a molecule. While he supported the atomistic theory (more precisely, the atomistic hypothesis of that time), the existence of physical atoms (that is, the smallest chemically unresolvable particles) was still regarded as unproved in the middle of the nineteenth century, and Butlerov preferred to use the concept of "chemical atoms." This precaution was fully justified at the time.

Having thus established the concept of chemical structure, Butlerov then went on to say: "The chemical nature of a complex particle is determined by the nature of its simplest components, the number of these components and by their chemical structure" [2].

Butlerov was thus the first to state that each molecule has a definite chemical structure, that this structure determines the properties of the substance, and that the study of the chemical transformations of the substance can reveal its structure.

Butlerov's views on the significance of chemical structural formulas follow from the central aspects of his theory. He thought that these formulas should not be "type-centered" or "reaction-centered," but rational. Thus each substance can have only a single rational formula, from which one can derive its chemical properties. Butlerov rightly regarded the manner of writing structural formulas as a secondary problem: "We should remember that the important thing is not the form but the essence of the matter, its underlying concept, the idea. If we then take into consideration the logic of the situation, that is, that formulas denoting isomerism should represent real particles—i.e., certain chemical relationships existing within these particles—then it follows that any method of formula writing will be satisfactory as long as it conveniently represents the prevailing relationships. In fact, it is even natural to use a variety of formulas, selecting the one that is best suited to the particular case. For example, it makes almost no difference which of the following formulas is used to represent ethane C_2H_6 :



However, if fundamentals are not well defined, then a different way of writing a formula may lead to confusion" [3].

With the creation of the theory of chemical structure, organic chemistry emerged at last from the labyrinth of type-centered formulas. The new theory showed the way toward the understanding of the internal structure of molecules; it provided a theoretical basis for understanding chemical processes and for predicting new synthetic pathways. And, what is most important, from its very beginning the theory of chemical structure allowed chemists to direct their experiments toward definite goals which could be set in advance.

One of the early and great achievements of the theory of chemical structure was its explanation of the phenomenon of isomerism, which was discovered early in the nineteenth century. Some time previously, at the end of the eighteenth century, Proust discovered the law of constant proportions, which says that each chemical species always has the same composition. For several decades afterwards it was thought that the reverse statement was also true; that is, a given composition was held to be the property of only one chemical species. Then, however, Liebig (1803-1873) proved in 1823 that the composition of silver fulminate was identical to that of silver isocyanate—an entirely different substance obtained in 1822 by Wöhler. This remarkable finding was rapidly followed by the discovery of other compounds that exhibited the same empirical

formulas but different properties. Following Berzelius (1799-1848), from 1830 on this phenomenon was called *isomerism* (which in Greek means "composed of the same parts"), the compounds exhibiting this property being known as *isomers*.

All attempts to explain isomerism by means of the theory of radicals or the theory of types were unsatisfactory, and the phenomenon remained theoretically unexplained for almost 40 years after its discovery, that is, until the advent of the theory of chemical structure. That theory stated that the properties of a substance depend not only on the nature and the number of its constituent atoms, but also on the structure of the molecule itself. Thus some substances could have the same composition and molecular weight, and yet because of structural differences be completely different.

Butlerov also discovered and explained the phenomenon of *dynamic isomerism*, whereby two or more isomers readily interconvert under certain conditions. Today this is known as tautomerism.

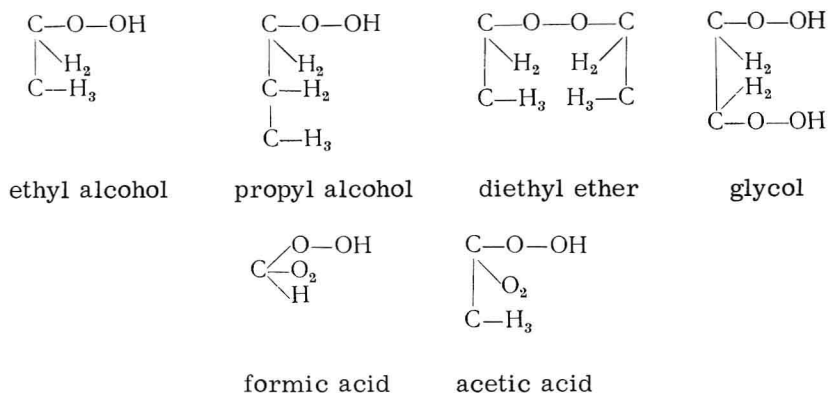
The two problems of static and dynamic isomerism were the first tests of the young theory of chemical structure, and it passed them with flying colors.

It is significant that Butlerov never regarded the molecule as some kind of a dead framework binding the individual atoms into a lifeless construction. He wrote: "Today we do not look upon a chemical compound as some inert, immobile entity; on the contrary, we hold that it is endowed with constant motion, present even in its smallest particles whose particular and mutual relationships are subject to constant changes which add up to some average result. There may also be constant changes in the chemical particles making up the bulk of the substance, but all this reduces to a certain average state of the substance itself. Thus, in the general case we are always faced with a state of dynamic equilibrium. With this approach to the nature of a chemical compound and to chemical reactions, we can clearly explain phenomena which were formerly completely incomprehensible. Consider, for example, how easily we now account for dissociation, reversible reactions, etc." [3].

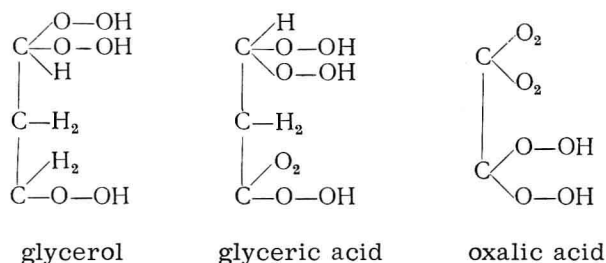
The simple and irrefutable tenets of the theory of chemical structure soon found general acceptance. However, there has always been a tendency to minimize Butlerov's contributions and to ascribe its discovery to Kekulé and Couper, so that soon after his formulation of the theory Butlerov was forced to defend his priority. While some foreign chemists at first did not subscribe to or even understand his work, they subsequently tried to claim for themselves the discovery of its basic propositions.

In 1858 Couper published a paper entitled "On a new chemical theory," in which he rejected the theory of types and suggested that all properties of organic substances can be explained by only two characteristics of atoms: their "selective affinity" (bonding) and the "degree of affinity" (valence) [4]. Couper wrote: "These two properties, in my opinion, explain all that is characteristic of organic chemistry, as I shall now prove. . . . A molecule may consist of three, four, five, etc., carbon atoms and equivalent quantities of hydrogen, oxygen, etc. While the latter elements can be replaced by others, the carbon forms an interrelated linkage. This means that carbons are bonded to each other. This property imparts to carbon a special character, and explains the until now incomprehensible superposition of carbon atoms in organic compounds" [4].

Having thus arrived at the important concept of carbon chains, Couper expressed his views on structure in graphic formulas. These were the first structural formulas*:



Couper thus was able to achieve a remarkably correct representation of the structures of these compounds, and of some even more complicated and then little known substances such as tartaric and racemic (paratar-taric) acid. However, none of these formulas was based on experimental evidence, because Couper never considered the problem of their experimental verification. His formulas, as one can readily see, were based on a formal interpretation of the concepts of valence and bonding of atoms, and to some extent simply on intuition. Obviously, such an approach is bound to lead to errors. For example, Couper's formulas for glycerol, glyceric acid, and oxalic acid:



are incorrect. For this reason his views, despite the talented and interesting manner of presentation, do not bear the earmarks of an orderly theory.

Another attempt to represent organic compounds by structural formulas was made in 1861 by Loschmidt [5], who regarded atoms as the smallest material particles subject to forces of attraction and repulsion. Loschmidt thought that these forces equilibrated as the atoms approached each other, and thus kept the atoms at a certain equilibrium distance. Loschmidt denoted the spheres of influence of these forces by circles. Carbon and

*Like other chemists of his time, Couper assumed the atomic weight of oxygen to be 8. He therefore always represented it as a double atom with a degree of affinity (valence) equal to 2.

hydrogen atoms thus were denoted by single circles, oxygen atoms by two concentric circles, and nitrogen by three. Some examples of Loschmidt's formulas are



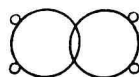
water



ammonia

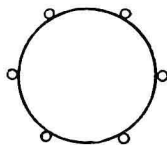


methane



ethylene

Without attempting to describe the bonding of the six carbons in benzene, Loschmidt denoted the latter by the symbol



benzene

Loschmidt derived his formulas on the basis of valence (*Pollenz*) but, in contrast to Couper, he was sometimes guided by chemical considerations. However, on the whole his method of formula derivation was abstract and often simply speculative. Thus, Loschmidt tried to infer the formulas of such complex substances as indigo, uric acid, etc., even though he lacked all chemical data. Not surprisingly these formulas turned out to be wrong. Although many of Loschmidt's formulas proved correct, his work passed almost unnoticed by the chemists of his day and had little effect on the development of theoretical organic chemistry.

On the other hand, the work of the German chemist Kekulé contributed considerably to the creation of the structural theory. Kekulé established the tetravalence of carbon, identified the type of methane, proposed the modern formula for benzene, and, most important, formulated one of the main problems of organic chemistry of his day.

In his paper "On the structure and transformation of chemical compounds and on the chemical nature of carbon" (1858) Kekulé wrote: "I think that the main task of chemistry today is not the discovery of atomic groups that, because of certain properties, can be regarded as radicals; nor is our task the classification of compounds into various types which can hardly have any meaning other than that of models for formulas. On the contrary, I suggest that we turn to the structure of the radicals themselves; the nature of the elements should be used to derive both the nature of the radicals and that of their compounds" [6].

Kekulé considered the startingpoints of this inquiry to be the "basicity" (valence) of elements and, in dealing with organic compounds, the nature of carbon. He also originated a number of other correct views about the bonding of atoms, which he expressed by graphic formulas.

However, even after 1861, Kekulé was not consistent in his views, and the second volume of his book (1863) was still based on the theory of types. Kekulé did not regard his formulas as denoting actual structures; he merely wanted to represent the reactivity of the compounds: "Rational formulas are only meant to give a certain idea of the chemical nature of a

compound, and therefore of its transformations and its relationships to other materials. . . . One should bear in mind that rational formulas only represent reactions and do not show the structure of the compound. One should bear in mind that these formulas are simply a means of representing the reactions of substances and for comparing various substances among themselves, and that they are in no way intended to express the structure, i.e., the arrangement of the atoms in a given compound.”*

Kekulé believed that the determination of the true structures of molecules belongs among the tasks of chemistry, but, like Gerhardt, he thought that this could be achieved not by studying chemical reactions but by comparison of physical properties of compounds.

Like other adherents of the theory of types, Kekulé represented individual compounds by several typical formulas. For example, he suggested that the then known properties of acetic acid be depicted by eight formulas. Thus although his views closely resembled modern structural considerations, and although he did make a substantial contribution to the theory of chemical structure, Kekulé could not quite free himself from the ideas of the theory of types.**

The decisive role of Butlerov in the creation of the theory of chemical structure was stressed in 1867 by Mendeleyev when he recommended Butlerov to the St. Petersburg University. Mendeleyev wrote that Butlerov “tries, by studying chemical reactions, to penetrate to the very chemical bonds linking various elements into a whole, assigns to each bond a natural tendency to enter in a certain number of combinations, and ascribes differences in the properties to the various ways in which the elements are bonded. No one else has carried through these thoughts so consistently, although they have appeared earlier. . . . To extend this approach to all classes of organic compounds, Butlerov published in 1864 the ‘Introduction to a Complete Study of Organic Chemistry,’ which recently was translated into German. Through his lectures and his fascinating ideas, Butlerov succeeded in forming around himself at Kazan a school of chemists working along his lines. The fame of Markovnikov, Myasnikov, Popov, the two Saytsevs, Morgunov, and others is based on the many discoveries due largely to the independence of Butlerov’s thought. I can personally vouch for the fact that such French and German scientists as Würtz and Kolbe regard Butlerov as one of the most influential movers of theoretical chemistry of our time.”*** And further: “Some of these ideas have surfaced before; they were proposed fragmentarily, as in Couper’s work; they could be gleaned from the writings of a number of scientists unwilling to follow Gerhardt, as pointed to or foreshadowed in the memoirs of men such as Kekulé, who showed clearly that they trusted nothing and regarded all theory as simply one of the methods for systematization” [8].

Butlerov held that the theory of chemical structure would develop with the accumulation of new factual material. He wrote: “I cannot fail to mention that the conclusions to which we are led by the principle of

*A. Kekulé, *Lehrbuch der organischen Chemie oder der Chemie der Kohlenstoffverbindungen* [Textbook of Organic Chemistry or the Chemistry of Carbon Compounds] Erlangen, v. 1, 1859-1861.

**On the roles of Butlerov and Kekulé in the creation of the theory of chemical structure, see [7]. [In the West the formulation of the theory of structure in organic chemistry is usually credited to Kekulé and Couper. See W. V. Farrar and K. R. Farrar, *Proc. Chem. Soc.*, 285 (1959).—Translation editor.]

***Zh. Minist. Narod. Prosveshch. (J. Ministry National Education). 1868 (*Uspekhi Khimii*, no. 1, 115, 1953).

chemical structure are in harmony with the known facts in thousands of cases. As in any other theory, we have here certain shortcomings and imperfections; we encounter some facts which do not strictly fit in with the concept of chemical structure. We should, of course, wish for more of such discrepancies; *facts which cannot be explained by existing theories are those which are most valuable to science, and it is primarily by their explanation that we can expect science to develop in the nearest future*" (italics mine—O.R.) [9].

Elsewhere Butlerov said, "He who fills his mind with the vain conviction of the infallibility of his scientific theory is in fact turning away from science and toward blind faith, i.e., to the very thing he thinks he is fighting," and also, "Blind trust in the infallibility of scientific theories leads to unscientific and completely unjustified skepticism, and often obscures the sight of real truths lying outside the domain of one's favorite theories" [10].

In the subsequent years, the theory of chemical structure was enriched by a number of new ideas, the most significant of which were the stereochemical theories of the Dutch scientist van't Hoff (1852-1911) and the Frenchman Le Bel (1847-1930), as well as the electronic theory of organic chemistry.

To summarize, the theory of chemical structure systematized the factual material of organic chemistry, explained the more important laws governing it, and provided a means for predicting new facts. It was the scientific foundation of modern organic chemistry.

Interaction of Atoms in Molecules

There is an enormous mass of evidence pointing to the fact that atoms or groups of atoms interact when bonded into molecules. We can distinguish the interaction between directly linked atoms and that of atoms not directly bonded. The former case can be illustrated with silicon tetrachloride SiCl_4 and carbon tetrachloride CCl_4 . The reactivities of the chlorines in these two compounds are very different. Thus, in the presence of water the chlorines in SiCl_4 are very readily replaced by hydroxy groups, while those in CCl_4 are not affected under these conditions. This difference is due to the differing effects exerted by silicon and carbon on the chlorines to which they are linked. In turn, the chlorines also affect the carbon and the silicon.

Indirectly bonded atoms also interact. Thus the chemical effect of the hydrogen in hydrogen cyanide $\text{H}-\text{C}\equiv\text{N}$ is different from that of the hydro-

gen in methane $\text{H}-\text{C} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$, even though in both cases we have a hydrogen

linked directly to carbon. This difference can only be due to the effects of other atoms in the molecule (in this case, nitrogen or the other hydrogens).

Obviously, comparison of only two substances cannot reveal the true nature of the interaction between atoms. Thus a comparison of $\text{H}-\text{CN}$ and $\text{H}-\text{CH}_3$ shows only that the nitrogen in the first case and the hydrogen atoms in the second affect the chemical reactivity of the indirectly connected hydrogen atom, but cannot explain how this one hydrogen atom affects the nitrogen in HCN and the other three hydrogens in CH_4 . A large number of compounds must be examined if the nature of the interaction