Table I. Incorporation of Labeled Precursors into Elaiomycin

expt no.	precursor ($^3H/^{14}C$)	incorpn, %	labeling pattern
1	(3-^{13}C)-DL-serine		9-fold enhancement of C-4
2	[3(*R*,*S*)-^{3}H,U-^{14}C]-L-serine (4.91)	0.02, $^3H/^{14}C = 4.86$	
3	(2-^{13}C,^{15}N)-DL-serine		16-fold enhancement of C-3; C-3 a doublet, $J_{CN} = 3.3$ Hz
4	(*methyl*-^{13}C)-L-methionine		40-fold enhancement of OMe
5	sodium (1,2-$^{13}C_2$)acetate		C-1, C-5–C-12 labeled; 4-fold enhancement of C-12, 6-fold enhancement of C-1
6	sodium (2-^{13}C)acetate		C-1, C-6, C-8, C-10, C-12 labeled; 4-fold enhancement of C-12 and C-1

Our initial efforts to elucidate the biosynthesis of the (methoxyamino)butanol moiety explored the possibility that this portion of the antibiotic was derived from the amino acid threonine. The specific incorporation of this amino acid was never observed, however. A second likely candidate as a precursor appeared to be serine. Accordingly, (3-^{13}C)-DL-serine was synthesized[8] and administered to cultures of *S. gelaticus*. Examination of the noise-decoupled ^{13}C NMR spectrum of the resulting antibiotic revealed a high degree of enrichment at C-4 (70.4 ppm) (Table I, experiment 1). The specific incorporation of C-3 of serine having been established, an experiment was carried out with [3(*R*,*S*)-^{3}H,U-^{14}C]-L-serine to determine whether the entire carbon skeleton of the amino acid was incorporated into elaiomycin. The results of this experiment (Table I, experiment 2) clearly show that C-2–C-4 of elaiomycin are derived from serine. This result led in turn to the question of the source of the α-nitrogen atom of elaiomycin. The question was answered by administration of (2-^{13}C,^{15}N)-DL-serine[9] to *S. gelaticus*. Examination of the noise-decoupled ^{13}C NMR spectrum of the elaiomycin produced in this experiment revealed that C-3 (64.8 ppm) of the antibiotic was coupled to ^{15}N (Table I, experiment 3) thereby proving that the α-nitrogen atom of elaiomycin is derived from the amino group of serine.

The incorporation experiments just outlined revealed the origin of a major portion of the (methoxyamino)butanol moiety of elaiomycin. However, the source of C-1 remained unclear. Administration of (*methyl*-^{13}C)-L-methionine to *S. gelaticus* led to antibiotic that exhibited a high level of enrichment in the *O*-methyl group (58.7 ppm), but no enrichment was discernible at C-1 (Table I, experiment 4). A clue to the origin of the C-1 carbon atom was obtained serendipitously. A precursor incorporation experiment was carried out with sodium (1,2-$^{13}C_2$)acetate to confirm the fatty acid origin of C-5–C-12 of the antibiotic. As expected, C-5–C-12 of the elaiomycin appeared as enhanced doublets in the noise-decoupled ^{13}C NMR spectrum. Unexpectedly, the signal for C-1 of the antibiotic (20.3 ppm) appeared as a strongly enhanced singlet (Table I, experiment 5). This result suggested that C-1 of elaiomycin is derived from one of the two carbon atoms of acetate. On chemical grounds, it seemed more likely that C-2 of acetate should serve as the source for C-1 of elaiomycin. Administration of sodium (2-^{13}C)acetate to *S. gelaticus* proved this to be the case (Table I, experiment 6). The donation of a methyl group from C-2 of acetate is an unusual process whose only precedents appear to be in the biosynthesis of pactamycin and virginiamycin M_1.[10] In the case of virginiamycin M_1, the methyl group is believed to be introduced by aldol condensation of malonyl-CoA with a preformed polyketide chain followed by decarboxylation. The introduction of C-2 of acetate into elaiomycin is probably best visualized as a Claisen condensation between an activated form of serine and malonyl-CoA to yield a β-keto ester, which is hydrolyzed, decarboxylated, and reduced.

Acknowledgment. We thank the National Institutes of Health (Grant CA-25142) and The Robert A. Welch Foundation (Grant C-729) for support of these investigations. We also thank Dr. J. B. Tunac of Warner-Lambert Co. for a culture of *S. gelaticus*.

Registry No. 1, 23315-05-1; L-serine, 56-45-1; acetic acid, 64-19-7; L-methionine, 63-68-3.

---

[8] King, J. A. *J. Am. Chem. Soc.* **1947**, *69*, 2738.

[9] (2-^{13}C,^{15}N)-DL-Serine was prepared by the methods used to obtain (1-^{13}C,^{15}N)-DL-serine: Murray, R., III; Williams, D. L. "Organic Synthesis with Isotopes, Pt. I"; Interscience: New York, 1958; p 175.

[10] (a) Weller, D. D.; Rinehart, K. L., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 6757. (b) Kingston, D. G. I.; Kolpak, M. X.; LeFevre, J. W.; Borup-Grochtmann, I. *J. Am. Chem. Soc.* **1983**, *105*, 5106.

*Book Reviews**

Developments in Polymer Photochemistry. Volume 2. Edited by Norman S. Allen (Manchester Polytechnic). Applied Science Publishers, London. 1981. x + 278 pp. $63.00.

This second volume of the series on polymer photochemistry together with Volumes 1 and 3 provide the interested reader with an excellent introduction to this area of polymer science. The editor has succeeded in collecting contributions from authors who have been actively involved in the field of photochemistry of synthetic or natural polymers for several years. The book begins with a review of photoinitiated cationic polymerization by sulfonium salts, including specific methods for the preparation of these compounds, the mechanism of photolysis, and the use of photosensitizers. This is followed by an extensive table listing general processes and applications of photografting of monomers onto polymer substrates. A detailed discussion of the photooxidation reactions of phenolic antioxidants is then presented, paying particular attention to reaction mechanisms that should be of interest to organic photochemists in this field. The remaining topics in the book deal with the photocatalytic (TiO_2 or ZnO) oxidation and photodegradation of synthetic (polypropylenes and polyundecanoamides) and natural polymers (cellulose), the latter including an interesting discussion on the singlet oxygen theory vs. the hydrogen-abstraction theory for dye-sensitized photooxidation, a subject of considerable debate for many years. Photostabilization of polymers and its mechanisms are also discussed in considerable detail. This book and its companion volumes should provide photochemists and polymer chemists with pages of stimulating material. We should expect the appearance of future volumes in this series dealing with other interesting areas in the field of polymer photochemistry.

Fernando A. Souto, *University of Puerto Rico at Mayaguez*

Compendium of Organic Synthetic Methods. Volume V. By Leroy G. Wader, Jr. (Colorado State University). John Wiley and Sons, New York. 1984. xvi + 552 pp. $37.50.

This hard-bound volume, modestly priced for its size, surveys the years 1980, 1981, and 1982 with respect to practical synthetic methods for

---

*Unsigned book reviews are by the Book Review Editor.

monofunctional and difunctional compounds. The content is organized in 15 chapters according to functional group, as in the earlier volumes in the series. The format remains the same: nothing but equations clearly laid out with full structural formulas, accompanied by conditions, yields, and reference. The organization within each chapter is succinctly set out in a 2-page chart that serves as an index. The great value of this series as a tool for retrieving recently published information and for keeping abreast of synthetic developments is maintained. One should note, however, that the series does not deal with the synthesis of heterocyclic rings.

It is easy to sympathize with the authors cri de coeur, "the reporting of actual, isolated yields and detailed experimental conditions will save a great deal of wasted effort on the part of other chemists hoping to apply the reported reactions to their own synthetic problems". Is anybody listening?

Molten Salt Techniques. Volume 1. Edited by David G. Lovering (R.M.C.S., Shrivenham, Swindon, UK, and Louisiana State University) and Robert J. Gale (Lousiana State University). Plenum Press, New York and London. 1983. xvii + 272 pp. $39.50.

Books on methods are much scarcer than books reporting results, expounding theory, and describing progress, and in the field of molten salts a how-to book is certainly welcome. The editors are to be congratulated on the first volume of a well laid out work. This and the projected volumes cover the territory quite adequately. The introduction provides an excellent overview. There are really two parts to this volume—one containing chapters about techniques for certain groups of melts as classified by the anion (halides, haloaluminates, hydroxides, sulfates, ionized organic salts) and the other chapters about spectroscopy, thermal methods, and reaction chemistry.

A few words from the preface deserve to be quoted here, because they characterize the approach of this book: "Avoid excessive reviews, and concentrate on practical issues, making copious use of tables, figures, and photographs". The authors seem to have followed this guideline without failing to give theoretical background wherever necessary.

In a field as diversified as this, it is difficult to be comprehensive. In the introduction the table of applications does not list electropolishing, and the one on impurities misses organic solvents, which although decomposing at higher temperatures may nevertheless leave residues. It is very surprising to find asbestos recommended as protection against the heat at a time when its use has been outlawed and it is no longer available from supply houses.

In the chapter on sulfates those containing hydrogen ions do not seem to be mentioned. Owing to their much lower melting points, they really form a separate group. Let us hope they will be included in a different chapter. Molten salts are often defined as melts of highly ionic salts, but one might also like to find more water-like melts (e.g., $SbCl_3$) treated in a book like this one, as aluminum halides already are.

Newcomers to the field and experienced workers alike will find this first volume a most useful adviser. The editors should be encouraged to continue this highly commendable undertaking and may they find authors of equally outstanding caliber for the volumes to follow.

Ragnar P. Tischer, *Research Staff, Ford Motor Company*

Treatise on Analytical Chemistry. 2nd Edition. Part I. Volume 3. Solution Equilibria and Chemistry. Edited by I. M. Kolthoff (University of Minnesota) and P. J. Elving (University of Michigan). John Wiley and Sons, Inc., New York. 1984. xxi + 592 pp. $70.00.

This volume continues the up-dating of the systematic presentation of "the theoretical fundamentals of analytical chemistry and their implementation" recently begun in the second edition of the classic "Treatise" by Kolthoff and Elving. The seven chapters in this volume [topics, authors (pages, references)] are: Chapter 24, Oxidation–Reduction Equilibria and Titration Curves, J. A. Goldman (82, 368); Chapter 25, Surface Chemistry: Utilization in Analysis, A. M. Schwartz and P. J. Elving (67, 83); Chapter 26, Solubility, E. S. Amis (117, 287); Chapter 27, Precipitates: Formation, Coprecipitation, and Aging, A. E. Nielsen (79, 45); Chapter 28, Precipitation Equilibria and Titrations in Aqueous and Nonaqueous Media, J. F. Coetzee (45, 65); Chapter 29, Reactive Groups as Reagents: Introduction and Inorganic Applications, H. Freiser (111, 336); Chapter 30, Reactive Groups as Reagents: Organic Applications, J. G. Hanna (62, 225).

Chapter 24 is outstanding as a comprehensive and detailed presentation concerning redox titration curves, end points, and the effects of various traditional approximations. Methods of end point detection are also discussed. Chapter 25 is also well-written and it covers theoretical and practical aspects of such topics as capillarity, adsorption, electrical effects, and colloidal systems. Chapter 26 includes the topics of gas-in-liquid, liquid-in-liquid, solid-in-liquid, and polymer-in-solution solubilities. There are some rather serious thermodynamic and mathematical errors in the equations on pp 232–3, and the discussion of (pseudo) standard state thermodynamic quantities that follows the equations is inadequate.

Chapters 27 and 28 very clearly explain and illustrate important phenomena and methods that must be considered in the application of solubility theory to actual analytical determinations. Chapter 29 briefly introduces the topic of reactive groups in general and then describes, tabulates, and explains in well-organized detail the various classes of metal complexation reactions and titrations. Chapter 30 describes redox, precipitation, complexing, addition, condensation, substitution, and other reactions and reagents useful for analysis of organic species.

In summary, this is a valuable reference work for researchers and serious students interested in any of the specific topics covered. The material is presented clearly, and examples are used in each chapter. Applications are discussed frequently, and references to the literature and to other books and monographs are presented.

Earl M. Woolley, *Brigham Young University*

Solubility Data Series. Volumes 12 and 13. Volume 12 edited by C. L. Young; Volume 13 edited by S. Sekierski, T. Mioduski, and M. Salomon. Pergamon Press, Oxford and New York. 1983. Volume 12: xvii + 477 pp; $100.00. Volume 13: xxiv + 490 pp. $100.00.

This ambitious series continues under the overall guidance of A. S. Kertes as Editor-in-Chief and under the auspices of IUPAC. Volume 12 is concerned with the solubility of five gases: sulfur dioxide, chlorine, fluorine, chlorine monoxide, and chlorine dioxide. More than half the book is devoted to the first of them. Volume 13 treats a very different group of substances: the nitrates of scandium, yttrium, lanthanum, and the lanthanide elements. As is characteristic in this series, the data have been critically evaluated and integrated, and the possible errors due to method of measurement and lack of purity have been carefully taken into account. There are many instances of recalculation of results by the compilers in order to make a consistent presentation. Access to the data is facilitated by three indexes: chemical system; registry number; and author. The collaborators in this effort have raised the compilation of data to a high standard not generally encountered in similar works.

Rodd's Chemistry of Carbon Compounds. 2nd Edition. Supplement. Volume III. Part F (partial) and Part G. Edited by M. F. Ansell. Elsevier Scientific Publishers, Amsterdam and New York. 1984. xvi + 290 pp. $95.75.

This supplement covers polybenzenoid hydrocarbons, including polyphenyl-substituted aliphatic hydrocarbons, and monocarboxylic acids of the benzene series, with their derivatives. It completes the supplementation of Volumes IIIF and IIIG. The preface is dated September 1983, but there is no specification as to the termination date of the coverage of the literature.

The content is, of course, a highly useful compilation of descriptive information in well-organized form, which allows one to become somewhat up to date on the chemistry of particular classes of compounds. It is necessary to use the word "somewhat", for casual scanning disclosed no references later than 1980. Structural formulas are laid out copiously and clearly, although in a much varied group of styles. A substantial index complements the elaborately detailed table of contents.

Some of the nomenclature used is nonstandard and occasionally mystifying, if not actually misleading. For example, on p 144, "aryloximes" are mentioned, without an accompanying structure. Although that term seems logically to mean $R_2C{=}N{-}OAr$, one is eventually led to the conclusion that $ArCH{=}NOH$, properly called "arenecarbaldoximes", is meant. On p 151, there is a table titled Some hydroxamic acids ..., in which the only identification of the compounds whose properties are listed is a column simply headed "substituents". One is left to infer, with some uncertainty, that "benzohydroxamic acids" are meant. Many other inappropriate terms can be found, such as "thioisocyanate" for "isothiocyanate" and "triazothiones" for "triazolothiones".

As in the case of previous supplements, this volume has been prepared by direct reproduction of typescripts. Some sloppily handdrawn symbols mar the result, but the most unnecessary and unpleasing feature is the use of two different sizes of type, elite and pica, indiscriminately. It is such a pity, when the situation could have been avoided by a simple directive from the editor. Running heads (the abbreviated subject of the chapter at the top of each page) could have been asked of the contributors and would have made the book considerably easier to use. Nevertheless, it is good to have this volume available.