
 BOOK REVIEWS

Lipide Chemistry. By DONALD J. HANAHAN, Department of Biochemistry, University of Washington, Seattle, Washington. With contributing chapters by Frank R. N. Gurd, Bureau of Medical Research, Equitable Life Assurance Society of the United States and Department of Biochemistry, Cornell University Medical College, New York, and Irving Zabin, Department of Physiological Chemistry, University of California, Los Angeles. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1960. ix + 330 pp. 15.5 × 23.5 cm. Price, \$10.00.

The study of the lipids has lagged behind that of the carbohydrates and proteins largely because of the difficulties of approach—peculiar solubilities and the habit of forming more or less stable combinations with many substances. Modern development has been made possible by the development of means of separation, especially by the chromatographic methods. Not less important are the improved methods of synthesis resulting in the formation of key compounds which can be used as a basis for comparison with the natural products. The apparently hopeless lipid combinations have now yielded to the modern treatment and there has resulted a startlingly rapid increase of relatively exact information. This book consists of an examination of the progress made during the last ten years in this fast-growing field. It covers in briefer form much of the material in Deuel's monumental work, but gives special attention to the organic structure of the lipids, their nature and synthesis. Very little attention has been given to the sterols, vitamins and other substances ordinarily classed with the lipids.

Each major class of lipids is discussed with special reference to its connection with the lipoproteins which constitute the form in which these substances occur in nature.

There are contributing chapters by Frank R. N. Gurd on the association of the lipids with proteins and with the naturally occurring lipoprotein systems; the sphingomyelins are given special consideration by Irving Zabin.

A companion volume—"Lipide Metabolism," edited by Konrad Bloch—is to be published soon.

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Theory of Detonation. By I. A. B. ZELDOVICH and A. S. KOMPANEETS. Academic Press Inc., 111 Fifth Avenue New York 3, N. Y. 1960. 284 pp. 16 × 23.5 cm. Prices, \$10.00.

This book is a translation from the original Russian edition published in Moscow in 1955. It is an excellent presentation of classical detonation theory which includes the important part of the theory for which the senior author shares honors with J. von Neumann and W. Doering, although the latter two great contributors to detonation theory are not mentioned in this volume. Failure to acknowledge the work even of the foremost of the many contributors to the theory of detonation outside Russia is unfortunate because, aside from the contribution of Zeldovich himself, the basic parts of the theory were not contributed by Russian scientists. For example, the thermohydrodynamic theory of detonation which forms the foundation of much of the theory discussed in this volume is largely the work of renowned British, French and German scientists of the late nineteenth and early twentieth centuries.

The first chapter is a concise but lucid presentation of conventional shock wave theory including the powerful method of characteristics. The second and third chapters deal with detonation waves with special emphasis on gaseous detonations. The approach is that of a shock wave followed by chemical reaction without coupling between them in which effects of diffusion, viscosity and conductivity in the reaction zone are neglected. This treatment has lately been referred to as the "zeroth-order" approximation. The case of strong intimate coupling of the shock wave with chemical reaction in the detonation wave associated with high thermal conductivity, maintained for some time by the reviewer, seems now to

be well-justified by the experimental facts. Hirschfelder and co-workers have considered such coupling in an elegant, general theory of detonation that includes the influence of transport phenomena. Still the great contribution of the zeroth-order solution of Zeldovich, von Neumann and Doering should not be discounted. Indeed, without it, bringing out so clearly as it does the consequences of negligible heat transport on the nature of the pressure-time contour in detonation, progression in the science of detonation waves would no doubt have been greatly retarded. Failure to observe the type of pressure-time curves predicted by the zeroth-order approximation is therefore no reflection on the magnitude of the contribution of these authors. In fact, it was the definitive character of their solution that pointed clearly the way to the more general theory including transport phenomena which more accurately accounts for the experimental facts.

Chapter 4 treats detonation in condensed explosives. It gives a number of brief, somewhat categorical, statements considered by the authors as most pertinent to detonation in condensed phase, and then presents a discussion of the equation of state applicable in condensed explosives. The discussion pertaining to condensed explosives, however, leaves very much to be desired, both regarding the real nature of the detonation in condensed phase and the equation of state. But it is nevertheless of considerable interest.

The final chapter discusses the motions of the products of detonation inside a detonation wave and the expansion characteristics of the waves propagated outside a charge. Within the limitations of the basic facts and concepts considered this section is also an excellent presentation. Unfortunately, the matters discussed are complicated by phenomena not considered in this volume. One of these is the "triangular region" or "detonation head" observed by flash radiography and clearly elucidated in shaped charge studies. Another is the influence of strong ionization in detonation on the motions of the products both inside and outside the original charge. However, the "dilute plasmas" associated with detonation waves were not recognized until after the original publication of this volume in 1955. It is now evident from the experimental facts that the highly luminous clouds ejected into surrounding media from free surfaces by detonation waves in condensed explosives are actually comprised to a large extent of highly ionized (intermediate) products of detonation that have apparently sieved through the otherwise distinct shock wave and practically obliterated it, the shock connected with the front of these brilliantly luminous clouds being merely a relatively weak bow wave. Any treatment of the luminous clouds ejected from free surfaces of detonating explosives as shock waves is thus clearly incorrect.

Despite limitations imposed on the theory by the most recent experimental observations, this volume represents a significant contribution to the theory of detonation with which all concerned with this complicated but fascinating field of science should become familiar.

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Aids to Biochemistry. Fifth Edition. By S. P. DATTA, B.Sc., M.B., B.S., Reader in Biochemistry in the University of London, and J. H. OTTAWAY, B.Sc., Ph.D., A.R.I.C., Senior Lecturer in Biochemistry, University of Edinburgh. The Williams and Wilkins Co., Baltimore 2, Maryland. 1960. viii + 266 pp. 10.5 × 16.5 × 1.6 cm. Price, \$3.75.

This pocket-size volume is stated by the authors to have been prepared primarily for the instruction of preclinical students of medicine and secondarily for the use of advanced students of medicine who need to refresh their biochemical knowledge. This reviewer doubts that either of these ends has been satisfactorily achieved.

In so small a text, comprising (apart from diagrams, tables and formulas) not much more than sixty thousand words, it would be practically impossible to present all the factual and

theoretical information which a medical student in this country is required to assimilate. Efficient use of the limited space would necessitate extremely careful selection of material, and there is no evidence of this. A student for whom it is deemed necessary, for example, to outline the elementary organic chemistry of esters and ethers (p. 22) is unlikely to be able to grasp the implications of the information summarized (pp. 25-27) concerning polysaccharides. He could, presumably, also make little out of the statement (p. 70) that "proteins can be made to sediment in very high speed centrifuges" unless it were at least hinted that the proteins were in solution.

Misstatements also abound. It is, for example, incorrect to assert that casein is a globulin (p. 69), that "all mono-saccharides can be converted into furfural if they are boiled long enough with strong acid" (p. 23) and that phenylalanine gives a positive xanthoproteic test. The validity is questionable of the general statement (p. 35) that "saturated fatty acids can be oxidized with difficulty to acids with two atoms less in the carbon chain, together with 2CO_2 ." There is also occasional evidence of lack of care in proof-reading: "toluidine" for "tolidine" (p. 91), "a copious excreta" (p. 200), the omission of an oxygen atom in the formula for cerebrosides (p. 44), the faulty ring structure for cholesterol (p. 48).

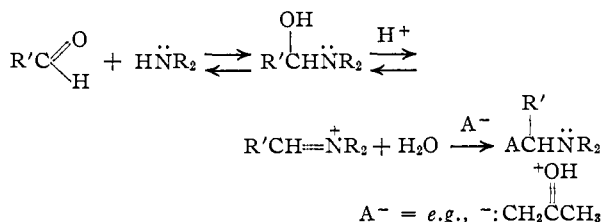
In textbooks intended for the instruction of unsophisticated beginners and other uncritical readers, errors of any kind may lead to misunderstandings and other difficulties.

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Die Mannich-Reaktion. By BENNO REICHERT, Dr. Phil., Apl. Professor and der Universität München. Springer Verlag, Heidelberger Platz 3, Berlin-Wilmersdorf, Germany. 1959. viii + 195 pp. 16 X 23.5 cm. Price, DM. 36.—

Dr. Reichert, a student of Mannich, has written an authoritative, well-documented, though not entirely complete account of the development and the synthetic applications of the Mannich reaction, covering the period up to and including 1957. The Mannich reaction is, as shown, the condensation of an aldehyde with ammonia, or a primary or a secondary amine, and a compound containing reactive hydrogen atoms (a CH- or NH- acidic reagent), to form what came to be called a C- or N-Mannich base.



The exploration of the general synthetic potentialities of this reaction, from 1917 on, was Mannich's life work, explained in some 70 articles published before his death in 1947.

Previous reviews of the reaction were published in *Archiv. der Pharmazie* by Karbe, in 1950, with emphasis on compounds of pharmacological interest, and in "Organic Reactions, Vol. I" by Blicke, in 1942, in more general terms. However, while Dr. Blicke's article cited 74 references, Dr. Reichert now cites over 1000. Of these approximately 700 cover the years 1942-1957, the period since the last review; six citations are included for the year 1958. Consequently Dr. Reichert's book is the best available record to date on the Mannich reaction.

Dr. Reichert divides his book into seven sections. After a brief historical survey he presents a section on the scope and the mechanism of the reaction. In it he credits Hellmann and Opitz with the clarification of the mechanism of the Mannich reaction, although in fact the late Eliot R. Alexander and E. J. Underhill carried out the quantitative kinetic study of it before the appearance of "Die Mannich-Reaktion." The book mentions their study very briefly, but does not discuss their data and conclusions; because of this omission the mechanism on p. 6 is not entirely satisfactory

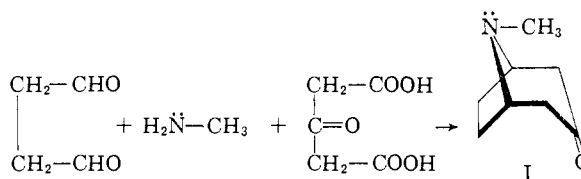
in all detail for the general case of the acid-catalyzed Mannich reaction. It should be mentioned here that in a very recent kinetic study Cummings and Shelton (*J. Org. Chem.*, **25**, 419 (1960)) have borne out Alexander and Underhill's findings, with only minor modifications. The chapter does not indicate specifically, either, that basic catalysis of the Mannich reaction is possible, nor does it cite evidence for the formation of aminomethyl ethers, $\text{R}_2\text{NCH}_2\text{OR}'$, as intermediates in alcoholic media, though such evidence was available.

The next section explains experimental procedures and conditions; it is not as well organized as similar chapters in "Organic Reactions." However, Dr. Reichert compensates for this by including in the rest of the text about 70 individual procedures for the preparation of particular compounds.

The bulk of this volume, 104 pages, deals in two sections with the various CH-acidic and NH-acidic components used in the Mannich reaction. Separate chapters cover ketones, aldehydes, acetylenes, carboxylic acids, di-, tri- and tetracarboxylic acids and their esters, β -keto-diester, phenols, nitro compounds, heterocyclic compounds, and aliphatic and heterocyclic amides as NH-acidic components. Thirty pages are devoted to ketones alone, five pages to Mannich bases with nitro compounds, a relatively recent field; eighteen pages cover Mannich bases derived from indene. As might be expected in a volume covering over 1000 separate sources, referencing and cross-referencing is not always complete; for instance, several articles on nitro compounds are not mentioned in the appropriate chapter. However, there is wealth of material in these two major sections, and Dr. Reichert has gone to great trouble to present it in digestible form. Some of the highlights from these pages are the formation of 2-methylenecyclohexanone, its dimerization and subsequent ring-contraction to a dispirane (no mechanism given); the failure of dihydrocodeinone to undergo aminomethylation; the preparation of *d,l*-cytisine, a vegetable alkaloid; the successful aminomethylation of various tetracyclines; and the syntheses of the plant growth factor heteroauxin and of tryptophan by way of Mannich reactions.

Two concluding sections give applications of the Mannich reaction in synthesis, and a list of C- and N-Mannich bases (with references). Both parts are very useful, but neither section is entirely complete. The section on synthetic applications omits a good example, with experimental procedure, for the formation of olefins from Mannich bases, and it omits also the preparation of pyrazolines, which is dealt with only briefly elsewhere. The reverse Mannich reaction is particularly interesting in these final chapters. At the end of the volume an author index is missing.

I should like to make one more point in connection with the coverage of the book. In 1917, the same year in which Mannich started his intensive work in Germany, Robert Robinson in England prepared tropanone (I) and thence atropine, from acetonedicarboxylic acid (or its dimethyl ester, or even acetone), succindialdehyde and methylamine hydrochloride, in a reaction that was clearly a double Mannich condensation.



He reasoned that tropanone, a precursor of atropine, could arise phytochemically in a similar non-enzymatic reaction. Clemens Schöpf investigated the Robinson condensation in Germany; his and Robinson's work had tremendous influence on biogenetic theory in the field of alkaloids. Not only were a host of tropanone and atropine derivatives, and other tropanone-like compounds obtained by this method for the first time, but the principle of the condensation was also applied to the synthesis of a large number of other alkaloids, or precursors. Furthermore, practically all contemporary workers in the biogenetic field postulate the Mannich-Robinson condensation as a fundamental reaction in the phytochemical formation of alkaloids.

Last year then, after the appearance of Dr. Reichert's monograph, Edward Leete demonstrated in isotopic tracer feeding experiments (*J. Am. Chem. Soc.*, **81**, 3948 (1959))