and hexadienynes in the benzene photolyses and indicate that at steady state a substantial fraction of hexadienyne is formed from fulvene.

Fulvene and the hexadienynes were also irradiated at 2537 Å under similar conditions, with results which differed markedly from those at 1849 Å or in solution at 2537 Å. In contrast to the behavior of fulvene in solution, where conversion to benzene does not occur[8] upon irradiation at 2537 Å, an almost quantitative yield of benzene was obtained in the vapor phase, $\Phi \sim 0.01$. The hexadienyne vapors exhibited not only the rapid *cis–trans* isomerization observed in solution, but also a slower, $\Phi \sim 0.01$, almost quantitative conversion to a 2:1 mixture of benzene and fulvene. As a consequence of these reactions, lower steady-state concentrations of fulvene, and particularly of hexadienyne, were obtained when benzene was photolyzed without exclusion of 2537-Å radiation.

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[8] H. J. F. Angus, J. M. Blair, and D. Bryce-Smith, *J. Chem. Soc.*, 2003 (1960).

[9] Participant in the CSUI-ANL Honors Program, spring 1967.

Louis Kaplan, S. P. Walch,[9] K. E. Wilzbach
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439

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Book Reviews

Extrusion Reactions. By B. P. Stark, M.A., Ph.D., Chief Research Chemist, CIBA (A.R.L.) Ltd., Duxford, Cambridge, and A. J. Duke, M.A., Ph.D., A.R.I.C., CIBA (A.R.L.) Ltd., Duxford, Cambridge (now Head of Coatings Department, Central Research Laboratories, Richard Thomas and Baldwins Ltd., Whitchurch, Aylesbury, Bucks). Pergamon Press Inc., 44-01 21st St., Long Island City, N. Y. 1967. x + 190 pp. 14 × 22.5 cm. $10.00.

The provocative title of this slim volume derives from a restricted group of the general class of fragmentation reactions. An "extrusion reaction" is defined as one "in which a small inorganic fragment (including carbon monoxide and carbon dioxide) is totally eliminated from a cyclic organic compound to form a (cyclic) product which either has a ring smaller than that present in the starting material (ring contraction) or has a smaller number of fused rings (bridge expulsion or ring degeneration)." Included under this definition are such familiar examples as the decarbonylation and decarboxylation reactions of bicyclic derivatives carrying bridged carbonyl systems to yield cyclohexadienyl and aromatic products, the elimination of nitrogen from pyrazolines to form cyclopropanes, and the decomposition of benzo[*c*]-2,5-dihydrothiophene dioxide to produce benzocyclobutene. Excluded by the restricted definition are reactions which lead to purely acyclic products (*cf.* the stereospecific fragmentations of 3-sulfolenes and diazene derivatives of 3-pyrrolines) or to more than one residual organic fragment.

In the first chapter, the authors introduce a rather elaborate classification system for extrusion reactions based on the structure of the intermediate *residuum*, formally conceived as the diradical or zwitterionic species immediately generated by expulsion of the inorganic moiety. Three general classes and four subclasses are recognized which differ in the kind and degree of internal stabilization available in the system of atoms comprising the residue. While systematics of this sort may appeal to some readers, this reviewer found the classification more distracting than useful.

In the chapters which follow, extrusion reactions are grouped according to the moiety expelled. Carbon monoxide and carbon dioxide extrusions from bridged carbonyl systems are treated in Chapters 2 and 3, other extrusions of carbon oxides in Chapter 4. Further subdivisions of these extrusions are made on the basis of the *residua* classification where appropriate. Extrusions of sulfur dioxide and other oxidized sulfur fragments are reviewed in Chapter 5; succeeding chapters deal with the extrusions of elemental sulfur, selenium, and oxygen. Nitrogen extrusions are treated in a sequence of four chapters and include the well-documented cases of extrusions from pyrazolines and triazolines as well as the possible intermediacy of oxadiazolines and thiadiazolines in the syntheses of oxirans and thiirans by the action of diazo compounds on carbonyl and thiocarbonyl systems. Extrusions of a few miscellaneous fragments, *e.g.*, cyanate ion and "sulfimide" (SO_2NH), and some examples of multiple extrusions are discussed briefly in later chapters. In a final chapter is presented a summary of such generalizations and interrelationships as do emerge from the material surveyed.

This monograph, brief as it is, contains a wealth of information and carries references to the relevant literature through September 1965. The compendium-like style in which it is written makes for rather tiresome reading; and there is little critical evaluation of the material presented. As a source book for the specialist who wishes to explore this somewhat artificially defined area of fragmentation reactions, however, it should prove quite valuable.

Sara Jane Rhoads
Department of Chemistry, University of Wyoming
Laramie, Wyoming 82070

Electrolyte Theory. An Elementary Introduction to a Microscopic Approach. By Pierre M. V. Résibois, Université Libre de Bruxelles. Harper and Row, 49 East 33D St., New York, N. Y. 1968. x + 166 pp. 16 × 24 cm. $11.25.

Changes in the most effective way to teach subjects like electrochemistry are often motivated by continuing progress in the statistical-mechanical theory of liquids. This book nicely illustrates such trends. Professor Résibois offers here a short introduction to some of the fundamental concepts of electrochemical theory in a distinctly modern manner. The text has grown out of a lecture series given by the author to advanced undergraduates, but it seems to be a potentially valuable guide not only to graduate students polarized toward theoretical work, but also to more mature electrochemists who wisely choose to stay abreast of current theoretical thinking.

The book's objective is relatively modest. The author sets out primarily to derive and explain the low-concentration limiting laws for both electrolyte thermodynamic behavior and linear transport properties. He accomplishes this task with erudition, but not arrogance. Although molecular distribution function theory provides the prevalent language, the approximations are honestly displayed and given clear motivation. Furthermore, simple intuitive explanations for the existence of the limiting laws are offered.

A substantial portion of the book is devoted to the theory of Brownian motion. This material is a valuable exposition in its own right, quite apart from electrochemical applications.

The reader might well be warned that the emphasis is on the physical (rather than chemical) aspects of electrochemistry. Nevertheless, it should become clear to anyone who studies this book carefully exactly where in the general theory the distinctively chemical differences between various salts and solvents would have to enter.

One important phenomenon which was not mentioned, but whose inclusion would be pedagogically consistent with the material offered, is ionic retardation due to solvent dielectric relaxation. Unfortunately, this effect (associated over several decades with the names Born, Fuoss, Boyd, and Zwanzig) seems to be totally unreported in textbooks of electrochemical principles.

The book seems to contain a rather large number of small errors and misprints, considering its size. The publisher could henceforth show concern for its reading public by inserting an Erratum sheet with further copies offered for sale.

Frank H. Stillinger, Jr.
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey 07974

Cycloaddition Reactions of Heterocumulenes. By HENRI ULRICH, The Upjon Co., D. S. Gilmore Research Laboratories, North Haven, Conn. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1967. ix + 364 pp. 16 × 23.5 cm. $16.50.

Monographs may be of several types, serving various ends. They may be synoptic, presenting a general view of the subject they cover. They may be encyclopedic, giving a detailed and comprehensive account of the state of knowledge in the field. They may be analytic, giving an interpretation in terms of a restricted number of principles of the accumulated body of knowledge in the field. Finally, they may be seminal, providing novel insights and ideas that will stimulate new approaches and extensions in the field. Although these ends are to some extent interrelated, most monographs make an important contribution in only one of these respects. The book under review is no exception, falling in the encyclopedic category.

It gives extensive coverage of the various types of cycloaddition reactions of heterocumulenes, to the study of which the author himself has made important contributions. The heterocumulene systems discussed include ketenes, carbon suboxide, isocyanates, isothiocyanates, carbodiimides, carbon dioxide, carbonyl sulfide, carbon disulfide, sulfenes, N-sulfinylamines, N-sulfinylsulfonamides, and sulfur diimides. The reactions of these systems involving polymerization and 1,2-, 1,3-, and 1,4-cycloaddition reactions are presented in detail. Indeed, the coverage is so extensive that under the heading of the 1,2-cycloaddition reaction are included several reaction types whose membership in this class is very dubious. Thus, many reactions leading to noncyclic products are included on the unverified, and in some cases unlikely, assumption that they may proceed *via* cyclic intermediates. No matter! The reader merely gets more than the title promises him.

Of equal importance to extensive coverage in an encyclopedic work is intensive coverage. The reviewer naturally first examines the coverage of the work he knows best—his own. The failure of the author to refer in his chapter on ketenes to the work of Clark on butenolide formation from ketenes [*Tetrahedron Letters*, 435 (1961)] and of Chandross on "camphoketene" dimers [*Tetrahedron Letters*, No. 20, 1 (1959); *cf.* J. E. Baldwin, *J. Org. Chem.*, **29**, 1880 (1964)] is a source of regret to the present reviewer. Although it could be concluded that the author, after judicious consideration, has decided that mention of this work was unnecessary, the reviewer is left with the unfortunate feeling, so common to newspaper readers, that lapses in accounts of areas with which he has close acquaintance may well be matched by lapses in the coverage of areas less familiar to him.

The presentation of the subject matter is acceptable, with one noteworthy exception. Throughout the book the double-headed arrow normally reserved for representing resonance hybrids is used both for this purpose and also for the representation of equilibria. To compound the confusion, in one case (p 124), the relationship between two contributing structures to a resonance hybrid is referred to as isomerization, and, in another (p 283), two structures are drawn as common contributors to a hybrid, although the difference in their geometries must surely preclude such a relationship.

The subject matter is clearly presented on the whole, although the writing style suffers on occasion from ungrammatical and unidiomatic phrases. The statement that "In the absence of sufficient data, only generalizations can be made" may most charitably be placed in this class. The present author, like many others, makes a habit of using expanded meanings of the words "dimer" and "trimer," as exemplified by the terms "mixed dimer," "mixed trimer," and "polymeric dimer." It is unfortunate that words with exact meanings should become diluted in this way; the resulting confusion is immortalized by the author's phrase "partial (formally) dimer character." The book has its usual quota of typographical errors, with perhaps more than usual in the case of the structural formulas and equations, among which sixteen errors have been noted.

In sum, this monograph is not without its blemishes; these, however, are far outweighed by its usefulness. It is recommended as a valuable source of information for workers in the field and for those planning to enter it.

Peter Yates
Department of Chemistry
University of Toronto, Toronto, Canada