COMPREHENSIVE ORGANIC CHEMISTRY

The Synthesis and Reactions of Organic Compounds

SIR DEREK BARTON, F.R.S.

AND

W. DAVID OLLIS, F.R.S.

Volume 1 Stereochemistry, Hydrocarbons, Halo Compounds, Oxygen Compounds

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Edited by J. F. STODDART
UNIVERSITY OF SHEFFIELD

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ORGANIC CHEMISTRY

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Foreword

During more than a century, the development of organic chemistry has been associated with extensive documentation. Vast numbers of textbooks, monographs, and reviews have been published with the objective of summarizing and correlating the results obtained by many thousands of organic chemists working in academic and industrial research laboratories. However, out of this colossal literature there is but a relatively small number of textbooks and multi-volumed works which have become generally accepted as representing real steps forward in the presentation of our subject.

During the classical era of organic chemistry (1820–1940), textbooks which had a profound influence on the teaching of the subject included, for example, works by Armstrong (1874), van't Hoff (1875), Roscoe–Schorlemmer (1878), Richter (1888), Gattermann (1895), van't Hoff–Werner–Eiloart (1898), Meyer–Jacobson (1902), Schmidt–Rule (1926), Karrer (1928), Freudenberg (1933), Richter–Anschütz (1935), and Gilman (1938). These texts provide an opportunity to comment on the relationship between the history of organic chemistry and its associated publications. The *Treatise on Chemistry* by Roscoe and Schorlemmer consisted of three volumes (5343 pages) published in nine parts over the period 1878–1892: the major component was Volume III (6 parts, 3516 pages) which was devoted to organic chemistry. Another instructive example is the important work *Lehrbuch der Organischen Chemie*, produced by Victor Meyer and Paul Jacobson. The increase in size from the edition (1735 pages) published during 1902–1903 to the edition (5115 pages) published over the period 1913–1924 is striking.

Many have expressed concern about the problems of maintaining effective contact with the expanding literature of organic chemistry, but few have allowed themselves to become involved with attempted solutions. The decision to publish Comprehensive Organic Chemistry was not taken lightly. The absence of a work reflecting the current rapid development of modern organic chemistry has been lamented by many eminent chemists, including the late Sir Robert Robinson (1886–1975) who played an important role in the initiation of this project shortly before his death. Comprehensive Organic Chemistry was conceived, designed, and produced in order to meet this deficiency. We realised that the current rate of growth of organic chemistry demanded speedy publication and, furthermore, that its interaction with other subjects including biochemistry, inorganic chemistry, molecular biology, medicinal chemistry, and pharmacology required the collaboration of many authors. The selection of topics to be included in order to justify the work as being comprehensive has not been easy. We recognize that some areas of organic chemistry have not been given the detailed treatment which can be justified, but we have done our best to meet the expectations of the majority of readers. In particular, we have not made a special section for Theoretical Organic Chemistry. This is not because of any lack of appreciation on our part of the importance of Theory. It is because a correct treatment of Theory cannot be made comprehensible in an abbreviated form. It is also because Theory changes with time more rapidly than the facts of the subject. Theory is better treated in our view in specialist monographs. The same arguments apply equally to the fundamental subject of Stereochemistry. Any comments regarding errors and omissions will be appreciated so that they can be dealt with in future editions.

The contents of each volume have been brought together so as to reflect what are judged to be the truly important facets of modern organic chemistry. The information is presented in a concise and logical manner with mechanistic organic chemistry being adopted to provide a constant and correlative theme. The dominating intention of the Editorial Board has been to ensure the publication of a contribution to the literature of organic chemistry which will be genuinely useful and stimulating. Emphasis has therefore been given throughout to the properties and reactions of all the important classes of organic compounds, including the remarkable array of different compounds prepared by synthesis as well as natural products created by biosynthesis. Of course, the study of natural products provided the original foundation stones on which modern synthetic organic chemistry now firmly stands.

As a major presentation of modern organic chemistry, Comprehensive Organic Chemistry will be doubly useful because we have provided, in a separate volume, an extensive index. Not only have the contents of the work been indexed in the ordinary way, but we have also added a substantial number of additional references from the original literature. These do not appear in the text itself. Thus, the reader who wishes to obtain additional information about reactions and reagents mentioned in the text will quickly be able to consult the original literature. The Index volume has been prepared by a team from Pergamon Press.

Our debt to the Authors and to the Volume Editors is considerable. We are very grateful to all our colleagues for the efficient way in which they have tried to meet the challenges (and the deadlines!) which have been presented to them. We hope that the Authors have enjoyed their association with this venture. In a lighter vein, we also trust that their feelings are different from the statement 'this task put system into my soul but not much money into my purse' attributed to Henry Edward Armstrong (1848–1937) after he had written his *Introduction to Organic Chemistry* in 1874.

We are delighted to acknowledge the masterly way in which Robert Maxwell, the Publisher, and the staff at Pergamon Press have supported the Volume Editors and the Authors in our endeavour to produce a work which correctly portrays the relevance and achievements of organic chemists and their contributions to knowledge by research.

D. H. R. BARTON
Chairman

W. D. OLLIS
Deputy Chairman

Preface to Volume 1

Chemistry assumes a ubiquitous status amongst the natural sciences. Not only does it seek, through the investigation of molecular structure and reaction mechanism, to answer questions posed by physical and chemical phenomena, but it also provides, through the medium of synthesis, a challenge to the innovative spirit and creative genius of man. It should always be a science and is sometimes an art. Often, the curiosity of the chemist in his quest to understand natural phenomena is surpassed only by his desire to emulate the chemical works of Nature. Nowhere across the wide spectrum of chemical disciplines has so much been accomplished by the practitioners in such a relatively short time span as within the domain — whatever that might be — of organic chemistry. A consideration in this volume to a range of topics which leads the reader through a somewhat arbitrary maze from hydrocarbons to quinones must, of necessity, pay some allegiance to the past glories of the subject. However, earlier achievements in no way overshadow more recent triumphs by organic chemists in manipulating molecular events involving the more mundane functional groups which will always provide the staple diet for chemical reactivity in organic compounds. Moreover, the last three decades have witnessed a technological revolution in the tooling of chemistry with the widespread introduction of, for example, chromatography and spectroscopy in their many and varied forms. In addition, interpretative and predictive powers have been increased enormously with the advent of modern high-speed electronic computers.

Stereochemistry has always provided a focal point within organic chemistry. It seemed not only reasonable but logical to allow recent conceptual developments in stereochemistry, coupled with the inevitable proliferation in nomenclature surrounding these advances, to provide a short introduction to this volume in Part 1. Aside from their very considerable commercial importance, hydrocarbons, be they saturated or unsaturated, aliphatic or aromatic, have captured the imagination of theoreticians and experimentalists alike in recent years. Chapters 1–6 in Part 2 illustrate how the interplay of theory and practice has provided a much needed fillip to progress in this area. A discussion of reactive intermediates in Chapters 7 and 8 of Part 2 provides a useful bridge to the remainder of the volume. The early pre-eminence of carbocations has now given way to the recognition of the synthetic utility of other reactive species — particularly carbanions, but also radicals, carbenes, and arynes. Part 3 is given over entirely to halo compounds—a situation which reflects their importance from both academic and industrial viewpoints. In Part 4, alcohols, phenols, ethers, and peroxides are discussed in six separate chapters. Here, the importance of the oxygen atom in naturally occurring compounds is providing the organic chemist with the incentive, not only to understand, but also to mimic, *e.g.* the dramatic developments around crown ethers in a decade. Finally, of course, the carbonyl group is the centrepiece of organic chemistry. Chapters 1–5 in Part 5 must be viewed not only as individual contributions but also as introductions to much of the chemistry to be discussed in subsequent volumes of this work.

Circumstances eventually dictated that I was joined by no less than eighteen contributors in this mission to produce Volume 1 of Comprehensive Organic Chemistry. In so far as we are judged to have been successful in producing an interesting and readable account, the credit belongs to the authors. In so far as we are judged to have erred in our task through omissions or worse, the responsibility is mine. Whatever the judgement might be, I thank all those who have helped me to collate the material for this volume.

Sheffield J. F. STODDART

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PART 1

NOMENCLATURE AND STEREOCHEMISTRY

1

Introduction and Stereochemistry

J. F. STODDART
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1.1 SCOPE

There is little doubt that the emergence of stereochemical concepts over more than a century or so has been reflected intimately in the development of organic chemistry as a scientific discipline. Although stereochemistry is as old as organic chemistry itself, it provides, nonetheless, a suitable introductory theme to a treatise such as this devoted to modern organic chemistry. In more recent times, the advent of conformational analysis as a result of the pioneering paper[1] published in 1950 by Barton heralded a new era of growth in organic chemistry. During almost three decades now, conformational ideas in particular and stereochemical concepts in general have fostered major advances in (i) our approach to structural elucidations, (ii) our knowledge of reaction mechanisms, and (iii) our development of new synthetic methods. In this brief introductory section, the more recent conceptual advances in stereochemistry will be brought under scrutiny since they impinge most directly upon structural aspects. Thereafter, some contemporary aspects of dynamic stereochemistry will be highlighted very briefly as a forerunner to the remainder of the work. Inevitably, a short introduction must of necessity ignore many important stereochemical topics in specialized fields. Thus, at the outset, we refer the reader to a selection of numerous[2–19] textbooks, monographs, and reviews on various aspects of stereochemistry in the hope that he might find there what he will not find here in this introductory chapter.

1.2 SYMMETRY AND CHIRALITY

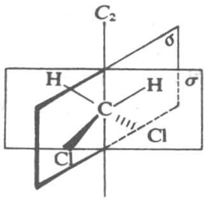
The symmetry properties of geometrical figures are characterized by symmetry operations which in turn define the symmetry elements (see Table 1) present in the particular simplex under examination.[6,20–24] If molecules can be assumed[20–28]—for the present at least—to generate geometrical figures, then it is possible to discuss their molecular structures in terms of their symmetry. In the first instance, it will be useful to restrict this discussion to (i) molecules which have defined structures by virtue of their rigidity and (ii) flexible molecules in which structures are defined as a consequence of selecting particular conformations. Basically, there are two kinds of symmetry elements — namely (i) axes of rotation and (ii) rotation-reflection axes — which a molecule can display through inspection of symmetry operations. Molecules that witness superimposition of structures upon their original structures as a consequence of rotation by $2\pi/n$ radians about an axis possess a so-called C_n axis (*n.b.* symmetry element descriptors are usually italicized). For example, dichloromethane (**1**) contains a C_2 axis and chloroform (**2**), a C_3 axis. All molecules, of course, contain an infinite number of trivial C_1 axes and, for this reason, they are often referred to collectively as the identity element, *E*. Molecules whose structures are indistinguishable from the original structures only after rotation by $2\pi/n$ radians followed by reflection in a plane perpendicular to the chosen axis of rotation possess a so-called S_n axis. When $n=1$, the trivial S_1 axis corresponds to a plane of symmetry (σ) perpendicular to the rotation axis. A σ plane is most easily recognized as a mirror plane which bisects the molecule such that the ligands on one side of the plane are reflected exactly upon those on the other side. For example, dichloromethane (**1**) possesses two, and chloroform (**2**) three, σ planes. When $n=2$, the S_2 axis corresponds to a centre of inversion (i) which demands that all ligands in the molecule are capable of inversion through a centre, *i.e.* any two particular ligands lie on a line going through the centre of the molecule such that the ligands are equidistant from the centre. The particular conformation (**3**) of *meso*-1,2-difluoro-1,2-dichloroethane contains a centre of symmetry. Higher order S_n (n must be an

TABLE 1

Symmetry Elements and Symmetry Operations

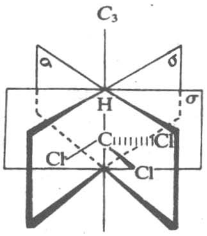
Symmetry elements	*Symmetry operations*
C_n (Axis of symmetry)[a]	Rotation about an axis through $2\pi/n$ radians
σ (Plane of symmetry)[b]	Reflection in a plane
i (Centre of symmetry)[c]	Inversion through a centre
S_n (Rotation-reflection axis of symmetry)	Rotation about an axis through $2\pi/n$ radians followed by reflection in a plane perpendicular to the axis

[a] All molecules have an infinite number of trivial axes which can be referred to collectively as the identity element, *E*. [b] A plane of symmetry corresponds to a S_1 symmetry element. [c] A centre of symmetry corresponds to a S_2 symmetry element.



C_{2v}

(**1**)



C_{3v}

(**2**)