

**Table I.** Variable-Temperature Photolyses

% <b>8</b> from (-)-thujone	<i>T</i> , °C	% <b>8</b> from (+)-isothujone
16.4 ± 0.3	89.0	17.1 ± 0.2
14.7 ± 0.1	49.8	15.4 ± 0.5
11.6 ± 0.1	10.8	11.7 ± 0.2
7.7 ± 0.1	-26.5	7.7 ± 0.1
4.4 ± 0.2	-74.5	4.8 ± 0.1

Preparative scale photolysis afforded a mixture of **7** and **8**, which were separated by preparative glpc and identified on the basis of infrared (ir) and nmr data. Compound **7**, obtained in 98.9% purity, was found to be *trans*-5-methylene-6-methyl-2-heptene<sup>2,13,14</sup> and **8**, obtained in 99.4% purity, was established as *cis*-5-methylene-6-methyl-2-heptene.<sup>15</sup>

Degassed samples of 0.125 *M* 99.7% (+)-isothujone or 0.068 *M* 99.5% (-)-thujone in isooctane were irradiated at 305 nm while maintained at various temperatures. The results, when appraised as a whole, indicate that the same mixture of photoproducts is produced by irradiation of either epimeric ketone (Table I).

A degassed sample of 0.086 *M* 99.6% (-)-thujone in 3-methylpentane as a glass at -196° exhibited strong, unstructured phosphorescence with an onset at 368 nm ( $E_T = 78$  kcal mol<sup>-1</sup>). When a degassed sample of 0.299 *M* 94.4% (-)-thujone or 0.055 *M* 99.7% (+)-isothujone in 3-methylpentane was irradiated at 305 nm while maintained as a glass at -196°, no decarbonylation or epimerization could be detected under conditions where 15–20% reaction occurred in liquid solution. Degassed isooctane solutions containing 0.129 *M* 99.7% (+)-isothujone and up to 0.10 *M* isoprene were irradiated in parallel at 305 nm while maintained at 30.5°. The ratio of photoproducts obtained was unchanged by the addition of triplet quencher. A Stern-Volmer plot of the data obtained at 5–8% conversion indicates a triplet lifetime

(13) C. H. Brieskorn and S. Dalforth, *Justus Liebig's Ann. Chem.*, **676**, 171 (1964).

(14) Ir (liquid film) 3080, 3020, 1640, 1378, 1362, 980, 894 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>-1%TMS) δ 1.02 (6 H, doublet, *J* = 6.5 Hz), 1.67 (3 H, multiplet), 2.24 (1 H, broad septet, *J* = 6.5 Hz), 2.71 (2 H, broad singlet), 4.67 (1 H, multiplet), 4.75 (1 H, multiplet), 5.46 (2 H, broad multiplet).

(15) Ir (liquid film) 3080, 3020, 1640, 1378, 1363, 893, 685 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>-1%TMS) δ 1.04 (6 H, doublet, *J* = 6.5 Hz), 1.63 (3 H, multiplet), 2.25 (1 H, broad septet, *J* = 6.5 Hz), 2.77 (2 H, broad doublet), 4.69 (1 H, multiplet), 4.75 (1 H, multiplet), 5.52 (2 H, broad multiplet).

of  $\tau = (3.4 \pm 0.7) \times 10^{-10}$  sec if diffusion-controlled quenching is assumed.

Attractive initial intermediates in photodecarbonylation are **3** and **4** formed by  $\alpha$  cleavage to give the more stable diradicals.<sup>16–19</sup> These species are almost certainly involved in the epimerization of the ketones.<sup>20–22</sup> In the formation of **3** and **4**, if nonadiabatic crossing from the bound triplet state at 78 kcal mol<sup>-1</sup> to an unbound state at about 75 kcal mol<sup>-1</sup><sup>23</sup> is a thermally activated process, an efficient explanation is generated for the strong phosphorescence and lack of reactivity at -196° in conjunction with the short triplet state lifetime and reactivity at higher temperatures. The existence and interconvertibility of diradicals **5** and **6** are moot.<sup>1–3,25–27</sup>

The experimental data do not require that the decarbonylation of (-)-thujone or (+)-isothujone proceed in a concerted fashion. In fact, an extremely fortuitous combination of orbital symmetry allowed pathways modulated by thermodynamic factors is necessary to explain the results in this way.

**Acknowledgment.** This work was initiated in the laboratories of Professor George S. Hammond at the California Institute of Technology where it was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, and the Monsanto Fund. Investigations at the University of Oregon were supported by the Research Corporation.

(16) S. W. Benson and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **64**, 80 (1942).

(17) F. E. Blacet and A. Miller, *ibid.*, **79**, 4327 (1957).

(18) H. M. Frey, *Chem. Ind. (London)*, 947 (1966).

(19) G. Quinkert, *Pure Appl. Chem.*, **9**, 607 (1964).

(20) A. Butenandt and L. Poschmann, *Chem. Ber.*, **77**, 394 (1944).

(21) B. Rickborn, R. L. Alumbaugh, and G. O. Pritchard, *Chem. Ind. (London)*, 1951 (1964).

(22) R. L. Alumbaugh, G. O. Pritchard, and B. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965).

(23) This estimate<sup>24</sup> is based on the CH<sub>3</sub>CO-CH(CH<sub>3</sub>)<sub>2</sub> bond dissociation energy and the difference in strain energy between cyclopropane and bicyclo[3.1.0]pentane.

(24) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

(25) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(26) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6259 (1970).

(27) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6267 (1970).

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Received April 29, 1971

## Book Reviews\*

**Chemical and Biological Aspects of Steroid Conjugates.** Edited by SEYMOUR BERNSTEIN (Lederle Laboratories) and SAMUEL SOLOMON (McGill University). Springer-Verlag New York Inc., New York, N. Y. 1970. xi + 453 pp + Author Index (19 pp) + Subject Index (53 pp). \$28.00

This collaborative work represents a careful effort to review the varied aspects of steroid conjugation from the chemist's laboratory to the clinic. It follows the 1968 publication by Bernstein, Dusza, and Joseph of "Physical Properties of Steroid Conjugates."

\* Unsigned book reviews are by the Book Review Editor.

There are nine chapters, each by different authors. Each chapter is followed by its own list of references. The indices, however, are to the entire book and are extensive. In cases there are as many as three subdivision orders under a given heading, for example, "Dehydroisoandrosterone sulfate-conversion-to plasma testosterone-in canine testes." However, compounds are indexed by trivial name only, and authors frequently are to be found only in the reference listing rather than on the page to which the author index refers one.

The chapter contributors are, in each case, prominent or leading figures in this field. Judged in terms of its authors, this volume presents a remarkable range of experience and authority. One

of the most rewarding features of these chapters is the freedom the authors have taken in expressing the opinions derived from their experience. Another major benefit of such expertise appears in the selection of that literature which remains pertinent in the light of present knowledge. While some of the contributions do occasionally lapse into a dull recording of a dull accumulation of data, the greatest part of the writing is cohesive. A work of this caliber will be the authoritative source for the subject until progress renders it out-dated.

The steroid conjugates were for many years only a nuisance in the isolation of the steroids from natural sources. It is now evident that the conjugates cannot be ignored in biological processes, and it may be that they cannot be ignored in understanding the disease states or in the treatment of disease. It is at once the disappointment and the challenge of the last chapters that the role of steroid conjugation in disease and in the treatment of disease has barely begun to appear.

G. W. Moersch, *Parke, Davis & Company*

**High Resolution NMR—Theory and Chemical Applications.** By EDWIN D. BECKER (National Institutes of Health). Academic Press Inc., New York, N. Y. 1969. xii + 310 pp. \$12.00.

This book is one of the best organized of the several available introductions to proton magnetic resonance. It would be suitable as a text for an advanced undergraduate or graduate level course. Likewise, it would be ideal for self-study by the nonexpert.

The discussion sections are replete with well-chosen examples which clearly amplify each topic. Ten of the twelve chapters also contain pertinent problems which allow the student to assess his comprehension of the chapter. Mathematical detail is provided whenever needed. Thus, the book might serve as an introduction to more advanced treatments. However, in every case mathematical results are clearly given and their significance is explained. Therefore, much of value can be extracted from these sections by those who lack mathematical interest or expertise.

Four useful appendices include a list of nuclear spins, magnetic moments and resonance frequencies for most isotopes, thirty-seven "unknown" pmr spectra, general nmr references, and answers to selected problems.

Some idea of the author's style and level of treatment may be obtained by reading an earlier paper (*J. Chem. Educ.*, **42**, 591 (1965)) from which several examples used in the book were obtained.

George H. Wahl, Jr., *North Carolina State University*

**Classical Scientific Papers. Chemistry, Second Series.** Edited by DAVID M. KNIGHT (University of Durham). American Elsevier Publishing Co., Inc., New York, N. Y. 1970. xiii + 441 pp. \$15.00.

This attractively produced volume contains facsimile reproductions of 48 classic papers dealing with the development of concepts of the nature of elements and their arrangement. They are arranged chronologically, beginning with Prout's hypothesis (1815) and ending with Ramsay's reports on the transmutation of atoms in radioactivity (1911). Most of the papers are in English, a result that has been attained by seeking out contemporary English versions of papers by those who customarily wrote in another language: papers by Mendeléeff in the *Journal of the Chemical Society* (1889), by Berzelius in *American Journal of Science* (1845), etc.

This collection makes fascinating and enjoyable reading, and the fact that the papers are reproduced unedited and in their original type-face helps to retain the atmosphere in which they appeared.

**The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, and Bismuth. Second Edition.** By F. G. MANN (Cambridge University). Wiley-Interscience, New York, N. Y. 1971. xxiii + 716 pp. \$42.50.

The first edition of this book, which is part of the series "Chemistry of Heterocyclic Compounds" edited by Weissberger and Taylor, appeared twenty years ago. Its 162 pages have now been more than quadrupled. Even so, there have had to be some omis-

sions, such as silicon heterocycles, which were in the first edition but would now require a book of their own, totally inorganic ring systems, which have been treated elsewhere, and many cyclic esters.

The vexing problem of nomenclature has been solved by adopting the Ring Index names throughout. One does not need to know the proper name of a ring system in order to find it easily, however, for the subject matter is systematically organized according to structure.

For a book of nearly encyclopedic reference, it is unusually easy to read; the author's sensitivity to style is evident. A particularly happy feature is the inclusion of melting or boiling points at the first mention of each compound, for this gives the reader an immediate sense that the compound has a physical reality and is not just an abstraction.

There is an author index and an extensive subject index. The references total 901, and some of them are dated 1969, although the cut-off date of the survey of the literature is not stated.

**Organic Solvents: Physical Properties and Methods of Purification. Third Edition.** By J. A. RIDDICK and W. B. BUNGER (Indiana State University). Wiley-Interscience, New York, N. Y. 1971. xi + 1041 pp. \$24.95.

This book has been nearly doubled in size over the second edition, and is a great value for the money. The authors state that one hundred new solvents have been added, none have been deleted, and twelve new properties have been added. The new authors appear to have completely rewritten the earlier editions and have obviously gone to an enormous amount of work to find and correlate useful information. In this they have made extensive use of private communication with the manufacturers and have performed calculations where necessary. The suggestions made by users of the earlier editions have been used extensively.

The staggering amount of information in this book can be gauged by the fact that Chapter III is composed entirely of tables of physical properties, and is 440 pages long—a book in itself. There are additional useful tables in the form of property indexes, in which solvents are arranged in the order of their boiling points, freezing points, density, cryoscopic constant, dielectric constant, and dipole moment, respectively. Nearly all the data are supported by references, a fact that adds greatly to the confidence of the user.

In the section on purification, it is helpful to find much information on toxicity and flammability, in addition to the valuable basic information on the most up-to-date methods.

This book will continue to be a workhorse in the library, and it is likely to become worn out from hard use in short order.

**Total Steroid Synthesis.** By AFANASII A. AKHREM and YURII A. TITOV (Academy of Sciences of the USSR). Translated by B. J. HAZZARD. Plenum Press, New York, N. Y. 1970. 362 pp. \$25.00.

This excellent monograph was first published in Russian in 1967. The authors added an appendix to the English translation which includes 1967 and several 1968 references, and brings the total number of references to 1126.

The authors elaborate on the term total synthesis to imply sequences in which the construction of specific side chains was intimately involved in the planning of the steroid skeleton. Such is, for example, the case of aldosterone and conessine, but not of equilin, diosgenin, and tomatidine, the syntheses of which start with naturally occurring steroids. Furthermore, special attention is paid to the construction of steroid skeleton rather than the introduction of side chains. Heterocyclic aza-, oxa-, and thiasteroids are included.

The book comprises four chapters. The first deals with general questions concerning total synthesis; the second, with total syntheses from AB, AC, and AD fragments, the third, with total syntheses from BC and BD fragments; and the fourth, with total syntheses from CD fragments.

I highly recommend this lucidly written and well-organized monograph. Future editions should include an author index.

Jacob Szmuszkowicz, *The Upjohn Company*