products from both additions is a mixture of cis- and trans-1-chloro-4-trichloromethylcyclooctane.[8]

The CCl_4–cyclooctene product mixtures were fractionally distilled at reduced pressure. Several low boiling products containing 1–3 chlorines per 8–9 carbons were obtained in combined yield of about 17% (yields of individual compounds varied from traces to 5%), and substantial amounts of hexachloroethane, confirming the free radical nature of the reactions, were also isolated. The major fraction, $C_9H_{14}Cl_4$, b.p. 97–116° (0.2 mm.), amounted to yields up to 73% and was separated into solid (33%,[9] m.p. 64.5–65.5°) and liquid (67%,[9] b.p. 127–130° (1.8 mm.)) isomers by low-temperature fractional crystallization from methanol. The geometrical isomerism was established by dehydrochlorination of either the solid or liquid isomer with 1.08 equiv. of potassium hydroxide in a mixed solvent of dimethyl sulfoxide, methanol, and water (10: 4:1 by volume) to the same 1-chloro-4-dichloromethylenecyclooctane, b.p. 121–123° (3.5 mm.) (90% yield).

The dichloromethylenecyclooctane reacted sluggishly with ozone in CCl_4 solution at 0° to form an ozonide which was reduced with zinc dust and acetic acid to 4-chlorocyclooctanone (54% yield; infrared absorption at 1706 cm.$^{-1}$; 2,4-dinitrophenylhydrazone m.p. 150–152°). This chloro ketone was identical with the one synthesized by conversion of 9-oxabicyclo[4.2.1]nonane[10] to 4-chlorocyclooctyl acetate (70% yield) by treatment with acetyl chloride and zinc chloride,[11] reduction of the ester to chloro alcohol with lithium aluminum hydride, and oxidation of the crude alcohol to 4-chlorocyclooctanone with chromic acid in aqueous acetone.

Photoinitiated (3500-Å. light) addition of bromotrichloromethane to cis-cyclooctene (4:1 molar equiv.) gives, along with small amounts of bromocyclooctenes and trichloromethylcyclooctane, addition product which is at least 97% 1-bromo-2-trichloromethylcyclooctane. The 1,2 isomer is readily distinguished from the 1,4 isomer by n.m.r. data.

N.m.r. signals for CH_2CX (X = Cl, Br, or CCl_3) and for $HCCCl_3$ appear at about -2.2 p.p.m. (A), while those for more remote methylenes appear at about -1.65 p.p.m. (B). For 1-chloro-4-trichloromethylcyclooctane, the ratio A:B (integrated areas) is 9:4, and the signal for $HCCl$ is an unresolved multiplet at -4.2 p.p.m. For 1-halo-2-trichloromethylcyclooctane, the ratio A:B is 5:8 and the signal for $HCCl$ or $HCBr$ is a doublet of triplets centered at -4.75 or -4.82 p.p.m., respectively.[12]

(8) Gas chromatographic analysis indicated that the $C_9H_{14}Cl_4$ fraction contained about 3% of material with retention time coincident with that of the 1,2 isomer.

(9) Analysis by comparison of infrared spectra of $C_9H_{14}Cl_4$ product mixture and standard mixtures prepared from separated isomers.

(10) (a) R. M. Moriarty and H. C. Walsh, Tetrahedron Letters, 465 (1965). (b) A. C. Cope, M. Gordon, S. Moon, and C. H. Park, J. Am. Chem. Soc., 87, 3119 (1965).

(11) A. C. Cope and A. Fournier, ibid., 79, 3896 (1957), describe the comparable reaction between 9-oxabicyclo[4.2.1]nonane and acetyl bromide. We found that the reaction of the less reactive acetyl chloride is facilitated by zinc chloride catalyst.

(12) (a) All chemical shifts are relative to internal tetramethylsilane. Data were obtained with a Varian HA-60 instrument. (b) The integrated n.m.r. spectrum of the 1-bromo-2-trichloromethylcyclooctane sample suggests about 3% contamination by the 1,4 isomer. (c) Analytical use of ratios similar to A/B has been described independently by C. L. McGehee and C. H. Sommers in "Developments in Applied Spectroscopy," Vol. 4, E. N. Davis, Ed., Plenum Press, New York, N. Y., 1965, p. 405.

Peroxide-initiated addition of trichloromethanesulfonyl chloride (0.45 mole) to cis-cyclooctene (0.35 mole) in refluxing benzene solution gave an 81% yield of $C_9H_{14}Cl_4$ addition product which was found by gas chromatographic and n.m.r. and infrared spectrophotometric analyses to be 30% 1-chloro-2-trichloromethylcyclooctane and 70% 1-chloro-4-trichloromethylcyclooctane (67% liquid isomer, 33% solid isomer).

Clearly the relative free energy requirements of the alternate reactions of intermediate 2-trichloromethylcyclooctyl radicals determine the course of the over-all reaction: Abstraction of chlorine from carbon tetrachloride requires more energy than transannular hydrogen migration, which requires more energy than abstraction of bromine from bromotrichloromethane; energy requirements for transannular hydrogen migration and for abstraction of chlorine from trichloromethanesulfonyl chloride are nearly the same.

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The Reactions of Carbon Atoms with Chlorinated Hydrocarbons

Sir:

Previous communications from this laboratory have reported on reactions of carbon atoms with olefinic[1-3] and saturated[4] hydrocarbon substrates. We now report the extension of these studies to reactions with chlorinated hydrocarbons.

The reaction system used has been described.[5] Reactions occur in condensed phase at liquid nitrogen temperature. Products were isolated by vapor phase chromatography and their retention times and infrared and mass spectra compared with those of known compounds.

The reaction of carbon atoms with carbon tetrachloride yields two products, tetrachloroethylene and octachloropropane.
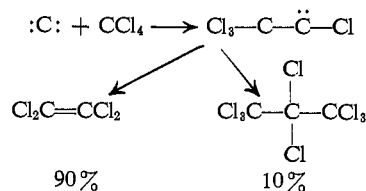
We postulate the initial reaction to be an insertion on a carbon–chlorine bond forming trichloromethylchlorocarbene as the intermediate. This intermediate can either stabilize by chlorine rearrangement, producing tetrachloroethylene, or can insert on the carbon–chlorine bond of a second carbon tetrachloride molecule, producing octachloropropane.

Carbon atoms react with chloroform in a similar manner, yielding trichloroethylene (84%) and 1,1,2,2,-3,3-hexachloropropane (16%). The possibility that some of the trichloroethylene is produced from tri-

(1) P. S. Skell and R. R. Engel, J. Am. Chem. Soc., 87, 1135 (1965).
(2) P. S. Skell and R. R. Engel, ibid., 87, 1135 (1965).
(3) P. S. Skell and R. R. Engel, ibid., 87, 2493 (1965).
(4) R. R. Engel and P. S. Skell, ibid., 87, 4663 (1965).
(5) P. S. Skell, L. D. Wescott, Jr., J.-P. Golstein, and R. R. Engel, ibid., 87, 2829 (1965).

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 β-carbon–hydrogen bond. 2-Chloro-3-methylbutene-2 is produced as a minor product; this could result from a methyl shift.

91%   9%
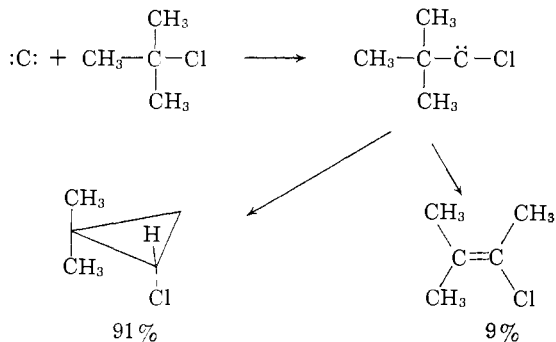
The free α-halocarbenes undergo cyclization to halocyclopropanes even when β-hydrogens are available for migration. For example, ethyl bromide reacts with carbon atoms to form cyclopropyl bromide, bromopropenes, etc.

$$CH_3CH_2Br \ + \ :C: \ \longrightarrow \ CH_3CH_2\ddot{C}Br \ \longrightarrow \ \triangleright\!Br$$
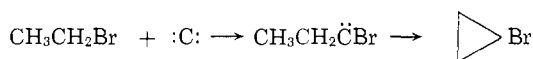
The reaction of carbon atoms with chloroform has been studied by the time-delay technique.[3] Whereas trichloroethylene is formed from both the ^1S and ^1D states of atomic carbon, 1,1,2,2,3,3-hexachloropropane is formed only by the higher energy ^1S. The insertion of dichloromethylchlorocarbene into a second carbon–chlorine bond would be expected to be a higher energy process than chlorine rearrangement. No products result from the ^3P ground state.

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

Insertion of carbon atoms into carbon–chlorine bonds produces substituted alkylmonochlorocarbenes as intermediates. Previously, substituted alkylmonochlorocarbenes have been produced either by the α-elimination of hydrogen chloride from 1,1-dichloroalkanes with strong bases[6,7] or by the interaction of dichlorocarbene with RLi or RMgX.[6,8] 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[6] 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.

(6) W. Kirmse and B. v. Bulow, *Chem. Ber.*, **96**, 3316 (1963).
(7) R. A. Moss, *J. Org. Chem.*, **27**, 2683 (1962).
(8) V. Franzen and L. Fikentscher, *Chem. Ber.*, **95**, 1958 (1962).

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Book Reviews

Titrations in Non-Aqueous Solvents. By Jiří 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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