

the  $\alpha$ -methyl-naphthyl-type intermediate.<sup>1,2</sup> This is not found in corresponding SCF calculations. Dewar and Thompson have found a single correlation for the relative rates of carbonium ion and carbanion formation.<sup>10</sup>

Further, Gleicher has shown by strain energy calculations that the nonbonded interactions are not as severe as predicted by the Hückel approach.<sup>11</sup> The failure of the Hückel calculation here is probably due to its neglect of the nonuniform electronic field in these ions.<sup>12</sup>

Our results for the SCF correlation of the rates of hydrogen abstraction show an excellent single correlation as is seen in Table II. The correlation coefficient of 0.977 for all points is, to our knowledge, better than any obtained in similar studies. It appears that even in uncharged odd-alternant systems, the SCF approach can yield more precise correlations than can be obtained from the Hückel treatment. This is probably due to the fact that the unpaired electron will interact differently with other electrons depending on whether

they are of the same or opposite spin.<sup>13</sup> This consideration is ignored in the HMO approach.

There is again improvement with a dual correlation. This may reflect a transition state of slightly higher energy for the  $\alpha$ -methyl-naphthyl-type compounds because of nonbonded interactions. The change, however, is small, and it is difficult to determine whether this small improvement is real or an artifact of the calculations.

**Acknowledgment.** The authors gratefully acknowledge the National Science Foundation and the Oregon State University Computing Center for support of this work.

(13) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 71, 264 ff.

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Received August 11, 1969

(10) M. J. S. Dewar and C. C. Thompson, Jr., *J. Am. Chem. Soc.*, **87**, 4414 (1965).

(11) G. J. Gleicher, *ibid.*, **90**, 3397 (1968).

(12) M. J. S. Dewar, *Rev. Mod. Phys.*, **35**, 586 (1963).

## Book Reviews

**Introduction to Mass Spectrometry. Instrumentation and Techniques.** By JOHN ROBOZ, Air Reduction Co., Inc., Murray Hill, N. J. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1968. xvii + 539 pp. 16 × 23 cm. \$20.00.

The Preface to this book states that it has three objectives: to present an introduction to the theory, design, and operation of the various types of mass spectrometers; to provide assistance in the selection of commercial mass spectrometer systems and components by discussing required instrument performance in many fields of applications; to acquaint the reader with the general experimental techniques employed in mass spectrometry and illustrate these methods in typical applications. It does not succeed in these objectives for several reasons.

The book begins with a good Introduction which defines the various terms used in mass spectrometry and gives a brief account of the scope of applications of mass spectrometry. This is followed by a chapter on mass analysis which covers electrostatic and magnetic analysis fairly fully as well as the principles of focusing the ion beam.

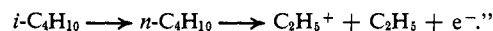
The remainder of the book is not up to the standard of these first two chapters and deals with the following subjects. Pages 65-276 are concerned with the remaining aspects of instrumentation and deal with types of mass spectrometers, ion sources, ion detectors, vacuum techniques, sample introduction, and commercial instruments. Part II of the book covers in a further 225 pages the subject of applied mass spectrometry and discusses types of ions in mass spectra, analytical techniques in organic and inorganic chemistry, mass spectrometry in physical chemistry, and miscellaneous applications.

All these chapters are difficult to read because coverage is uneven and aspects of the same topic are dealt with in several places and the cross references are to sections rather than pages so that they are not easily found. For example, in the section entitled "Isotope Ions" which is only three pages long, there are cross references to an appendix, a table, and six other sections.

Much of the material presented consists of trivial information which is often contradicted in other sections (see, for example, the chapter on Vacuum Techniques where elastomeric seals are discussed several times). Again, the chapter on commercial instru-

ments is not at all critical and the mass of trivial facts presented make it very difficult to pick out the real differences in performance and application. Much of the detail cataloged for one specific instrument equally well applies to several other instruments. And many of the figures quoted for performance are lower than those guaranteed by the manufacturers. But, more seriously, many of the statements made are wrong. For example, a cycloidal analyzer is said to give first-order double focusing.

The book is filled with generalized half-truths, and this, coupled with the large number of completely erroneous statements, makes it a book which cannot be recommended. The errors are particularly frequent in the sections which deal with chemical applications where terms such as ion, molecule, atom, and group are used loosely and almost interchangeably. As an example of the statements made, the section on "Re-arrangement Ions" contains in its first paragraph the remarkable statement about the origin of the peak at  $m/e$  29 in the mass spectrum of isobutane that "its appearance can only be explained by assuming isomerization followed by dissociation,



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**Applications de la Dispersion Rotatoire Optique et du Dichroïsme Circulaire Optique en Chimie Organique.** By PIERRE CRABBÉ, Directeur des Recherches, Syntex S. A., Professeur à l'Université Ibéroaméricaine et à l'Université Nationale Autonome de Mexico. Gauthier-Villars, Paris, France. 1968. 611 pp. 16 × 24.5 cm. 128 F.

This book represents the second edition of a work first published in English, under the title "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry" (Holden-Day, San Francisco) in 1965 (see review in *J. Amer. Chem. Soc.*, **88**, 1340 (1966)). As Professor Djerassi says in his Introduction the development of these two techniques in the past 4 years has been most striking and

a new version was certainly due. It is most appropriate that this new version should be in French, since so much important work, classical and modern, has come from French laboratories.

The new French version is approximately twice the size of the American version of 1965, and stands as the *only* up-to-date work in any language on these two techniques—now conveniently described together as the “chiroptical” techniques. The appearance of this new work in French is an ingenious and well-justified plot to make those of us who normally speak English (or American) practice our French, since we shall not get the benefit of Dr. Crabbé's work otherwise. It is a salutary reminder that not all chemical literature is published in the language of Shakespeare, Winston Churchill,—or James Thurber.

The emphasis of the book is essentially practical, as its title implies. Theory and instrumentation are dealt with rather briefly (74 pp) and are followed by a general chapter on application of the techniques to structural problems (38 pp).

Two chapters, extending over 246 pages, then describe the Cotton effects of saturated ketones of all kinds. There must be few stereochemical problems in the alicyclic field for which useful analogies cannot be found in this mass of material. The reference numbers in the two chapters add up to over 400, and the total number of papers cited must be well over 1000.

Chapter 7 (76 pp) deals with aromatic chromophores of all kinds, a field where much more work is necessary. Chapter 8 (76 pp) covers  $\alpha,\beta$ - and  $\beta,\gamma$ -unsaturated ketones; these are less well explored than the saturated ketones, but nonetheless a rich field for studies, past and future. Chapters 9 and 10 (84 pp) cover the remaining chromophores; exploration of many of these has been hindered by lack of adequate penetration into the ultraviolet. This reminds us that the progress of all physical techniques, if their application is to be extensive, depends on the instrument manufacturer.

A final very short chapter touches on the Faraday effect (magnetic ORD and CD). These techniques, which will be applicable to very different groups of problems from those where “natural” ORD and CD are used, are still in their infancy. A book on these magnetic techniques is desirable.

The book is illustrated by numerous excellent tables, formulas, and figures reproducing curves; perhaps some space could have been saved by “telescoping” formulas.

Dr. Crabbé is to be congratulated on a very thorough and useful guide in a subject where theory and application are still too far divorced from one another. No organic chemist working with chiral compounds can afford to be without access to this book, though the price may compel him to use a library copy. We are doubly in Dr. Crabbé's debt for his bilingual efforts.

The whole field of study (not merely the “magnetic” aspect) is developing rapidly, and no doubt a third version of Dr. Crabbé's book may soon be required; perhaps we shall then have to polish up our Spanish, as the author works in Mexico.

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**Carbocyclic Ring Expansion Reactions.** By C. DAVID GUTSCHE, Department of Chemistry, Washington University, St. Louis, Mo., and DEREK REDMORE, Petrolite Corporation, Webster Groves, Mo. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1968. viii + 243 pp. 15.5 × 23 cm. \$13.50

This book is Supplement 1 to the series “Advances in Alicyclic Chemistry,” edited for Academic Press by Harold Hart and G. J. Karabotsos. The authors have collected a large number of literature references dealing with the expansion of carbocyclic rings, although they have not attempted to exhaustively treat the subject in the manner of “Organic Reactions.” The various methods which have been utilized for ring expansions are organized into the following categories: Chapter II, Wagner–Meerwein Rearrange-

ments; Chapter III, Pinacol-Type Rearrangements; Chapter IV, Diazoalkane Ring Expansions of Cycloalkanones; Chapter V, Ring Expansions *via* Anionic Intermediates; Chapter VI, Ring Expansions *via* Carbene or Radical Intermediates; Chapter VII, Photochemically Induced Ring Expansions; Chapter VIII, Ring Expansion Sequences *via* Bicyclo[*n*.1.0]alkane Intermediates; Chapter IX, Ring Expansion by Two Carbon Atoms; Chapter X, Ring Expansion by Three or More Carbon Atoms. Within each chapter, the reactions are usually subgrouped in terms of the ring sizes involved (*e.g.*, cyclopropyl → cyclobutyl, cyclohexyl → cycloheptyl). The over-all classification scheme is generally effective, but breaks down in several instances, as for example when the solvolytic rearrangement of a 1,2-diol monotosylate (LiClO<sub>4</sub>–CaCO<sub>3</sub>–tetrahydrofuran) is included with “Base-Induced Rearrangements of 1,2-Glycol Monotosylates” in Chapter V.

In the introduction, the book is referred to as a “... catalog of ring expansion procedures (which) will be primarily useful to chemists interested in synthesis applications...” However, several obvious errors were noted which suggest that the various references included were not critically reviewed prior to inclusion, a situation which could seriously diminish the value of the book for its intended purpose.

Several examples, which are of special interest to the reviewer, should serve to illustrate the point. On page 133, in footnote 377, we find the reaction of copaene with HCl given as an example of a ring enlargement *via* a bicyclo[*n*.1.0]alkane, when it is now known that this terpene does not contain a cyclopropane ring (De Mayo, Büchi, 1963). In the same vein, on page 128, we are told that bicyclo[4.1.0]heptane and bicyclo[3.1.0]hexane open hydrolytically to cyclohexylcarbinol and cyclopentylcarbinol, when the actual products are the respective *trans*-2-methylcycloalkanols (ref 366).

In their presentation of the vinylcyclopropane rearrangement as a ring expansion procedure (pp 163–170), the authors imply that the only structural feature which is deleterious to facile cyclopentene formation occurs when the double bond contains a methyl group *cis* to the cyclopropane ring. The well-known 1,5-hydrogen shift, which leads to ring scission in 2-alkylvinylcyclopropanes (Ellis and Frey, 1964), is ignored. The omission of such an important side reaction, which completely obviates the vinylcyclopropane rearrangement as a ring expansion process in many cases, is unfortunate. It is further stated that “... current sentiment appears to favor a completely synchronous bond-breaking and bond-making mechanism for most of the vinylcyclopropane rearrangements which have been studied...” even though a recent review by a leader in the field concludes that the reaction proceeds *via* diradical intermediates (H. M. Frey, “The Gas Phase Pyrolyses of Some Small Ring Hydrocarbons,” in “Advances in Physical Organic Chemistry,” Vol. 4, V. Gold, Ed., Academic Press, New York, N. Y., 1966).

Several other mistakes were noted, including one glaring nomenclature error (cyclododecane instead of cycloeicosane on page 195) and one most perplexing case (pp 91–92, compound 423 to compound 424) in which one of the structures is either in error, or a most remarkable reaction has occurred. Unfortunately, it is impossible to decide, since the textual names agree with the structures as given, and the literature citation is to unpublished observations from the author's laboratory.

The volume is attractively bound and printed. However, it is rather difficult to read since structures are numbered consecutively throughout (up to compound 886!) and frequent use is made of general structures (for example, see page 74, where structures 349–351 each represent 12 different compounds). In addition, the structural formulas are often separated from the text by two or more pages.

The book will probably be useful as a quick source of leading references on various ring expansion procedures, provided the user is careful to check the original literature before relying on factual statements.

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