

^{14}C label at C-2 of the precursor was retained in the same position in the C_{17} acid. These results show that neither the methyl end nor the carboxyl end of 8,11,14-eicosatrienoic acid contributes to the three carbon atoms which are eliminated.^{11a}

It is therefore suggested that the elimination of the three carbon atoms occurs by way of the cyclic peroxide II, which was earlier postulated to be an intermediate in the formation of prostaglandins.¹² This hypothetical intermediate can be visualized to be converted, by expulsion of a three-carbon fragment,¹³ to 12-hydroxy-8,10-heptadecadienoic acid. Since the two side chains attached to the five-membered ring are *trans* to each other, this mode of formation is also

(11a) NOTE ADDED IN PROOF. Recent experiments with $[3\text{-}^{14}\text{C}, 10\text{-}^3\text{H}]8,11,14\text{-eicosatrienoic acid}$ demonstrate that the tritium label is lost during the conversion to III.

in agreement with the established *trans* configuration of the Δ^8 double bond of the product. No labeled heptadecadienoic acid could be isolated, indicating that the hydroxyl group is introduced prior to elimination of the carbon atoms.

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(12) B. Samuelsson, *J. Am. Chem. Soc.*, **87**, 3011 (1965).

(13) The three-carbon fragment shown in Scheme I as malonaldehyde has not been identified. However, substrate-dependent formation of material giving a positive thiobarbituric acid test (see F. Bernheim, M. L. Bernheim, and K. M. Wilbur, *J. Biol. Chem.*, **174**, 257 (1948)) could be demonstrated during the incubation.

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Book Reviews

The Chemistry of Alkenes. Edited by SAUL PATAI, The Hebrew University, Jerusalem, Israel. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1964. xi + 1315 pp. 16.5 × 23.5 cm. \$37.00.

This volume is the first of a planned series under the editorship of Professor Patai of The Hebrew University on the chemistry of various functional groups. Its aim is an up-to-date presentation of the chemistry of the carbon-carbon double bond. Emphasis is on a comparative and critical discussion addressed to the advanced student and research chemist; encyclopedic coverage is not intended nor achieved. Theoretical and mechanistic aspects of the subject are stressed. Except for the first chapter which discusses wave mechanical aspects of the alkene bond, treatment of the material is limited to reactions in which this bond is formed or is the site of reaction. The literature is generally covered through 1962; some references to papers published during 1963 will be found. Each chapter presents a single aspect of the chemistry of alkenes. The result is a valuable collection of individual monographs by authors who are authorities in the specialty involved. This review will comment on each monograph.

Chapter 1. Wave Mechanics and the Alkene Bond. Professor C. A. Coulson is the senior author of this interesting chapter which is next to the longest in the book. It was indicated that the general purpose was "to enable the reader without previous knowledge of quantum-chemical procedures to appreciate the significance and also the limitations of wave-mechanical calculations, but not to enable him to perform such calculations himself or to encourage him to investigate subtle problems in valence theory. . . ." The authors state that ". . . a wave-mechanical description of bonding in organic molecules requires far more than just the assimilation of a little quantum-chemical terminology into the language of classical organic chemistry. We would do wrong not to make it clear at the outset that, from the wave mechanical point of view, the σ - π systems with which this book is concerned are by no means as straightforward as is often suggested. Any worthwhile study of the bonding in an alkene or polyene molecule (or, indeed, any polyatomic molecule) demands, quite inescapably, a prior understanding of the quantum chemistry of much simpler molecules. . . ." With regard to the mathematics needed to understand the chapter the authors say, "It is idle to pretend that any but the most trivial features of organic quantum chemistry can be presented in non-mathematical terms. For our purposes, however, the mathematical analysis required is very straightforward and well within the repertoire of the average chemist. Although we have not tried to avoid any essential mathematics, we have assumed nothing more than a knowledge of the differentiation and integration of simple trigonometric and

exponential functions, and we have explained other routine mathematical procedures wherever necessary."

The reviewer believes that the authors have seriously overestimated the degree of mathematical sophistication of the average organic chemist. However, if a reader does possess sufficient facility with mathematics or is willing to spend enough time to acquire it, the chapter should be very useful. The authors' conviction that a prior understanding of the quantum chemistry of much simpler molecules is required before olefins can be examined is demonstrated by the fact that two-thirds of the chapter is devoted to the former and only one-third to alkenes (under sections on the π -electron hypothesis, the Hückel approximation and spectra). It seems somewhat irrational to place this chapter first when it is so different in emphasis from the remaining chapters.

Chapter 2. Elimination Reactions in Solution. This relatively brief chapter presents little of the massive amount of experimental data which has been obtained on elimination reactions, but does give a well-organized understandable discussion of the mechanisms of olefin formation by removal of H and an adjacent leaving group. Pyrolytic elimination reactions are left for Chapter 3 and reactions in which neither group lost is hydrogen are not covered. There is no emphasis on synthesis, and references to elimination of HX, where X is other than the more usual groups, are not included. Literature coverage is roughly through 1962 so that a number of significant papers which have appeared during the last 3 years could not be included.

Chapter 3. Olefin-Forming Elimination in the Gas Phase. This brief chapter is concerned primarily with the evidence that there is a class of homogeneous gas phase elimination reactions which are essentially heterolytic in character and in which the effects of substitution on the rates can be discussed in terms of effects in the heterolytic bond dissociation energies. Analogies between such reactions and eliminations occurring by the unimolecular mechanism in polar solvents are stressed. Discussion of the groups that leave with the β -hydrogen includes halogens, RCO_2 , $\text{CH}_2=\text{CHO}$, OCS_2CH_3 , OH, NH_2 , and ClCO_2 . Although the author states that interest in these reactions lies in two areas, one of which is their synthetic application, and that the synthetic importance derives from those cases where more than one olefin can be formed, he does not in fact deal with this area beyond pointing out the differing proportions of 1- and 2-butene obtained from *sec*-butyl chloride and acetate. Gas phase eliminations which occur by chain or heterogeneous mechanisms are not discussed.

The author is well known for his advocacy of the mechanism propounded again in the chapter under review. A more recent review has appeared in *Advan. Phys. Chem.*, **3**, 91 (1965) [Academic

Press, London and New York, V. Gold, Ed.], and a short paper defending the analogy is found in *J. Am. Chem. Soc.*, **87**, 3774 (1965).

Chapter 4. Alkene-Forming Condensation Reactions. This brief chapter contains little more than textbook material; it is somewhat useful for recent references.

Chapter 5. Detection and Determination of the Alkenes. This is an excellent chapter which gives a rapid review of almost every detection or determination method that has been applied to alkenes and excellent leading references on each; difficulties encountered are fairly well covered. The discussion of ozonization was not good but other chemical methods received adequate coverage. The discussion of vapor phase chromatography was good, but the possibility of rearrangement on the column should have been discussed (examples as of allylic or allenic systems might have been cited). The elementary introduction on infrared methods might well have been omitted. The author appears to underestimate the importance of nuclear magnetic resonance, and the improved Raman spectrophotometers should make that method of greater importance.

Chapter 6. Alkene Complexes of Some Transition Metals. This chapter describes complexes of di- and oligo-olefins with some of the transition metals; complexes arising from reactions between such olefins and metal carbonyls receive major attention. No attempt is made to review π -cyclopentadienyl-, π -arene-, and π -allylmetal complexes. It seems more surprising that complexes of monoolefins with metals such as silver, copper, mercury, etc., are excluded. The approach is purely factual; a variety of compounds is described and evidence for the proposed structures is reviewed. There is no discussion of the mechanism of formation of the complexes and very little on the nature of the bonds involved. A number of other reviews are cited in the present chapter and still more have continued to appear in publications such as *Advances in Organometallic Chemistry*, *Advances in Inorganic Chemistry and Radiochemistry*, and *Progress in Inorganic Chemistry*.

Chapter 7. Alkene Rearrangements. This excellent chapter is divided as follows: *cis-trans* isomerism, prototropic rearrangements, anionotropic rearrangements, and miscellaneous alkene rearrangements. The section on allylic rearrangements might well have been omitted because it duplicates material which is presented more completely in Chapter 10, but some of the examples of more extended systems are not covered in the latter. The final section is very brief. It might be mentioned that the review of prototropy in enyne systems (p 433) is so brief that it is misleading; there has been extensive work in this field.

Chapter 8. Nucleophilic Attacks on Carbon-Carbon Double Bonds. This fine chapter covers material not well reviewed elsewhere. Included are nucleophilic additions, ring formation, vinylic substitution, fragmentation reactions, cyclodimerization, and nucleophilic isomerization. No attempt is made to cover the many synthetic studies which involve such nucleophilic attacks, but papers which afford clarification of mechanisms involved are very well summarized. The subjects of vinylic substitutions and fragmentation reactions are very active at present and much has transpired since this chapter was written.

Chapter 9. Reaction of Alkenes with Radicals and Carbenes. The subject of reactions of alkenes with radicals is indeed a broad one, and even after the wise decision to omit radical polymerizations was made, it is clear that the subject has not been covered completely. The result is a thought-provoking treatment which does present much of the newer material in well-organized fashion.

Although reactions of alkenes with carbenes do not as yet possess as extensive a literature, the subject is growing even more rapidly. The material presented in the present chapter is provocative but far from complete. Very recently two book-length reviews of the chemistry of carbenes have appeared.

Chapter 10. Allylic Reactions. This brief chapter consists of three parts. The first on nucleophilic substitution reactions of allylic compounds summarizes and brings up to date the much larger review of this subject published in 1956. The second section on allylic isomerization reactions covers material which was barely mentioned in the earlier review. The chapter concludes with a short section on allylic Grignard reagents; this topic was covered in the earlier review and is now brought up to date. There has been much work on allylic compounds since 1956 and this excellent review is most welcome.

Chapter 11. Cycloaddition Reaction of Alkenes. This excellent chapter, the longest in the book, defines and classifies cycloaddition reactions; it then discusses these under the headings three-membered rings, four-membered rings, 1,3-dipolar cycloadditions, and the Diels-Alder reaction. The relatively short section on three-membered rings duplicates the earlier treatment (Chapter 9) on

carbenes and might have been omitted. The other sections present excellent well-organized coverage of these important topics.

Chapter 12. Conjugated Dienes. This brief chapter is well written but provides no more than minimal coverage of this important class of olefins. Some idea of how brief the treatment is can be gained by comparing the number of references (147) with the number for the following chapter on the far-less-common cumulenes (377). The discussion is organized in sections on synthesis, physical properties (boiling points, magnetic properties, electronic absorption spectra, nuclear magnetic resonance spectra, and chemical properties); the treatment is modern and useful. It seems surprising that polyenes should not have received more thorough discussion in the present treatise, although there is some mention of these higher conjugated compounds in the present chapter.

Chapter 13. Cumulenes. No review of allene chemistry has appeared previously in English and the present survey is welcome. The field is very active at present and the 50 pages devoted to the subject is somewhat meager; however, excellent tables of the allenes synthesized by the different methods help to make the chapter more comprehensive. Coverage of the mechanisms side of various allene reactions is inadequate, but otherwise the review is quite complete through 1962. Other cumulenes are discussed under the headings pentatetraenes and cumulenes with an odd number of double bonds (butatrienes, hexapentaenes, octaheptaenes, and decanonaenes). A feature of the review is a fine section on the theory of the cumulene bond (thermodynamics, electric and magnetic properties, vibration-rotation phenomena, and electronic theory). The reader should be warned that a variety of recent developments has already made a few parts of the review out of date.

Chapter 14. Ketenes. This well-organized review of the syntheses and reactions of ketenes is timely and will be useful. Coverage of dimerizations and other cycloaddition reactions of these compounds is more complete than in Chapter 11.

In summary it may be said of this treatise on alkenes that the objectives set forth by the editor have in general been achieved. This book should be in every research library of chemistry, and organic chemists working directly in the alkene field will doubtless want to own a copy in spite of the high price. The editor has explained the omission of two very important topics in alkene chemistry by the fact that chapters on "Electrophilic Attacks on Alkenes" and on "Biochemical Formation and Reactions of Alkenes" were promised but were not delivered. It is to be hoped that these omissions can be remedied by publication of a suitable supplementary volume.

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Theorie und Praxis der Gravimetrischen Analyse. Band III. Bestimmung der Nichtmetalle. By Dr. LASZLO ERDEY, Professor an der Technischen Universität Budapest, Mitglied der Ungarischen Akademie der Wissenschaften, Akadémiai Kiadó, Verlag der Ungarischen Akademie der Wissenschaften, Alkotmány utca 21, Budapest V. Hungary. 1964. 340 pp. 17 × 24 cm. \$13.00.

This volume is the last in a three-part series on gravimetric analysis. According to the publisher's statement on the book jacket, the plan of the series is the following: the first volume deals with theoretical topics; the second covers methods for determining individual cations; and this, the third volume, is given over to methods available for the gravimetric determination of various anions of F, Cl, Br, I, S, N, P, C, Si, and B. The text also includes an account of methods for carrying out separations of ions that might interfere with a specific gravimetric analysis.

The procedures described in the volume under review are generally familiar to the analytical chemist. For a number of the procedures the author provides supplementary information derived mainly from experiments in his own laboratory. As examples of the latter, one can cite the thermal analytical curve for ammonium phosphomolybdate and a procedure for separating the phosphates by paper chromatography. The material in the volume is well organized and can therefore be useful in many circumstances. It is to be noted, however, that the volume is not a complete treatise. Thus, no mention is made whatever of certain procedures (e.g., the Schöniger flask method for organo-sulfur compounds) that are as well known as some of those described by the author (e.g., the