PETER SYKES

A Guidebook to Mechanism in Organic Chemistry

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A GUIDEBOOK TO MECHANISM
IN ORGANIC CHEMISTRY

FOR
JOYCE

FOREWORD

THE great development of the theory of organic chemistry or more particularly of our understanding of the mechanism of the reactions of carbon compounds, which has occurred during the past thirty years or so, has wrought a vast change in outlook over the whole of the science. At one time organic chemistry appeared to the student as a vast body of facts, often apparently unconnected, which simply had to be learnt, but the more recent developments in theory have changed all this so that organic chemistry is now a much more ordered body of knowledge in which a logical pattern can be clearly seen. Naturally enough during the long period of development from the initial ideas of Lapworth and Robinson organic chemical theory has undergone continuous modification and it is only in comparatively recent times that it has become of such evident generality (although doubtless still far from finality) that its value and importance to the undergraduate student has become fully realised. As a result the teaching of organic chemistry has been, to some extent, in a state of flux and a variety of experiments have been made and a substantial number of books produced setting out different approaches to it. While it is the writer's opinion that it is unsatisfactory to teach first the main factual part of the subject and subsequently to introduce the theory of reaction mechanism, he is equally convinced that at the present time it is quite impracticable to concentrate almost entirely on theory and virtually to ignore the factual part of the subject. Organic chemical theory has not yet reached a level at which it permits prediction with any certainty of the precise behaviour of many members of the more complex carbon compounds which are of everyday occurrence in the practice of the science. Sound theory is vital to the well-being of organic chemistry; but organic chemistry remains essentially an experimental science.

In Cambridge we are seeking the middle way, endeavouring to build up both aspects of the subject in concert so that there is a minimum of separation between fact and theory. To achieve this the student is introduced at an early stage to the theoretical principles involved and to the essential reaction mechanisms illustrated by a modest number of representative examples. With this approach is coupled a more factual treatment covering the chemistry of the major groups of carbon compounds. Dr. Sykes [who has been intimately associated with this approach] has now written this aptly-named 'Guidebook' to reaction mechanism which sets out in an admirably lucid way what the student requires as a complement to his factual reading. I warmly commend it as a book which will enable students to rationalise many of the facts of organic chemistry, to appreciate the logic of the subject and in so doing to minimise the memory work involved in mastering it.

A. R. TODD.

26th April, 1961.

PREFACE

THE last twenty-five years have seen an enormous increase in our knowledge of the reactions of organic compounds and, in particular, of the actual detailed pathway or mechanism by which these reactions take place. This understanding has largely come about from the application of electronic theories—so successful in other fields—to organic chemistry, and has resulted not only in an extremely valuable systematisation and explanation of the vast, disparate mass of existing facts, but has also made it possible to specify, in advance, the conditions necessary for the successful carrying out of many new and useful procedures.

The new approach avoids the learning of vast masses of apparently unconnected facts—which has been *the* characteristic of organic chemistry in the past—and helps and encourages the chemist to think for himself: far from requiring a chemist to know more, it enables him to make infinitely better use of what he already does know. It marks the greater effectiveness of really understanding the underlying principles rather than merely knowing by rote. At the same time it is well to emphasise that the complexity of organic compounds in general is such that the *rigorous* application of quantum-mechanical principles to them is impossible. Assumptions and approximations have to be made before useful generalisations can be worked out and it is at this point that there is particular need for strictly chemical skill and insight: the day of organic chemistry from the armchair is far from being with us yet!

This new and effective way of thinking about organic chemistry has been the subject of several large monographs but a smaller, compact book is still required that introduces the essentials, the very vocabulary of the subject, to the scholarship candidate, to the beginning undergraduate and technical college student, and to the chemist whose professional education has been along strictly classical lines. That is the aim of this book which has grown out of the author's lecture courses at Cambridge and his many years spent in supervising undergraduates.

The minimum of space has purposely been spent on valency theory as such for not only is that adequately treated elsewhere, but the student's real need is to gain as much experience as possible in seeing how theoretical ideas work out in practice: in explaining the course taken by actual reactions. Thus the first chapter is intended to give a succinct statement of the basic principles employed and the rest of the book shows how they work out in explaining the variation of reactivity with structure, the occurrence of three main classes of reagent—electrophiles, nucleophiles and radicals—and their behaviour in the fundamental reactions of organic chemistry—substitution, addition, elimination and rearrangement. In all cases, the examples chosen as illustrations have been kept as simple as possible so that the essential features of the process are not confused by extraneous and inessential detail.

Detailed references to the original literature are not included as the author's experience leads him to believe that in a book of such a size and scope the limited space available can be better employed. A select bibliography is, however, included in which the student's attention is drawn to larger sources of information to which he can now progress and reference is made to the particular virtues of a number of the sources quoted.

I am most grateful to my mentor of many years, Professor Sir Alexander Todd, for his Foreword and to my colleagues Dr. J. Biggs (now of the University of Hull), Dr. V. M. Clark, Dr. A. R. Katritzky, Dr. D. H. Marrian and to my wife, who have read the manuscript in whole or in part and made very many useful suggestions. I should also like to express my gratitude to the Rockefeller Foundation for a grant which enabled me, in 1959, to visit the United States and stay at Harvard University, Northwestern University, the University of Illinois, Oberlin College and the Georgia Institute of Technology to study the teaching of mechanistic organic chemistry to undergraduates and graduate students. Many interesting discussions, particularly with Professors F. G. Bordwell, Nelson J. Leonard and Jack Hine, influenced a number of the ideas developed in this book. My indebtedness to the original literature and to other publications, in particular Ingold's *Structure and Mechanism in Organic Chemistry*, Gould's *Mechanism and Structure in Organic Chemistry*, Alexander's *Ionic Organic Reactions* and Hine's *Physical Organic Chemistry* will be apparent to many who read here. Finally I should like to express my deep appreciation to Longmans, and to the printers for their unfailing patience and for the extreme trouble to which they have gone to produce that rare phenomenon, structural formulae that are both clear and aesthetically satisfying.

PETER SYKES.

Cambridge,
April 1961.

CONTENTS

1 STRUCTURE, REACTIVITY AND MECHANISM

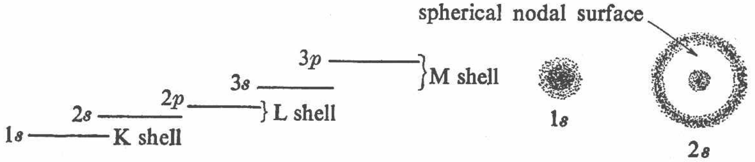
THE chief advantage of a mechanistic approach to the vast array of disparate information that makes up organic chemistry is the way in which a relatively small number of guiding principles can be used, not only to explain and interrelate existing facts but to forecast the outcome of changing the conditions under which already known reactions are carried out and to foretell the products that may be expected from new ones. It is the business of this chapter to outline some of these guiding principles and to show how they work. As it is the compounds of carbon with which we shall be dealing, something must first be said about the way in which carbon atoms can form bonds with other atoms, especially with other carbon atoms.

ATOMIC ORBITALS

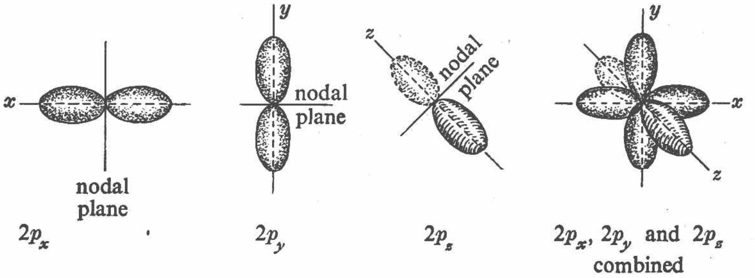
The carbon atom has, outside its nucleus, six electrons which, on the Bohr theory of atomic structure, were believed to be arranged in orbits at increasing distance from the nucleus. These orbits represented gradually increasing levels of energy, that of lowest energy, the 1*s*, accommodating two electrons, the next, the 2*s*, also accommodating two electrons, and the remaining two electrons of a carbon atom going into the 2*p* level, which is actually capable of accommodating a total of six electrons.

The Heisenberg indeterminacy principle and the wave-mechanical view of the electron have made us do away with anything so precisely defined as actual orbits, and instead we can now only quote the relative probabilities of finding an electron at various distances from the nucleus. The classical orbits have, therefore, been replaced by three-dimensional *orbitals*, which can be said to represent the shape and size of the space around the nucleus in which there is the greatest probability of finding a particular electron: they are, indeed, a sort of three-dimensional electronic contour. One limitation that theory imposes on such orbitals is that each may accommodate two electrons only, these electrons being distinguished from each other by having opposed ('paired') spins.

It can be shown from wave-mechanical calculations that the 1*s* orbital (corresponding to the classical K shell) is spherically symmetrical about the nucleus and that the 2*s* orbital is similarly spherically symmetrical but at a greater distance from the nucleus; there is a region between the two latter orbitals where the probability of finding an electron approaches zero (a *spherical nodal surface*):



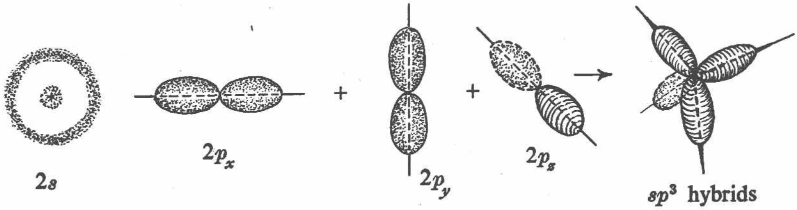
As yet, this marks no radical departure from the classical picture of orbits, but with the 2*p* level (the continuation of the L shell) a difference becomes apparent. Theory now requires the existence of *three* 2*p* orbitals, all of the same energy and shape, arranged mutually at right-angles along notional *x*, *y* and *z* axes and, therefore, designated as $2p_x$, $2p_y$ and $2p_z$, respectively. Further, these three 2*p* orbitals are found to be not spherically symmetrical, like the 1*s* and 2*s*, but 'dumb-bell' shaped with a plane, in which there is zero probability of finding an electron (*nodal plane*), passing through the nucleus (at right-angles to the *x*, *y* and *z* axes, respectively) and so separating the two halves of each dumb-bell:



We can thus designate the distribution of the six electrons of the carbon atom, in orbitals, as $1s^22s^2\ 2p_x^12p_y^1$; orbitals of equal energy (e.g., $2p_x$, $2p_y$, $2p_z$) accommodating a single electron, in turn, before any takes up a second one—the $2p_z$ orbital thus remains unoccupied. The $2s$ orbital takes up its full complement of two electrons before the $2p$ orbitals begin to be occupied, however, as it is at a slightly lower energy level. This, however, represents the *ground state* of the carbon atom in which only *two* unpaired electrons (in the $2p_x$ and $2p_y$ orbitals) are available for the formation of bonds with other atoms, i.e. at first sight carbon might appear to be only divalent. The carbon atom can, however, be raised to an *excited state* in which the $2s$ electrons are unpaired and one of them is promoted to the vacant $2p_z$ orbital, with the result that *four* unpaired electrons, i.e. $2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$ are now available in orbitals for the formation of bonds with other atoms, i.e. carbon is now exhibiting its normal and characteristic quadrivalency, the energy required for the $2s \rightarrow 2p$ promotion being more than compensated by that produced on forming the two extra bonds.

HYBRIDISATION

It does not, however, exert its quadrivalency by the direct use of these four orbitals to form three bonds of one type with the three $2p$ orbitals and one of a different nature with the $2s$ orbital. Calculation shows that by blending these four orbitals, a more stable arrangement results in which four, new, mutually indistinguishable (i.e. identical) orbitals are obtained, inclined to each other at 109° 28′, which will form stronger bonds; thus quantum mechanical calculations from first principles lead to the tetrahedral carbon atom long known empirically. These four new orbitals are designated as *sp^3 hybrids* and the process by which they are obtained as hybridisation:



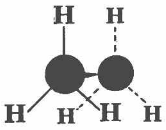
BONDING IN CARBON COMPOUNDS

Bond formation between two atoms is then envisaged as the progressive overlapping of the *atomic* orbitals of the two participating atoms, the greater the possible overlapping, the stronger the bond so formed. When the atoms have come sufficiently close together, it can be shown that their two atomic orbitals are replaced by two *molecular* orbitals, one having less energy and the other more than the sum of the energies of the two separate atomic orbitals. These two new molecular orbitals spread over both atoms and either may contain the two electrons. The molecular orbital of reduced energy is called the *bonding orbital* and constitutes a stable bond between the two atoms; the molecular orbital of increased energy is called the *anti-bonding orbital* and need not here be further considered in the formation of stable bonds between atoms.

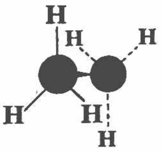
In the stable bond so formed the two bonding electrons tend to be concentrated along the line joining the nuclei of the two participating atoms, i.e. the molecular orbital is said to be *localised.* Such localised electrons are often referred to as σ electrons and the covalent bond so formed as a σ bond. Thus on combining with hydrogen, the four hybrid sp^3 atomic orbitals of carbon overlap with the $1s$ atomic orbitals of four hydrogen atoms to form four identical, strong, hybrid sp^3 or σ bonds, making angles of 109° 28′ with each other (the regular tetrahedral angle), in methane. A similar, exactly regular, tetrahedral structure will result with, for example, $\mathbf{CCl_4}$ but with, say, $\mathbf{CH_2Cl_2}$, though the arrangement will remain tetrahedral, it will depart very slightly from exact symmetry; the two large chlorine atoms will take up more room than hydrogen so that the **H—C—H** and **Cl—C—Cl** bond angles will differ slightly from 109° 28′ and from each other.

(i) Single bonds

The combination of two carbon atoms, for example in ethane, results from the overlap of two sp^3 atomic orbitals, one from each carbon atom, to form a strong σ bond between them. The carbon–carbon bond length in saturated compounds is found to be pretty constant—1·54 Å. We have not, however, defined a unique structure for ethane; the σ bond joining the two carbon atoms is symmetrical about a line joining the two nuclei, and, theoretically, an infinite variety of different structures is still possible, defined by the relative relationship of the hydrogens on one carbon to those on the other. The two extremes of the possible species are known as the *eclipsed* and *staggered* forms; they and the infinite variety of structures lying between them are known as *conformations* of the ethane molecule. Conformations are defined as different arrangements of the same group of atoms that can be converted into one another without the breaking of any bonds.



Eclipsed



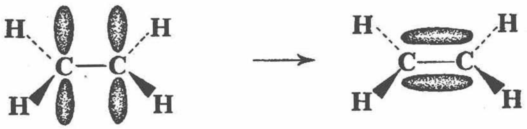
Staggered

The staggered conformation will obviously be the more stable of the two for the hydrogen atoms are as far apart as they can get and any interaction is thus at a minimum, whereas in the eclipsed conformation they are suffering the maximum of crowding. The long cherished principle of free rotation about a carbon–carbon single bond is not contravened, however, as calculation shows that the eclipsed and staggered conformations differ by only 3 kcal/mole in energy content and this is small enough to allow their ready interconversion through the agency of ordinary thermal motions at room temperature. That such crowding *can* lead to a real restriction of rotation about a carbon–carbon single bond has been confirmed by the isolation of two forms of $\mathbf{CHBr_2 \cdot CHBr_2}$, though admittedly only at low temperatures where collisions between molecules do not provide enough energy to effect the interconversion.

(ii) Double bonds

In the formation of a carbon–carbon double bond, Hückel has suggested a different mode of hybridisation of the 2*s* and 2*p* atomic orbitals than the sp^3 mode occurring in saturated compounds. Here hybridisation of the 2*s* and *two only* of the 2*p* orbitals can be shown to lead to the formation of *three* sp^2 hybrid orbitals, all lying in the same plane and inclined at 120° to each other (*plane trigonal orbitals*). In forming the molecule of ethylene, two of the sp^2 orbitals of each carbon atom are seen as overlapping with the 1*s* orbitals of two hydrogen atoms to form two strong σ C—H bonds, while the third sp^2 orbital of each carbon atom is used to form a strong σ C—C bond between them.

This then leaves, on each carbon atom, one unhybridised 2*p* atomic orbital at right angles to the plane containing the carbon and hydrogen atoms. These two 2*p* atomic orbitals are parallel to each other and can themselves overlap to form a molecular orbital, spreading over both carbon atoms and situated above and below the plane containing the two carbon and four hydrogen atoms (dotted lines indicate bonds to atoms lying *behind* the plane of the paper and ◄ to those lying in *front* of it):



The electrons occupying this new molecular orbital are known as π electrons and the orbital itself as a π orbital. The new π bond that is thus formed has the effect of drawing the carbon atoms closer together (C═C distance in ethylene is 1·34 Å compared with a C—C distance of 1·54 Å in ethane) but it is weaker than a σ bond and it is found that the energy of a carbon–carbon double bond, though more than that of a single bond is, indeed, less than twice as much. Thus the C—C bond energy in ethane is 83 kcal/mole, while that of C═C in ethylene is only 143 kcal/mole.

The overlap of the two 2*p* atomic orbitals, and hence the strength of the π bond, will clearly be at a maximum when the two carbon and four hydrogen atoms are exactly coplanar, for it is only in this position that the *p* atomic orbitals are exactly parallel to each other and thus capable of the maximum overlapping. Any disturbance of this coplanar state by twisting about the σ bond joining the two carbon atoms would lead to reduction in π overlapping and hence a decrease in the strength of the π bond: it will thus be resisted. A theoretical justification is thus provided for the long observed resistance to rotation about a carbon–carbon double bond. The distribution of the π electrons in two layers, above and below the plane of the molecule, and extending beyond the carbon–carbon bond axis means that a region of negative charge is effectively waiting there to welcome any electron-seeking reagents (e.g. oxidising agents), so that it comes as no surprise to realise that the characteristic reactions of a carbon–carbon double bond are predominantly with such reagents (*cf.* p. 124). Here the classical picture of a double bond has been superseded by a view in which the two bonds joining the carbon atoms, far from being identical, are believed to be different in nature, strength and position.