It is to be noted that complete degeneracy arises after a minimum of four cleavages and recombinations of doubly allylic C–C bonds in one given direction. Because the indicated deuterium scrambling necessarily takes place in stepwise fashion (Scheme I), isotopic transposition to the remaining four pairs of carbon atoms in **8** is predicted to occur in the sequence b → a → c → e → d. The experimental findings (Table I) indicate that at least a prominent component, and possibly all, of the degenerate lumibullvalene rearrangement proceeds in the free-radical mode. Thus, positions a acquire deuterium label relatively rapidly as expected from the fact that carbons a and b become equivalent (excluding isotopic influences) after the first cleavage–recombination sequence. Difficulty was realized in achieving structural automerization which would position deuterium at carbons d because of the marked proclivity of the lumibullvalene molecule for conversion to *cis*-9,10-dihydronaphthalene under conditions which are relatively mild for such interconversions.[10] It is to be recalled that the d positions are not expected to acquire isotopic label until a minimum of four steps has been traversed (Scheme I).

Further experimentation[11] with **9** likewise attested to the capability of this $(CH)_{10}$ isomer to exchange its constituent sp^2- and sp^3-hybridized carbon atoms faster than irreversible conversion to *cis*-9,10-dihydronaphthalene (Table II). Should the conversion of **4** to semibullvalene (**7**) which proceeds with great facility at 25° [5] likewise occur by initial homolytic cleavage to give **5**,[12] the differing pericyclic constructs of **2** and **5** as defined by Goldstein and Hoffmann[4] could be the source of the significant energetic differences in the rate-determining steps of these closely related reactions.

Table I. Deuterium Atom Distribution in Pyrolyzed Samples of Monodeuteriolumibullvalene (**8**) (60 MHz, $CDCl_3$ Solutions)

Temp, °C	Pressure, mm	**8**:*cis*-9,10-dihydronaphthalene in pyrolysate, %	Rel deuterium atom distribution, %[a] a	b	c	d	e
240	12	100:0	7	93	1	0	0
290	30	45:55	30	48	11	0	11
310	30	60:40	28	47	9	5	9
280 (2×)[b]	25	60:40	32	28	28	0	12

[a] The percentage composition values were derived by careful integration of the various pmr absorptions (total area = 9 H), computation of the hydrogen count at each site, subtraction of these values from the maximum possible values (2 H), and multiplication of the numbers so obtained by 100. The chemical shifts of the various multiplets and their assignments are: c, δ 6.57; e, 5.81; d, 5.51; a, 3.10; b, 2.38. [b] Experiment conducted by preparative vpc separation of lumibullvalene from *cis*-9,10-dihydronaphthalene and repeat treatment under identical conditions.

Table II. Deuterium Atom Distribution in Pyrolyzed Samples of Hexadeuteriolumibullvalene (**9**) (60 MHz, $CDCl_3$ Solutions)

Temp, °C	Pressure, mm	**9**:*cis*-9,10-dihydronaphthalene in pyrolysate, %	Rel deuterium atom distribution, %[a] a	b	c	d	e
(Before pyrolysis)			0	0	38	36	27
285	18	79:21	8	3	33	31	25
300	20	58:42	9	7	29	30	25
300	20	58:42	11	7	28	29	24
312	18	37:63	16	13	24	25	21
320	18	30:70	18	13	24	24	21

[a] Calculations performed as before, assuming 5.98 protons per molecule (nmr and mass spectral data for **9**).

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(10) At the experimental level, only a very small temperature region (280–320°) was available which would allow return of sufficient lumibullvalene for characterization.

(11) All pyrolyses were conducted in the gas phase under a nitrogen atmosphere in a quartz tube packed with quartz chips as previously described: L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **93**, 2459 (1971).

(12) In this instance, the possible alternative operation of the concerted pathway remains to be established. See, however, H. M. Frey and R. G. Hopkins, *J. Chem. Soc. B*, 1410 (1970). Meinwald and Zimmerman[5] have proposed the diradical pathway in their original reports of this reaction (**4** → **7**).

Book Reviews

Mass Spectrometry: Techniques and Applications. Edited by G. A. W. MILNE (National Heart and Lung Institute, National Institute of Health). Wiley-Interscience, New York, N. Y. 1971. x + 521 pp. $24.95.

This compendium consists of twelve chapters strongly oriented toward organic and biochemical mass spectrometry. The first 216 pages (seven chapters) are devoted to techniques: two on photographic and electric recording by Desiderio and by McMurray, one on GC–MS by Ryhage and Wikstrom, three on automated data acquisition and computer applications by Venkataraghavan, by Fennessey, and by Buchanan, Duffield, and Robertson; newer ionization techniques are discussed by Fales, with emphasis on chemical ionization. Applications chapters deal with peptides (Shemyakin, Yu A. Ovchinnikov, and A. A. Kiryushkin), stable isotopes in biochemistry (Grostic and Rinehart), problems in medicine and biochemistry (Milne), and fragmentation mechanisms (Bursey and Hoffman). The last chapter by Jennings is on metastable transitions and covers techniques and principles more so than uses. The overall caliber of the book is consistently high; only one chapter seems weak and there are several which could be termed outstanding in clarity, completeness, and levels of insight and expertise displayed.

There is little duplication in the chapters dealing with similar topics, and the editor has obviously done a very careful job in coordinating the book. Topical coverage is fairly complete within the restrictions of the intent of the book, which is very much defined by the preface which begins with "The affair between organic chemistry and mass spectrometry . . . ." About the only subjects which are either not at all or only insufficiently covered are the use of negative ions for analysis, and ion cyclotron resonance. In general, the approach of each chapter is to take its topic and to summarize the present state of knowledge in a well-coordinated fashion, rather than to abstract all recent papers; there are one or two exceptions which do not seriously detract from the book. The literature coverage appears to be complete through 1969 and there are some references to work published in 1970.

The twelve chapters serve very well as a summary of the subjects they cover and should be highly useful to those mass spectrometrists who are well grounded in fundamentals and need a reference work which summarizes accomplishments, problems, and generally the state of the art in areas with which they themselves do not deal regularly. Moreover, the book should prove quite useful to all who are interested in the use of mass spectrometry in organic and biochemistry, and it can even serve very well as broad supplementary material in an advanced course in mass spectrometry.

G. G. Meisels, *University of Houston*

Flame Spectroscopy: Atlas of Spectral Lines. By M. L. PARSONS and P. M. MCELFRESH (Arizona State University). Plenum Press, New York, N. Y. 1971. vii + 96 pp. $11.50.

This book is an atlas of the usable lines for atomic absorption, emission, and fluorescence flame photometry. The information for each type of flame spectroscopy is contained in a separate section. The authors indicate that their purpose was to place under one cover the information available. The intensities of the lines are listed on a scale of 10 for the strongest and permit an evaluation of those available when less intensity may be desirable for more concentrated solutions.

Unfortunately the latest information is that published in 1969. At that time not much work had been done on fluorescence and much more useful information has appeared for both atomic absorption and emission photometry.

This book only lists and evaluates the useful spectral regions for the various elements, and as such would be of interest to the investigator who has the knowledge and interest or need to adapt his instrument to conditions other than those given in the instruction manuals accompanying most instruments. It does not contain any information on the use of any of the instruments.

If the column headings were included on every page, the information would be a lot easier to use.

Taft Y. Toribara, *School of Medicine and Dentistry University of Rochester*

Lactic Acid. Properties and Chemistry of Lactic Acid and Derivatives. By C. H. HOLTEN (Danmarks Ingeniørakademi) with contributions by A. MÜLLER (C. H. Boehringer Sohn), and D. REHBINDER (Bioscientia G.m.b.H.). Verlag Chemie, Weinheim. 1971. 515 pp. DM 135.

The International Research Association Stichting Ilra, comprising the main European producers of lactic acid, decided some years ago to collect all available knowledge of lactic acid and its derivatives and to publish the collected material in the form of a systematic and critical monograph which should be equally useful for pure and applied chemistry, taking into consideration that (1) lactic acid, being one of the simplest compounds with a center of chirality, has been intensely studied from a theoretical point of view and (2) that this compound, containing two different functional groups, may take part in numerous intermolecular reactions leading to esters, ethers, amides, macromolecules, and heterocyclic compounds, many of the derivatives thus formed being of very considerable technological importance.

More than 3000 publications have been studied and about 2500 of these are entered as references. The collected information is reviewed with sufficiant details to allow anyone looking for the preparation and properties of a particular derivative of lactic acid to get an impression of the procedure to follow and reference to papers where procedures are more fully described. The many tables and figures facilitate the selection of derivatives with specified properties.

The object aimed at in planning the monograph has been fully achieved. The present volume is of equal usefulness for scientists and for industrial research laboratories and deserves to find widespread distribution.

Stig Veibel, *Technical University of Denmark*

Phase Transitions. By SOLVAY INSTITUTE. John Wiley & Sons, Ltd., London. 1971. xi + 256 pp. $16.50.

This book contains the proceedings of the Fourteenth Conference on Chemistry held at the University of Brussels in May 1969. Both the papers presented at the conference and the ensuing discussions are reported. Most of the papers and discussion are referenced.

The first half of the book contains reports and communications by J. E. Mayer, S. A. Rice, E. Lieb, J. S. Langer, L. Verlet, and A. Bellmans dealing with the theory, mathematics, and mechanics of phase transitions. A paper by A. R. Ubbelohde is concerned with the relation of crystal structure to melting and the various mechanisms which have been advanced to explain melting. G. B. Benedek reports on some studies of divergences in transport properties from light scattering near critical points. This is followed by a short communication by P. Résibois concerning dynamical phenomena close to the critical point. G. Busch and H. J. Güntherodt report on the electronic structure of pure liquid metals and several alloys as determined from measurements of electrical resistivity, the Hall coefficient, and magnetic susceptibility. Finally, the last paper by S. Lifson is concerned with equilibrium properties related to transitions in chain molecules with special attention focused on polypeptides and polynucleotides which undergo helix–random coil transitions.

Richard E. Wilde, *Texas Tech University*

Photochemistry and Spectroscopy. By J. P. SIMONS (University of Birmingham). Wiley-Interscience, London. 1971. xiii + 343 pp. $16.50.

This text is an interesting one and does provide different emphasis from most of its predecessors. It is divided into three main sections: the first deals with basic quantum chemistry as of interest to the photochemist; the second part concerns photophysical processes; and the last section discusses aspects of photochemistry.

The emphasis might be considered by some as more appealing to physical rather than organic photochemists; at least, it appears that this is the author's intent. Section I covers the topics of electromagnetic radiation, atomic energy levels, MO's and electronic states, vibrations and rotational energies, electronic transitions, and selection rules. Section II covers atomic and diatomic spectra, the various modes of excited state decay, polyatomic spectra, and decay. Part III covers primary processes in simple molecules and a short, selected coverage of some organic photochemistry.

The book is a difficult one for the present reviewer to assess since it has many good points and some weaknesses. The Edward John Phelps quotation that "The man who makes no mistakes usually does not make anything" is the book's introduction. The reviewer agrees with this philosophy but would not have begun the book with it. The book does have some errors. It also has many stimulating sections.

One error is the definition of the noncrossing rule as a vibration carrying a molecule through an intersection of states. This is serious and seems likely due to misplacement of the sentence on page 131 saying "This is known as the non-crossing rule." If the sentence occurred slightly earlier, it would have been correct. The description of the di-π-methane rearrangement on page 241 as a bond-switching process, with just an indication of the change in atomic positions, is overly primitive, and no indication is given of current thinking about the reaction. Figure 1.7 on page 22 has two orbitals improperly filled in with wave function signs; this is clearly an error in drawing. Thus, the book does have its share of errors. The discussion of organic photochemical reactions is the weakest since it is short and the coverage is a bit light in breadth and depth. However, this, too has its redeeming features in providing a survey of some interest. In fairness, one has to note that it is really quite impossible these days to give anything approaching complete coverage to organic photochemistry.

On the other hand, the book is very readable and covers some very interesting topics in very large number. The expert reader will not be deterred by the errors, and the positive thinker will pay more attention to the very large fraction of the text which is easy and informative reading.

In summary, the book should be on library shelves and is indeed a good contribution.

Howard E. Zimmerman, *University of Wisconsin*