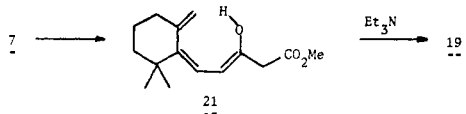


of this dichotomy.<sup>13</sup> The partitioning of photoproducts from **3** between pyran **8** and ketone **16** apparently reflects the position of equilibrium of the 4,5-cis dienone **19** with its enolate **20**, the neutral species undergoing the well-precedented tautomerization to **8**,<sup>6</sup> whereas for **20** a triene electrocyclicization<sup>14</sup> to **16** prevails (see Scheme I). Cis isomer **19** probably originates from **7** via a 1,7-prototropic shift of enol **21**;<sup>15</sup> in any case, di-



rect photochemical trans  $\rightarrow$  cis isomerization of **3** (in polar solvents) as well as enolate **18** is excluded by these results. A consequence of the reversibility<sup>16</sup> of the cis-dienone-pyran tautomerism in Scheme I is that access to **20**, and hence **16**, may also be gained via **8**.<sup>17</sup> Thus, irradiation of **8** in methanolic sodium methoxide furnished a mixture of **16** and **17** similar in all respects, including yield, to that obtained from **3** under the same conditions. No enone was produced when **8** and sodium methoxide were mixed in the dark.

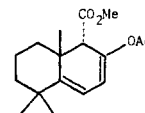
These results suggest that the photochemical behavior of conjugated enolates can be modulated in synthetically useful ways through pathways which differ significantly from those followed by the corresponding uncharged species.

**Acknowledgments.** We are grateful to the National Science Foundation and to the M. J. Murdock Charitable Trust for financial support. One of us (R.W.S) thanks the N. L. Tartar Research Fellowship Fund for financial support.

#### References and Notes

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- (8) *E* isomer (CDCl<sub>3</sub>):  $\delta$  5.55 (1 H, s), 6.60 (1 H, d,  $J = 16$  Hz), 7.40 (1 H, d,  $J = 16$  Hz). *Z* isomer (CDCl<sub>3</sub>):  $\delta$  5.64 (1 H, s), 6.00 (1 H, d,  $J = 16$  Hz). Assignment is based on the downfield shift ( $\Delta\delta = 1.2$ ) of the C-4 vinyl proton due to the deshielding effect of the carbomethoxy group in the *E* isomer.
- (9) *E* isomer (CDCl<sub>3</sub>):  $\delta$  3.76 (2 H, d,  $J = 7$  Hz). *Z* isomer (CDCl<sub>3</sub>):  $\delta$  3.14 (2 H, d of d,  $J = 2.7$  Hz).
- (10) With  $>2.5$  equiv of sodium methoxide the yields of **16** and **17** diminish owing to decomposition. An as yet unidentified yellow compound is one of the decomposition products. It was established that **17** arises from **16** through base-catalyzed isomerization.
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(1)

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- (18) National Institutes of Health Research Career Development Awardee, 1976-1981.

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## Book Reviews

**Low Temperature X-Ray Diffraction Apparatus and Techniques.** By REUBEN RUDMAN (Adelphi University). Plenum Press, New York, N.Y. 1976. xvi + 344 pp. \$35.00.

This book is a review and consolidation of all the techniques and apparatuses that have been used over the years to study low-temperature X-ray diffraction behavior of both polycrystalline and single crystal samples. The theory of the technique is discussed and a comparison of low temperature diffraction and room temperature diffraction is included. There are many detailed discussions and drawings of specific equipment and techniques, some of which are of historical interest.

The book covers such topics as temperature control, frost prevention, crystal stability, phase transitions, choice of adhesives, film properties, absorption, window materials, sample preparation, crystal growing techniques, and data collection and reduction. Discussion and drawings of low-temperature apparatus for powder cameras, single crystal cameras, and diffractometers are included. The Bibliography is extensive and included are a list of suppliers, an apparatus code number listing, and a techniques and applications code number listing to aid in the location of specific information.

William M. Butler, *University of Michigan*

**Chemical Pharmacology of the Synapse.** By D. J. TRIGGLE (State University of New York at Buffalo) and C. R. TRIGGLE (Memorial University of Newfoundland). Academic Press, New York, N.Y. 1976. ix + 654 pp. \$43.75.

This excellent book, with two chapters by both authors and the other three by only the one (D.J.T.), has some of the immediacy of a symposium proceeding together with the pedagogical qualities of a graduate-level textbook, an advanced one to be sure. Biochemists, pharmacologists, and physiologists, to cite only the broad classic divisions, cannot afford to be without this book. We recognize that a work of such wide appeal is difficult to aim for a consistent readership. Thus there are many simplistic diagrams of nerve endings to illustrate neurotransmitter synthesis, storage, and release, whereas the steric aspects of structure-activity relationships might have been improved by some introductory simplification. The chapter on ligand-receptor interaction contains a review of the formal models for cooperative behavior which is wide ranging. For example, not only are the well-known concerted and sequential models dealt with, but also reviewed are some nonequilibrium kinetic schemes which should generate cooperative behavior, as well as an example illustrating cooperativity generated by events other than those based on multiple binding site

mechanisms. This section might have been improved by noting that Changeux's cooperative lattice model (which is discussed here) has much in common with Tasaki's "two stable state" model of axonal conduction (which is not mentioned). The molecular basis of neurotransmitter-receptor interactions has probably been most evenly handled, moving progressively from the simple Nernst equation through voltage clamp technology, ionic channels, membrane biochemistry, and the most recent highly speculative models. While the chapter on receptor isolation and characterization seems rather brief, this is a subject in such a rapid state of advancement that undoubtedly when a revision of this book comes out it will include the more recent findings which tend to move the experimental spot light away from the use of reversible and irreversible affinity agents as the sole receptor probes. An example illustrating the direction of recent progress would be the proposed phosphorylation of nicotinic receptors by an endogenous kinase.

Such a revision will, we hope, correct the only serious flaw in this otherwise well-organized book, namely the subject index. Two examples: The organophosphorus cholinesterase inhibitor diisopropylphosphorofluoridate is dealt with on several pages (even a reference to its action on synaptic membranes) but is not indexed under any of its several names. Curare is at the very core of synaptic pharmacology and is even depicted in structural formulas, but is not indexed under any of its various names.

Donald A. Farquharson, Francis C. G. Hoskin  
Illinois Institute of Technology

**Trace Element Contamination of the Environment.** By DAVID PURVES (Edinburgh School of Agriculture). Elsevier Scientific Publishing Co., Amsterdam and New York. 1977. x + 260 pp. \$34.75.

This book is written along the lines of H. J. M. Bowen's 1966 book, "Trace Elements in Biochemistry", and presents a welcome update of information in specific areas.

The author deals primarily with the first transition series of metals plus lead, mercury, and boron with minor reference to arsenic, selenium, sulfur, and fluorine. He traces the dispersion of these elements from their original ore deposits through their use in industry to their entry into the environment from industrial and municipal sources.

The focus of the book, and the area where the most significant information is contained, is on the entry of trace elements into the soil and their subsequent potential uptake by vegetation and ultimate incorporation into the food chain. The data concentrate on the British Isles and include the author's own research.

The final sections of the book deal with the methods of disposal of municipal and industrial sludge and compost from the point of view both of dispersion of a valuable natural resource and of contamination of the environment. Suggestions are made as to needed changes in methods of recovery and to disposal on a world-wide basis.

This book will be valuable to researchers in the soil science area because of the large amount of data contained and the excellent list of over 400 references. The only serious drawback is the lack of a subject index which makes it very difficult to refer back to specific items.

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Ann Arbor, Michigan

**An Introduction to Radiation Chemistry. Second Edition.** Edited by J. W. T. SPINKS and R. J. WOODS (University of Saskatchewan). John Wiley & Sons, New York, N.Y. 1976. xiv + 504 pp. \$24.95.

The first edition of this book (1964) has served radiation chemists for many years as a starting point in their studies. The usefulness of the first edition was primarily due to its practical approach to problems which radiation chemists meet in the laboratory. Among other features, actinometry was treated with sufficient exhaustiveness to be of immediate use to those who have to determine radiolytical yields. After a 12-year interval the second edition has now appeared and, according to the authors, it takes into account the changes which have occurred in radiation chemistry during the last decade. However, as the number of pages has only modestly increased (by 27), it might be hoped that the content of the new edition would have been revised to reflect the new state of knowledge of the subject.

Here and there the authors have shortened somewhat the descriptive content, e.g., sources of radiation, interaction of radiation with matter (Chapter 2), dosimetry (Chapter 3), and formation of reactive species by ionizing radiation (Chapter 4). Chapter 5 on radiolysis kinetics is

entirely new; beginning with an elementary development (16 pp), it continues with 20 pages of qualitative description of pulse radiolysis equipment and techniques, as well as picosecond laser spectroscopy. Chapter 6 on the radiolysis of gases is a slightly shortened version of the corresponding chapter in the first edition, with about 20 new references added to bring the total to 125. Considering the advances during the last decade in the area of gas phase radiolysis, this addition seems indeed small.

The real innovation in the second edition is found in Chapters 7 and 8, which deal with water and aqueous solutions and with organic compounds, respectively. The new edition includes more than 100 new references, most of them from the 70's. Well-documented tables of rate constants of reactions in aqueous solutions are provided. The radiation chemistry of organic compounds is illustrated by a few examples of radiolysis of some representative compounds chosen from different groups: normal hexane and cyclohexane for saturated hydrocarbons; hexene for the unsaturated ones; methyl iodide, chloroform, and carbon tetrachloride for halogenated compounds; methanol for alcohols, acetone and its esters; etc. The complexity of the radiolytical processes occurring in these compounds is emphasized, and the treatment of this subject could serve as a source of inspiration to beginners in the field for further study.

Chapter 9, dealing with radiation effects on solids, is merely a repetition of the first edition. As substantial progress has been made in this area, the reader wishing to become acquainted with it still has to search through the recent literature. The last chapter deals briefly with industrial applications of ionizing radiation. The book ends with 14 solved problems which are typical of those encountered in radiation chemistry. It is a pity that a chapter on radiation polymerization and radiation effects on polymers has not been included, as this field is very active and is particularly important in applications.

In summary, the second edition of this book has preserved its practical approach to problems in radiation chemistry and, as such, will be useful for those new to the field. However, unless owners of the earlier edition have a special interest in the relatively small amount of new material, they will not find it necessary to purchase the second edition.

Jan A. Herman, *Université Laval*

**Neighboring Group Participation. Volume 1.** By BRUCE B. CAPON (The University, Glasgow) and S. P. MCMANUS (The University of Alabama in Huntsville). Plenum Press, New York and London. 1976. x + 280 pp. \$29.50.

This is the initial volume of a projected two-volume set dealing with the title subject. The authors' stated objectives in the set are not to treat neighboring group participation in a comprehensive manner—providing, however, for the inclusion of all significant examples—and to discuss the topic in a systematic and critical manner. In this reviewer's opinion, they have indeed achieved these objectives.

The first three chapters of the book encompass the vocabulary, history, theory, and experimental methodology of the subject and provide an overview of the various factors known to influence anchimeric assistance. The final three chapters deal, respectively, with participation by oxygen-, sulfur-, and nitrogen-containing groups, all of which are classified as donors of nonbonding electrons. Other  $n$ -electron donors as well as donors of  $\sigma$  and  $\pi$  electrons will be considered in the companion work, as will be ambident (referred to as "ambient" in the text, presumably as the result of a typographical error) species such as ester and amide groups. The coverage of the relevant chemical literature appears to extend through mid-1976.

Sufficient space has been allotted to the fundamentals of the topic so that a background equivalent to a junior-senior level course in mechanistic organic chemistry should allow mastery of the material. The presentation is complete, logical, and concise, and specific criticisms are rather minor, e.g., the use of the terms,  $k_c$  and  $k_\Delta$  some seven pages prior to their careful definition, the absence of labeling on the rather unconventional free energy diagrams presented in Chapter 1, and the failure to define the arrows used in Fig. 2.1. There is a more important conceptual error in the discussion (p 43) of the increase in the number of vibrational modes that occurs as the consequence of a bimolecular reaction; the increase is six rather than three.

This book represents a valuable addition to the literature of organic chemistry and should find a place in both institutional and private collections. Hopefully the high standards established here will be maintained in the final volume.

John C. Gilbert, *University of Texas—Austin*