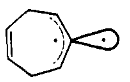
rangement to 1,2,5-cycloheptatriene. The kinetics were followed in the uv at five temperatures between 30 and 48° in ethanol. Plots of log Co/C vs. time were found to be linear through three half-lives with the sole observable product being dimer **3**. Thus the reaction appears to be first order with rate-determining Cope rearrangement being followed by very rapid bimolecular dimerization. An Arrhenius plot of the data yielded a good straight line the equation of which was obtained by a least-squares analysis:

$$\log k/\text{sec}^{-1} = (9.98 \pm 0.22) - (19{,}893 \pm 310)\text{cal mol}^{-1}/2.303RT$$

This corresponds to $\Delta H^{\ddagger} = 19.3$ kcal/mol and $\Delta S^{\ddagger} = -15$ eu at 39°, activation parameters which are certainly compatible with a rate-determining Cope process.

It thus appears that *cis*-1-ethynyl-2-vinylcyclopropane rearranged to 1,2,5-cycloheptatriene with a facility equal to that of conversion of *cis*-1,2-divinylcyclopropane (**7**) to 1,5-cycloheptadiene ($\Delta H^{\ddagger} = 19.4 \pm 1.8$ kcal/mol and $\Delta S^{\ddagger} = -5 \pm 7$ eu).[14] While the overall process of dimer formation should be very exothermic ($\Delta H_0 = -40$–50 kcal/mol of *c*-**5**)[15] the rate-determining formation of **2** should be *endothermic* by ~12 kcal/mol.[15] This is in contrast to the exothermicity of ~23 kcal/mol for the *cis*-1,2-divinylcyclopropane rearrangement.[15] Moreover, it appears that the Cope process of *cis*-1,2-diethynylcyclopropane, which could lead initially to an even more strained diallenic intermediate, occurs with a rate constant similar to those of *c*-**5** and **7**.[16]

While the source of the bulk of the dimer from these pyrolyses has not been unambiguously ascertained,[17] it does appear reasonable that the major, if not only, primary fragmentation product is *cis*-1-ethynyl-2-vinylcyclopropane,[18] and that this then rearranges to 1,2,5-cycloheptatriene[20] which rapidly dimerizes. The structure of this highly reactive allenic intermediate is a matter of some significance. The question yet unanswered experimentally is whether this allene is a planar diradical or dipolar species, such as **8**, or a twisted, strained-but-bonded allene. Calculations by Dillon and Underwood indicate that a *planar* structure may be most stable and that a triplet, biradical species may be the ground state.[22]



8

The unexpected, low-activation-energy Cope rearrangement of *cis*-1-ethynyl-2-vinylcyclopropane is presently receiving further attention in our laboratories, as are probes of the nature of 1,2,5-cycloheptatriene.

Acknowledgment. We wish to acknowledge with thanks partial support of this research by the National Science Foundation.

References and Notes

(1) For a general review of such processes see W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971.

(2) (a) J. M. Walbrick, J. W. Wilson, and W. M. Jones, *J. Am. Chem. Soc.*, **90,** 2895 (1968); (b) W. M. Jones and D. L. Krause, *ibid.*, **93**, 551 (1971).

(3) T. Sasaki, E. Eguchi, M. Ohno, and T. Umemura, *J. Org. Chem.*, **38**, 4095 (1973), and references therein.

(4) A. M. Foster and W. C. Agosta, *J. Am. Chem. Soc.*, **95**, 608 (1973).

(5) The anti ketone has been reported earlier.[6] A mixture of syn and anti-ketone was generated by the decomposition of *cis*-diazomethylketo-2-vinylcyclopropane. GLPC or column chromatographic separation led to the pure isomers. The syn isomer was especially unstable to thermal or acid catalyzed decomposition.

(6) J. J. Gajewski and C. C. Shih, *Tetrahedron Lett.*, 2967 (1970).

(7) Flash pyrolytic techniques used were: D-S, whereby salt was dropped onto a hot Pyrex surface; S, the static technique used frequently by Shechter[6] and others; and T, whereby salt was dropped through a hot vertical Pyrex tube 40 cm in length; all pyrolyses carried out at $\sim 10^{-5}$ Torr.

(8) T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *J. Am. Chem. Soc.*, **94**, 5366 (1972).

(9) All new compounds gave satisfactory elemental analyses.

(10) This compares favorably with the λ_{max} 252 nm (ϵ 8600) for the dimer of the relatively stable allene, 1,2,6-cyclononatriene,[11] which dimerized at 120°.

(11) K. G. Untch and D. J. Martin, *J. Am. Chem. Soc.*, 87, 4501 (1965).

(12) The dimers from **1-S** and **1-A** appear to be identical in all respects although the stereochemistry of the cyclobutane ring has not yet been elucidated. **3** was extremely air sensitive and subject to facile thermal decomposition in solution. Thus, no Diels–Alder adducts could be obtained with either tetracyanoethylene or maleic anhydride.

(13) S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, **28**, 1413 (1963).

(14) J. M. Brown, B. T. Golding and J. J. Stofko, Jr., *J. Chem. Soc., Chem. Commun.*, **319** (1973).

(15) Approximations of heats of formation of **2, 3,** and **5** were made utilizing Benson's group values: S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968. $\Delta H_f°$ for **2** was approximated by assuming no unusual ring strain but a structure similar to **8** (vide infra) and assuming an allenic π bond energy of 60 kcal/mol—8 kcal/mol usual allene strain—15 kcal/mol allyl radical resonance stabilization.

(16) M. B. D'Amore, Ph.D. Thesis, California Institute of Technology, 1972; and personal communication from R. G. Bergman. See also T. J. Henry and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 5103 (1972).

(17) Such ambiguities are common in flash pyrolytic studies of tosylhydrazone sodium salts. Localized high pressure zones may be the cause of such extensive dimer formation with little evidence of monomeric species.

(18) A similar fragmentation was observed in the pyrolysis of tetracyclo[3.2.1.0^{2,7}.0^{4,6}]octan-3-ylidene, although in this case there was no evidence of subsequent conversion to an allene species.[19]

(19) R. G. Bergman and V. J. Rajadhyaksha, *J. Am. Chem. Soc.*, **92**, 2163 (1970).

(20) An earlier attempt was made to generate **2** in hopes that it would rearrange to *c*-**5**.[21]

(21) G. W. Klump and J. J. Vrielink, *Tetrahedron Lett.*, 539 (1972).

(22) P. W. Dillon and G. R. Underwood, *J. Am. Chem. Soc.*, **96**, 779 (1974).

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Received May 20, 1975

Book Reviews

Introduction to Organic Electrochemistry (Techniques and Applications in Organic Synthesis Series). By M. R. RIFI and FRANK H. COVITZ (Union Carbide, Research and Development Department). Marcel Dekker, Inc., New York, N.Y. 1974. vii + 417 pp. $26.50.

This book is designed to initiate organic chemists into the mysteries of electrochemical synthetic methods.

The first chapter includes a frank discussion of the advantages and disadvantages of the method and a historical background. The second chapter covers the basic principles in about 60 pages, touching on the Nernst equation and diffusion as well as such esoterica as double layer capacitance, adsorption, *iR* drop effects, junction potentials, etc. It includes a particularly lucid discussion of charge-transfer rate constants. The third chapter covers apparatus and techniques. The discussion of electrode materials and their pretreatment, solvents, supporting electrolytes, and practical synthetic cells is excellent. The authors also discuss measurement and recording devices, coulometers, and potentiostats and provide a partial list of vendors. The discussion of the techniques, polarography, linear sweep voltammetry, and rotating disk methods is disappointing in contrast to the rest of the material. The chapter includes a recommended list of start-up equipment and procedures which is invaluable. The final section of the chapter is a discussion of the realities of scaling up a synthesis from the gram level to the multiton-a-day level.

Most of the remaining two-thirds of the book deals with representative oxidations and reductions of functional groups, what happened in specific cases, and how the course of the reaction can be altered. There are also brief sections on the relatively untouched areas of electroinitiated polymerizations and electrocoating. Throughout these sections the authors include helpful hints and practical cell designs.

The final section includes a helpful glossary of terms and questions and answers for each chapter.

This book is recommended for any chemist looking for a starting place in electrochemical synthesis, or for an electrochemist interested in understanding the viewpoint of the synthetic organic chemist.

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Permutation Groups, Symmetry and Chirality in Molecules (Topics in Current Chemistry, Volume 49). By C. A. MEAD (University of Minnesota). Springer-Verlag, Berlin-Heidelberg-New York. 1974. 88 pp. $12.30.

This volume of "Topics in Current Chemistry" contains just one article concerned with the applications of group theory to chemistry. In light of the increasingly recognized utility of group theoretical approaches to the study of complicated problems in molecular geometry including chirality, this article is a timely effort to bridge the mathematical gap between the chemist's usual expertise in group theory and some less familiar aspects, including the representation theory of the symmetric and hyperoctahedral groups and the idea of induced representations. If the reader has already developed some expertise in group theory, this volume will be very useful in expanding his knowledge and potential applications of group theory in problems concerning molecular geometry.

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Introduction to Chemical Kinetics. By GORDON B. SKINNER (Wright State University). Academic Press, New York, N.Y. 1974. x + 214 pp. $12.50.

Compared to most chemical kinetics textbooks intended for first-year graduate students, this is a somewhat slender volume with modest goals. Developed in a course attended primarily by students majoring in polymer, analytical, and inorganic chemistry, it contains chapters in collision theory of reaction rates and activated complex theory, Lindemann rate constants and RRKM theory, chemical reactions in solution, and surface reactions and catalysis by solids. Exhibiting a "strong practical slant", this text solicitously alleviates confusion over conversion of units and arithmetic computations with an ample selection of numerical problems. Several experimental kinetics techniques (e.g., nmr, shock tubes, and flash photolysis) are described in a final chapter, though some important current trends (ir and visible chemiluminescence, laser-induced fluorescence studies, and time-resolved laser spectroscopy) are not mentioned.

Little will be gleaned here by instructors searching for useful complementary insights into the topics covered in popular books by Benson, Laidler, or Frost and Pearson. It appears likely that this text will be found most useful for its simplified condensation of a potentially thorny subject for students who are tangentially concerned with physical chemistry. Skinner's personal experience with such students may lend greater clarity to this work, intended for people with limited backgrounds in thermodynamics and statistical mechanics.

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Progress in Mass Spectrometry. Edited by HERBERT BUDZIKIEWICZ. **Volume 1. Indolalkaloide.** By MANFRED HESSE (Organisch-Chemisches Institut der Universität Zurich). Verlag Chemie, Weinheim/Bergstr. 1974. xiv + 261 pp (Teil 1); vii + 98 pp (Teil 2). DM98 (Teil 1 and Teil 2 are not available separately).

The editor indicates in his preface that the purpose of this series is to provide a comprehensive and up-to-date critical account of specific areas of research in the field of mass spectrometry which will enable the nonspecialist to find a footing and which will provide the expert with easy access to the information in the original literature. Although the initial volumes deal with mass spectrometry of natural products, plans call for future volumes dealing with additional aspects of this diverse field. Volume 1 deals with the indole alkaloids, is printed in German, and is presented in two separately bound parts. Teil 1 is effectively divided into five chapters dealing in turn with indole bases, carbazole derivatives, β-carboline derivatives, Iboga alkaloids, and pyrrolidino-indole alkaloids. It is well indexed and referenced, provides a brief introduction to the mass spectral behavior of specific indole alkaloids, and provides an indication in tabular form of the type of information present in the various literature sources cited (e.g., discussion of fragmentation, similar compounds, isotopic labeling studies, configuration, and reproduction of spectra). Extensive references through 1971 are presented at the end of each section. Known indole alkaloids are listed in order of molecular weight in a table at the end of the book and may prove of value in structure elucidation. Teil 1 also serves as the index for Teil 2, which presents the spectra of 173 of the alkaloids discussed in Teil 1. Although some may be reluctant to tackle a subject such as this in the German language, the effective presentation and efficient indexing make this a somewhat less formidable chore than one might expect. The volume should prove to be useful as a reference source, particularly to those active in the field.

Volume 2: Chroman and Related Compounds. By SIEGFRIED E. DREWES (University of Natal). Verlag Chemie, Weinheim/Bergstr. 1974. 138 pp. DM58.

Volume 2 is divided into six chapters dealing with chroman and chroman derivatives, coumarins, xanthenes and xanthones, simple flavenoids, C_{16} flavenoids, and higher flavenoids. The characteristic fragmentations of these types of compounds are discussed in reasonable detail and illustrated by specific examples. Almost two-thirds of the book is devoted to the flavenoids. A tabular compound index to the biblography is included which facilitates access to the original literature (through 1971), indicating via a code whether complete spectra, partial spectra, or information on fragments is discussed. Although a table of contents is included, the absence of any subject or compound index to this volume may be considered an unnecessary inconvenience. The volume will serve as an introduction to the field for the investigator contemplating this area, and for the mass spectroscopist currently active in the area should be a valuable reference.

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Enzyme Engineering. Volume 2. Edited by E. K. PYE (University of Pennsylvania) and L. B. WINGARD, JR. (University of Pittsburgh). Plenum Press, New York and London. 1974. xiv + 470 pp. $27.50

"Enzyme Engineering 2" is an indexed compilation of most of the papers from a second well-organized conference on the new interdisciplinary field of enzyme engineering. In order to employ an enzymic reaction for industrial, analytical, and human therapeutic purposes, the new field appears to be the marriage of enzyme chemists and engineers in order to acquaint each other with the problems of their new "mutual state of the art".

The papers are grouped under nine sections, corresponding to the nine conference sessions, and include new sources of enzymes, purification techniques, immobilization (three sections including papers on the immobilization of enzymes requiring cofactors), reactor design, and industrial and commercial aspects (three sections).

Most of the papers are well written and the text subject matter is coherent, a credit to the editors. The text of the compilation will serve as an authoritative introduction to this interdisciplinary subject, and some novel techniques are discussed, such as the immobilization of an enzyme on iron oxide powder and recovery of the enzyme with a magnet. The references cited can also be used as a more detailed introduction to the subject.

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