

pair of FMNH· radicals¹⁴ at the cross-over point in terminal oxidation in biochemical systems.¹⁵

A number of significant possibilities stem from our preparation of the radical (1). The factors stabilizing free radicals and the reactivity of free radicals may now be examined with simpler radicals than heretofore possible. Pyridinyl radicals represent a new class of chemical reagents for which there is little direct analogy. The procedures described in this communication are clearly applicable to a whole variety of quaternary salts, including those derived from heterocyclic rings, phosphines, arsines, sulfides, etc. Experiments designed to test some of these implications are now underway.

(14) Q. H. Gibson, V. Massey and N. M. Atherton, *Biochem. J.*, **85**, 369 (1962).

(15) E. M. Kosower, "Molecular Biochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 226.

The physical properties of such stable free radicals as well as the theoretical problems posed by their stability will also be of much interest. All of these matters will be reported in full publications at a later time.

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BOOK REVIEWS

The Interpretation of NMR Spectra. By KENNETH B. WIBERG, Yale University, and BERNARD J. NIST, University of Washington. W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1962. vii + 593 pp. 19 × 27 cm. Price, \$25.00.

With the wide-spread availability of spectrometers, the interpretation of high-resolution nuclear magnetic resonance spectra has become the concern of a large number of organic chemists. The authors of the present book use the word "interpretation" in a rather narrow sense. Thus, the extremely important problem of obtaining chemical and structural information is completely omitted. What is dealt with is the problem of obtaining chemical shifts and especially coupling constants from a spectrum, with the important proviso that the spectrum, or a part of it, must belong to one of the categories found in this volume.

The book is essentially a compilation of theoretical spectra, calculated and printed with the aid of a computer, for systems involving up to five spins and with selected values of chemical shifts and coupling constants.

The spectra are presented in two ways: (a) tables of line positions and intensities, and (b) a visual representation where crosses are used to indicate band positions and intensities, with a fixed width for each line. The representation is effective if not aesthetically pleasing.

The greater part of the book is concerned with the following important spectra: ABX and ABC, A₂X₂ and A₂B₂ (including cases with two different AB or AX coupling constants). The well known and relatively simple AB, AB₂, AB₃, AB₄ and A₂B₃ cases take relatively few pages.

The ABC system is split up into a number of different sections, depending on the relative chemical shifts of A, B and C. With ν_A and ν_B at -3 and $+3$, respectively, results are given for (A), $\nu_C = +3$; (B), $\nu_C = +4$; (C), $\nu_C = +5$ and (D), $\nu_C = +7$. One other case (E) has $\nu_A = -6$, $\nu_B = 0$ and $\nu_C = +6$. Altogether about five hundred spectra are given, with different combinations of coupling constants, including negative ones, in the range of 1 to 18.

There is about the same number of A₂B₂ spectra, all with $\nu_{AB} = 6$, and with coupling constants similar to those mentioned above.

Each set of spectra has a short, but invariably excellent introduction on its particular characteristics.

While this is undoubtedly a valuable book, a number of important criticisms must be made. One is the remarkable absence of cases with one coupling constant equal to zero in the lengthy list of ABC and A₂B₂ spectra. The only cases where zero J 's are given are completely trivial ones such as in the AB_n systems. A second is the duplication which occurs in the AB₂ spectra and the ABC spectra (case A) with $J_{AB} = J_{AC}$. Indeed, it would appear that little effort has been made to weed out unnecessary spectra. For example, many of the A₂B₂ spectra with large J_{AB} 's are of the uninformative "skyscraper" type. A book of half the size would have been as useful and much cheaper.

In spite of the mass of information about line positions and intensities published with each spectrum, the captions to the spectra do not mention chemical shifts explicitly. This is a most annoying feature, especially in the ABC spectra. One either has to remember the chemical shifts for cases A to E mentioned above or continuously refer back to a difficultly-found table in the text.

Although this book was published rapidly, it does not include any reference to recent work on the analysis of spectra, particularly the use of computers to obtain converging solutions from a set of experimental parameters.

In spite of its shortcomings, the book should prove useful as an aid in the analysis of n.m.r. spectra.

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Ergebnisse der Alkaloid-Chemie bis 1960 unter besonderer Berücksichtigung der Fortschritte seit 1950. By PROFESSOR DR. HANS-GÜNTHER BOIT, Humboldt University, Berlin. Akademie-Verlag G.m.b.H., Leipziger Strasse 3–4, Berlin W 8, Germany. 1961. x + 1082 pp. + unbound supplement of viii pp. 18 × 24.5 cm. Price, DM 140.

From the title of this volume and that of a previous one, Fortschritte der Alkaloid-Chemie seit 1933 (1950), one may deduce that Professor Boit has set himself the valuable but unenviable task of publishing a monograph surveying developments in the chemistry of alkaloids every ten years. At least one implication in this initial deduction is not quite correct. This new book does not simply take the previous one as a point of departure; it is, rather, a complete and self-contained review of the state of alkaloid chemistry to the end of 1960. The emphasis is upon those elucidations of structure, those transformations, those alkaloids newly discovered since 1950. But ample space is allotted to that earlier material necessary for a reference work, so that the discussion of any particular family of substances is complete even if the central members of that family have been known for a long time.

The volume is divided into 59 chapters and two supplements, with three indices. The chapters cover the alkaloids divided into families in the traditional way by structural similarity. Each chapter contains: (1) a brief introduction to the family by discussion of salient features of the principal members; (2) a substantial table listing all known members of the family, with melting point, optical rotation, melting points of selected derivatives, all known plant sources, and recent references for each entry as appropriate; (3) the discussion, substance by substance, of the chemistry new since 1950. The material covered is diverse: new transformations of well known substances, reports, however incomplete, of new alkaloids, and full presentations of degradative and synthetic studies leading to structures and solutions to stereochemical problems. For example, the complex chain of degradation and synthesis of fragments that led to the structures of cevine and its congeners is allotted more than seven pages. The two supplements, one bound with the volume and one inserted afterward, are for the purpose of making coverage of the literature as complete up to the publishing date as possible—they cover those developments in 1960 and a few in 1961 that are omitted from the main body of the text, and the larger supplement has references to the pages elsewhere in the book where the same substance is discussed. The three indices index the contents under the divisions plants and plant products, animals and animal products, and chemical compounds. It is unfortunate that there is no author index; however, it may have

been prohibitively expensive, as there are more than 5300 references to the original literature.

The book is useful in those ways in which any fine monograph is useful. It pulls together a vast body of information scattered through the world's literature, chemical and botanical. Even the specialist who works only with members of a few alkaloidal families will probably not have read all the difficultly accessible journals from which the reports of this volume are drawn. Not only are the original citations given, but reference is made to the abstract either in "Chemical Abstracts" or "Chemisches Zentralblatt." Thus this book will be a useful addition to his reference shelf. The introduction to each class of substances includes a brief presentation of the biogenetic theories advanced to account for the structures of the principal members. These theories are not discussed in any critical fashion, although admittedly the experimental evidence on which sound criticism may be based is only now beginning to be published in quantity. The book does not include description of the pharmacological action of the various substances, but seems otherwise remarkably complete.

Two minor criticisms may be made of the work: The more serious is that it is not particularly critical of the material included. To cite but a single example, the reported syntheses of apyohimbine and yohimbine from yohimbone by Preobrasenskii, *et al.*, are presented without comment, although the syntheses are implausible both from a mechanistic point of view and from the poor correspondence between the reported properties of the synthetic and natural substances. A less serious criticism is concerned with an aspect of the format. The stereochemistry of the majority of the substances discussed is known. Unfortunately, much of their chemistry is presented with formulae lacking this known stereochemistry. Toward the end of a particular section the stereochemistry is given; then one must go back and reread the transformations to see how their course is made the more plausible by the additional knowledge.

With the single exception mentioned above, the format is excellent. In quality of paper, printing and binding, the volume approaches that offered by the Swiss publishers, though it does not achieve it. There are a number of typographical errors, the majority of which are cited and corrected in the unbound supplement. Though it is quite expensive, this work is less expensive than recently available sets on the chemistry of alkaloids and much more complete, and is to be recommended.

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Collection of Problems in Physical Chemistry. By JIŘÍ BAREŠ, ČESTMÍR ČERNÝ, VOJTĚCH FRIED and JIŘÍ PICK. Translated by HELENA WATNEY. Addison-Wesley Publishing Company, Inc., Reading, Massachusetts. 1962. xvii + 608 pp. 16.5 × 23.5 cm. Price, \$9.75.

Until some twenty-five years ago no collection of numerical problems in physical chemistry was available that was not based on experiment and theory at least twenty years behind the advancing frontier of the science. It is gratifying to note that the past ten years has seen the appearance of at least three further collections of problems. They vary in form and emphasis; some hope to lure the student into reading the paper from which the data are taken and others clearly attach little importance to this fringe benefit; all recognize and to varying degrees satisfy the need for problems related to areas of current research interest.

The volume under review comes from four members of the faculty of the Institute of Chemical Technology in Prague; it is a welcome addition to the growing family of problem collections. It is at least as comprehensive as any of its predecessors; it includes almost all areas of physical chemistry. Each of eleven chapters covers a region of the subject and consists of a number of worked examples followed by a set of unworked problems with their numerical answers. Some but by no means all of the unworked problems are accompanied by literature references; the latter include a good many from journals written in English. It should perhaps be added that in some chapters the unworked problems include some rather pedestrian calculations; an extreme example of this is provided by the inclusion of three routine Beer's law calculations in the total of fourteen unworked problems in the chapter on "Molecular Structure and Physical Properties."

The price of the book is probably too high for general student purchase, but it is to be noted that its length is greater than that of other collections and the typographical format is generous and appealing. The number of worked illustrations is around two hundred and the number of unworked problems is over four hundred. Certainly no teacher of physical chemistry would find it other than a rewarding investment and a useful teaching tool.

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The Chemical Basis of Carcinogenic Activity. By G. M. BADGER, Ph.D., D. Sc., Professor of Organic Chemistry, University of Adelaide, Adelaide, South Australia. Charles C Thomas, Publisher, 301-327 East Lawrence Avenue, Springfield, Illinois. 1962. xiii + 72 pp. 6 × 23.5 cm. Price, \$5.00.

This book, by one of the leading contributors to organic chemical research in carcinogenesis, is a useful and up-to-date reference source for the carcinogenic activity of chemical compounds. In keeping with the spirit of the "Living Chemistry Series," the book is neither long nor encyclopedic. The style of writing is clear, concise, and quite readable. Although the references are not profuse (numbering 157 in all), they are useful and, for the most part, well selected; key references will allow the interested reader to investigate further.

Beginning with the suggestion by Pott in 1775 that constant exposure to soot was responsible for the development of skin cancer in chimney sweeps, the author classifies the important chemical compounds now known to be carcinogenic in animals or in man. The major categories include polycyclic aromatic hydrocarbons, aromatic amines and azo compounds; carcinogenic activity has also been demonstrated for alkylating agents, urethanes, *Senecio* alkaloids, steroids, inorganic compounds, polymers and a number of miscellaneous compounds that defy classification in structural groups. In fact, the variety of chemical structural types producing tumors in animals is nothing short of bewildering.

Dr. Badger discusses not only the historical background, chemistry and structures of chemical carcinogens but also the metabolism and postulated mechanisms of chemical carcinogenic action, wherever possible, and he includes a brief discussion of *in vivo* bioassay techniques for the evaluation of carcinogenic activity. He appropriately restricts his structure-carcinogenic activity correlations to related compounds of a given structural type, and emphasizes the impossibility of delineating a single structural configuration or moiety that is generally responsible for carcinogenic activity. By the same token, a single mechanism of action for carcinogenic compounds in general is highly improbable; on the other hand, it is equally unlikely that a separate and distinct mode of action will be found for each of the several hundred chemical carcinogens now known. It is regrettable that very little substantial information on the mechanism or mechanisms of chemical carcinogenesis has been derived from the extensive studies carried out to date on the metabolism, biochemistry and experimental pathology of carcinogenic agents.

The author discusses the two-stage mechanism theory of carcinogenesis involving an initiation phase, in which normal cells are altered, and a promotion phase, in which the altered cells can be recognized as malignant. He also reviews the observations on the binding of certain carcinogens to cell proteins as related to possible mechanisms of carcinogenesis.

The book can be criticized only in that it is too brief and superficial to be of any real value to the investigator in the field of chemical carcinogenesis. For example, the work of the Pullmans, Coulson, and others on the attempted correlation of electron densities at the K and L regions of polycyclic aromatic hydrocarbons with carcinogenic potency is inadequately and only indirectly mentioned. However, the book is recommended for the non-specialist, especially those desiring an introduction to chemical carcinogenesis.

It should be pointed out that, with few exceptions, compounds known to be carcinogenic in animals have not been unequivocally proved to be carcinogenic in man. The author takes the conservative and eminently reasonable position that any compound carcinogenic in animals should be regarded as potentially carcinogenic in man. This somewhat controversial subject is of great importance at the moment in the evaluation of the potential carcinogenic activity in man of chemical substances that will come into physical contact, either internally or externally, with human beings. Dr. Badger's philosophy is summed up in his closing sentences: "... all the different carcinogens are worthy of study. Such studies can not only point to potential human hazards, but may be of the utmost value in providing some understanding of the mechanism of carcinogenesis."

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Physical Aids to the Organic Chemist. By M. St. C. FLETT, Research Chemist, I. C. I. (Dyestuffs Division) LTD., Blackley, Manchester, Great Britain. American Elsevier Publishing Company, Inc., 52 Vanderbilt Avenue, New York 17, N. Y. 1962. 388 pp. 13.5 × 19.5 cm. Price, \$8.00.

This book is on the whole well written and free of typographical errors. The book contains chapters on Chromatographic Separation, Gas-Liquid Chromatography, Zone Refining, Electronic Absorption Spectroscopy, Infra-Red Spectroscopy, Electron