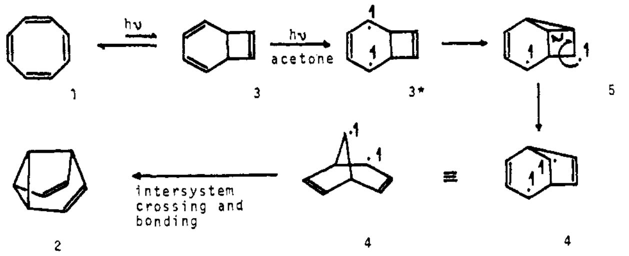
the present reaction is the reverse of the previously observed[2a,b] conversion of semibullvalene (**2**) to cyclooctatetraene (**1**).

Two molecular pathways seem reasonable possibilities for the reaction. One is based on the presumption that there is an appreciable concentration of bicyclo-[4.2.0]octa-2,4,7-triene (**3**).[4–6] A di-π-methane rearrangement[7] of the type noted by us earlier[2b] as being general, when applied to this bicyclic intermediate (*i.e.*, **3**),[8] leads to semibullvalene (**2**) (note Chart I).

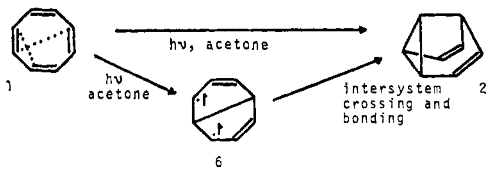
Chart I. Di-π-methane Route from Cyclooctatetraene to Semibullvalene



Interestingly, this mechanism proceeds *via* the same triplet biradical **4** that was demonstrated[2b] in the photolysis of barrelene to lead to semibullvalene.

The second pathway available is by 1,5 and 2,8 (or 4,6) bonding as depicted in Chart II.[9] However, the correct mechanism need not be the reverse of that utilized in the semibullvalene (**2**) to cyclooctatetraene reaction[2a] since, as has been pointed out,[12] microscopic reversibility is not easily invoked in photochemistry.

Chart II. Direct Route from Cyclooctatetraene to Semibullvalene



We are presently pursuing the mechanistic ramifications of this unusual new reaction.

Acknowledgment. Appreciation is expressed to the National Institutes of Health for support of this research by Grant GM07487.

(5) It is possible that **3**, available thermally (R. Huisgen and F. Mietzsch, *Angew. Chem.*, **76**, 36 (1964)), is utilized in the reaction.

(6) In the present study no direct evidence was adduced for photochemical formation of **3**. Further studies on this point, the photochemistry of **3**, and detailed mechanistic investigations of the conversion are in progress.

(7) We now prefer the term di-π-methane rearrangement for this transformation since aryl-substituted methanes undergo the process as well as divinylmethanes, as has been noted.[2b]

(8) This compound has been independently synthesized by E. Vogel, H. Keifer, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964).

(9) Such 1,5 bonding, as well as bonding of 1,3 related atoms in a π system, has been noted by us earlier[10] to be energetically favorable photochemically. More recently this has been considered by Woodward and Hoffmann.[11]

(10) H. E. Zimmerman, *J. Am. Chem. Soc.*, **88**, 1566 (1966).

(11) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(12) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *J. Am. Chem. Soc.*, in press.

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Book Reviews

Catalytic Hydrogenation over Platinum Metals. By Paul N. Rylander, Research and Development Division, Engelhard Industries, Inc., Newark, N. J. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1967. xii + 550 pp. 16 × 23.5 cm. $22.50.

Catalytic hydrogenation is now a classical procedure for reducing a wide variety of functional groups, but few chemists are aware of the many different catalysts available or the most advantageous way to carry out a particular reduction. This information is widely scattered throughout the literature, and much of it has been published during the past 15 years. The object of this book is to collect, summarize, and interpret this information. The emphasis is on recent literature and on the practical side of the art; historical aspects are barely mentioned, and there is little mechanistic speculation. Only the platinum metals and their oxides are considered. The reader will have to look elsewhere for a discussion of other metal oxide catalysts and of sulfide catalysts which are competitive with the platinum metals and are preferable in certain situations. Nickel catalysts are mentioned only occasionally.

After a 50-page discussion of general matters (types of catalysts, certain of their properties, reactors, and reaction conditions), the work is organized according to the nature of the functional group to be reduced: acetylenes, olefins, imines, hydrazones, aldehydes, etc. A few of the interesting new catalytic procedures in the book are described below in order to give some idea of the newer material included. Iridium catalysts are especially useful in stereospecific hydrogenation of certain 16-methylene steroids to the β-methyl derivatives. Rhodium on alumina is superior to platinum and palladium for hydrogenation of vinyl or allylic halides to haloalkanes; the latter catalysts cause extensive hydrogenolysis. Certain optically active olefins are hydrogenated over platinum oxide with almost no racemization, but over palladium on carbon considerable racemization occurs; this indicates that double bond migrations during hydrogenations are more likely with palladium than with platinum. Reduction of oximes over a rhodium-on-carbon catalyst gives largely primary amines, whereas over platinum or palladium under similar conditions, secondary amines may be the principal products. Both the aromatic ring and the nitro group of aromatic nitro compounds can be hydrogenated in a single operation over a ruthenium catalyst. A trace of stannous chloride is a superior promotor for the reduction of aldehydes over platinum oxide, but it acts as a poison with a prereduced platinum catalyst. Palladium is often ineffective as a catalyst for the hydrogenation of ketones whereas platinum is usually satisfactory. Protonation of a ketone by hydrogenating in an acid medium greatly increases the rate of reduction over platinum catalysts, but rhodium and ruthenium catalysts are more active in neutral or basic solution. These are only some of the examples which show that organic chemists who employ catalytic hydrogenation have a wide variety of useful catalysts at hand, and that this book will be a source of many new ideas about how to carry out practical hydrogenations.

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Stossrohre. Shock Tubes. Theorie, Praxis, Anwendungen, Mit einer Einfuhrung in die physik der Gase. By Herbert Oertel. Springer-Verlag, Molkerbastei 5, A-1010, Wien, Germany. 1966. xxi + 1030 pp. 18 × 24.5 cm. $80.00.

This extensive summary, written in "easy-to-read" German, consists of 857 pages of text, 621 diagrams, 152 tables of data and compilations of equations, and 220 pages of references to the literature (through 1964) with titles of the reports, listed alphabetically by authors. The text is divided into nine sections. About half of the text is devoted to the physics of gases; it is a compendium of elementary thermodynamics, statistical mechanics, kinetic theory and transport processes, fluid mechanics, ultrasonics and relaxation processes, and several topics on atomic and molecular structure. The material appears to have been selected on the basis of anticipated frequency of use of equations, tables, and graphs, to which a beginning student would turn for rapid reference. As such it will indeed prove useful. For those who might be misled into believing that they could in this manner bypass a careful study of the fundamentals of chemical physics and gas dynamics, this will prove a trap. There is little discussion of basic concepts, and the presentation on the whole is uncritical.

In the next seven sections a large amount of practical material has been abstracted from the literature and organized primarily for the experimentalist. After pouring over the mass of material I became convinced that, prior to the design of any experiment in this area, a careful study of the appropriate section in this portion of the book will prove rewarding, because the author did prepare a full compilation of the various apparatus configurations which have been tested. The many diagrams which relate the appropriate reduced variables will also be useful. The last section of 150 pages on *applications* suffers the most from having been completed in the fall of 1963 and somewhat patched to include references to papers which appeared in 1964. It is clearly impossible to maintain such a section up to date, and of necessity it lags most behind the other parts of this handbook at its first printing. The author was consistent in his objective, in that he arranged the topics in this section on the basis of the physical variables which were measured. Obviously as shock-tube techniques become generally exploited, the emphasis must shift to an organization of material on the basis of the physical and molecular concepts involved. Indeed, this is the striking contrast between the book by Oertel and the two volumes on the "Physics of Shock Waves and High Temperature Hydrodynamic Phenomena" by Zel'dovich and Raizer, now available in English translation. However, the effort to prepare such a handbook seems heroic to the reviewer. Reproduction of the beautiful schlieren photographs of gas dynamic processes, prepared under Professor Schardin's direction, is appreciated.

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The Structure and Reactions of Heterocyclic Compounds. By Michael H. Palmer, Lecturer in Chemistry in the University of Edinburgh. St. Martin's Press, 175 Fifth Ave., New York, N. Y. 1967. vii + 462 pp. 15.5 × 23.5 cm. $13.95.

Despite the fact that, by current estimates, some 65% of all published work in organic chemistry deals with some aspect of heterocycles, textbooks on this subject covering basic principles of structure, properties, and synthesis are not only of very recent origin but generally fall far below the standard set for textbooks in the general field of organic chemistry. The present book is no exception. It deals with a reasonable cross section of heterocyclic chemistry, with perhaps more emphasis than other introductory texts on relationships between ground-state properties and MO calculations, and between reactivity and localization energy calculations. Its intended scope is indicated by the chapter headings: nomenclature and definitions; pyridines; diazines; triazines and tetrazines; bicyclic heterocycles; diazanaphthalenes; pteridines; pyrylium salts and pyrones; benzopyrylium salts and benzopyranones; tricyclic heterocycles with six-membered rings; heterocycles with one heteroatom in a five-membered ring; benzo derivatives of pyrrole, furan, and thiophene; condensed pyrroles, porphyrins, and phthalocyanines; five-membered ring heterocycles with more than one heteroatom; the mass spectra of heterocycles. Palmer's book thus gives the superficial appearance of presenting an up-to-date treatment of heterocyclic chemistry.

It is a gamble to write a textbook in a field with which one is not familiar and in which one has not had extensive research experience. To this reviewer, the present book fails completely to convey to the reader any sense of excitement or interest in heterocyclic chemistry. A striking illustration is given by the section on purines, which is almost entirely concerned with interrelationships among the various methylated xanthines (theobromine, caffeine, theophylline) and with uric acid chemistry. These were interesting topics in purine chemistry at the turn of the century, but surely the student studying heterocyclic chemistry today should be given some realization of the contemporary importance of this field—the impact of biogenetic considerations on chemotherapy, the synthesis of adenine from hydrogen cyanide and ammonia under simulated primitive earth conditions, and the biological importance of purines as bases in nucleic acids, as plant growth hormones, and as antibiotics. An entire chapter is devoted to pteridines without a single mention of *why* this ring system is important, and without mention of any of the many important pteridine derivatives (folic acid, aminopterin, xanthopterin, biopterin, etc.). The reader is not even told that pteridines occur as natural products and is left with the impression that chemists study them only as substrates for measurements of pK values and for alkylations.

Similar omissions plague the entire book. The chemistry of heterocyclic systems appears, from the discussion given here, to be confined to the determination of the position of tautomeric equilibria, to nitrations, chlorinations, sulfonations, and acylations, and to nucleophilic displacement reactions. There is no mention of the Alder–Rickert reaction, of the oxidation of furans to 2,5-dialkoxy-2,5-dihydrofurans and their use as synthetic intermediates (*e.g.*, in the synthesis of vitamin B_6), of the usefulness of Reissert compounds in heterocyclic synthesis, or of the synthesis of morphine or chlorophyll (despite a discussion of structure proof). Photochemistry of heterocycles, an extremely active and productive contemporary field of research, is dismissed with the statement that 2-pyranone "is converted to a bicyclic isomer by ultraviolet irradiation." The majority of the synthetic reactions leading to heterocycles which are cited were discovered more than 40 years ago and only a few have any practical significance today. In fact, except for a number of references to papers published in 1965 and 1966, this book could have been written 25 years ago.

I do not recommend this book either to students, who will be neither informed nor excited about heterocyclic chemistry, or to research workers, who will find in it little that is relevant to the actual world of present-day research.

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Photochemistry and Reaction Kinetics. Edited by P. G. Ashmore, F. S. Dainton, and T. M. Sugden. Cambridge University Press, 32 East 57th St., New York, N. Y. 1967. xvi + 378 pp. 14.5 × 22 cm. $13.50.

This book is dedicated to R. G. W. Norrish, Nobel Laureate and Emeritus Professor of Chemistry, University of Cambridge, to commemorate his lasting contributions to photochemistry and reaction kinetics. It's twelve chapters were written by fourteen distinguished men, most of whom acquired their major scientific training and their enthusiasm for chemistry in his laboratory. Throughout the text runs the incredibly diverse thread of Norrish's contributions to photochemistry and free-radical chemical kinetics.

However, only the first two chapters are concentrated primarily upon the work of Norrish in the fields of photochemistry and combustion. The remaining ten chapters are critical review articles which coordinate and evaluate the published information which, in the opinion of the respective authors, contributed significantly to current general concepts and theories concerning the mechanisms of important chemical processes.

These review chapters cover photochemistry in the liquid phase, gaseous photochlorination, flash photolysis, flash photolytic studies of free radicals in the gas phase, energy transfer in molecular collisions, polymer chemistry, the mechanism of hydrocarbon oxidation in the gas phase, the interpretation of cool-flame and lowtemperature combustion phenomena, the sensitization and inhibition of ignitions, and the pyrolyses of paraffins.

Students who plan to do research in any of the above fields would do well to start with a careful reading of this book. The selected references at the end of each chapter could be a valuable guide to additional study. This volume should be in every chemistry research library and most interested scientists will want it in their personal collections.

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