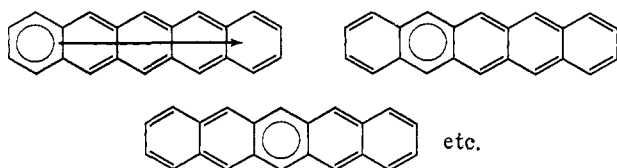


direct continuation of Volume 1; the only apparent reason for dividing the treatise into two parts is the desire to avoid an oversized single book. However, the principal advantage appears to be the perhaps inadvertent one, that individuals interested in understanding Clar's rather novel approach to polycyclic hydrocarbon chemistry need only purchase Volume 1 and rely on library copies for reference to compounds treated in Volume 2. Perhaps this possibility did not escape the publishers because each volume has a separate author index. Volume 2 starts with Part III and continues through Part XI; Parts III to IX inclusive treat what Clar calls "Peri-Condensed Hydrocarbons" and Parts X and XI treat some exotic hydrocarbons.

The theory discussed in the early chapters is rather weak, besides being occasionally wrong, and frequently ambiguous; much of it could have been omitted altogether. Chapters 6 through 9 are fascinating. These contain the heart of Clar's approach. They demonstrate how a master of the field can wield his material into powerful empirical generalizations that bring order and understanding out of the chaos of the multitudinous possible arrangements of fused hexagons. Here are elaborated the remarkable correlations Clar has been able to develop between absorption spectra, reactivity, and his annellation principles. His semi-empirical analysis of the spectra of the polycyclic hydrocarbons in terms of the p -, α -, and β -band systems is now classic and is an extremely powerful tool.

According to the basic Clar classification, the polycyclic hydrocarbons may be divided into two main classes: Kata-annellated (frequently anglicized by other authors to cata-condensed), and peri-condensed. The cata-condensed hydrocarbons are those in which ring fusion is achieved by the sharing of only two carbon atoms between adjacent rings and thus all the carbon atoms in the system are on the periphery. The cata-condensed hydrocarbons are then further divided on the basis of the maximum number of linearly fused (or annellated) rings: one for benzene; two for naphthalene, phenanthrene, triphenylene, chrysene, 3,4-benzophenanthrene, picene, hexihelicene, etc.; three for anthracene, 1,2,5,6-dibenzanthracene, etc. When the bond distribution in the ring systems is drawn strictly in accord with the notation introduced (1925) by Sir Robert Robinson, to whom incidentally these volumes are dedicated, much is revealed about their properties. In this notation, the aromatic sextet only is indicated by a circle inside a hexagon. Thus, *e.g.*, the five equivalent resonance structures of pentacene are written



The five structures written as shown imply that two π -electrons migrate through the entire five rings of the acene and four π -electrons remain localized in each ring. (The arrow is intended to convey the concept of the mobility of the two π -electrons.) One sextet is thus shared among five rings and hence the benzenoid character is highly diluted. As a matter of fact, the linear seven-ring acene, heptacene, is so reactive it has yet to be prepared in a pure state. The higher acenes finally lose all aromatic character and become chemically similar to cyclic polyenes. The use of the circle to symbolize only the aromatic sextet not only emphasizes relative stability, but indicates the site of reactivity. Thus phenanthrene, the first member of the phene (systems with angular rings) series; is written with circles in each of the terminal rings and a double bond in the 9,10-position suggesting that this angular system is more stable than its linear isomer anthracene and that its reactivity is centered in the 9,10-bond.

Chapters 10 through 17 average about three pages each! Chapter 18 contains an authentic, if limited, account of the work that has been done on the carcinogenic properties of polycyclic hydrocarbons and is written by a guest author, Regina Schoental, who has herself made substantial contributions to this field. However, since there is no essential integration of this material with other portions of the book it seems somewhat out of place.

Volume 2 is devoted principally to the peri-condensed hydrocarbons. Most of these hydrocarbon systems have some carbon atoms which are common to more than two rings and hence there are usually carbon atoms present that are internal and are not on

the perimeter of the system. The admirable practice of including the absorption spectrum of each ring system under discussion is continued in this volume. Although there does not appear to be any drastic revision from the earlier German version, a substantial number of references to papers which have appeared since 1951 are given.

These books are made less valuable than they otherwise might have been by the lack of a subject index even though there is a generous table of contents. It is also regrettable that no serious effort was made to relate the absorption spectra analysis to the free electron model for cata-condensed hydrocarbons so brilliantly developed by Platt. However, these are on the whole minor drawbacks to a valuable contribution. Anyone interested in polycyclic hydrocarbons must have access to these books, and workers in the field will be rewarded by at least owning Volume 1.

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Alkylation with Olefins. By A. V. TOPCHIEV, S. V. ZAVGORODNI, and V. G. KRYUCHKOVA, Petroleum Institute, U.S.S.R. Academy of Sciences, Moscow. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1964. ix + 306 pp. 15 × 23 cm. \$16.00.

The reviewer was unable to see a copy of the original Russian edition of the book and therefore he is uncertain whether the title was properly translated into English. If so, it is a most unfortunate selection of title, which seems to implement the treatment of alkylation with olefins as the general topic.

Perhaps the title should have read: "Some Preparative Aspects of Boron Trifluoride Catalyzed Alkylation with Olefins." The book in fact consists of selected specialized reviews of fields in which the authors themselves were active. The late Topchiev and his co-workers have done outstanding work in alkylation of carboxylic acids, aromatic hydrocarbons, phenols, and their derivatives, using alkenes as alkylating agents. Their studies predominantly involved the use of catalysts based on boron trifluoride. These studies are well summarized in the four chapters the book is composed of: "Alkylation of Organic Acids with Olefins," "The Alkylation of Aromatic Hydrocarbons with Olefins," "Alkylation of Phenols and Alkyl Aryl Ethers with Olefins in the Presence of BF_3 Catalysts," and "Alkylation of Halophenols and Haloanisoles with Olefins in the Presence of BF_3 Catalysts." There is an additional fifth chapter on "Autoxidation of Alkylaromatic Hydrocarbons" which does not fit too well into the scope of this collection although in their forward the authors stress their reasons for inclusion of this chapter. There is much merit in publishing summary reviews of the work of large research groups in its own field of specialization. It is, however, obvious that claiming that a collection of review papers of this type represents a comprehensive and fundamental coverage of a large field, such as alkylation with olefins, is misleading. The publisher of the translation claims on the dust jacket that the book is a recognized general standard text in its field. In my view this statement is not in accordance with the facts. The authors own introduction clearly states that only the results of Russian chemistry and in particularly those of the research group of the late Topchiev were reviewed.

The coverage of Russian literature pertaining to these catalysts appeared satisfactory and complete even to the extent of reproducing many detailed tables of operating conditions, yields, and physical properties of the products. But the coverage of non-Russian references is extremely sketchy. Therefore no attempt is made for comparison with recent comprehensive reviews.^{1,2} Little or no account is given of the many interesting and significant side reactions which often accompany alkylation which other workers have described in considerable detail. For example, the work of Malchik and Hannan is dismissed with the mere statement that they studied the effect of BF_3 catalyst concentrations. Papers by Schmerling and West (skeletal isomerization), Ipatieff, Pines, and Olberg (hydride transfer), and Friedman and Morritz

(1) S. H. Patinkin and B. S. Friedman in "Friedel-Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience Div., John Wiley and Sons, Inc., New York, N. Y., 1964, Chapter XIV.

(2) "The Chemistry of Alkenes," S. Patai, Ed., Interscience Div., John Wiley and Sons, Inc., New York, N. Y., 1964.

(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