

(disproportionation of alkylating group) are merely listed. The section on the reaction of phenols and alkyl phenyl ethers with diolefins omits reference to any of the important papers by Bader, etc.

There are about two references to the alkylation of thiophenol and none to thiophene compared to the 13 and 27 in a recent review.¹ The ring alkylation of aniline types, N-heterocyclics, hydroxybenzoic acids, aryloxy acids, polyhydric phenols, diaryl ethers, naphthols, indanols, and tricyclic fused-ring aromatic hydrocarbons, are not covered—many not even mentioned.

Obviously the over-all coverage is very uneven and incomplete, and the discussion of mechanism quite elementary.

The treatment throughout all review chapters is entirely based on experimental data, obviously dating back to the time before the general use of spectroscopic and vapor phase chromatographic methods, and through present day eyes seems somewhat outdated.

Anybody spending \$16 for the present book of 306 pages (an extremely high pro page price even in these times of skyrocketing book prices and puzzling in view of the known difficulties western authors have in collecting royalties for Russian translations of their books) should be aware that he is buying a collection of summary papers of one specific research group and not a comprehensive treatise of alkylations with olefins. As such the translation is a welcomed addition to the chemical literature, familiarizing us with some of the otherwise not easily accessible results of Russian chemistry.

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Carbene Chemistry. By WOLFGANG KIRMSE, *Chemisches Institut der Universitaet Marburg, Marburg, Germany.* Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1964. vii + 302 pp. 16 × 24 cm. \$9.50.

This is the second book to appear within a span of less than a year devoted exclusively to the chemistry of divalent carbon compounds. Kirmse is well known among workers in the carbene field through his own research contributions and through the valuable services he provided earlier by writing several excellent review articles on the subject.

This book attempts a compromise between the classical monograph, usually written by a single authority, and the modern, multi-authored version of the "Progress in..." variety. The main author, Kirmse, presents a thorough discussion of most of the aspects of carbene chemistry in the first ten chapters. In the remaining two chapters, subjects of more physico-chemical nature are treated by three other experts. In Chapter 11, Frey discusses the chemistry of methylene in the vapor phase and the associated problems of excited molecules. The last chapter is written by Gaspar and Hammond, who give an excellent review on the many problems arising from the possibility of carbenes reacting in states of different spin multiplicities. It appears that this approach has considerable merit because a unified treatment is preserved by the contribution of the main author, and only little duplication of material treated in the first ten chapters is found in the remaining two. At the same time those aspects which are somewhat removed from the principal theme are discussed by authors who may, by nature of their research interests, be somewhat better qualified for the task.

Following a brief introduction, Kirmse describes the chemistry of methylene and its derivatives using a clear and logical guideline. The nine chapters are arranged according to the functional groups attached to the divalent carbon. Thus, the discussion on methylene is followed by chapters on alkylcarbenes, olefinic and acetylenic carbenes, arylcarbenes, carbalkoxycarbenes, ketocarbenes, halocarbenes, carbenes containing other heteroatoms, and dicarbenes. At the beginning of each chapter a summary is given of all methods used to generate the carbene. Following this is usually a rather complete listing of reactions presumably involving the intermediacy of the species under discussion. The emphasis in these sections is on mechanistic aspects although the preparative angle of the field is very adequately treated. It should be pointed out that a large fraction of the reactions discussed in this book probably do not proceed through the intermediacy of true divalent carbon species. In recent years it has become increasingly apparent

that "complexed" carbenes, in which the formal valency of carbon is greater than two, are intermediates in many reactions. Since Kirmse's research has largely centered on α -eliminations frequently proceeding through such intermediates, it is not surprising that he critically examines the literature data for information regarding this problem. Although Kirmse's conclusions are at present in perfect agreement with the sometimes rather limited data of mechanistic significance, it is a safe prediction that many changes will be necessary, should there ever be a second edition. This should not be read as criticism of the book but should rather serve to illustrate the difficulties the author had to cope with when he was writing on a subject that is young enough to require frequent reinterpretation of even the older data.

The chapter on gas phase reactions of methylene is competently written by Frey who is almost in a unique position to do so. Most of the work described here originates with relatively few people and Frey is certainly the leading contributor. The average organic solution chemist will greatly profit from being introduced to an area of mechanistic chemistry where in addition to many other complications he has to cope with the concept of "hot" reaction products and the accompanying molecular rearrangements.

This reviewer was especially delighted with the last chapter. Here Gaspar and Hammond succeed admirably in presenting the material of one of the most exciting aspects of carbene chemistry. Extremely valuable is the much needed criticism of many interpretations which have been advanced to relate chemical reactivity with multiplicity of the reacting methylene derivative. The authors show that chemical intuition can provide valuable working hypotheses which at present cannot be deduced from adherence to strictly theoretical principles. But they also warn the reader that these hypotheses should not be taken as the gospel, as is too frequently done. Adding to the reading pleasure is the very good sense of humor displayed throughout this chapter and culminating in the last reference cited in the book.

Literature coverage is essentially complete through the first third of 1964. A special word of praise is due to the publisher who kept the production time to a few months. In summary, it should be emphasized that this is an extremely good book which can be recommended to all organic chemists who have any interests in reaction mechanisms.

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Chemical Kinetics of Gas Reactions. By V. N. KONDRAT'EV, Member of the Academy of Sciences of the U.S.S.R. Translated from the Russian by J. M. CRABTREE and S. N. CARRUTHERS. Translation edited by N. B. SLATER, Professor of Applied Mathematics, University of Hull. Addison-Wesley Publishing Co., Inc., Reading, Mass. 1964. xiii + 812 pp. 16 × 24 cm. \$17.50.

Although the author does not make this classification, I find it very convenient to think of gas phase chemical kinetics at three different "levels of abstraction," that is, degrees of averaging: (1) over-all chemical reactions, (2) elementary chemical reactions, and (3) elementary chemical-physical reactions. An ideal elementary chemical-physical reaction involves the transition of reactants each in a definite quantum state to products each in a definite quantum state; such transitions are purely mechanical processes and independent of temperature. An elementary chemical reaction consists of one type of elementary chemical-physical reaction averaged over a steady (not necessarily equilibrium) distribution of states, such a distribution depending on only a small number of macroscopic variables. Elementary chemical reaction rates depend on temperature, concentration, and perhaps other variables. Practical, over-all reactions typically involve a set of elementary chemical reactions, occurring in series or in parallel or both; the set of elementary steps is often referred to as the "mechanism." In this book, there is a well-balanced coverage of each of these three aspects of kinetics.

Elementary chemical-physical reactions treated here include intermolecular energy transfers: translational-translational, translational-rotational, and translational-vibrational. Electronic excitation of a molecule by absorption of radiation, the inverse process of fluorescence, and the collisional quenching of electronically excited molecules are included. The impact of electrons and ions on molecules to produce excitation and ionization is covered. In

actual experimental work the ideal of only single quantum-state transitions is not attained; almost always averaging over some type of state is involved; and the definition of "elementary chemical-physical reaction" needs to be extended to cover single-state transitions for one type of energy even when other types of energy have the usual distribution over states.

Elementary chemical reactions are given separate chapters of "Theory of Elementary Chemical Processes," "Bimolecular Reactions," and "Unimolecular and Termolecular Reactions." Kondrat'ev follows the highly commendable practice of regarding a real reaction system only as the sum of its component elementary steps.

Many types of over-all reactions are treated briefly in the chapter "Chemical Mechanism of Reactions." In the chapters on "Photochemical Reactions," "Chemical Reactions in Electrical Discharges," and "Combustion Processes," there is a blending of the three levels of abstraction: physical, chemical, and mechanistic. The long chapter on "Chain Reactions" includes Semenov's formal kinetics of chain reactions and an interesting, detailed treatment of the combustion of hydrogen as a model reaction.

A well-balanced presentation is given to collision theory, to activated-complex theory, and to other theoretical approaches. Experimental data are discussed critically, and there are extensive (but, of course, by no means complete) tables of data to illustrate each topic. For each type of chemical reaction there is presented the theory, discussion of data, and tables of data.

Reference to the Russian language literature is extensive, 310 references, and impartial; non-Russian literature is given by 1024 references, many with a, b, etc. subtitles. The primary coverage of the literature seems to be through about 1954 or 1955, but a substantial number of references in the period 1955-1959 are inserted. There appear to be no references after 1960.

The translation from Russian to English seems to be excellent.

For parts of the book, Kondrat'ev had the assistance of N. D. Sokolov, who contributed the long chapter on the "Theory of Elementary Chemical Processes" and portions of certain other chapters. There is some appearance of less than perfect coordination between the two hands: on page 151 Sokolov dismisses Kassel's theory of unimolecular reactions with a curt footnote, but in Chapter 5 Kondrat'ev gives a good review of Kassel's theory.

For a book as broad as this one, it seems almost impossible for one or two men to rederive all the theories, to reinterpret all the experimental data from the journals, and to present the whole from a unified, critical point of view. It seems inevitable that some theoretical derivations would be copied from the literature, certain discussions must only paraphrase original authors, and entries in tables of experimental data must surely be taken directly from the literature. Some such paraphrasing was recognized; for example, the incorrect formula for the moment of inertia of linear $A-B-C$ that appears in Glasstone, Laidler, and Eyring is reproduced on page 254. On the other hand, the book does seem to contain a large fraction of critically re-evaluated material. Also, certain sections on photochemistry, ionic reactions, chain reactions, spectroscopy, and energy transfer give the feeling of immediacy and authority that comes from being written by the man who has done that sort of work.

The book is clearly and attractively printed, sturdily and handsomely bound, and priced out of reach of graduate students for whom it would make an excellent textbook or regularly used reference book.

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