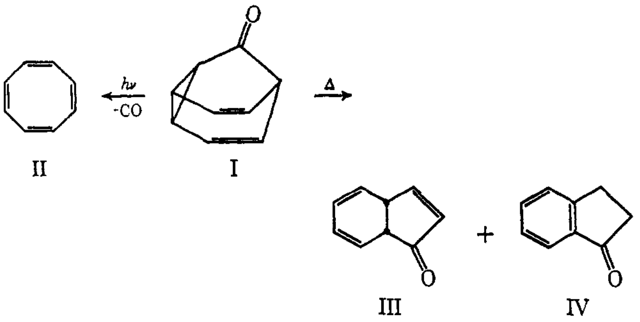
product III was found to be identical with *cis*-dihydroindenone by means of vpc analysis and nmr spectroscopy and by the formation of an adduct, mp 241°,[12] with maleic anhydride. The structure of IV was assigned as indanone on the basis of the formation of a semicarbazone, mp 236°, in addition to the spectral data. As is well known, the product IV was a secondary thermal product of III.

On electron impact, I exhibited the following peaks (m/e): 132 (M, 42%), 131 (M − 1, 71%), 104 (M − CO, 100%), and 78 (M − CO − C_2H_2, 69%). This spectrum seems to resemble more closely that which would be expected as a result of the photolysis rather than that of the pyrolysis of I.



II I III IV

The mechanistic pathways for both photolysis and pyrolysis of I are intriguing, especially when these reactions are compared with the photochemical and thermal reactions of bullvalene (V) or with the photolysis of the bicyclo[4.1.0]hept-4-en-2-one system (VI).[13] The compound I is considered to be a keto analog of V, that is, I differs from V by bearing a keto group in the place of an ethylene group. It has been reported that the irradiation of V gave bicyclo[4.2.2]-deca-2,4,7,9-tetraene,[14] whereas the pyrolysis of V at 350° afforded dihydronaphthalene.[15] On the assumption that the photolysis of I behaves in a way similar to that of V, bicyclo[4.2.1]nona-2,4,7-trien-9-one comes out as a possible intermediate for the formation of II. It should also be noted that, although I has a structure partially common to VI, the irradiation of a bicyclo[4.1.0]hept-4-en-2-one derivative afforded a penta-2,4-dienylketene derivative *without decarbonylation.*[13] The mechanism of the photodecarbonylation of I is ambiguous at present, but it should add a new example to the photocheletropic decarbonylation of cyclic unsaturated ketones if it occurs as a concerted process.[16] On the other hand, the mechanistic pathway for the pyrolysis of I as well as that of bullvalene would be complicated, because the reaction was carried out at a high temperature. However, one of the possible paths from I to III is *via* cyclohepta-1,3,5-trienylketene and its valence isomer.[17] In order to clarify these ambiguities, we are continuing the studies on the photochemical and thermal reactions of I and its related compounds.

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Received February 27, 1970

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(16) Although our trapping experiments do not completely rule out nonconcerted processes such as α cleavage of the carbonyl group followed by ring opening and decarbonylation, the decarbonylation of I could also be explained by a concerted mechanism on the basis of the molecular orbital consideration (private communication from Professor K. Fukui). Details will be reported in our full paper.

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Book Reviews

Topics in Phosphorus Chemistry. Volume 6. By K. Darrell Berlin, G. M. Blackburn, J. S. Cohen, D. E. C. Corbridge, and D. Michael Hellwege. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1969. vii + 309 pp. 15.5 × 23 cm. $27.50.

The sixth volume of "Topics in Phosphorus Chemistry" is as welcome as were the first five. The editors and contributors are to be congratulated for their continued diligence in providing timely reviews in a rapidly expanding subject.

The first chapter by Berlin and Hellwege covers carbon–phosphorus heterocycles. The review is extensive and thorough. An appendix containing Tables of Compounds will be of considerable value to investigators who wish to find out which compounds have been prepared. The review is organized on the basis of the syntheses of the heterocycles starting with three-membered ring compounds and proceeding to large-ring heterocycles. The second section discusses reactions, stereochemistry, and spectral properties.

The following chapter by Blackburn and Cohen covers chemical oxidative phosphorylation. This is a subject which has received considerable mechanistic study, and the authors do a good job in discussing the various pros and cons of the proposed mechanisms. Of particular interest is the section on quinol phosphates, both because of the mechanistic complexity and the possible relationship to oxidative phosphorylation in biological systems. The authors note, however, "that there may be *no actual phosphorylation* of quinones during the complex of biological processes grouped under the term oxidative phosphorylation."

The third and final chapter by Corbridge reviews the infrared spectra of phosphorus compounds. The review is broad in scope, and it covers all of the multitude of types of known phosphorus compounds. There is an extensive series of tables which cover the total fundamental frequencies of simple molecules such as phosphine and phosphorus trichloride. They also cover particular group frequencies. The review covers theory and vibrational studies of simple molecules and then turns its attention to spectra–structure correlation. There is no question that this chapter and the others will be of considerable value to organophosphorus chemists.

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Linear Free Energy Relationships. By P. R. Wells, Department of Chemistry, University of Queensland, St. Lucia, Brisbane, Australia. Academic Press Inc., Ltd., Berkeley Square House, Berkeley Square, London W1, England. 1968. vii + 116 pp. 15.5 × 23.5 cm. $5.95.

Proposals for linear free energy relationships have been with us virtually since the beginnings of physical organic chemistry. As this important area of study has progressed, more and more such relationships have been suggested, their scope and limitations more clearly defined, and their implications more critically evaluated.

Dr. Wells' short monograph provides a very reasonable reflection of the state of development of LFER's into the late 1960's. A brief introduction sets a critical tone which is carried through the body of the text, after which the book's major chapter gives a lucid treatment of the Hammett and Taft equations. Chapters which follow discuss the origins of substituent effects, correlations of changes in reaction medium (including the Grunwald–Winstein treatment, the Swain equation, and acidity functions), and correlations of reagent changes (including the Brønsted and Edwards equations). The final chapter, which deals with linear free energy relationships involving spectroscopic data, appears to be the weakest, mirroring in part the limited success of such treatments in this area.

Since relatively recent reviews of linear free energy relationships have appeared as portions of popular texts by Leffler and Grunwald and by Wiberg, it may be asked what Wells' volume contributes that the others do not. Most obviously, the present monograph postdates the other works by half a decade. This edge in timeliness is not vastly important, for although details in the subject have been filled in between 1963 and 1968, its complexion has not altered greatly. (Indeed, of the 121 references given at the end of Wells' chapters, only 13 fall in the interval 1964–68). Wells' exposition is substantially more detailed than that by Wilberg, who devotes only 60 pages to the subject, and less terse than his own earlier review (*Chem. Rev.*, **63**, 171 (1963)). It is, however, a much less ambitious effort than the careful, profound, and rigorous treatment which constitutes the major portion of Leffler and Grunwald's "Rates and Equilibria in Organic Reactions" (Wiley, 1963).

Nevertheless, for the reader who wishes to build up a working knowledge of this subject from minimal beginnings, Wells' book will probably be the more useful. It is economically written, its language is unusally direct, and the text is more nearly free of algebraic formulations which tend to decrease readability. Although he explores fewer implications than do Leffler and Grunwald, Wells is critical where he should be critical, and, as was particularly appealing to this reviewer, his *caveats* are often stated in very bald form. The following excerpts illustrate his no-nonsense approach:

> "Additional parameters inevitably improve the correlations without necessarily providing additional information." (p 7)
>
> "...but, as with most four-parameter treatments, the correlations may be deceptively good." (p 33)
>
> "...the status of hyperconjugation is still unclear." (p 55)
>
> "The conclusion seems clear that a direct electrostatic mechanism for substituent-to-reaction-site interactions is consistent with observed results, whereas σ-bond induction is not. The latter is then an unnecessary postulate." (p 50)

There are surprisingly few evident typographical errors (*e.g.*, pp 53, 88, and 100), fewer lapses of other types (δ_R in eq 2.19 is not defined in the text), and Wells may perhaps be forgiven for falling once into the type of trap he warns others about when he appears to overinterpret substituent constants in the naphthalene series (p 30). Such slip-ups will almost certainly be corrected in subsequent printings and do not seriously detract from the quality of the book.

In short, although Wells does not say all that can be said about linear free energy relations, he says a great deal, tersely, skeptically, and, in some cases, distinctively. The book is therefore strongly recommended as an intensive introduction to the subject. Moreover, in the present inflationary era it is seldom indeed that one may obtain a hard-cover scientific book dealing definitively with any topic for the rather modest list price of this monograph.

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ESCA Applied to Free Molecules. By K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, Institute of Physics, University of Uppsala, Uppsala, Sweden. North-Holland Publishing Co., 305–311 Keizergracht, Amsterdam, Holland. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 10017. 1969. vii + 200 pp. 19.5 × 27 cm. $15.00.

The technique called Electron Spectroscopy for Chemical Analysis, popularly referred to as ESCA, consists basically of measuring the kinetic energy distribution of the electrons liberated from a sample exposed to high-energy monochromatic ionizing radiation. Application of the Einstein photoelectric law then yields the binding energies of the electrons in the sample. This monograph presents a detailed account of the significant research performed by the authors in the development of photoionization techniques employing soft X-radiation.

After an almost too brief review of the necessary instrumentation, the book begins with a presentation of ESCA data for each of the noble gases. Included are numerous Auger spectra; these are the energy spectra for the secondary electrons produced when an excited state of the ionized species relaxes to a state of the doubly ionized species. Other processes are called "shake-off" and "shake-up," the former involving secondary collisions between photoelectrons and neutral atoms, and the latter involving simultaneous inner-shell and valence-shell excitations. Thus ESCA yields considerable information about atomic dynamics.

The interpretation of ESCA data for small gaseous molecules is the main theme of the book. The molecules include various diatomics, water, sulfur hexafluoride, the xenon fluorides, and numerous hydrocarbons and their derivatives. In each case binding energies are given for all electrons that can be ionized with soft X-radiation, usually from a magnesium target. These electrons are, for example, from carbon 1s, sulfur 2p, and xenon 3d levels, as well as from the valence shells. The most discussed aspect of the data is the large dependence of the binding energy of an inner-shell electron on the chemical environment of the atom. These "chemical shifts" are interpreted both in terms of the one-electron energies obtained from molecular orbital calculations and in terms of a simple electrostatic model. Indeed throughout the book extensive use is made of the energies and charge distributions obtained from molecular orbital calculations of the CNDO (complete neglect of differential overlap) variety.

Several appendices contain autoionization and Auger data for the noble gases, while others describe the formalism of self-consistent-field molecular orbital theory and the group-theoretical description of molecular electronic states. A selection of group character tables is also included. The book is beautifully printed and not unreasonably priced. Its timely publication should be welcomed not only by researchers who will find numerous ideas for further experimentation and for theoretical consideration, but also by all who are interested in the electronic structures of molecules.

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BOOKS RECEIVED. *May 1970*

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