of chlorohydrins **4a** and **4b** can be isolated. The major diastereomer is the threo adduct which on treatment with NaH/THF at 50 °C gave only the cis epoxide **5**, δ 0.31 (9 H, s), 2.78 (1 H, d, J = 5.0 Hz), 4.40 (1 H, d, J = 5.0 Hz), 7.5 (5 H, s). No vinyl chlorides were formed from the elimination of trimethylsilanol, which could have been a competing reaction. When the reaction mixture of CTC (**3**) with benzaldehyde is warmed from −55 to 20 °C, the initially formed chlorohydrins **4a** and **4b** are converted in situ into the trans and cis epoxides, **5** and **6** (1:3.4), respectively. The threo chlorohydrin **4b** is converted more slowly into the cis epoxide **6** than the erythro chlorohydrin **4a** is converted into the trans epoxide **5**.

All of the substrates listed in Table I react rapidly and cleanly with CTC (**3**) to give α,β-epoxysilanes. The only limitations noted from the examples are that sterically hindered or readily enolizable carbonyl groups cause a lowering of yields. We have not examined the direct hydrolysis of the epoxides listed in Table I using optimum conditions with respect to yield and purity. The conditions described in the literature appear to suffice, and in all cases gave clean and rapid conversion of the α,β-epoxysilanes into aldehydes.[4] Treatment of the epoxides **5** and **6** with $MeOH/BF_3{\cdot}OEt_2$ gave phenylacetaldehyde dimethyl acetal (90%), whereas 5% aqueous $HClO_4$ in THF or 10% aqueous $H_2SO_4/MeOH$ gave phenylacetaldehyde (80%). Furthermore we have converted the α,β-epoxysilane **7** into cyclohexanecarboxaldehyde ethylene acetal, dithioethylene acetal, and 1,3-dithiopropane acetal by treatment with $HOCH_2CH_2OH/TSOH/PhH$, $HSCH_2CH_2SH/TSOH/PhH$, and $HSCH_2CH_2CH_2SH/TSOH/PhH$, respectively.[5] All conversions proceed in excellent yields (≥95%), thus providing a homologation procedure that leads directly to a protected aldehyde or derivative (dithiane) capable of further elaboration. No existing procedure has this simple versatility.

Apart from α,β-epoxysilanes being precursors to carbonyl groups they can react with dialkyl cuprates to give β-hydroxysilanes which can be stereospecifically converted into alkenes.[6] α,β-Epoxysilanes serve as useful precursors to vinyl ethers, bromides, and enamides.[7] Recently α,β-epoxysilanes have been deprotonated to give an α-lithio epoxide synthon.[8]

The α-chloro-α-trimethylsilyl carbanion serves as a nucleophilic acylating species ($\ominus$ CHO synthon) where reduction has occurred at the original electrophilic carbonyl group—*reductive nucleophilic acylation.* While reagents exist for this transformation, none offer the flexibility for further conversion nor the mild and specific conditions that provide the homologated aldehyde.[9] Furthermore the new method described here for making α,β-epoxysilanes uses a commercially available reagent[10] and the only other product formed in their hydrolysis to an aldehyde is trimethylsiloxane.

The procedure described here requires no special techniques or experience with organosilicon chemistry and should find wide use in organic synthesis.

The chemistry of the α-chloro-α-trimethylsilylcarbanion is being actively pursued in these laboratories.

References and Notes

(1) For a leading review covering general organosilicon chemistry, see C. Eaborn and R. W. Bott, "Organometallic Compounds of the Group IV Elements", Part I, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N.Y., 1968; R. F. Cunico, *J. Organomet. Chem.*, **109**, 1 (1976). For reviews describing the synthetic uses of organosilicon chemistry, see I. Fleming, *Chem. Ind.* (*London*), 449 (1975); S. S. Washburne, *J. Organomet. Chem.*, **83**, 115 (1974), and **123**, 1 (1976).
(2) Several silicon stabilized carbanions have been used in synthesis. $Me_3SiCH_2^-$: D. J. Peterson, *J. Org. Chem.*, **33**, 780 (1968); T. H. Chan, E. Chang, and E. Vinokur, *Tetrahedron Lett.*, 1137 (1970). Me_3SiC^-HSR and $Me_3SiC^-HPR_2$: F. A. Casey and A. S. Court, *J. Org. Chem.*, **37**, 939 (1972); H. Gilman and R. Tomasi, *ibid.*, **27**, 3647 (1962); N. E. Miller, *J. Inorg. Chem.*, **4**, 1458 (1965). $Me_3SiCHSeR$: K. Sachdev and H. S. Sachdev, *Tetrahedron Lett.*, 4223 (1976). $Me_3SiC^-HSiMe_3$: B.-T. Gröbel and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **13**, 83 (1974).
(3) R. L. Kreeger, Ph.D. dissertation, The Ohio State University, 1976 (with Professor Shecter) has studied the reactions of bases with trimethylsilyl bromide to give α-bromo-α-trimethylsilylcarbanion which undergoes efficient alkylation with *tert*-butylbromide. Seyferth has prepared the carbanions $Me_3SiCCl_2^-$, $(Me_3Si)_2CCl^-$, $Me_3SiCBr_2^-$, and $Me_3SiCHBr^-$: D. Seyferth, E. M. Hansen, and F. M. Armbrecht, Jr., *J. Organomet. Chem.*, **23**, 361 (1970); D. Seyferth, R. L. Lambert, Jr., and E. M. Hansen, *ibid.*, **24**, 647 (1970). No products from α-elimination of CTC have been observed.
(4) G. Stork and B. Ganem, *J. Am. Chem. Soc.*, **95**, 6152 (1973); G. Stork and E. Colvin, *ibid.*, **93**, 2080 (1971); G. Stork and M. E. Jung, *ibid.*, **96**, 3682 (1974); R. K. Boeckman, Jr., and K. J. Burza, *Tetrahedron Lett.*, 3365 (1974).
(5) Mr. Glenn Roy is thanked for carrying out these experiments.
(6) P. F. Hudrlik, D. Peterson, and R. J. Rona, *J. Org. Chem.*, **40**, 2263 (1975).
(7) P. F. Hudrlik, A. M. Hudrlik, R. J. Rona, R. N. Misra, and G. P. Withers, *J. Am. Chem. Soc*, **99**, 1993 (1977).
(8) J. J. Eisch and J. E. Galle, *J. Am. Chem. Soc.*, **98**, 4646 (1976).
(9) O. W. Lever, Jr., *Tetrahedron Rep.*, **No**, **19**, 1943 (1976). This review describes in detail the reagents that have been used for nucleophilic acylation.
(10) α-Chloromethyltrimethylsilane is commercially available from Petrarch Systems, Inc.
(11) The Upjohn Co. is gratefully acknowledged for supporting this work.

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Book Reviews

Fluorocarbon and Related Chemistry, Volume 3. By R. E. BANKS and M. G. BARLOW (University of Manchester, England). The Chemical Society, London. 1976. ix + 491 pp. £35.00.

For that small band of chemists who concern themselves primarily with highly fluorinated compounds, this book is indispensable. The third volume in a biennial series, it is a 450-page running abstract of new work in fluorine chemistry appearing in 1973 and 1974. It maintains and may even improve the high standard set by its predecessors.

The literature coverage is excellent and an astonishing amount of information is conveyed, not only concerning reaction conditions and yields but also about secondary products, mechanisms (where possible), and related or previous work. This is not a book which tantalizes one with offhand references; insofar as the extremely condensed format permits, the data are given.

The faults of the book are not attributable to the authors but are inherent in its nature. Although it contains a tremendous amount of information valuable to nonfluorine chemists, this is very difficult to disinter since there is no index and the arrangement of chapters is rather rudimentary, being generally based on structure rather than process. There are, however, a few subject headings such as "The Chlorofluorocarbon-Ozone Question" and "Inhalation Anaesthetics", as well as a good number of cross-references. The style of writing is so dense as to require more nearly translation than reading; this is not a volume to be picked up for a little technical browsing. In places, the British habit of using a dot for an electron-pair bond, in conjunction with efforts to save an em here and an em there, make comprehension momentarily difficult for an American reader; it would certainly be less confusing if a slash were used rather than a hyphen to denote a mixture in $CF_2{:}CF_2{-}CF_2{:}CFOCF_3$, and the symbol R_F is employed mistakenly to mean $-(CF_2)_n-$. As would be expected in such a highly condensed presentation, there is little or no critical comment by the authors.

Overall, the authors' objective of collecting in one location a brief description of all the new work on highly fluorinated "organic, organometallic, and organometalloidal" compounds over this two-year period has been brilliantly achieved. Not only fluorine chemists but many others—pesticide, polymer, or environmental chemists, to name but a few—will find this volume well worth study in whole or in part.

John A. Young, *Universidad Autonoma de Guadalajara*

Ion Cyclotron Resonance Spectrometry, By THOMAS A. LEHMAN (Bethel College) and MAURICE M. BURSEY (University of North Carolina at Chapel Hill). Wiley-Interscience, New York, N.Y. 1976. xi + 230 pp. $21.50.

Ion cyclotron resonance spectrometry is a relatively new experimental method which has been found to be extremely useful for the study of ion-molecule reactions. This is the first book entirely devoted to the theory, applications, and consequences of the ICR technique.

The first chapter presents the physical basis for the method and includes sections on double resonance, signal intensity, and ion-trapping cells. The mathematics are kept as simple and concise as possible. Chapters 2 and 3 treat reaction processes and their chemistry: specific ion-molecule reactions are discussed along with their important implications for solution chemistry. The authors have included fascinating sections on acid-base reactions and nucleophilic, electrophilic, and other reactions observed in the gas phase. Chapter 4 deals with more theoretical aspects, such as resonance phenomena, and different methods of measuring reaction rates. The last chapter concerns itself with the effect of light on ions and molecules.

The bibliography is exhaustive. The authors claim to have references to every publication through 1973 and include many into 1976.

This is an excellent introductory book which will be useful to all chemists interested in ICR spectrometry.

Joel C. Colburn, *University of Michigan*

Electron Spin Resonance, (Specialist Periodical Reports), Volume 3, Senior Reporter: R. O. C. NORMAN (University of York). The Chemical Society, London. 1976. x + 311 pp. £17.00 ($46.75).

This volume is a continuation in a series that should be well received by all those who have an interest in ESR spectroscopy and its applications. The literature is surveyed from November 1973 to June 1975. The chapters are very well written and the coverage is extremely broad including over 1900 references, some of which may not be readily available to the average chemist. Where a particular reference pertains to the subject matter of more than one chapter, that reference is included in the appropriate chapters.

The only shortcoming of this volume is the lack of a subject index, although an author index is included. While a detailed table of contents ameliorates this somewhat, such an index would be greatly appreciated.

The cost of this volume may be unattractive to some chemists but, in all, it will be an asset to any library.

Howard S. Friedman, *University of Michigan*

Mechanisms of Oxidation by Metal Ions, By D. BENSON (Halton College of Further Education, England). Elsevier Scientific Publishing Co., New York and Amsterdam. 1976. viii + 225 pp. $33.95.

This work is the tenth in a series of monographs devoted to the topic "Reaction Mechanisms in Organic Chemistry". The book is primarily a review volume, which has been carefully limited to discussion of metal-ion oxidations for which kinetic studies of mechanism have been carried out. Although the main concern of the author has been to present mechanistic features of the oxidation of organic substrates, some discussion of mechanisms of oxidation of inorganic species has been included as background material. The relevant literature has been covered through 1973/1974 (depending on the chapter). The book is aimed primarily at the research worker who wishes to utilize mechanistic information to understand and control the course of metal ion oxidations in organic systems, and should be a valuable reference source for those concerned with this area.

The organization of the book is based on the identity (and oxidation state) of the metal ion oxidant. Each of the three main chapters concerns itself first with general features of the oxidants, such as stability, hydrolysis, and means of production. This is followed by a short discussion of typical mechanisms of oxidation reactions with inorganic reductants (both metal ions and nonmetallic species). The main body of each chapter then deals in detail with mechanisms of oxidation of organic reductants. This section is organized according to the type of compound oxidized (hydrocarbons, alcohols, glycols, aldehydes, ketones, carboxylic acids, phenols, ethers, amines, and sulfur compounds). With regard to particular oxidants, the second chapter reviews the mechanistic literature for the oxidants cobalt(III), cerium(IV), vanadium(V), manganese(III), iron(III), copper(II), and silver(II). The third chapter concerns oxidation mechanisms of lead(IV), thallium(III), mercury(II), and palladium(II), while the final chapter is devoted exclusively to oxidation mechanisms of chromium(VI) and manganese(VII).

Oren P. Anderson, *Colorado State University*

Comprehensive Chemical Kinetics, Volume 15, Non-Radical Polymerization, Edited by C. H. BAMFORD (Liverpool) and C. F. H. TIPPER (Liverpool). Elsevier, New York and Amsterdam. 1976. vii + 660 pp. $100.00.

This book is a most welcome addition to the highly regarded series "Comprehensive Chemical Kinetics". It deals with all types of polymerization except those proceeding by free-radical mechanisms which, because of their interest and importance, are to be treated separately in Volume 14A. The twelve contributing authors are all well known in this area of organic polymer chemistry and have produced what is clearly a definitive treatment of the subject.

The first two chapters cover homogeneous anionic (65 pp) and cationic (65 pp) polymerizations, respectively. The third chapter (125 pp) deals with Ziegler-Natta-type catalysts, the fourth (72 pp) covers the polymerization of cyclic ethers and sulfides, and the fifth (47 pp) and sixth (93 pp) deal with the polymerization of aldehydes and lactams, respectively. The last two chapters are concerned with polycondensation reactions (109 pp) and the polymerization of N-carboxy-α-amino acid anhydrides (55 pp).

J. E. Mark, *University of Michigan*

Methodicum Chimicum, Volume 8, Edited by K. NIEDENZU and H. ZIMMER. Academic Press, New York-London-San Francisco. 1976. x + 579 pp. $110.00.

The volume reviewed is an English translation of the German edition published in 1973; it surveys synthetic methods for the preparation of transition metal complexes. With some exceptions, i.e., the lanthanides and actinides, each metal is discussed individually by chapter. The metal is usually considered from its lowest to its highest oxidation state. In the chapters dealing with more than one metal, the complexes are discussed by type: hydrides, halides, oxides, etc. Although both inorganic and organometallic complexes are discussed, emphasis is placed on classical synthesis of inorganic complexes. The final four chapters are devoted to the prolific areas of metal carbonyls, ferrocenes, other sandwich compounds, and heteropoly ion synthesis. Of the latter, the first three cover some, but not all, of the omissions in the area of organometallic synthesis.

As noted by the editors, ". . . the extreme delay . . ." in publishing the English translation is unfortunate and is perhaps the major disadvantage of the text. Since the work considers the literature through 1970 (with a few 1971 references), many recent but extremely important advances are not included. Of the materials covered, however, the discussions are quite comprehensive considering the enormity of the subject matter.

The incredible number of primary and secondary sources cited in the discussions further compensates for the text's datedness. While the text emphasizes synthetic methods, it also allows easy entry into the literature concerning chemical and theoretical aspects of the complexes discussed. The use of the text as a tertiary source is further facilitated by a thorough volume index.

In summary, this volume of "Methodicum Chimicum" provides a comprehensive description of methods used for the synthesis of a wide range of transition metal complexes. Although the text is somewhat dated, the fact that it is so well referenced would make it a valuable contribution to the reference section of both academic and industrial libraries. My copy has, in fact, already proven useful on a number of occasions.

David M. Floyd, *Harvard University*