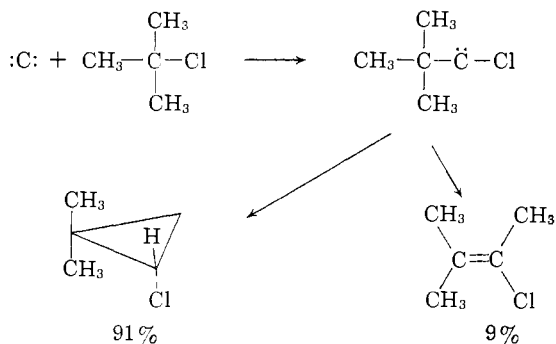
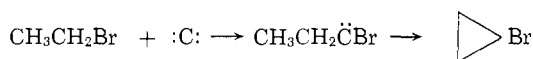


chloromethylcarbene (insertion of the carbon-hydrogen bond) has not been rigorously excluded.

The reaction of carbon atoms with *t*-butyl chloride produces 1-chloro-2,2-dimethylcyclopropane as the major product. This is postulated as an initial insertion on the carbon-chlorine bond, forming *t*-butylchlorocarbene as the intermediate, followed by intramolecular insertion on a  $\beta$ -carbon-hydrogen bond. 2-Chloro-3-methylbutene-2 is produced as a minor product; this could result from a methyl shift.



The free  $\alpha$ -halocarbenes undergo cyclization to halocyclopropanes even when  $\beta$ -hydrogens are available for migration. For example, ethyl bromide reacts with carbon atoms to form cyclopropyl bromide, bromopropenes, etc.



The reaction of carbon atoms with chloroform has been studied by the time-delay technique.<sup>3</sup> Whereas trichloroethylene is formed from both the <sup>1</sup>S and <sup>1</sup>D states of atomic carbon, 1,1,2,2,3,3-hexachloropropane is formed only by the higher energy <sup>1</sup>S. The insertion of dichloromethylchlorocarbene into a second

carbon-chlorine bond would be expected to be a higher energy process than chlorine rearrangement. No products result from the <sup>3</sup>P ground state.

When *t*-butyl chloride was studied by the time-delay technique, it was found that both products were formed from the <sup>1</sup>S and <sup>1</sup>D states. No product results from the <sup>3</sup>P states.

Insertion of carbon atoms into carbon-chlorine bonds produces substituted alkylmonochlorocarbenes as intermediates. Previously, substituted alkylmonochlorocarbenes have been produced either by the  $\alpha$ -elimination of hydrogen chloride from 1,1-dichloroalkanes with strong bases<sup>6,7</sup> or by the interaction of dichlorocarbene with RLi or RMgX.<sup>6,8</sup> In these cases there is probably a degree of association between the carbenes and the salts (*e.g.*, LiCl in the case of RLi) present in solution. Carbenes generated in a dilute chlorocarbon matrix are not subject to this kind of interaction and are thus closer to being "free carbenes."

Kirmse<sup>6</sup> has attempted to prepare *t*-butylchlorocarbene by treating 1,1-dichloro-2,2-dimethylpropane with *n*-butyllithium and by treating *t*-butyllithium with chloroform. No 1-chloro-2,2-dimethylcyclopropane was obtained in either case. The free *t*-butylchlorocarbene produces 1-chloro-2,2-dimethylcyclopropane as the major product.

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## Book Reviews

**Titration in Non-Aqueous Solvents.** By JIŘI KUCHARSKÝ, R. N. Dr., Pharmaceutical and Biochemical Research Institute, Prague, and LUDĚK ŠAFAŘÍK, Ph. Mr., State Institute for Control of Drugs, Prague. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1965. xi + 286 pp. 16 × 23 cm. \$12.50.

The first edition of this book was published in 1961 in Czech. The present second edition is in English and has been enlarged by about one-third with a review of more recent papers dealing with nonaqueous titrations. The theory is covered from a qualitative viewpoint in 50 pages in the first two chapters. The first chapter discusses the historical development of acid-base theories, including the G. N. Lewis theory, but no examples of the conductometric and other types of titration of Lewis acids are given in the practical part. The second chapter reviews the classification and properties of nonaqueous solvents and includes a section of 12 pages dealing with their purification. The third chapter discusses end-point determination by potentiometric, coulometric, and conductometric techniques. Actually, by the coulometric technique solvated protons are produced, but it is not an end-point detection method. Amperometric and thermometric titration methods are not mentioned. The theory of the visual end-point determination with

acid-base indicators refers mainly to behavior in acetic acid, but it is quite different in solvents with an intermediate dielectric constant. The last 200 pages are of a practical nature. Procedures are presented for the preparation of standard solutions of perchloric acid and of tetraalkyl hydroxides and their standardization. Some 110 pages are devoted to the titration of a host of acids and bases of various charge types, with considerable emphasis on pharmaceuticals. The book concludes with an author and a very extensive subject index.

The book is not very stimulating to those interested in the further development of nonaqueous titrations on the basis of a knowledge and understanding of acid-base equilibria. For example, these equilibria are completely understood in dilute solutions of glacial acetic acid and they have been very helpful in calculating titration errors and errors caused by the presence of water. No references to such studies are made in the book. This does not detract from the value of the monograph, as the main objective of the authors was to offer a book which serves as a practical manual for the analyst; as such it is very useful.

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