



tion by base. Although the carbanion might be hydrogen bonded by external deuteron (proton) donors in the medium, deuteron (proton) capture at sites distant from the cation of the ion pair would generate dissociated ions. Such a process is favorable only in solvents of high dielectric constant. Recapture by a new site of the proton (deuteron) originally abstracted to form the carbanion produces an ion pair when metal alkoxides serve as bases, and a neutral molecule when amines are used.

The intramolecular rearrangements of III to IV and of V to VI probably occur by migration of protons

(deuterons) as conjugate acids of the catalyst across the face of a π -cloud of electrons containing a negative charge. Migration from the front face of the π -cloud to the rear face by the migrating group would involve breakage of the hydrogen bond and at least partial dissociation of the ion pair, and is an unlikely process in those solvents which exhibit high intramolecularity. Therefore, these results imply that if suitable optically active analogs of III and V were submitted to conditions that gave high intramolecularity, the products would be of high optical purity. Thus asymmetric induction over several bond lengths is anticipated. The stereochemical experiments of Bergsen and Weidler^{2d,e} and of Jacobs and Dankner⁷ give force to this expectation, which is currently being tested.

(7) T. L. Jacobs and D. Dankner, *J. Org. Chem.*, **22**, 1424 (1957).

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BOOK REVIEWS

Divalent Carbon. By J. HINE, Professor of Chemistry, Georgia Institute of Technology. The Ronald Press Co., 15 East 26th St., New York 10, N. Y. 1964. vii + 206 pp. 15 × 21 cm. Price, \$7.00.

Considering the volume of published material on the chemistry of methylenes, it is amazing that the publication of the first comprehensive and acceptable review in English appeared only after this field has enjoyed an immense popularity for more than a decade. It is fortunate that the first book entirely devoted to methylenes has been written by an author who has revitalized the interest in divalent carbon compounds through his pioneering studies on the mechanisms of haloform hydrolyses.

The book consists of eight chapters which proceed from a discussion of the physical and physical-organic chemistry of methylene itself to a treatment of the chemistry of a variety of methylene derivatives. Included in the latter are dihalomethylenes, alkoxy-, alkylthio-, and monohalomethylenes, double-bonded derivatives of divalent carbon, and miscellaneous other substituted methylenes. The last three chapters present a discussion of mechanisms of α -eliminations, of pyrolytic and photolytic decompositions of diazo compounds, and of a number of other reactions which may proceed through the intermediacy of divalent carbon species. The 218 references are taken from the literature available to the author to mid-1962. This includes some material with publication dates of 1963. Throughout the book, Hine has avoided the term "carbene"; instead he seems to prefer the Chemical Abstracts system which names all divalent carbon compounds as derivatives of methylene.

In the authors own words, the emphasis of the book is on "mechanisms of reactions involving methylenes and the effect of structure on reactivity in these reactions." As a consequence of this guideline, many references of interest mainly to the synthetic chemist are dealt with rather briefly, or are omitted entirely. Undoubtedly other books on divalent carbon will be published soon, and since it is likely that synthetic aspects will be stressed in one or the other, this restriction cannot be considered a shortcoming. The real strength of this monograph lies in its attempt to develop a general and consistent framework into which the vast volume of experimental data may be fitted. In the discussion Hine does not shy away from giving his own interpretations of many experimental observations even if his conclusions are not the same as those of the original authors. Another enjoyable aspect is the large number of suggestions of experiments which should be done to solve remaining problems. Considering

the size of the book, most aspects of mechanistic methylene chemistry in solution have been covered adequately. A somewhat more detailed description of the vapor phase work might have added to the value of the book. The only severe criticism must be directed towards the publisher. A production time of 18 months cannot be tolerated when the subject of the monograph is in a state of dynamic development. As a result of this time lag, the most exciting recent developments in methylene chemistry, such as the information on ground-state properties of divalent carbon compounds obtainable from e.s.r. studies, are only mentioned in a few words.

In conclusion, Hine succeeded in writing a very useful and stimulating book. Acquisition can be highly recommended to any one interested in organic reaction mechanisms. It should be included in the reading list for organic graduate students. They will profit not only from being familiarized with divalent carbon chemistry, but, more important, they will be given an excellent view on the methods and techniques used to study short-lived reactive intermediates in general.

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Electronic Spectra and Quantum Chemistry. By C. SANDORFY, Professor of Chemistry, University of Montreal. Prentice-Hall, Inc., Englewood Cliffs, N. J. 1964. xiii + 385 pp. 16 × 23 cm. Price, \$14.95.

This book was originally published in French in 1959 as "Les Spectres Electroniques en Chimie Theorique," and its German translation (1961) was previously reviewed in this journal (*J. Am. Chem. Soc.*, **84**, 2656 (1962)). The present volume, as the author remarks in his preface, is a greatly augmented version of these previous editions.

After a short introduction on units, and a somewhat longer one on the basis of the variation and perturbation methods in quantum mechanics, there is a short chapter on energy calculations by the Hückel MO method, and another considerably longer one on the corresponding valence bond technique using "structures." The emphasis is on the presentation of complete detail of each treatment, so that not even the smallest arithmetic steps are passed over.

A 20-page section on transition probabilities is followed by a 70-page section on classification of electronic states, selection rules, and symmetry of molecules containing the briefest of introductions into the use of group representations in this connection. Character tables are included in the text. The next two chapters consider the calculation of spectral quantities first by the molecular orbital method and then by the valence bond method. The examples of butadiene, the polyenes, benzene, and the acenes are considered in some detail.

The remainder of the book (100 pp.) consists of short chapters on "Antisymmetrized Molecular Orbitals" (*sic*), "The Semi-empirical Method of Pariser and Parr" (5 pp.), "The Self-Consistent Field Method" (11 pp.), "Summing Up. What Next?" (8 pp.), "Free-Electron Methods" (17 pp.), and "A Brief Review of Chemical Spectroscopy" (25 pp.).

The book is clearly written in simple easy-to-follow style. It is perhaps best regarded as a source book on the cookbookery of the empirical techniques used in the simple MO and VB methods some 15 to 20 years ago. The book is weak in more modern approaches and in providing sufficient discussion of the pitfalls, drawbacks, and limitations of the various procedures.

The earlier review of previous editions of this work commented explicitly on the distribution of references by year. One would have hoped that the present volume, published in 1964, might have included considerable recent literature as an aid to the student. Of the 460 references, however, only 34 are dated within the past five years, and only 87 are within the past decade. The bulk of the references are more than 15 years old. In this day of rapidly advancing science, such a distribution can hardly be said to "enable the reader to introduce himself to actual research work in the field of electronic spectra of larger molecules."

Summarizing, we can say that the book is well conceived, clearly written, but disappointing in its lack of up-to-date viewpoint. It will serve a useful function, but no modern course or program of self-study should be based on this volume alone.

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Free Radical Reactions in Preparative Organic Chemistry. By GEORGE SOSNOVSKY, Associate Professor, Illinois Institute of Technology, Chicago, Ill. The Macmillan Co., 60 Fifth Ave., New York 11, N. Y. 1964. xvi + 438 pp. 16 × 24 cm. Price, \$17.00.

Scientists concerned with synthetic organic chemistry, or those who have a general interest in free radical chemistry, will find this book of value. The author's aim has been to deal comprehensively with a selected series of synthetically useful reactions—mainly additions to unsaturated systems—which are known to proceed, or which may likely proceed *via* free radical intermediates.

The volume contains eight chapters which are set up in a format similar to the one used in the well-known series on "Organic Reactions" (Wiley). Of the 416 pages of text, 169 are devoted exclusively to tables which illustrate the specific reactions; over 2000 fully documented examples are included.

The world-wide literature of the subject is represented in the 1481 references given at the ends of chapters. Of these, almost 200 are to articles in Russian journals (mainly since 1957), and about 180 are to patents. British, German, French, and Japanese works, among others, are also reviewed. A detailed check of over twenty references which were of particular interest to the reviewer, including those to foreign journals, showed full accuracy in citation and in quoting of data.

Very few references to studies later than 1960 are given. A subject index (20 pages) is included, but an individual author index is not. The latter omission is not very serious, however, since the alphabetical reference lists are easy to scan. The type, formulas, and tables are exceptionally clear, the book is quite free of typographical errors, and the general physical makeup is good.

In view of its extent, the author wisely omitted the topic of free radical reactions in the preparation of polymers, as such; however, many of the reactions cited are of direct interest for polymer studies. The following are the headings for individual chapters: I (13 pp.), "Addition of Hydrogen Halides to Unsaturated Compounds"; II (43 pp.), "Addition of Alkylpolyhalides to Unsaturated Compounds"; III (58 pp.), "Reactions

of Sulfur Compounds"; IV (33 pp.), "Addition-Type Reaction of Water, Hydrogen Peroxide, Alcohols, Acetals, Ethers, Carbonyl Compounds, and Saturated Compounds with Unsaturated Compounds"; V (40 pp.), "Reactions of Phosphorus Compounds"; VI (20 pp.), "Additions of Silicon and Germanium Compounds to Unsaturated Compounds"; VII (69 pp.), "Reactions of Nitrogen Oxides and Related Compounds"; VIII (132 pp.), "Halogenations."

Although the preparative theme of the book is fully adhered to, the fundamental lists of references and the supplementary reading lists lead the reader to specific theoretical aspects of the subject, and the author has interwoven comments thereto throughout the text. In seeking a rationale for including free radical reactions of preparative value, a liberal basis was resorted to. The author recognized the uncertainties inherent in assuring that a particular reaction under chosen conditions does, indeed, involve free radical intermediates, but includes those reactions in which free radicals have been well demonstrated, those which are catalyzed by free radical initiators (such as peroxides, azobutyronitrile, and organometallic compounds), or those reactions which are initiated by irradiation or thermal means—ostensibly under nonionizing conditions. Assurance of free radical intermediates is sometimes tenuous, as, for example, in the additions of water to crotonic acid or to ergot alkaloids, effected by ultraviolet irradiation; but such reactions are of considerable interest, both chemically and biochemically, and in view of the mechanistic possibilities they have been included.

Some limitations of the volume may be noted. Since the discussion of mechanism is incidental to the main theme, there are some cases where references are given to particular discussions of reaction mechanisms without including also significant later considerations. An example is the reference to the proposal of homolytic mechanisms for thermally induced additions of elementary sulfur to olefins, without further notation to the later views of Bateman, Moore, and co-workers on the probable polar courses of these reactions. It is obvious that subjects as extensive and as complex as the olefin-sulfur reactions, the free radical reactions of sulfonyl chloride with olefins or alkanes, and the behaviors of numerous other nitrogen, sulfur, and phosphorus reagents cannot be dealt with fully in a relatively short monograph. The author has, however, generally accomplished his purpose to provide basic examples of preparative value, and to cite the major references. Particularly with the series of studies of M. S. Kharasch, F. R. Mayo, W. H. Urry, and co-workers, in the several fields of investigations which they pioneered, the author has provided an exhaustive and valuable summary of the original studies and of their later extensions, besides citing the earlier review works. Much of the work of other early investigators is also brought into perspective. The text also contains descriptions of many less well-known reactions which are of potential value and which are intriguing for further study. Experts in particular areas will certainly, however, recognize many additional examples of importance which could equally warrant inclusion. In larger areas of study, the preparative aspects of semi-quinonoid radical reactions (as, *e.g.*, the oxidative formations of thyronines from iodotyrosines) and of homolytic arylation reactions, among others, are not included.

This book will help the general reader to recognize that a number of key factors have now fully combined to set the stage for a renewed growth of interest in preparative free radical chemistry. Among these are (1) the availability of a greater selection of radical initiators, (2) the availability of suitable apparatus for selective irradiation studies of all types, (3) the capability for effective separations of mixtures by preparative gas chromatography, (4) the comparative ease with which products can now be identified by combinations of chromatographic, spectroscopic, and conventional means, and (5) the realization of differences of specificities among various reagents, as for example, various halogenating agents which react by free radical paths. Hence, the timing of this volume can be viewed as fortuitous, for it marks and emphasizes the end of an era of about thirty years during which the pioneering works of many academic and industrial investigators have been integrated to lay a sound basis for future work. The earth was indeed fertile, and it has been tilled well.

A comment to the question of whether the earlier investigators have, in fact—as has been lamented by some—taken the "cream off the top" may be appropriate. From the mechanistic side, this is certainly not the case, for numerous facets of the mechanisms of the synthetically useful reactions require study by classical and new techniques, and these studies can yield infor-