PUBLISHER'S ANNOUNCEMENT

COMPREHENSIVE ORGANIC CHEMISTRY

The Synthesis and Reactions of Organic Compounds

Chairman of the Editorial Board: Sir Derek Barton, FRS
Deputy Chairman: W. David Ollis, FRS

Reviewed by Lord Todd, PRS, Cambridge:

Volume 1 (Stereochemistry, Hydrocarbons, Halo Compounds, Oxygen Compounds; edited by J. F. Stoddart, Sheffield)

When I was a young doctoral research worker in organic chemistry—and that was nearly fifty years ago—I, like all practising organic chemists of the day, had quite a problem on my hands. Ours was a large and growing subject with a high factual content and a rather primitive theoretical base. As a result it was difficult to systematise or abbreviate by generalisation. To master it and to use it required real familiarity with the various compound types and with reactions and methods. To this end the practising organic chemist needed not just a simple textbook (of which quite a few existed) but something a good deal more comprehensive which he could have on his own bookshelf. He needed a source book from which he could quickly get basic information on the behaviour and reactions of organic compounds and in which he could browse and increase not just his factual knowledge but also his chemical insight. But no single work existed to fill this need. Of course there were vast encyclopaedic works like Beilstein and many individual monographs but no single comprehensive work on a reasonable scale. And so we fell back to using two books: (a) a general text, usually Karrer, Lehrbuch der Organischen Chemie, and (b) a book on methods like Houben-Weyl, Methoden der Organischen Chemie or, if we were hard up, the shorter and cheaper Meyer, Analyse und Konstitutionsermittlung Organischer Verbindungen. During the fifty years since then the situation has not improved. Certainly we have extensive and detailed works like Rodd's Chemistry of Carbon Compounds which is an invaluable source of factual information, but is so large that it can be regarded as essentially a library work of reference rather than one which individuals keep on their own shelves and read regularly. This is perhaps the inevitable consequence of the staggering growth of organic chemistry during the past half-century; this growth no doubt accounts in part for the enormous expansion of Houben-Weyl. The 3rd Edition of that work, which ran to four substantial volumes, although immensely valuable was close to the limit in size for the individual reader; but the new 4th Edition is so enormous that it is quite beyond the pocket of the individual (and perhaps even of some libraries) and has lost some of its original character. Both of these reference works incidentally have a major defect inherent in their slow rate of publication: earlier volumes of each are not infrequently out-of-date before some later ones appear.

There remains therefore a gap in the literature of organic chemistry which is even more serious today than it was in the past. For this reason one must applaud the task which the editors and publishers of *Comprehensive Organic Chemistry* have set themselves in trying to fill this gap and by undertaking to publish the entire work on a mid-1977

i

coverage deadline during the first 3 months of next year. If this is achieved it will be a spectacular technical achievement. The intention is to issue the whole work in 6 volumes of around 1200 pages each and this article is specifically concerned with Volume 1. My comments on the work as a whole rest therefore on the assumption that Volume 1 is typical of them all; from its layout, its list of contents, and my perusal of the individual chapters this would seem a not unreasonable assumption to make.

I confess that I have been much impressed by Volume 1, largely, of course, because it meets my criteria for a personal reference text for the practising organic chemist. The coverage is on orthodox lines and comprises aliphatic and alicyclic hydrocarbons, arenes, halo-compounds, alcohols, phenols, carbonyl compounds and ethers. It contains the essential factual matter on individual groups of compounds but employs what I would call the Houben-Weyl approach to methods and reactions modernised on the basis of mechanistic ideas and it gives copious and, on the whole, well-chosen references to more detailed sources of information. Volume 1 includes, in addition to chapters on individual compound groups, others on theoretical topics such as stereochemistry and aromaticity which are dealt with in a thoroughly up-to-date manner. On first approaching it I felt the opening chapter on stereochemistry was curiously located, but on further reflection I think that this may be rather unfair. This book is in no sense an introductory text on organic chemistry for undergraduates and to give a comprehensive treatment of modern stereochemistry as a kind of introduction may well be desirable. One criticism which I would make is that the balance is not in my opinion always perfect; for instance I find it hard to believe that quinones warrant no more than 12 pages (and these mainly on benzoquinones) whereas 40 pages are devoted to annulenes. Of course, there are always differences of opinion on the relative importance of individual topics just as there are differences in style of presentation by individual authors, but although there is, here and there, a little unevenness in style, the editors have done such an excellent job in controlling general treatment of topics that any unevenness is not obtrusive. Some other minor criticisms could be made but they would not affect my view that this promises to be a real contribution to the literature of organic chemistry. It is not in competition with the encyclopaedic works of reference which we have but is a comprehensive first source to which the chemist can turn for information and in which he can browse for inspiration. If the other five volumes adequately match the first then Comprehensive Organic Chemistry will fill a long-felt need and should be a success.

Reviewed by G. Ourisson, Strasbourg:

Volume 2 (Nitrogen Compounds, Carboxylic Acids, Phosphorus Compounds; edited by I. O. Sutherland, *Liverpool*).

The present volume is probably typical of the complete series. It is "medium-sized", has a very wide coverage, relies heavily on existing reviews and books, and is definitely up-to-date.

Its medium size is in line with the British tradition of Rodd's Chemistry of Carbon Compounds, and runs opposite to the German ideal of the exhaustive Handbuch, as well as to the American one of the specialised monograph. This intermediate character makes it certainly easier for the reader to scan for the essential points in a domain new to him, at a level deeper than that made accessible by textbooks, and with the provision of key references to the primary literature, and to specialised reviews. In most chapters, the bibliography contains the essential recent books, mentions extensively chemical Reviews or Organic Reactions, Houben-Weyl or Patai, in brief does not make-believe that the author has read all the primary references quoted, and only primary literature. This is of course all to the advantage of the reader, who will certainly want to begin his reading by such reviews. Let us note at this stage that the latest references mentioned are from 1976 to 1977, and that in most chapters, the patent literature is practically ignored. (In this

respect recourse to Houben-Weyl would provide often a completely different picture.)

The coverage is very wide. In this volume of some 1300 pages, eighteen chapters describe classical functions (amines of diverse types, nitriles, esters, etc.), as well as more special ones (e.g. nitrones, nitroxides, phosphazenes...). In each case, a classical plan is followed: preparations and reactions are covered in turn, with usually only a very brief mention of the physical properties and of structural aspects. In general, mechanisms are hardly discussed, except when they have a direct bearing on the preparative aspects.

The various chapters are treated in a similar manner, but not at the same level of detail. For instance, the chapter on imines, nitrones, nitriles and isocyanides is exceptionally thorough (nearly 200 pages, 650 references), whereas aromatic amines, to which certainly much more work has been devoted, are covered in 50 pages, with some 200 references. In fact, I believe this is probably once again favourable for the reader, who gets most of what he needs most: help with the less accessible information.

It is extremely difficult to gauge such a large book by scanning it or by reading parts of it; it is also certainly not meant to be read through. An impression can however be gained easily in the few hours I have spent probing, reading, comparing. It is definitely very favourable. I am convinced that the emphasis is right; that the book, and certainly the series, will find daily use in most organic chemical laboratories, for quite a long time. Of course, it will be most useful only to those who have access to a well-stocked library, but it must be pointed out that, even from that point of view, the reader has been favoured; at least the Anglo-Saxon reader, as the bulk of the references are to American and British articles, with only occassional intrusion of German (few), Japanese (very few), Swiss, Russian or French papers (rare).

Reviewed by G. Stork, New York:

Volume 3 (Sulphur, Selenium, Silicon, Boron, Organometallic Compounds; edited by D. Neville Jones, Sheffield).

This volume starts with the organic chemistry of sulfur, from thiols to thiocarbonyl compounds, via sulfinylamines and thiosulfonates, which it covers in some 480 pages with almost 2000 references. This is followed by organoselenium and tellurium compounds (46 pages, 279 references), organic compounds of silicon (145 pages, 633 references), and of boron (251 pages, 842 references). We then encounter organometallic compounds of groups I, II, III and IV, and of antimony and bismuth (175 pages, 777 references). The volume closes with organic compounds of the transition metals (196 pages, 179 references). This is a breath-taking accomplishment for many reasons.

The sixteen writers of Volume 3 are not only possessed of what appears to be an encyclopaedic knowledge of their subject. They are, without exception, deeply involved in research in the field they cover and are, indeed, immediately recognized as among the foremost contributors to its recent developments. That such a galaxy of authors could be assembled, that it could bring such a project to fruition on schedule, that it could maintain some unity of presentation and a largely successful concern for relevance to synthetic organic chemists, is an extraordinary achievement. The Chairman of the Editorial Board, Professor D. H. R. Barton, his Deputy, Professor W. D. Ollis, as well as the Editor of this particular volume, Dr. D. N. Jones, have our admiration and deserve our thanks.

Judging by this volume, which I take to be representative of the whole work, it is clear that every serious chemistry library will have to acquire this set.

This being said, I will now comment more specifically on the material in Volume 3 if only to show that my recommendation is based on actual reading of this volume. I will start with some minor criticism. The book is completely oriented toward leading the practising chemist to recent, operationally useful, literature references on a particular reaction. In this it has succeeded, and this is obviously a major strength, but a corollary is that this is not a book which can be consulted to get a sense of the history or intellectual

background of a method. To give but three examples, the rearrangement of penicillin sulfoxide to cephalosporins is discussed without mention of the seminal work of Morin and the Lilly Laboratories; the alkylation of carbanions to thiolsulfonates is discussed with no references to Smiles; the contribution of Tsuji in the use of palladium complexes to form carbon-carbon bonds is mentioned, but there is no suggestion of its pioneering nature. This is not so much a criticism as a reminder to the users of the book.

The book is not especially concerned with mechanism and its usefulness is, therefore, not really affected by the (very few) questionable statements one inevitably encounters, such as comments on the addition of benzoylsulfene (p. 419), on the reason for the formation of allylic alcohols from selenoxides (compare p. 494 with p. 501), on what is, perhaps unfortunately, termed 1,3-additions to carbonyl compounds (p. 981), on the nature of Zn enolates (p. 992). Misleading statements are, as one would expect, extremely rare, one such concerning the suggested generality of the addition of Grignard reagents to imines.

There are some surprising omissions, inter alia, no explicit mention of the opening of epoxides with ethynyl alanes, the reduction of nitriles to aldehydes with dissobutyl-aluminum hydride, the use of β -heterosubstituted lithium and magnesium reagents, the conjugate reduction of α,β -unsaturated carbonyl compounds with tin hydrides, oxidative and protic destannylation. Some qualitative mechanistic statements would sometimes have helped, e.g. formation of aziridines from oximes (p. 978). On the other hand, the rather esoteric and somewhat limited opening of epoxides with HCo(CO)₄ is mentioned twice with equations (p. 1149 and 1236).

The editors have obviously struggled to minimize differences in style and presentation. Even then, two chapters (organic compounds of group I and II metals) do not quite come up to the standards of the others. They will probably not add much to the fund of knowledge of the average synthetic chemist. This is perhaps understandable since these areas are covered quite extensively in widely available monographs. On the other hand, the chapter by Ian Fleming on organosilicon chemistry is superb in every respect. I recommend its reading not only to the aficionados, but to anyone contemplating writing a book or a chapter. This is not meant to slight other chapters or their writers: the chapter by D. St. C. Black, J. J. Swan and W. R. Jackson represents a signal accomplishment in organising enormous amounts of material, as do the chapters by A. Pelter and K. Smith on boron compounds, to mention only two among several.

In conclusion, with the very few exceptions noted above, every important reaction (that I knew about) is covered here: from thio Claisen rearrangement to the use of Burgess' salt for dehydration, and of methylene thiosulfoxides as carbanion equivalents. Many more transformations that one would like to be familiar with are now presented in convenient and completely up-to-date fashion.

Comprehensive Organic Chemistry will be an all but essential companion in synthetic explorations.

Reviewed by R. U. Lemieux, FRS, Edmonton,

Volume 4 (Heterocyclic Compounds; edited by P. G. Sammes, London).

This fine contribution well surveys the exceedingly complex and ramified field of heterocyclic chemistry while remaining pleasantly readable. The focus is on the unsaturated heterocyclic ring systems with concentration on synthesis, chemical properties, reactions and mechanisms of reaction. These fundamental aspects are discussed and interpreted in uniformly competent, modern and critical modes. Some insights are provided to the great significance of heterocyclic chemistry to such areas as chemotherapy, photography, agriculture and dyestuffs. The quality of presentation and documentation in these latter regards is highly variable. Such a shortcoming was inevitable. The work is already of heroic proportions.

The volume is divided into five parts: the azines (7 sections, 272 pages), the azoles (6 sections, 329 pages), oxygen systems (6 sections, 179 pages), sulphur and other heteroatom systems (3 sections, 168 pages), and mixed heteroatom systems (4 sections, 267 pages). All sections are introduced with a table of contents and thereby usefully self-indexed. The work by 22 authors and edited by P. G. Sammes contains near 4000 references to, or to parts of, the near 500 review articles. The vast literature which has appeared in the more recent years appears well covered. The texts are assisted by well chosen and presented formulae, diagrams and tables.

The volume will serve as a sound base and guide to a vast field of chemistry which is harvested by virtually all chemists. It will undoubtedly find extensive use in both industrial and academic libraries. Consultants and research chemists should consider it for office usage—the retrieval in a coherent fashion of a wide range of important factual knowledge has been made reliably convenient.

Reviewed by W. S. Johnson, Stanford:

Volume 5 (Biological Compounds; edited by E. Haslam, Sheffield).

As stated in the Introduction, the contents of this volume have "been assembled not so much to be fully comprehensive as to be comprehensible, to reflect what are judged to be the truly important facets of the present state of biological organic chemistry". I am pleased to say that these aims have been achieved admirably. To a synthetic organic chemist the chapters are not only comprehensible but interesting and highly informative. As is seen by the comments below, which include some of those (paraphrased by me) of a number of my colleagues who kindly examined selected sections falling within their own specialty, the book on the whole does indeed cover the aforementioned important facets in a truly scholarly manner. The exceptions noted represent a rather trivial part of the whole.

Part 21 Biological Chemistry: An Introduction by E. Haslam. This is an eloquent statement that hits the center of the bullseye. I could have wished only that the term "biomimetic" had been adopted in place of the older more awkward expressions "biogenetic like" or "biogenetic type"—a trivial matter indeed.

Part 22 Nucleic Acids, by G. M. Blackburn; Nucleosides, by R. T. Walker; Nucleotides and Related Organic Phosphates, by D. W. Hutchinson; Nucleic Acids: Structure and Function, by G. M. Blackburn. Reviewed with G. W. Daub. Besides providing the organic chemist with a good exposure to fundamentals of the field, new developments and some of the more sophisticated aspects are treated to promote understanding at a higher level. The coverage includes work up through 1977.

Part 23 Proteins: Amino-Acids and Peptides: Introduction, by E. Haslam; Amino-Acids Found in Proteins, by P. M. Hardy; Peptides and the Primary Structure of Proteins, by D. T. Elmore; Naturally Occurring Low Molecular Weight Peptides, by W. Bycroft; B-Lactam Antibiotics, by G. Lowe; Peptide Synthesis, by R. C. Sheppard; Conformations of Polypeptides, by G. C. Barrett; and Part 24 Proteins: Enzyme Catalysis and Functional Proteins: Enzyme Catalysis, by A. J. Kirby; Chemistry of Other Proteins, by D. T. Elmore; Coenzymes, by H. C. S. Wood; Vitamin B₁₂, by B. T. Golding. Reviewed with D. H. Rich. Entire monographs have been devoted to each of the major topics covered in these sections; hence it has been possible to give only an abbreviated treatment. Nevertheless the exposition is eminently suitable for introducing the subject matter to chemists lacking biochemical backgrounds. A few minor criticisms are noted. The chemistry of bleomycin could well have been covered a little more thoroughly since this antitumor compound is an important therapeutic agent. A rather uncritical view of the state-of-the-art of peptide synthesis is projected, in particular some delineation of difficulties encountered, with side reactions (including references), would have been welcome. A number of important literature citations have been omitted, e.g. in connection with the reaction of $89 \rightarrow 90$ (equation 9) on page 345.

Part 25 Lipid Chemistry and Biochemistry: Fatty Acids, by F. D. Gunstone; Lipids, by F. D. Gunstone; Membranes and Lipoproteins, by P. F. Knowles. Reviewed with H. M. McConnell. This is a first-class treatment of the subject. Even from the point of view of the biochemist or biophysicist its weaknesses are principally matters of omission. It is perhaps worth noting that these latter scientists would regard cholesterol (as well as natural derivatives of fatty acids) as a lipid. One also might question the implication that the majority of proteins occurring in membranes are enzymes. Be that as it may, this is a splendid exposition of the subject for a chemical audience.

Part 26 Carbohydrate Chemistry: Monosaccharide Chemistry, by L. Hough and A. C. Richardson; Oligosaccharide Chemistry, by L. Hough and A. C. Richardson; Polysaccharides, by J. F. Kennedy and C. A. White; Polysaccharides: Conformational Properties in Solution, by D. A. Rees. Reviewed with G. A. Crosby. In addition to a clear and concise treatment of monosaccharide chemistry, an interesting section on sugars containing heteroatoms is included, i.e. amino- and halosugars. A timely addition would have been some illustration of the use of sugars as chiral synthons and templates for asymmetric synthesis of natural products. The four-page section on oligosaccharide chemistry is probably too brief as it barely touches on the subject. The polysaccharide section is especially good and up-to-date (48% of the references ≥ 1970). More attention could have been given to reactions of polysaccharides. The section on conformation seems to be very good and up-to-date (95% of the references ≥ 1970).

Part 27 Synthesis of Organic Macromolecules and their Uses in Organic Chemistry, by P. Hodge. Reviewed with G. A. Crosby. This section is well-written, easy to comprehend, accurate and interesting. However, the coverage is too brief (30 pages) and some important topics are almost ignored. For example, the treatment of the synthesis and properties of macromolecules covers only 19 pages as compared with 40 in Roberts and Caserio's Basic Principles of Organic Chemistry (2nd ed.). In the section on applications, the treatment of cross-linked polymers is excellent, but there are some other important subjects which could have been covered, including reactions of soluble polymers and selected industrial applications.

Part 28 Bio-Organic Chemistry: Biosynthesis, by R. Thomas; Photosynthesis, Nitrogen Fixation and Intermediary Metabolism, by E. Haslam. Part 29 Biosynthetic Pathways from Acetate: Polyketide Biosynthesis, by J. D. Bu'Lock; Terpenoid Biosynthesis, by J. R. Hanson; Carotenoid Biosynthesis and Vitamin A, by G. Britton. Part 30 Biosynthesis—A General Survey: Alkaloid Biosynthesis, by R. B. Herbert; Porphyrin, Chlorophyll, and Corrin Biosynthesis, by M. Akhtar and P. M. Jordan; Shikimic Acid Metabolites, by E. Haslam. Reviewed with R. J. Parry. Aside from a slight organizational problem, i.e. all of Part 29 seemingly belongs under the heading of Part 30, these chapters are extremely well-written. The material is quite up-to-date through 1975, and the important aspects of the field have been covered in a scholarly manner. In seeking perfection one can find only minor areas for improvement, i.e. Chart 2 on page 919 and Chart 4 on page 925, particularly the former, are difficult to interpret; in Scheme 7, p. 1053, it is incorrectly implied that the mechanism of reduction of the pyridine ring of nicotinic acid has been established; the representation of the adduct of thiamine pyrophosphate and α -ketoglutaric acid (in Schemes 16, 33 and 34, pp. 1184, 1200 and 1201) as a naked carbonion (having acidic hydrogens) is not very satisfactory.

In conclusion, Haslam and his collaborating coauthors are to be congratulated for producing such a magnificent segment of the Barton-Ollis magnum opus which indeed represents a major contribution to scholars of organic chemistry.

To be reviewed by J. E. Baldwin, FRS, Oxford:

Volume 6 (Author, Formula, Subject, Reagent, Reaction Indexes; edited by C. J. Drayton, Oxford).

This review will be published in a subsequent issue.

Comprehensive Organic Chemistry is published in six volumes (approximately 8000 pages) by Pergamon Press, Oxford and New York. Price US \$1250 (£625).