

with the carbon bearing the bulky phenyls canted considerably farther away from the diene (Figure 2). At the rate-determining transition state there is then considerable bonding between C<sub>1</sub> of the diene and the sp carbon of **1** but essentially none between C<sub>2</sub> of the diene and the sp<sup>2</sup> carbon of **1**.

Nevertheless, in the subsequent step, and because of the original approach geometry, the ketene's sp<sup>2</sup> carbon finds itself closer to C<sub>2</sub> of the diene than to C<sub>4</sub>, and thus the intermediate<sup>33</sup> closes to give only the (2 + 2) product.

If this picture is correct, it not only illustrates the power of isotope effect studies to help determine the structures of transition states but suggests that less bulky substituents on the ketene may lead to some bonding at both C<sub>1</sub> and C<sub>2</sub> of the diene (and hence to inverse 2°D KIE's at both positions) as the cycloaddition is

(33) Our present information is insufficient to describe the intermediate as either a diradical or a zwitterion, although it is interesting that a (2 + 2) cycloaddition known to traverse a dipolar intermediate shows one 2°D KIE as inverse and the other as normal.<sup>34</sup>

(34) von Gustorf, E. K.; White, D. V.; Leitich, J.; Henneberg, D. *Tetrahedron Lett.* **1969**, 3113.

sterically allowed to become concerted (but not necessarily synchronous). Studies designed to test this hypothesis are underway, but some support is already available from the work of Isaacs,<sup>35</sup> who found a substantial *inverse* 2°D KIE at the α-carbon of styrene reacting with dimethylketene, in contrast to the large *normal* effect at the same position when styrene reacts with **1**.<sup>20</sup>

**Acknowledgment.** We are grateful to Professor J. J. Gajewski, Indiana University, for the NMR measurements and a helpful discussion and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

**Supplementary Material Available:** Crystal and data collection parameters, final positional and thermal parameters, bond lengths and angles, torsion angles, and observed and calculated structure amplitudes (11 pages). Ordering information is given on any current masthead page.

(35) Isaacs, N. S.; Hatcher, B. G. *J. Chem. Soc., Chem. Commun.* **1974**, 593.

## Book Reviews

**Heterocyclic Chemistry. Volume 1.** Senior Reporters: H. Suschitzky and O. Meth-Cohn. The Royal Society of Chemistry, London. 1980. 522 pp. £69.00; \$194.50.

This new member of the Specialist Periodical Report series contains a combination of the type of material previously reviewed in other volumes in the series, namely "Saturated Heterocyclic Chemistry", "Aromatic and Heteroaromatic Chemistry" (both of which are now discontinued), and the heterocyclic portion of "Organic Compounds of Sulphur, Selenium, and Tellurium" (which will still continue to report on β-lactam antibiotic chemistry).

The reporters state that the literature covered is essentially based in volumes 89 and 90 of "Chemical Abstracts", i.e., July 1978 to June 1979, with some later papers included to provide continuity.

The style and format follow those of the revered "Annual Reports of the Chemical Society", providing almost encyclopaedic coverage of the subject (with some notable exceptions, vide infra) for the period. Syntheses and/or reactions are mentioned *very* briefly, an equation or a structure may be given, the occasional mechanism outlined, and the appropriate literature reference given (occasionally, reference is made to another Specialist Periodical Report rather than to the original article: this makes it difficult for the reader to check since the paper may well be available while the Report may not).

The format is traditional, with small rings being treated first, going from small to large rings, and giving preference to the smaller heterocycle in fused systems. In addition, articles on "Bridged Systems" and on "Conformational Analysis" are included because of their relevance to saturated heterocycles. References to reviews published during the period are given at the beginning of each chapter. The chapters (and reporters) are: 1. Three-membered Ring Systems (T. J. Mason). 2. Four-membered Ring Systems (R. C. Storr). 3. Five-membered Ring Systems (Thiophenes, and their Selenium and Tellurium Analogues by S. Gronowitz; Systems Containing Nitrogen and Sulphur, Selenium, or Tellurium, by P. A. Lowe; Other Five-membered Ring Systems, by G. V. Boyd). 4. Six-membered Ring Systems (Azines, Oxazines, and Thiazines, by R. K. Smalley; other Six-membered Ring Systems, by G. P. Ellis). 5. Seven-membered Ring Systems (D. J. LeCount). 6. Eight-membered and Larger Ring Systems (including macrocycles) (G. M. Brooke). 7. Bridged Systems (J. M. Mellor). 8. Conformational Analysis (F. G. Riddell).

The treatment is purely descriptive and uncritical (and is meant to be so). As might be expected in a review as extensive as this one, many errors creep into it. For example, a CH<sub>2</sub> is missing from structure **73** (p 14); an extra methyl group is present in **115** (p 19) and the need for a lithiating agent is not mentioned; formation of diazolidines (**760**) (p 234) requires the use of aroyl isothiocyanates; in **878** (p 244), R = H only, and a hydrogen is missing on the nitrogen of **879**; a methyl group

is missing in **43** (p 339) and a double bond in the ring at the bottom of that page; the dichloronorcaranes on p 331 are really dichloro-2-oxanorcaranes; on p 115, it is the *N*-(chlorothio)-1,2-benzisothiazol-3-one 1,1-dioxides that undergo reaction with arenethiols and *not* the *N*-chloro compounds; in the product (**34**) R = ArS, *not* R = Ar; methyl groups are missing in **880** and **881** on p 244, but are present (as required) in Scheme 28 (p 282) where the same reaction is discussed again. There are also a number of misstatements, e.g., p 26, *Direct Insertion* rather than *Direct Addition*; p 28, indole *N*-oxide rather than (3*H*)-indole (or indolenine) *N*-oxide; bicyclo-derivatives **81** (p 276) are classified as dihydropyridines; on p 337 it is stated that substituents or hydrogen in pyrylium salts are susceptible to nucleophilic *displacement*, but no example of this is given—instead the *addition* of methoxide ion is referred to. Such errors are almost inevitable in such an extensive, broad-ranging treatment. Many will stimulate the curiosity of the reader (as they did this reviewer) and send him to the literature for an explanation. Many unusual transformations are mentioned but not explained—once again, a trip to the library is thereby encouraged!

In spite of the very extensive coverage, much had to be left out to maintain the chapters to a "prescribed length", e.g., much of the patent literature on 1,4-benzodiazepines and tricyclic antidepressants, about one third of the articles on Other Five-membered Ring Systems. Virtually no mention is made of any biological activity in the compounds. This brings up an important point regarding such Specialist Reports. In spite of their covering a great deal of the literature on a given topic, they are not—and probably cannot be—exhaustive in their coverage and the reader will have to go to the original sources for a complete literature search. Presumably, then, the reports will be of use to heterocyclic chemists who will leaf through them in search of inspiration or look at them more carefully for leading references, realizing they may be missing something important to their research work. Certainly, the format does not make for casual reading! Indeed, one has to be either very dedicated or a reviewer to read more than a few pages in detail at one sitting! The very high price of the volume almost surely ensures that most heterocyclic chemists will not be able to afford their own copy—even some large university libraries may have a difficult time justifying the expense, particularly when the research chemist will have to go to the primary literature anyway to get all the information he wants and needs.

The senior reporters and reporters have done a monumental job with this compilation and, overall, have done it very well. This reviewer feels that a copy should be available in all research libraries that can afford it so that students and researchers can browse through it and see the many things they themselves have missed in their own general survey of the literature of heterocyclic chemistry, and occasionally find inspiration (as this reviewer did more than once) in a reaction or structure. It is no substitute—and was obviously not meant to be—for a thorough literature search of areas of immediate concern.

R. A. Abramovitch, *Clemson University*

**Management of Insect Pests with Semiochemicals: Concepts and Practice.** Edited by E. R. Mitchell (U.S. Department of Agriculture). Plenum Press, New York, 1981. xiv + 514 pp. \$59.50.

Semiochemicals, comprising pheromones, kairomones, oviposition deterrents, and other behavior modifying chemicals, have been the subject of several recent books. But the present, "Management of Insect Pests with Semiochemicals: Concepts and Practice", is the only one that deals in detail, as the title suggests, with the role of semiochemicals in insect pest management. The book is a compendium of papers presented at an international colloquium on management of insect pests with semiochemicals, held in 1980 in Gainesville, Florida.

The 36 contributions have been edited into five sections as follows: I, Biomonitoring; II, Mass Trapping; III, Mating Disruption; IV, Formulation, Toxicology, and Registration; and, V, Oviposition Disruptants and Antiaggregants. Following each of the first four sections is a summary of the recommendations made by a panel of experts on future research and development and transfer of technology.

Section I, Biomonitoring, deals with the use of semiochemicals in monitoring insects in situations such as storage areas, orchards, forests, and agricultural crops. Monitoring pest populations with pheromone traps appears to be simple enough at first glance, but there are inherent problems in interpreting trap catch data which are exacerbated by various biotic and abiotic factors. This problem is not faced in situations where precise population estimates are not required—such as quarantines. The mere presence of insects, detected by pheromone traps, warrants appropriate suppressive measures. As the panel recommendations suggest, the obvious and major bottleneck to more fully developing pheromone monitoring systems is to be able to correlate trap catch to population densities and ultimately damage levels. In fact, progress toward solving this problem is slow and few people are even working in this area. The panel also recommends high priority be given to further identification of the sex pheromone for key pest species.

Section II, Mass Trapping, deals with mass trapping programs using pheromones (and attractants) for various groups of insects. The results show great promise in suppressing pest populations. One of the chapters deals with a mass trapping program on a beetle pest of spruces on 4 million hectares in Scandinavia utilizing a million pheromone-baited traps. The information to date is that this program was successful in preventing an increase in tree mortality. The panel on Mass Trapping emphasized the need for increased research on basic behavioral studies; isolation, identification, synthesis, and formulation of attractants and pheromones; and optimization of pheromone dispensers.

The topic of Mating Disruption is dealt with in section III. Descriptions of the successful (and unsuccessful) use of mating disruption technology for a few species of insects in the United States and other parts of the world are provided in this section, including some of the problems encountered in the use of this technique. In fact, registration has already been obtained for using the technique of mating disruption for a few species of insects. Other chapters deal with the mechanisms of mating disruption, methods used to discover new disruptants and to evaluate formulations in the field, and the use of attractants and inhibitors in suppressing southern pine beetle populations. One of the major obstacles to successful implementation of mating disruption technology is the development of suitable formulations for application with existing spray technology. A major area of need seems to be the identification of sex pheromones (and of complete blends) for key insect species with special emphasis on chemical identification of sex pheromones and other disruptants of the entire pest complex of selected orchard, vegetable, and field crops. Also, there is need to improve large-scale commercial synthesis of pheromones at reduced cost.

In the last decade, the feeling existed that registration was still a serious constraint to the utilization of semiochemicals in pest management. But this is dispelled by the chapters in Section IV dealing with Formulation, Toxicology, and Registration. Although the Environmental Protection Agency has stated implementation of special guidelines for registration of biorational pesticides (such as semiochemicals), the panelists felt that there is still need for continued efforts on the toxicology of these compounds. There is also a need for coordinating the activities of international agencies such as NATO and the World Health Organization.

Section V, Oviposition Disruptants and Antiaggregants, is comprised of chapters on the nature and utility of such compounds in pest management. These compounds, unlike sex pheromones, are persistent and are amenable to being integrated into pest management systems. Again, there seems to be a great need for chemical identification of putative compounds.

This book is exceptional in all regards except for a few typographical errors. The copy reviewed had a page (page 214) entirely missing.

As some of the chapters in the book suggest, the potential of semio-

chemicals in insect pest management is only recently being realized. But as all the panelists agreed, there seems to be a great need for increased and continuing emphasis on basic behavior, chemical identification of sex pheromones, large-scale synthesis of semiochemicals, and better formulations and delivery systems. This book has appeared at a time when there is increasing awareness among scientists and administrators regarding the potential of semiochemicals in pest management. The recommendations from panel discussions at the end of each of the first four sections would be of particular interest to both the scientist and the administrator. The specialist and the advanced student would be well served to possess a desk copy.

Sonny B. Ramaswamy, *Mississippi State University*

**Gas Chromatography of Organometallic Compounds.** By T. R. Crompton (North West Water Authority at Preston, England). Plenum Press, New York, NY, 1982. x + 589 pp. \$75.00.

The author states that this book is the first complete review of the use of gas chromatography for the analysis of organometallic compounds. From over 1000 literature reports, 528 references are provided.

A major objective of this survey is to provide detailed analytical procedures for the analysis of organometallic compounds by gas chromatography (GC) without the need for referring to the original literature. For the topics discussed, this objective is reached. Specific directions for sample preparation and introduction are provided along with detailed descriptions of column packing supports, separation conditions, and means of detection. In many instances, different experimental parameters and procedures are compared. Several diagrams of apparatus and various component devices are included also. Example gas chromatograms are shown, and the problems of detector response and intensity calibration are discussed.

Organometallic compounds of 24 elements are covered in this review. Major emphasis is given to compounds of Si, Pb, Sn, Hg, B, and As. Approximately 30% of the text is devoted to the GC analysis of silicon compounds. Elements receiving more moderate review include Cr, Al, Mn, Fe, Mg, Ge, and Zn. Only minor reference is made to the GC analysis of organometallic compounds of Li, Ga, Se, Be, Sb, Mo, Te, Co, Cu, Ni, and Ru. Some nonorganometallic compounds, such as main-group metal hydrides and tetraalkoxysilanes, are discussed also. The principal transition metal organometallic compounds reviewed include: (arene)M(CO)<sub>3</sub> complexes of Cr and Mo, (C<sub>5</sub>H<sub>5</sub>R)Mn(CO)<sub>3</sub> complexes, ferrocene and analogous complexes, and (diene)Fe(CO)<sub>3</sub> compounds. Several of the main-group organometallic compounds of Li, Mg, and Zn are analyzed indirectly after alcoholysis or hydrolysis of the initial compound.

The author accomplishes his goal of providing a detailed source of GC analytical methods for selected organometallic compounds. This book would be of great value to those persons having a specific need to analyze samples of (or containing) organometallic compounds of the representative elements. This reference text would be particularly valuable to those who analyze biological or environmental samples for the presence of organometallic compounds. The transition-metal chemist would make only minimal reference to this review book.

Charles M. Lukehart, *Vanderbilt University*

**The Alkaloids. Volumes 9 and 10 (Specialist Periodical Reports).** Senior Reporter: M. F. Grunden (New University of Ulster). The Chemical Society, London. Volume 9 (1979). xii + 273 pp. £27.00 (\$70.00). Volume 10 (1980). xii + 263 pp. £49.00 (\$131.50).

These volumes of the "Specialist Periodical Reports" review the whole field of alkaloid chemistry including isolation, synthesis, and biosynthesis. Volume 9 covers the literature published between July 1977 and June 1978, and Volume 10 covers that between July 1978 and June 1979. In addition to the common 14 chapters, a chapter is devoted to *Erythrina* and related alkaloids in Volume 9. Volume 10 provides a two-year coverage of *Lycopodium* alkaloids which was omitted in the ninth volume. Not surprisingly, slightly more than 100 pages are spent to cover indole and isoquinoline alkaloid chemistry in both volumes. The organization of the books is excellent. The presentation is uniformly succinct. Many selected synthetic schemes scattered throughout the volumes certainly entertain synthetic chemists in general.

Any organic chemist interested in natural products will find it worthwhile to read all or parts of these books. Unfortunately, it is getting more and more difficult to buy these invaluable books as personal copies because of their skyrocketing prices.

Tohru Fukuyama, *Rice University*