# BOOK REVIEWS

**Organic Chemistry.** By E. E. TURNER, M.A., D.Sc., F.R.S., Professor of Chemistry in the University of London (Bedford College) and MARGARET M. HARRIS, Ph.D., Lecturer in Chemistry, Bedford College. Longmans, Green and Co., Inc., 55 Fifth Avenue, New York 3, N. Y. 1952. xi + 904 pp. 17.5 × 25.5 cm. Price, $10.00.

This work is described by the authors as "not intended as an examination text book," but it is also stated that "a study of this book should leave a student ready to begin the reading necessary for a research in any branch of organic chemistry." Certain other statements in the Preface present rather accurately the general nature of the work, especially, "The three main branches of organic chemistry are concerned with molecular configuration, mechanism of reaction and the constitution of naturally occurring substances." This outlines the scope of the book if one also heeds the additional statement, "It will be apparent that we have been more interested in some parts of the subject than in others."

The general make-up resembles, in many features, that of the first edition of Whitmore's "Organic Chemistry," including the regrettable policy of giving no references other than the names of investigators followed by a date (year). Specific features differ considerably from Whitmore's book, however. Although the present book has a reasonably large fraction of its content, perhaps one-third, devoted to a description of reactions useful for organic synthesis, this material is of the rather elementary sort found in general text books on organic chemistry. The scope and limitations of synthetic procedures are not discussed, and the simplicity of the presentation is sometimes deceiving. For example, in the discussion of the conversion of alcohols to alkyl halides no mention is made of the numerous rearrangements which may be encountered, in fact, it is stated that the "cation R+" is "never free." Space is also devoted to such things as explaining how line formulas are used to indicate benzene (p. 355).

On the contrary, there are numerous discussions of reaction mechanisms which appear to be complete and informative. These include, among others, Hughes' pioneering work on replacement of halogen by hydroxyl, the mechanisms of hydrolysis and esterification, and the structure and reactions of the diazonium salts. Discussions of this type should be regarded as a very useful feature of the book. Particular mention should be made of the section on free radical reactions, since this topic has not been treated in the secondary literature to such an extent as have ionic reactions. It is of interest that such terms as "carbonium ion," "$SN_2$," etc., appear to have been carefully avoided, although there is free use of such terms as mesomeric shift and hyperconjugation.

For those interested in the historical development and evolution of concepts and theories, the book contains much of this nature. For example, about seven pages are devoted to developments leading up to present concepts of the structure of benzene; also, presentation of the structures of sugars is developed along historical lines.

In various appropriate places, there is considerable useful discussion of the nature of valences and of molecular structure. Molecular orbital theory is mentioned but rather briefly, not entirely correctly, and in a manner wholly inscrutable to anyone not fully conversant with the language of and definitions used in such discussions. For example, the following three sentences constitute the complete treatment of the nature of the C,C double bond. "The single bond is formed from *s* electrons. In ethylene, the carbon atoms still have a $\sigma$ (bonding) orbital, but in addition there is a $\pi$ orbital (p electrons) perpendicular to the symmetrical $\sigma$ orbital of the *s* electrons. (The $\pi$ orbital is responsible for the inhibition of free rotation.)" The only other discussions of molecular orbitals noted by the reviewer are a single page in connection with *cis,trans* isomerism and a half-page in connection with the structure of benzene. The index does not contain an entry, "molecular orbitals."

There is considerably more space devoted to heterocyclic compounds than is common in American books of a general nature, and this would appear a useful feature. The reviewer discovered a surprisingly small number of typographical errors, and the factual errors (such as continuous removal of isopropyl alcohol by distillation during an Oppenauer oxidation) appear not excessive for a book of this scope. The price is sufficiently reasonable to justify a favorable exclamatory comment!

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
UNIVERSITY OF CALIFORNIA JAMES CASON
BERKELEY 4, CALIF.

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**Glycols.** By GEORGE O. CURME, JR., Editor, and FRANKLIN JOHNSTON, Associate Editor, Carbide and Carbon Chemicals Company, A Division of Union Carbide and Carbon Corporation. Reinhold Publishing Corporation, 330 West 42nd Street, New York, N. Y. 1952. xii + 389 pp. 16.5 × 23.5 cm. Price, $12.00.

Written from the viewpoint of the industrial chemist and engineer, this monograph carries the reader in logical fashion through the history, commercial production, physical properties, applications, and derivatives of industrial import of the glycols in commercial production today. As acknowledged by the editors, the major sources of information were Union Carbide and Carbon Corporation, Dow Chemical Company, E. I. du Pont de Nemours and Company, and the Mellon Institute. In addition, extensive surveys of the chemical and patent literature were incorporated in the review.

In undertaking the compilation of a vast amount of data, much of it previously unpublished, the authors have been eminently successful in emerging with a readable as well as informative review. The several chapters on physical properties of the more important glycols (industrially) render the book useful as a handbook for those interested in the field. The inclusion throughout the book of detailed descriptions of preparative methods for the glycols and their derivatives will also prove of considerable value to the chemist or engineer working in the field. The final chapter on Analysis and Test Methods will find especially grateful readers in that department.

The typography is generally good, the editing well above average. In beginning the second chapter one gains the feeling that this is the history of the growth of the various divisions of Union Carbide and Carbon. However, this is an interesting and probably necessary portion of any proper narration of the commercial development of a large tonnage chemical.

This book is recommended reading for all industrial chemists interested in a comprehensive and lucid treatment of the production and utilization of glycols and all academic chemists interested in bringing up to date their lectures in this field.

PETROLEUM CHEMICALS RESEARCH AND
DEVELOPMENT DEPARTMENT
CELANESE CORPORATION OF AMERICA O. V. LUKE
CLARKWOOD, TEXAS

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**Hydrogen Ion Concentration—New Concepts in a Systematic Treatment.** By JOHN E. RICCI. Princeton University Press, Princeton, New Jersey. 1952. xxxvi + 460 pp. 16.5 × 24 cm. Price, $10.00.

The purpose of this book is to consider the problem of hydrogen ion concentration in aqueous acid–base equilibria "without special assumptions and without dependence on theories of the mechanism of the process of ionization, but purely on the basis of mathematical definitions, and to present a systematic derivation of interrelated formulas for calculations involving the hydrogen ion concentration in various aqueous solutions of almost any degree of complexity."

The author has accomplished this objective in scholarly fashion, but some of the definitions are a little unusual even for the reader with considerable experience in the field of acids and bases. For example, a "strong acid" is one for which the un-ionized fraction is zero. The author recognizes this as a limiting case where the dissociation constant of a monobasic acid is infinity but mathematically considers the degree of dissociation of a "strong" monobasic acid to be always strictly 1 or never strictly 1. The concentration of the anion is set equal to the stoichiometric concentration of the acid but not equal to the hydrogen ion concentration as this would be inconsistent with the most fundamental definition of all, namely, the ion product of the concentration of the hydrogen and hydroxyl ions in aqueous solutions. The treatment applies only to aqueous solutions, and "neutrality" means equal hydrogen and hydroxyl ion concentration, "electrolytes" are solutes which contribute foreign ions to solution, "non-electrolytes" introduce no foreign ions, the word "salt" does not imply neutrality, the "degree of hydrolysis" for a salt is a term not mathematically definable.

The principle of electroneutrality plays an important role in the equations developed in the text and although it is recognized that equilibrium constants are only constant in terms of activities, activity coefficients are set equal to unity to retain the possibility of adding or subtracting activities in place of concentrations in the equation of electroneutrality. The author is well aware of the difficulty of extrapolation to infinite dilution but might have introduced the principle of "swamping salt" in his treatment.

Chapter V gives the *exact* equations for the determination of equilibrium constants for acids and bases and gives examples of the reduction to approximate equations used in the literature. Chapter VI gives an interesting interpretation of ionization constants. Subsequent chapters give the exact relations for hydrogen ion concentration, the feasibility of titrations for single acids and mixtures, for interdependent ionization constants and for some complex cases.

Chapters XVII through XXI take up the problem of the solubility and solubility product of acids, bases and salts, and the author's experience in phase rule studies has enabled him to give graphical as well as exact mathematical presentations of solubility relationships.

The book is a scholarly mathematical presentation of the problem of the equilibrium involved between acids, bases and ampholytes in aqueous solution. The book cannot be read casually, but with careful study of the definitions presented it serves as a useful reference work for the exact equations with hydrogen ion concentration as the independent variable.

ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO 16, ILLINOIS MARTIN KILPATRICK

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**Electrochemical Data.** By B. E. CONWAY, Ph.D., D.I.C., The Chester Beatty Research Institute, London. Elsevier Publishing Company, 402 Lovett Blvd., Houston, Texas. 1952. xx + 374 pp. 16.5 × 23.5 cm. Price, $8.75.

Out of the 359 pages of tables, literature references and notes of this volume, 152 are identical with the full contents of Chapter XIV of Volume II of the "Textbook of Electrochemistry" by Kortüm and Bockris (Elsevier, 1951), this Chapter being contributed by Dr. Conway. One wonders why the present volume could not have constituted Volume III of the Textbook, the duplication of tables being thus avoided and the high cost of Volume II being then correspondingly reduced.

There is no doubt that Dr. Conway has performed a most valuable task in assembling such an imposing mass of up-to-date data pertaining to such a wide range of properties, some of which, however, appear rather remote from electrochemistry. For instance, do vapor pressure data for mixed liquids really belong to a compilation of electrochemical data? The material is distributed between ten chapters, each one containing, in addition to tables, about two pages of general remarks on the selection of data, abundant notes in small print and detailed but not exhaustive bibliographies. The topics covered are as follows: I. Universal constants and ratios and some conversion factors (9 pages). II. General data on physical properties (45 pages). III. Molecular and ionic interaction in the liquid phase. Data on activity coefficients, osmotic coefficients, hydration, salting-out and salting-in (86 pages). IV. Transport in solutions of strong electrolytes. Electrolytic migration and diffusion (42 pages). V. Dissociation constants, solubilities and buffer solutions (34 pages). VI. Properties of the electric double layer at interfaces (24 pages). VII. Transport and general properties of colloids and macromolecular electrolytes of biological importance (22 pages). VIII. Electrochemistry of melts at high temperatures (47 pages). IX. Reversible electrode processes (47 pages). X. Parameters of electrode kinetics (25 pages). The space occupied by these last two chapters seems small compared with that occupied by thermodynamic, conductance and transport data for solutions of electrolytes, particularly in view of the fact that Chapter IX contains a great deal of blank space, lengthy bibliographies, etc. The main table of this chapter, that of Standard Electrode Potentials, contains 58 cases against nearly 250 in Latimer's corresponding table in the 1952 edition of his "Oxidation Potentials." Since Dr. Conway appears to have attempted a critical assessment in his selection of data (see his Preface), it is interesting to note a number of differences between his standard electrode potentials and those presented by Latimer. Further examination of these and of many other electrochemical data by suitable committees, preferably at the international level, appears imperative. The restriction of overvoltage data to those contributed by a small group of workers, all no doubt excellent, will probably appear too one-sided in some quarters. The function H is called *enthalpy* in the list of symbols but *heat content* in the various tables in the body of the book (with one exception: Table VI, 17), while the function G is called *free heat content* in the list of symbols but *free energy* in the tables. Enthalpy and free heat content do not appear in the Index, while heat content and free energy do.

In a vast compilation such as that undertaken by Dr. Conway inconsistencies will unavoidably appear and certain desirable connections and cross-references are missed. For instance, Table II, 8 on page 31 giving "Electron Work Functions of Metals" on the basis of data of Klein and Lange accurate to ±0.03 volt should be linked or contrasted with Table IX, 32 on page 329 giving a "Volta Potential (*vs.* Pt) Series in Air in Volts" on the basis of a private communication by Uhlig (references at least to other good determinations of Volta potentials would have been desirable here). Volta potentials derived from the former table are, understandably, not all identical with those of the latter table, but some values, however, are amazingly close to each other. It is interesting to note in passing that both tables imply a value of 0.8 volt for the Volta potential difference from zinc to copper. If one reasonably assumes that the Galvani potential difference is close to this 0.8 volt value, there is only $1.1 - 0.8 = 0.3$ volt left for the resultant of the two metal–solution potential differences in the Daniell cell. We found ourselves carried away toward many other attractive speculations while perusing "Electrochemical Data" which do indeed provide a great deal of food for electrochemical thought.

Our remarks are presented as suggestions for possible improvements in later editions. This reviewer fully realizes the difficulties involved in an effort such as that accomplished, apparently single-handed, by Dr. Conway and he greatly appreciates having the result of this effort available for daily consultation. He feels that the same appreciation will be forthcoming from many other workers in the various fields of theoretical and applied electrochemistry.

The general appearance of the book is pleasing, the tables are clearly printed and generously spaced. The price, although high, cannot shock anyone aware of present trends.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OREGON PIERRE VAN RYSSELBERGHE
EUGENE, OREGON

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**Hyperconjugation.** By JOHN WILLIAM BAKER, Reader in the Mechanism of Organic Reactions in the University of Leeds. Oxford University Press, 114 Fifth Avenue, New York 11, N. Y. 1952. vii + 158 pp. 14.5 × 22 cm. Price, $3.50.

The concept of hyperconjugation, as in the case of several other principles in organic chemistry, first arose as an hypothesis to explain certain experimental results and only later did it receive more adequate theoretical and physical justification. It was J. W. Baker, on the basis of irregular orders of electron release by alkyl groups, who first clearly proposed that β C–H bonding electrons are capable of conjugation with an unsaturated center (Baker–Nathan effect) and it is fitting that Baker should write the present monograph on hyperconjugation, as the generalized phenomenon has come to be known.

Baker's presentation is non-mathematical and is in the terminology and symbolism of C. K. Ingold, to whom Baker dedicates the monograph in the Preface. In addition to the more familiar Ingold notation, Baker uses some new symbolism, but the reader who is not very familiar with the English terminology will be assisted by a summary in the Appendix. Where the discussion is qualitatively wave mechanical Baker stresses the valence-bond approach and resonance language, and he justifies rather well his preference for this type of discussion. Nevertheless, he borrows some of the language arising from the molecular orbital approach to organic chemistry.

An impression of the organization and contents of the monograph may be gained from the list of chapters: I. Hyperconjugation: The Historical Development of the Concept; II. Physical Evidence for Hyperconjugation; III. Hyperconjugation and Aromatic Substitution; IV. The Role of Hyperconjugation in Tautomeric Equilibria; V. Addition Reactions; VI. Hyperconjugation in Olefine Chemistry. 1. The Formation of Olefines; VII. Hyperconjugation in Olefine Chemistry. 2. Heterolytic α-Methylenic Reactions of Olefines; VIII. Hyperconjugation and Homolytic Reactions.

The present reviewer was favorably impressed with the earlier chapters. In the later chapters the reviewer felt that the presentation was marred by several features. One defect arises because of the organization, so that one obtains an impression of repetition when there are two discussions which are necessarily very similar. For example, this is the case for the discussions of anionotropy and addition of halogen to conjugated polyolefins. The other defect is a tendency to apply explanations based on hyperconjugation to too many reactions whose mechanism is still uncertain. Thus the reviewer felt that the discussion of the reaction between toluene and maleic anhydride and much of the discussion of α-methylenic reactivity of olefins could be modified or omitted. Similarly, in the chapters on homolytic reactions there is a tendency to make hyperconjugation the basis of an explanation of methylenic reactivity by ascribing the reactivity of methylenic hydrogen atoms to hyperconjugation with adjacent double bonds rather than by stressing resonance stabilization of the free radical obtained by removal of a hydrogen atom.

The reviewer was disappointed by the lack of discussion of two aspects of the hyperconjugation phenomenon. The first of these aspects is the question of C–H *vs.* C–C hyperconjugation. Baker and Nathan, in their original hypothesis, proposed that C–H bonding electrons were capable of conjugation with an unsaturated center, but that C–C bonding electrons were incapable of such conjugation, and this general approach is pretty well preserved in the monograph. Actually, there is no theoretical basis for a complete qualitative difference between C–H and C–C bonding electrons, and the author gives no summary of evidence regarding the extent of the superiority of C–H *vs.* C–C bonding electrons in hyperconjugation in different electronic situations. The author makes no attempt to prove that C–H electrons are even always superior to C–C bonding electrons in this respect. The second aspect has to do with the steric requirements for hyperconjugation, but this subject is essentially untouched except for one brief reference to the work of Baddeley.

The general make-up of the book is pleasing and it is certainly a convenience to have available the collection of the subject matter in the convenient form Dr. Baker has provided. Many of the tables, such as in connection with tautomeric equilibria, will be useful for rapid reference. The reviewer feels that this monograph will have wide usefulness to organic chemists.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIFORNIA
S. WINSTEIN

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**Organic Syntheses—An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals.** Volume 32. By RICHARD T. ARNOLD (Editor-in-chief). John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1952. vi + 119 pp. 16 × 23.5 cm. Price, $3.50.

For thirty-two years chemists have been welcoming slim red-covered volumes of Organic Syntheses, confident that the methods described therein are reliable and practical. Volume 32 is no exception. Printed in clear and legible type, sturdily bound to withstand hard usage, it presents methods for the laboratory preparation of forty-five organic compounds. Four of these are new and presumably better syntheses for compounds described in earlier volumes. Nine represent methods of such general applicability that the number of specific syntheses is thereby increased by more than twenty. These features make the collection considerably more valuable than a hasty examination of its table of contents would indicate.

The index covers Volumes 30, 31 and 32. A ten-year cumulative index appeared in Volume 29.

Twenty-two universities, three government laboratories and six industrial laboratories have contributed methods for the synthesis of Abietic acid, Acrolein acetal, Alloxan monohydrate, 2-Aminobenzophenone, ε-Aminocaproic acid, 1,1′-Azo-bis-1-cyclohexanenitrile, β-Bromoethylphthalimide, *t*-Butyl hypochlorite, 1-Chloro-2,6-dinitrobenzene, *p*-Chlorophenyl salicylate, β-Chlorovinyl isoamyl ketone, Cyanogen iodide, 3-Cyano-6-methyl-2(1)-pyridone, 1,2-Cyclohexanedionedioxime, Cyclohexene sulfide, Cyclopentadiene and 3-chlorocyclopentene, 2,4-Diamino-6-hydroxypyrimidine, 2,2-Dichloroethanol, 1,1′-Dicyano-1,1′-bicyclohexyl, 1,2-Di-1-(1-cyano)-cyclohexylhydrazine, Diethyl $\Delta^2$-cyclopentenylmalonate, Diethyl ethylidenemalonate, Dimethyl acetylenedicarboxylate, 4,6-Dimethylcoumalin, 5,5-Dimethyl-2-pyrrolidone, asym-Dimethylurea, α,α′-Diphenylsuccinonitrile, 2-Ethylhexanonitrile, Ethyl orthocarbonate, 1,1′-Ethynylene-bis-cyclohexanol, Flavone, Isodehydroacetic acid and ethyl isodehydroacetate, β-Ketoisooctaldehyde dimethyl acetal, Methyl *p*-acetylbenzoate, Methylglyoxal-ω-phenylhydrazone, Methyl γ-methyl-γ-nitrovalerate, Naphthalene-1,5-disulfonyl chloride, Neophyl chloride, Phenylacetamide, Sodium nitromalonaldehyde monohydrate, β-Tetralone, Thiobenzoic acid and 10-Undecynoic acid.

No laboratory engaged in synthesizing organic compound can afford to be without this book.

UNIVERSITY OF BUFFALO
BUFFALO 14, NEW YORK
HENRY M. WOODBURN