

The compounds, **1**<sup>6</sup> and **2**,<sup>7</sup> have now been prepared and their variable-temperature <sup>1</sup>H and <sup>13</sup>C spectra have been investigated. The <sup>1</sup>H NMR spectrum, 80 MHz, of **1** in CD<sub>2</sub>Cl<sub>2</sub> showed only one resonance at δ 4.05, on cooling to -55 °C a broad two-line pattern was found, and at -85 °C fine structure was observed in the two-line pattern. Addition of *N,N*-diethylaminotrimethylsilane, a known acid and water scavenger, led to an extremely complicated but symmetrical ambient spectrum centered at δ 4.07. It appears that in the untreated sample that ring opening was occurring rapidly on the NMR time scale and this led to the equivalency of the protons. The treated sample shows quite clearly that the pure material has nonequivalent protons and the spectrum is that of an AA'BB' system. The <sup>13</sup>C NMR spectrum of either the treated or untreated material had only one resonance at δ +65.65 at ambient temperature and at -75 °C.

The <sup>1</sup>H NMR spectrum of **2** in CH<sub>2</sub>Cl<sub>2</sub> at ambient temperature has two resonances at δ 1.20 and 1.25 for hydrogens of nonequivalent pairs of methyl groups. At -110 °C in CFCl<sub>3</sub>-CD<sub>2</sub>Cl<sub>2</sub> a broad absorption was found. The ambient <sup>13</sup>C NMR spectrum of **2** in CD<sub>2</sub>Cl<sub>2</sub> had absorptions for pairs of nonequivalent methyl group carbons at δ 24.40 and 24.70. A single resonance for quaternary carbons was found at δ 81.40. At -112 °C in CFCl<sub>3</sub>-CD<sub>2</sub>Cl<sub>2</sub> compound **2** exhibited a broad absorption, half-height width of 101 Hz, for methyl group carbons and two absorptions separated by 76 Hz at δ 79.0 and 82.8 for nonequivalent quaternary carbons. The room temperature carbon and <sup>1</sup>H NMR spectra suggest that there is an intramolecular ligand reorganization process between trigonal-bipyramidal (TBP) structures or that **2** is square pyramidal (SP). An ionization process would render the methyl group carbons and hydrogens equivalent. The low-temperature carbon spectrum eliminates an SP structure and strongly supports a TBP or near-TBP structure. The Δ*G*<sup>‡</sup> for the ligand reorganization is 8 kcal/mol<sup>8</sup> with a coalescence temperature of -105 °C.

It is interesting to compare the result of this study with those found for five-membered ring containing oxyphosphoranes and sulfuranes. Many such phosphoranes exist as SP structures in the crystalline state,<sup>9</sup> whereas the sulfuranes favor TBP<sup>10</sup>

structures as solids or in solution. The solution structures of the oxyphosphoranes are not known; it is clear though that SP structures have not been eliminated. The structures of **1** and **2** follow the pattern found for the sulfuranes with a very similar activation energy for the ligand reorganization process.<sup>11</sup>

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## References and Notes

- (1) R. Luckenbach, "Dynamic Stereochemistry of Pentaco-ordinated Phosphorus and Related Elements", Georg Thieme Verlag, Stuttgart, 1973.
- (2) (a) L. J. Adzima and J. C. Martin, *J. Org. Chem.*, **42**, 4006 (1977); (b) G. W. Astrogloges and J. C. Martin, *J. Am. Chem. Soc.*, **98**, 2895 (1976).
- (3) (a) H. Reich, *J. Am. Chem. Soc.*, **95**, 964 (1973); (b) E. L. Muetterties and W. D. Phillips, *ibid.*, **81**, 1084 (1959); (c) E. F. Perozzi, J. C. Martin, and I. C. Paul, *ibid.*, **96**, 6735 (1974); (d) J. C. Martin and T. M. Balthazor, *ibid.*, **99**, 1521 (1977).
- (4) R. Paetzold and M. Reichenbacher, *Z. Chem.*, **10**, 307 (1970).
- (5) R. Paetzold and M. Reichenbacher, "Organic Selenium Compounds, Their Chemistry and Biology", D. L. Klayman and W. H. H. Gunther, Ed., Wiley, New York, N.Y., 1973, Chapter IX.
- (6) Compound **1** had the properties reported.<sup>4</sup>
- (7) Compound **2** was prepared by allowing selenium tetrachloride, pinacol, and triethylamine to react in THF. The triethylamine hydrochloride was removed by filtration. The THF solution was concentrated and **2** was crystallized at -25 °C. A sublimed sample had mp 89-91 °C. Anal. Calcd for C<sub>12</sub>H<sub>24</sub>O<sub>4</sub>Se; C, 46.30; H, 7.77. Found: C, 46.57; H, 7.73. The <sup>77</sup>Se chemical shift of **1** is δ 1261 relative to dimethyl selenide and that of **2** is δ 1203.
- (8) The maximum separation may not have been achieved at -112 °C. A further separation of the two resonances would lead to a slightly lower activation energy.
- (9) (a) J. A. Dieters, J. C. Gallucci, T. E. Clark, and R. R. Holmes, *J. Am. Chem. Soc.*, **99**, 5461 (1977); (b) P. Narayanan, H. M. Berman, F. Ramirez, J. F. Marecek, Y. Chaw, and V. A. V. Prasad, *ibid.*, **99**, 3336 (1976).
- (10) J. C. Martin and E. F. Perozzi, *Science*, **191**, 14 (1976).
- (11) A referee has noted "that a ring puckering equilibrium between pseudo-square pyramidal structures is also consistent with the NMR data. However, 8 kcal/mol may be considered too high for this process".

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## Book Reviews

**Herbicides: Physiology, Biochemistry, Ecology. Second Edition. Volumes I and II.** Edited by L. J. AUDUS (Bedford College, London University). Academic Press, New York-London-San Francisco, 1976. Vol I: xii + 608 pp. \$48.00. Vol. II: xx + 564 pp. \$38.25.

This two-volume set consists of review articles that deal with aspects of herbicides ranging from chemical classification to mechanism of action, from physical behavior to herbicidal selectivity. As such, they will be of greatest interest to researchers specializing in herbicide synthesis, to agricultural chemists, and plant biochemists. Analytical chemists, toxicologists, and ecologists will also discover a wealth of research opportunities in the articles which review the literature of the field to 1974.

Volume I is concerned primarily with studies of the mechanism of action of nearly 150 common herbicides. The mechanism studies are discussed in a systematic way, focusing in separate articles on the different sites at which disfunction affects normal growth and development of the plant, i.e., at the level of growth hormone control, cell membrane formation, or by interference with photosynthesis, respiration, metabolism, RNA transcription, or protein synthesis. Encyclopedic reviews of the literature detail the effects of specific herbicides

on a wide variety of plant species. A particularly interesting chapter shows the power of electron microscopy in revealing alterations in the fine structure of cellular components induced by chemical treatment. The strategy of using sublethal levels of herbicides to study the mechanisms of control of normal plant development is implicit in the discussion.

The behavior of herbicides in the soil and the fate of the chemicals in the environment are considered in Volume II. Articles describing the known routes of detoxification of herbicides by target plants, biodegradation by other organisms, and nonbiological modes of herbicide decomposition are particularly interesting mechanistically. The point is made that of the 150 chemicals used as herbicides worldwide, few have been completely studied to determine their metabolic and environmental degradation products.

Other articles in Volume II discuss the effects of herbicides on nontarget plants, soil microorganisms, and higher animals. Discussion also focuses on the variables which determine the selectivity and effectiveness of herbicides, with particular emphasis on environmental factors and selectivity resulting from differential absorption or metabolism by various plant species. An extensively referenced article

reviews the published analytical methods for detecting specific herbicides. The concluding article outlines the logistics and economics of development of new herbicides for specific applications. Commonly used screening tests are described and techniques for correlating structure and activity of potential herbicides are presented. These volumes have updated and considerably expanded upon the coverage of the single volume first edition (1963). They will be useful references for research libraries.

William R. Bartlett, *Saint John's University (Minnesota)*

**Solid-Liquid Phase Equilibria.** By JAROSLAV NÝVLT (Research Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences). Elsevier Scientific Publishing Co., New York, N.Y. 1977. 248 pp. \$32.75.

The concern of this book is the solubilities of electrolytes in water, and it is naturally divided into the main sections: graphical representation of saturated compositions, experimental measurement of solubilities, and methods for their correlation. In addition, an introductory section presents the basic thermodynamic framework with the inevitable Gibbs phase rule and the Helmholtz equation for the calculation of heat effects from solubilities at various temperatures. Two appended tables of solubilities at the end contribute to the usefulness of the book. The first table presents solubilities of various single electrolytes. The next table contains solubilities in the presence of a second electrolyte.

Details are not spared in the description of the experimental methods and the graphical presentation of the data. Correlation methods are divided into two categories: methods based on geometrical concepts and methods that correlate activity coefficients. The geometrical methods are based on assumed additivity of the properties of the components with various corrections derived from the geometry of the composition diagram. There is no rigorous justification for these methods, and the author observes, "Hence these methods need not yield correct results."

Correlation of activity coefficients starts with the classic Debye-Hückel theory and includes subsequent development of the theory, the theory of conformal ionic solutions, the Zdanovskii method, and the author's own expansion of relative activity coefficients.

Even though the publication data of the book is 1977, the source material of the book is the periodical literature of 1960's and before. Little wonder that the activity coefficient correlations of H. P. Meissner, L. A. Bromley, and others published in the seventies are not discussed.

A source of frustration to the readers is the omission of the kind of information one takes for granted in books. Often left out are the steps of the derivations, the original authors, the references to the original literature, the assumptions, and limitations. An example is in the discussion of activity coefficients. From the Debye-Hückel equation, two sentences lead to an extended equation containing four empirical parameters. Similarly a nomogram (Figure 1.1) is given for the calculation of the heat of solution from the temperature dependence of the solubility which includes an "appropriate empirical correction" for non-ideal solution effect. There is no mentioning, however, of the nature of the correction, accuracy, source, or author.

Viewed in this light, the book can hardly be said to be fulfilling its intended purpose as a supplementary text for university students in chemistry and chemical engineering. Nevertheless, it is a useful monograph for the technologists in industry, particularly those specializing in crystallization.

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**Metal-Ligand Interactions in Organic Chemistry and Biochemistry.** Edited by BERNARD PULLMAN and NATAN GOLDBLUM. D. Reidel Publishing Co., Dordrecht, Holland/Boston, Mass. 1977. x + 396 pp. \$39.50.

The "Proceedings of the Jerusalem Symposia on Quantum Chemistry and Biochemistry" (Volume 9, Part 1) contain a collection of 22 papers (all in English) by workers from throughout the world. About half of the papers contain theoretical and crystallographic material and half are experimental.

The lead paper (Pullman) considers the general features in cation-ligand binding via ab initio SCF studies. Followup papers treat metal ion binding to nucleic acids, phospholipids, DNA, amides, proteins, enzymes, and crown ethers.

The experimental papers discuss a variety of interesting topics. For instance, Kistenmacher's work on purines probes "whether or not interligand interactions can induce activity". Papers follow on the conformational sensitivity of DNA to ionic interactions, the effect of Gd(III), Mn(II), and Cu(II) on nucleotide structure, and the influence of heterocyclic nitrogen atoms on the interaction between purine analogues and metal ions. Two papers from the Indian Institute of Technology investigate the influence of alkali and alkaline earth metal ions on amides, polyamides, and polypeptides. J. Corset (France) reports on the IR and Raman findings on the organization of carbonyl groups of organic ligands around salt cations. Papers on specific metal-ligand interactions include Cu-proteins, La<sup>3+</sup>-lysozyme (while there are several bonding sites, only one ligand bonds strongly), and Co(III)-ATP complexes which are used as tools to elucidate interactions of enzymes with nucleotide-metal ions. The final paper discusses metal-ion-ligand interactions for the tetracycline derivative antibiotics using a structural approach.

Each paper is amply illustrated with structures, graphs, and tables, gives complete references, and is followed by a record of the question-answer discussion period.

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**Science and Technology of Gelatin.** Edited by A. G. WARD (The University of Leeds) and A. COURTS (Imperial College of Science and Technology). Academic Press Inc., London and New York. 1977. vii + 534 pp. £18.00/\$39.50.

This book fills a real need for an up-to-date text on the technology of gelatin. It is surprising how few texts there are that deal with this widely used substance. The authors of this "collage" book have done extremely well in covering the subject in both breadth and depth. In spite of 15 collaborating authors, the style is notably uniform throughout the entire text.

The character of collagen, the basic raw material for gelatin manufacture, is described in appropriate detail. Molecular aspects and physical structure of collagen provide a basis for understanding the ready formation of gelatin therefrom. The variety of anatomical sources of collagen is well described. Next, chemical and physical properties of gelatin are clearly defined. Comments on the molecular structure of gelatin support an imaginative contention that gelatin in solution may be "alive". The gelatin can revert back toward collagen as a result of cross-linking or hydrogen bonding. Simultaneously, smaller and smaller molecular weight peptides are formed as a result of an autolytic-like action taking place at 35 to 40 °C. Renaturation, the reversion phenomenon, seems strikingly parallel to retrogradation of amyloses back to native starch.

The latter half of the book deals authoritatively with the processing aspects: how raw materials are selected and prepared for production of gelatin, the choice of two broad processing operations and the consequences of each, the equipment required at each of several crucial steps in manufacturing, and controls used to achieve desired quality.

The principal outlets for gelatin in the food, photographic, pharmaceutical, adhesives, and paper industries are well documented. This raises a somewhat curious aspect of gelatin technology. Much more unpublished data on gelatin may exist than that which is already in the scientific literature. It is rumored that the highly competitive photographic industry is responsible for this clandestine state of affairs. Although this would be a natural apology to be included in the introductory section of the present book under review, only one collaborator chose to mention this as an aside, lamenting that "like the iceberg, a considerable amount of know-how is submerged in the files of industry".

The final sections of the book contain useful information on a considerable variety of chemical and physical methods for the characterization and analysis of gelatin.

Minor flaws, yet worthy of note, are (1) the scanty nature of the subject index (eight pages vs. twenty-one for the author index) and (2) rather poor proofreading, not only misspellings but also confused or incorrect sentences due to word distortion.

Even so, the book should be in the hands of all those who have a close working relationship with gelatin, a substance often the subject of attempted duplication, but thus far unmatched by any synthetic material created in the laboratory.

J. Controulis, *Parke, Davis & Company*