

CARBENE CHEMISTRY

Second Edition

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1971

ACADEMIC PRESS

New York and London

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ACADEMIC PRESS, INC.

111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1 7DD

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 64-21669

PRINTED IN THE UNITED STATES OF AMERICA

CARBENE CHEMISTRY

Second Edition

This is Volume 1 of
ORGANIC CHEMISTRY
A series of monographs
Editors: ALFRED T. BLOMQUIST and HARRY WASSERMAN

A complete list of the books in this series appears at the end of the volume.

PREFACE TO THE SECOND EDITION

Active interest in carbene chemistry has been steadily growing since the first edition of this book appeared in 1964. The number of original papers dealing with various aspects of the elusive carbene species has almost tripled within the last six years. Distinct progress has been made in many areas of carbene chemistry: correlation of spectroscopic studies of isolated carbenes with quantum chemical calculations; new carbene precursors; differentiation of carbenes and carbenoids; carbene complexes of the transition metals; mechanisms of singlet and triplet carbene reactions; structure-reactivity relationships for both carbenes and their substrates; applications in synthetic organic chemistry.

In order to cover these diverse aspects within a reasonable volume, the second edition of "Carbene Chemistry" has been reorganized according to the reaction scheme: precursor \rightarrow carbene (carbenoid) \rightarrow product. The first part (four chapters) reviews the many reactions known to transfer a formally divalent carbon fragment from one molecule to another, with emphasis on the mechanism and a critical evaluation of the evidence for carbene intermediates. The multitude of product-forming reactions of carbenes and carbenoids with various substrates is treated in the second part (six chapters). The two parts are linked by two chapters on the spectra and structural theory of carbenes. They are supplemented by a review of Si, Ge, and Sn analogs of carbenes. The subject of carbene "analogs" outside of group IV (nitrenes, etc.) was considered to exceed the scope of the present volume.

Throughout the book, important mechanistic problems have been discussed in detail, with a supply of relevant experimental data. Much synthetic and kinetic work, on the other hand, which did not produce exceptional results has been condensed into tables which provide access to the original papers. Literature citations extend through 1969 and, more selectively, into 1970. The largely increased number of references (ca. 2500) has undoubtedly also increased the number of inadvertent omissions. As in the first edition, I have tried to augment my knowledge with the help of expert coauthors who supplied the chapters on structural theory and carbene analogs. It is a pleasure to thank Professors J. F. Harrison, P. P. Gaspar, and B. J. Herold for their valuable contributions.

Furthermore, I wish to express my gratitude to numerous colleagues who have participated in the preparation of this volume by stimulating discussions and constructive criticism. I am especially indebted to Professor B. M. Trost who read large portions of the manuscript.

WOLFGANG KIRMSE

PREFACE TO THE FIRST EDITION

Carbene chemistry has experienced a tremendous growth and wide interest in the past decade. The investigation of divalent carbon intermediates proved to be rewarding to both physical and preparative organic chemistry. Many research groups have excelled in contributing to our present knowledge of the elusive carbene species.

By now, carbene chemistry has outgrown the dimensions of review articles, and the task of providing a comprehensive monograph seemed timely. On considering the objectives of such a publication, it appears that full coverage is best achieved by a single author, whereas the most authoritative treatment may come from various experts dealing with their own fields of research. The present volume attempts to combine the advantages of both procedures. In the first ten chapters, I have tried to give an essentially complete survey of carbene chemistry. Literature citations extend through late 1963, and a few early 1964 references have been included. Scope and emphasis devoted to the various topics are undoubtedly influenced by the author's personal interests. Therefore, advance apologies are tendered to any of my colleagues who find their own work discussed inadequately, and to those whose findings I have inadvertently overlooked. Although the subject demanded a careful and critical discussion of mechanistic problems, the discussion has been kept to a minimum in the first ten chapters in anticipation of the contents of Chapters 11 and 12. In these chapters, theory is applied consistently to the interpretation of carbene reactions in those fields where it is most advanced. It is a pleasure to thank Professors H. M. Frey, P. P. Gaspar, and G. S. Hammond for their valuable contributions.

Furthermore, I wish to express my gratitude to numerous colleagues who have participated in the preparation of this volume by stimulating discussions, by constructive criticism, and by disclosure of unpublished results. I am especially indebted to Dr. Robert B. Hager who read the entire manuscript.

Marburg/Lahn
May 1964

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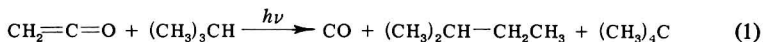
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CHAPTER 1

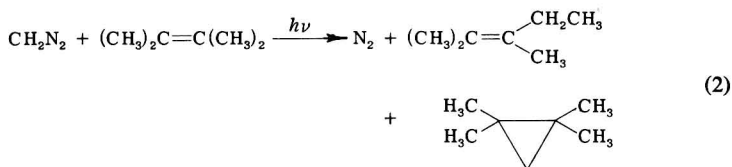
Introduction

I. EXAMPLES OF METHYLENE TRANSFER

FOR MANY YEARS, a group of organic reactions has been recognized in which a formally divalent carbon atom with two ligands is transferred between a pair of reactants. A somewhat arbitrary set of examples is presented in Eqs. (1)–(8). The term “methylene transfer” provides a purely phenomenological description, without mechanistic implications, in much the same way as we speak of “displacement,” “addition,” “elimination,” etc.

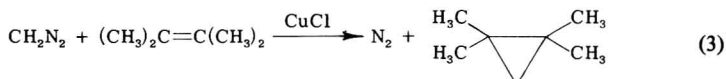


In Eq. (1), CH_2 is transferred from ketene to isobutane, under the action of light. With respect to isobutane, the process involves the “insertion” of CH_2 into the carbon–hydrogen bonds. Isopentane might also arise by insertion of CH_2 into the carbon–carbon bonds of isobutane, but the use of a suitable label would reveal that ketene furnishes C-4, rather than C-3, of 2-methylbutane. Insertion has been observed with other σ bonds such as C–Cl and C–O.

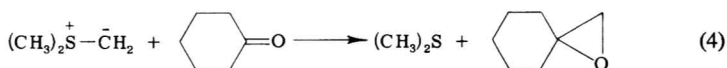


Equation (2) introduces another “methylene donor,” diazomethane. Photolysis of diazomethane in the presence of 2,3-dimethyl-2-butene affords not only the product of C–H insertion, 2,3-dimethyl-2-pentene, but also 1,1,2,2-tetramethylcyclopropane. Methylene transfer to the π bond is responsible for cyclopropane formation. With respect to the olefin,

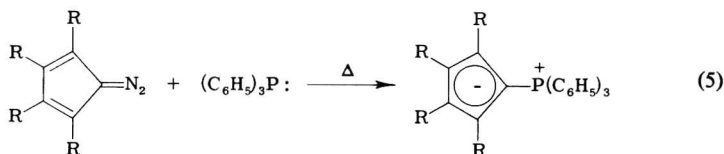
this process involves "addition" of CH_2 . (Some authors refer to the cyclopropane formation as "insertion" into π bonds, but the term addition serves better to distinguish the competing reactions and has been widely accepted.)



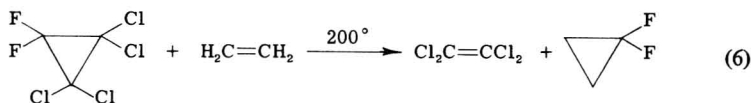
Equation (3) utilizes the same reactants as Eq. (2). Methylene transfer is effected, however, by CuCl catalysis rather than by irradiation. As a consequence, exclusive transfer of CH_2 to the π bond is observed and insertion into $\text{C}-\text{H}$ bonds does not take place. Obviously the two reactions, Eqs. (2) and (3), proceed by different mechanisms.



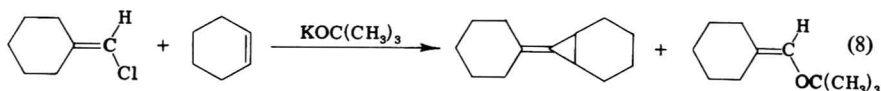
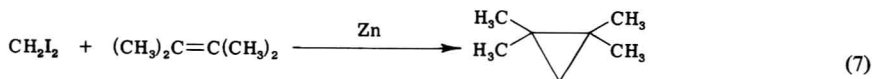
In contrast to the nonpolar $\text{C}=\text{C}$ bonds mentioned so far, Eq. (4) features the polar carbonyl group as a methylene acceptor. Dimethylsulfonium methylene acts as a methylene donor.



An ylide is the reaction "product" in Eq. (5), arising from transfer of a rather complex substituted methylene to the lone electron pair on the phosphorus of triphenylphosphine.



CX_2 transfer from polyhalocyclopropanes to olefins takes place at elevated temperatures in the gas phase. Significantly, only the CF_2 group is transferred in Eq. (6).

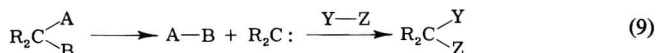


Reactions (1)–(6) proceed thermally or photochemically. The last two examples of methylene transfer, Eqs. (7) and (8), involve additional reagents which take over parts of the methylene donor [$\text{Zn} \rightarrow \text{ZnI}_2$; $\text{KOC}(\text{CH}_3)_3 \rightarrow \text{KCl} + \text{HOC}(\text{CH}_3)_3$]. Otherwise, reaction (7) is comparable to reaction (3): Addition of CH_2 to 2,3-dimethyl-2-butene proceeds without competing insertion. Reaction (8) affords two products: Transfer of an unsaturated methylene to the double bond of cyclohexene is accompanied by insertion into the O–H bond of *t*-butyl alcohol.

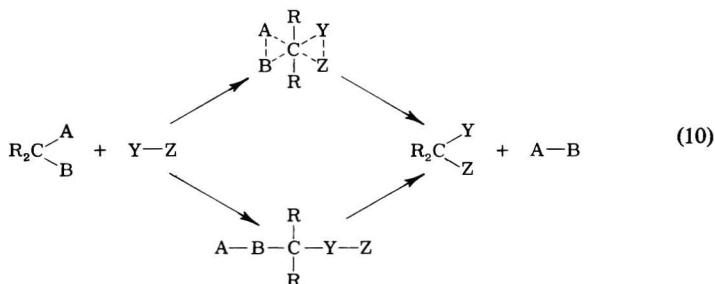
II. MECHANISMS OF METHYLENE TRANSFER

A simple and attractive way of explaining methylene transfer reactions is the assumption of a divalent carbon "intermediate," generally referred to as a "carbene." Methylene transfer is thought to proceed in two steps, (i) dissociation of the methylene donor to produce a carbene, and (ii) reaction of the carbene with the methylene acceptor.

The long-lasting fascination of the carbene concept for organic chemists appears to have emotional rather than empirical grounds. The desire to prepare compounds of divalent carbon can be traced back to the early nineteenth century, when the quadrivalency of carbon was not yet established. Thereafter a sort of *recherche du temps perdu*, the search has been continued on the more sophisticated level of divalent carbon intermediates. As is shown below, the unequivocal identification of transient carbenes is a difficult problem which, in many cases, still awaits final resolution. Oversimplification in favor of Eq. (9) has been a source of many pitfalls and, more importantly, a strong incentive to research.

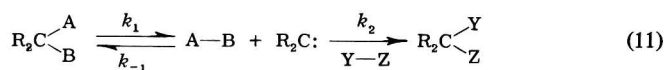


The other mechanistic extreme is a bimolecular reaction between methylene donor and methylene acceptor which leads to a concerted or successive displacement of the groups A, B by the groups Y, Z.



In order to distinguish between mechanisms (9) and (10) one has to determine at what stage in the overall reaction the groups A and B are detached from the methylene donor. The problem resembles that of distinguishing between the unimolecular and bimolecular mechanisms of substitution at a saturated carbon atom, and the general procedures employed are indeed quite similar.

a. Kinetics. If mechanism (9) operates, the rate of disappearance of the methylene donor R_2CAB should be independent of the concentration of the methylene acceptor $Y-Z$. This criterion is based on the premise that carbenes are highly reactive, i.e., their subsequent reactions are fast compared to the rate of formation. The kinetic criterion would be clearly invalid in case of an equilibrium, Eq. (11), with $k_{-1} \gg k_2$.



b. Partitioning between Competing Reaction Paths, e.g., insertion and addition; cf. Eq. (2). For a series of methylene donors R_2CAB , $R_2CA'B'$, ..., the relative reactivity should be independent of the nature of the groups A and B if the methylene transfer involves a common carbene intermediate, $R_2C:$. Variation of the groups A and B should lead to different product patterns in the bimolecular mechanism, Eq. (10). Thus, if reaction (2) possibly proceeds via free CH_2 , reactions (3) and (7) clearly do not.

c. Identification of Carbenes by Spectroscopic Methods. Although such physical evidence is most conclusive, it is rarely, if ever, obtained under the conditions of chemical transformation. Some doubt remains whether the spectroscopically observed species has any significance in methylene transfer reactions.

Variation of the groups A and B imparts much flexibility to the transition state of the bimolecular reaction (10). Weak bonding of A and B to carbon in the transition state minimizes the difference between mechanisms (9) and (10). The epithet "carbenoid" has been suggested to classify such borderline cases of methylene transfer. Again, the analogy with solvolytic displacement reactions is obvious. In both fields, however, the "first approximation" provided by the unimolecular and bimolecular mechanisms has proved to be extremely useful.

Additional problems arise from the fact that many methylene donors are themselves transient intermediates. For instance, diazomethane does not react with 2,3-dimethyl-2-butene at moderate temperatures unless