conclusion, when coupled with rate data, that the rate of *racemization* of α-NpPhMeSi*Cl by c-$C_6H_{11}NH_3Br$ exceeds the rate of chloride–bromide *exchange* for these reactants by a factor of more than 15.

Previously, it was found that the racemization rate of α-NpPhMeSi*Cl with c-$C_6H_{11}NH_3X$ in chloroform is somewhat insensitive to the nature of X (X = Cl, Br, or I), a fact which also suggested a siliconium ion-pair mechanism; reaction rate variation was less than a factor of 4.[1] Although these data pointed to a certain lack of dependence of rate on the anionic component of the cyclohexylammonium salts investigated, the critical experiment, using cyclohexylammonium perchlorate, could not be carried out because of the extreme insolubility of this salt in chloroform. However, very recent work shows a sharp decrease in the rate of racemization of α-NpPhMeSi*Cl when the anionic component of quaternary ammonium and phosphonium salts is perchlorate. Thus, in chloroform solvent, comparing racemization rates with $PhCH_2Et_3NCl$ and $PhCH_2Et_3NClO_4$ gives a relative rate for the perchlorate salt of $\sim 10^{-3}$. Comparing racemization rates with $Ph_3(PhCH_2)PCl$ and $Ph_3(CH_3)PClO_4$ in chloroform solvent gives a relative rate for the perchlorate salt of $\sim 10^{-3}$.

It should be noted here that the fine work of Grant and Prince[2,3b] with $Li^{36}Cl$ in acetone–dioxane has shown that chloride–chloride exchange with α-NpPhMeSi*Cl in this system occurs with inversion of configuration for each act of exchange. Also, in another recent report, these authors have found for $(n\text{-}C_4H_9)_4N^{36}Cl$ in *benzene solvent* with α-NpPhMeSi*Cl that in this system the rate of exchange far exceeds the rate of racemization, k_{ex}/k_{rac} = 40–80. Thus, in this latter system the vast majority of exchanges are proceeding with retention of configuration.[6] For chloride–chloride exchange at asymmetric silicon, this work coupled with the new results reported herein demonstrates that the observed stereochemistry (per cent inversion *vs.* per cent retention) and the operation of competitive mechanisms are a sensitive function of the nature of the solvent, the reagent, and the chlorosilane structure. This is in sharp contrast to the usual situation for reactions of optically active acyclic chlorosilanes with strong nucleophiles which provide entering groups more basic than Cl—for such reactions an inversion SN2–Si mechanism operates in the vast majority of cases.[7,8]

Further discussion of the mechanistic implications of the above new data, and other data including the relative rate of chloride–chloride exchange at bridgehead silicon, will be presented in a later article.

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[6] M. W. Grant and R. H. Prince, *Nature (London)*, **222**, 1163 (1969).

[7] For example, c-$C_6H_{11}NH_3F$ and c-$C_6H_{11}NH_3OCOCH_3$ in chloroform solvent with α-NpPhMeSi*Cl give the fluorosilane and acetoxysilane products with better than 90% inversion of configuration; see L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *J. Amer. Chem. Soc.*, **89**, 857 (1967).

[8] L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965, Chapter 4.

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*Book Reviews**

The Alkaloids. Chemistry and Physiology. Volume XII. Edited by R. H. F. Manske, Uni Royal Limited Research Laboratory. Academic Press Inc., New York, N. Y. 1970. xvii + 637 pp. $29.00.

Alkaloid chemists throughout the world will welcome the appearance of this twelfth volume of this standard and most comprehensive of treatises on all phases of alkaloid chemistry.

A number of varied topics are reviewed in this new volume, which consists of seven chapters. Chapters 1 and 2, by S. W. Pelletier and L. H. Keith, constitute a book within a book on the subject of the diterpene alkaloids of *Aconitum*, *Delphinium*, and *Garrya* species. Chapter 1 discusses the C_{19} diterpene alkaloids (*e.g.*, the aconitine type), while Chapter 2 discusses the C_{20} diterpene alkaloids (*e.g.*, the atisine type). The authors are to be congratulated for having accumulated most of the very complex chemistry of these polycyclic multifunctional bases, especially the C_{19} alkaloids, into one critical but thorough review.

Chapter 3, by J. E. Saxton, is concerned with *Alstonia* alkaloids. It is mostly a very readable account of the superb structure determinations of the unusual dimeric indole bases of *Alstonia* species, as carried out in recent years by Schmid, Hesse, Taylor, and their collaborators.

Chapter 4, by F. L. Warren, brings up to date the earlier review of N. J. Leonard on the "Senecio alkaloids," a special but large subgroup of pyrrolizidine alkaloids. Not only are the individual alkaloids described but also their hydrolysis products, the necine bases and the necic acids. The practical utility of this fine chapter would have been increased by the addition of a special section devoted to spectroscopic properties.

Chapter 5 by F. Šantavý, concerns recent studies of the alkaloids of the family *Papaveraceae*. The author has done an impressive job in discussing a wide variety of topics, from chemotaxonomy and biosynthesis to the chemistry of the fifteen different structural types of benzylisoquinoline-derived bases found to date in the *Papaveraceae*.

Chapter 6, by R. H. F. Manske, is a collection of brief abstracts of recent reports of alkaloids from various plant sources, Well-known alkaloids and new alkaloids of all types, some of which are of unknown structure, are included. This is a chapter of primarily practical use for the investigator doing current phytochemical research.

The volume closes with Chapter 7, by E. G. C. Clarke, on the subject of the forensic chemistry of alkaloids. This chapter appears to be a very good general review of such topics as poisoning and addiction by alkaloids, legal control of alkaloids, and extraction and analytical detection of alkaloids in animal tissues. This type of review is well worth publishing somewhere although one wonders

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* Unsigned book reviews are by the Book Review Editor.

whether any natural products chemist using the remainder of the book will ever use any of this material. One can argue that the "physiology" aspects of future volumes in this series should be limited to simplified sections on alkaloid pharmacology which would help natural products chemists to realize the potential practical uses of the compounds which they are studying. For example, the brief section (VI) on pharmacology in the present Chapter 4 seems just right for this purpose.

Finally, this reviewer would like to echo some of the sentiments expressed by E. Wenkert in his review (*J. Amer. Chem. Soc.*, **88**, 3681 (1966)) of an earlier volume of this series. It is to be hoped that future volumes may be organized more on the basis of alkaloid structural types than according to botanical origin. For example, Chapter 3 could have been more usefully organized as a review of the recent chemistry of dimeric indole alkaloids in general, not only the bases from *Alstonia* species. Chapter 5 of the present volume illustrates best how well nature can frustrate us in trying to use a botanical organization: the author has been forced to try to discuss some fifteen structural types of alkaloids, most of them not exclusively found in the genus *Papaveraceae*, in the space of a single chapter.

Despite these criticisms, this volume and the earlier ones in this series remain as an indispensible part of the library of any practicing alkaloid chemist.

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Topics in Heterocyclic Chemistry. Edited by R. N. CASTLE, University of New Mexico. Interscience Publishers (John Wiley & Sons, Inc.), New York, N. Y. 1969. 264 pp. $14.95.

This book consists of the eight plenary lectures given at the First International Congress of Heterocyclic Chemistry (1967). It includes references and a substantial index.

Analytical Chemistry of Nitrogen and Its Compounds. Edited by C. A. STREULI and P. R. AVERELL, American Cyanamid Co. Wiley-Interscience, New York, N. Y. 1970. vii + 763 pages in two volumes. $35.00 per set.

This work is divided into seven chapters on inorganic nitrogen and nine on organic, ranging from "Determination of Total Nitrogen" to "Amino Acids, Polypeptides, and Proteins." Each chapter contains background information, data on qualitative detection, separation, and determination, and in many instances descriptions of specific methods. There is also much useful information in tables. A chapter on nuclear magnetic resonance of nitrogen is particularly timely.

References are abundantly given; in one chapter there are over 800. The Preface is dated October 1969, but there seem to be very few references later than 1966. The chapter on amines refers the reader to the 1949 edition of "Sidgwick's Organic Chemistry of Nitrogen," for example, in apparent unawareness of the revised edition by Millar and Springall in 1966.

The collecting together of the various analytical methods is a great service to both inorganic and organic chemists engaged in laboratory work, applied or fundamental. If the presentation is not always as critical as one might desire, this can be largely excused by the paucity of published comparisons and the authors' reluctance to engage in unsupported speculation. It is a pity this same reluctance did not carry over to the discussions of structures and mechanisms in the introductory sections, which include some truly incredible misinformation and are the weakest part of this work. The structure of sodium nitrolates, for example, is shown with a four-membered ring (oxadiazete), nitroalkane anions are confused with *aci*-nitro tautomers, and 3-diaziridinol is represented as a canonical resonance form of urea, in some way meant to explain the acid–base properties of the latter. Although such gaffs are not excusable, they occur in the nonessential portions of the work and do not materially reduce its usefulness.

The index, which is less than nine pages, is somewhat skimpy for the amount of information covered in the two volumes and does not include, for example, an entry under "nitrosamines," a class of compound of much current interest as pollutants.

Taken as a whole, this is a valuable compendium whose usefulness will surely outweigh its faults.

A Dictionary of Named Effects and Laws in Chemistry, Physics and Mathematics. Third Edition. By D. W. G. BALLENTYNE and D. R. LOVETT, Imperial College and University of Essex. Chapman and Hall Ltd. (distributed in U. S. A. by Barnes & Noble, Inc.), New York, N. Y. 1970. viii + 335 pp. $9.50.

This book lists in alphabetical order a large number of laws, theorems, effects, methods, reactions, etc., commonly known by proper names, and defines each briefly. The definitions range from one line to one and one-half pages; no references are given. It is certainly very useful for orientation and refreshing, especially for phenomena outside one's own field. One might not expect it from the title, but a large number of organic "name reactions" are included. The definitions or explanations are rather out of date in some cases; for example, the Wolff–Kishner reaction is described as a sealed-tube reaction with sodium ethoxide. The coverage is impressively comprehensive, even though the Woodward–Hoffmann rules are not included—but then, neither is Parkinson's law.

The orthography is rather unfortunate in some places; umlauts are annoyingly omitted from all the familiar German names, and benzene rings are sometimes shown in a form indistinguishable from cyclohexane rings. Terminology is a bit strange in places; witness "Markownikoff's Replacement Rule." The book is a poor teacher, but its value as a reminder is great, and it should see heavy use in the reference section of any technical library.

Organic Reactions. Volume 18. Edited by W. G. DAUBEN, University of California. John Wiley & Sons, Inc., New York, N. Y. 1970. vii + 475 pp. $19.95.

The newest volume in this familiar and important series contains four chapters, which cover preparation of ketones from organolithium compounds and carboxylic acids, the Smiles and related rearrangements, formation of cyclopropanes and cyclopropenes from diazoacetic esters, and the Stevens and Sommelet–Hauser rearrangements. They follow in tradition of an encyclopedic treatment with extensive tables of examples. The cut-off date for the literature surveys is not stated, but casual examination shows some references dated 1969. In addition to the volume index, cumulative author and chapter topic indices are included. It is interesting to note that ten authors have contributed twice during the 28 years spanned by the first 18 volumes, but no one has yet contributed three times.

This series continues to be an indispensable part of an organic chemistry library.

Selective Organic Transformations. Volume 1. Edited by B. S. THYAGARAJAN, University of Idaho. Wiley-Interscience, New York, N.Y. 1970. 400 pp. $19.95.

This is the first volume in a new series. It consists of eight unnumbered chapters by different authors and a short index. Each chapter is concerned with a particular type of reaction, such as "Triazoline Formation" or "Stereoselectivity in Quaternizations of Tertiary Amines"; it is interesting that no classical "name" reactions are included. The reactions are discussed from a strongly mechanistic viewpoint, such that each chapter constitutes a critical analysis of the reaction mechanism and the evidence for it, drawing carefully reasoned inferences about the scope. The result is to give the reader a rational basis on which to make his own predictions and extrapolations to new situations. The pragmatic side is not neglected, however, for there are much data presented in tables, and the bibliographies are quite extensive (although not encyclopedic).

The type of selectivity implied by the title may be stereoselectivity or site selectivity, or even selectivity among substrates of different reactivity. Comparison with the "Organic Reactions" series is inevitable, but the relation is largely complementary, for the latter series is relatively pragmatic and focused more closely on preparative features. The new series is thus by no means redundant and does, in fact, satisfy a need. This first volume is both useful and stimulating and will appeal especially to those who feel that organic chemistry has moved a long way toward becoming a more exact science.

Survey of Organic Syntheses. By C. A. BUEHLER and D. E. PEARSON, University of Tennessee and Vanderbilt University. Wiley-Interscience, New York, N. Y. 1970. ix + 1166 pp. $27.50.

This is a remarkable work, which succeeds in digesting all the important material on synthetic methods, including all that is in "Organic Reactions," "Organic Syntheses," and Theilheimer, and presenting it in a well-organized state and in a critical, brief, yet readable form. The book covers twenty classes of organic compounds, from alkanes to nitro compounds, devoting a chapter to each. All reasonable methods of generating a particular functional group from another are presented, arranged in a logical classification. It is particularly impressive that in a work of this enormity, the authors have been able to include critical discussions of the merits of the various methods and often to say something of mechanism.

A weakness of some previous attempts to produce a comprehensive book on synthetic methods—the inclusion of substantial numbers of obsolete methods without indicating their status, and omitting many of the newest methods—has been avoided with remarkable success. Outdated methods are signaled when given, and the proportion of references to the last twenty years is high. The literature coverage appears to be through 1968. The number of literature citations is so large that to have grouped them at the ends of the chapters would have been quite inconvenient. As it is, the authors have put them in groups of convenient size after each subsection. They are well chosen and include many reviews and compilations as well as copious quantities of original articles.

Examples are given throughout, and the authors have clearly gone to a lot of trouble to provide yields and precise experimental conditions, a fact that greatly increases the value of the book. They have also avoided the usual aliphatic–carbocyclic parochialism, and have included lots of examples taken from heterocyclic chemistry, in recognition of the often ignored fact that heterocyclic chemistry is a major part of current activity in organic chemistry.

An author index and a large subject index are included. The latter is good in spite of the fact that there is no entry under either "isocyanides" or "isonitriles"; although the synthesis of this functional group is not within the scope of the book, their reactions are discussed in the chapter on amides.

The aim of the authors to produce a useful reference work for researchers and advanced students has been achieved surpassingly, and they well deserve the success that their book will undoubtedly attain.