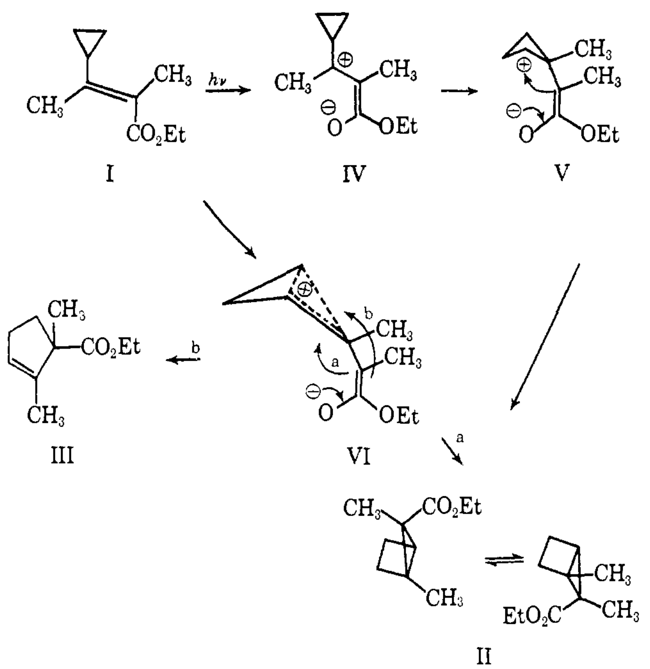
Chart I



labile σ bond. Two ring systems, the bicyclo[1.1.0]butane and the bicyclo[2.1.0]pentane, fit these specifications.[5] Although the former skeleton is readily derivable by a cyclopropane δ-hydrogen abstraction,[3a] the expected structure based on such a reaction mode is not reconcilable with the observed nmr spectrum. On the other hand, all the observed properties are consonant with a bicyclo[2.1.0]pentane structure. The very presence of this structural feature in the photoproduct was confirmed by hydrogenation experiments. In the presence of platinum both isomers reacted slowly with hydrogen, yielding ethyl 1,2-dimethyl-1-cyclopentanecarboxylate.[7] The structural assignment rests on spectral comparison of the hydrogenated product with ethyl 1,2-dimethyl-1-cyclopentanecarboxylate prepared by an independent synthetic route.[8]

Two structures, both mechanistically relatable to starting material, fit these data: these are ethyl 1,5-dimethylbicyclo[2.1.0]pentane-5-carboxylate (II) and ethyl 1,2-dimethylbicyclo[2.1.0]pentane-2-carboxylate. The absence of the characteristic cyclopropyl methylene absorption in the nmr and infrared spectra eliminates the second possibility, and II is presented, accordingly, as the structure of the new photoproduct. "Ring flip" isomerism accounts for the existence of two isomers of II.[9]

An attractive mechanism for the origin of II from I can be formalized by way of the cationic intermediates IV and V. This formulation is prompted by the striking resemblance of the photochemical ring expansion reaction to that commonly taking place among the reactions observed of simple cyclopropylcarbinyl cations in the ground state.[10] It is particularly interesting to note that such ring expansion reactions take place only in the cyclopropylcarbinyl cation and are not observed in the radical or anion in the ground state.[11] The latter two can undergo ring-opening reactions to give allylcarbinyl systems.[12] Alternatively, it is tempting to view the pathway as proceeding concertedly *via* the delocalized bicyclobutonium ion VI, as the common precursor to both II and III.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of these studies.

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[5] Isomerization about the central bond in bicyclo[1.1.0]butane derivatives is expected but has not been observed: A. Cairncross and E. P. Blanchard, *J. Am. Chem. Soc.*, **88**, 496 (1966). Isomerization about the internal bond in bicyclo[2.1.0]pentane has been reported in the 2-methyl derivative.[6]

[6] J. P. Chesick, *ibid.*, **84**, 3250 (1962).

[7] The hydrogenation is stereospecific. Each isomer yielded predominantly a different one of the two possible stereoisomers of 1,2-dimethyl-1-cyclopentanecarboxylate.

[8] R. Granger and H. Techer, *Compt. Rend.*, **250**, 1282 (1960).

[9] Exploratory rate studies indicate that thermal equilibrium, to a ratio of 28:72, is established within 30 min at 175°. The isomerization is, hence, considerably more facile than that reported for the simpler 2-methylbicyclo[2.1.0]pentane.[6]

[10] For a review of the cyclopropylcarbinyl rearrangement, see R. Breslow in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963. Under solvolytic conditions tertiary cyclopropylcarbinyl cations are known not to rearrange; under acid-catalyzed conditions rearrangements have been reported. See, for example, H. Hart and J. M. Sandri, *J. Am. Chem. Soc.*, **81**, 320 (1959); N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, **87**, 4533 (1965); H. M. Walborsky and L. Plonsker, *ibid.*, **83**, 2138 (1961); T. A. Favorskaya, *et al.*, *Zh. Obshch. Khim.*, **29**, 2894 (1959), and previous papers. It is evident that under these equilibration conditions the ultimate products which form are those derived from ring opening to give the more stable allylcarbinyl systems. The photochemical conditions of the irradiation of I resemble those of equilibrium control. If no other pathway for reaction other than return to I is open to IV, slow rearrangement to the less stable ions V and its corresponding allylcarbinyl ion is to be expected. While I is continuously reexcited to give IV, products II and III which correspond to the rearranged ions are stable under the photochemical conditions and should accumulate during the reaction course.

[11] M. E. H. Howden and J. D. Roberts, *Tetrahedron Suppl.*, **2**, 403 (1963); J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951); P. T. Lansbury, V. A. Pattison, W. A. Clement, and J. D. Sidler, *ibid.*, **86**, 2247 (1964).

[12] The rearrangements of I to III corresponds to a cyclopropylcarbinyl → allylcarbinyl interconversion. Employing ground-state analogy, this rearrangement can be formulated as well *via* an anionic or radical state.

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Book Reviews

Polyesters. By V. V. Korshak and S. V. Vinogradova. Translated from the Russian by B. J. Hazzard. Translation edited by J. Burdon. The Macmillan Co., 60 Fifth Ave., New York, N. Y. 1965. xv + 548 pp. 16.5 × 23.5 cm. $30.00.

This scholarly work will be particularly appealing to the industrial polymer researcher as a text book and reference book of polyester science. The book fulfills a real need for a compendium of polyester chemistry, mechanisms, analytical methods, structure, and properties of this important segment of polymeric materials.

It is well organized. The content of the individual chapters is complete which leads to some repetition, but this is not a fault. To aid the reader, extensive use has been made of page references and cross indexing when necessary, for the tables and the topical content of the text. Diagrams of laboratory equipment used for the preparation and analysis of polyesters are included and, in a few cases, flow diagrams of commercial practice. The interpretation and importance of the functional relationships of the many variables involved are amply illustrated by many graphs and figures (203) and tables of data (177) quoted verbatim from the literature.

As stated in the Preface to the English Edition, "We wrote the book 'Polyesters' on the basis of our many years of personal experience of scientific research work in the field of polyesters and a wide coverage of the relevant scientific literature. We set out to give the most detailed possible, and where necessary, critical account of the results both of our own work and that of other investigators." This has been accomplished. Polyesters of all types are discussed in a cohesive manner including linear, branched, crosslinked, and mixed systems. A thorough review is given the chemistry and mechanisms of the polycondensation reaction including the role of such destructive processes as esterolysis, alcoholysis, and acidolysis. These exchange and chain cessation reactions are related to the polydispersity obtained in the resulting polymer. The influence of these reactions is shown to result in molecular weight distributions different from those predicted from the theory for the "most probable distribution." Unfortunately it is not clear whether the polydispersity of polyesters made by continuous processes are included in this discussion. Preparative methods, analytical procedures, and physical and chemical properties are covered. The detail given to explanations of physical and structural properties and their measurement and the interpretation of the results are particularly noteworthy. Various investigators in the field of polyesters will find several items with which to take issue with the authors, but this is no serious detraction from the general over-all excellence of the work presented.

In spite of the extensive scope of the book, it does have several shortcomings. The major portion of the material presented is now at least 10 years old as it was written earlier for distribution in the USSR. Literature references are cited only to 1956 except for the revision of the last chapter (Polyarylates) which covers polycarbonates, etc., to 1960. In the 10 years not covered by the book, many new industrial methods of manufacture, new polyesters of commercial importance, and new structural interpretations and concepts have appeared in the patent and scientific literature. The most glaring shortcoming is the lack of reference, with a few exceptions, to the information available in the patent literature of the time. Usually, important technical information on polyesters is covered first in patents and only appears later in the scientific literature. As a result, the changes brought about by various orientation and heat treatments of films and fibers with their concomitant structure and property modifications are not discussed.

In a book of this magnitude (more than 1000 references are cited) errors usually occur. This reviewer has noted several instances where data were attributed to the wrong authors, names misspelled, and tabular data labeled incorrectly. Nevertheless, this book serves the very useful purpose of bringing together, in very readable form, a voluminous amount of factual information on a subject of considerable commercial importance gathered from the experience of many investigators.

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Radiochemical Survey of the Elements. Principal Characteristics and Applications of the Elements and Their Isotopes. By M. Haissinsky, Scientific Director, Laboratoire Curie, Centre National de la Recherche Scientifique, Paris, and J.-P. Adloff, Professor of Nuclear Chemistry, Centre de Recherches Nucleaires, Strasbourg-Cronenbourg (Bas-Rhin). American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1965. viii + 177 pp. 15.5 × 23 cm. $12.00.

The contents and format of this survey are well described by the original French title as a radiochemical "dictionary" of the elements. A one- or two-page discussion is devoted to the nuclear, chemical, and physical properties of each of the elements. Properties covered include: discovery of the element and derivation of its name; naturally occurring isotopes and their abundances; half-lives and radiations of some of the radioactive isotopes (particularly those convenient as tracers or in activation analysis); the electronic configurations, oxidation states, chemical reactions, and compounds of the element and their principal uses; some geochemical data including important minerals and crystal and cosmic abundances; and brief mention of any unusual nuclear or chemical properties.

I wonder for whom this book was intended (especially at its price!). Scientific workers would be frustrated by the lack of references or an index. Much of the data could have been better presented in tabular form. Standard nuclide charts, for example, contain essentially all of the nuclear data given in the book (and they are free). Instead of grouping the elements in some scientific way, the authors have arranged them alphabetically. The style of the book is not well suited for the elementary chemistry student or curious layman. It does not lend itself to cover-to-cover reading nor does it convey the excitement and historical interest that may be gained from books on the discovery of the elements.

The coverage is up to date, including such recent topics as ^{8}He, rare-gas compounds, and element 104. Some rather interesting phenomena, *e.g.*, delayed-neutron and -proton emission, were ignored. There are few serious errors although the presentation of some topics is confusing. The translation is generally good with occasional lapses such as "α-filiation" instead of "α-decay" and "retrodiffusion" for "back-scattering."

On the general subject of translations, including this one, I am left very puzzled. Why are publishers so anxious to do them? I can think of very few (and here I would include Professor Haissinsky's major radiochemical classic) that were worth the effort. Although not true for the case in point, the books are generally out of date by American standards when originally written and are certainly so by the time they are translated. Can't the publishers find more discriminating scientific consultants?

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Interpretation of Organic Spectra. Edited by D. W. Mathieson, The School of Pharmacy, London University, England. Academic Press Inc., Ltd., Berkeley Square House, Berkeley Square, London W.1, England. 1965. ix + 179 pp. 16 × 23.5 cm. $7.00.

With a few reservations, this is a book which can be recommended to advanced undergraduate and postgraduate students who need to develop and exercise their knowledge of spectroscopy in relation to organic chemistry. "Interpretation of Organic Spectra" is composed of three sections devoted successively to problems in the application of nmr, infrared, and mass spectral methods in structural analysis.

The longest section, by J. A. Elvidge, is excellent. With a limited knowledge of nuclear magnetic resonance spectroscopy the reader is led through a succession of examples for which the analysis of the spectrum is clearly and concisely written. The examples chosen increase in complexity and are used to develop broadly many aspects of nmr spectroscopy. Correlation tables of proton magnetic resonance frequencies and coupling constants with structure follow, and the section is rounded off with six unknowns for consideration by the reader. For one of these unknowns, number 5, the solution given is incorrect and should have an additional methyl group α to carbonyl. The footnote referred to on page 20 is on page 12 and not page 11. Perhaps the only disconcerting feature to the reader will be the variable use of sweep offset which could have been noted more distinctively through the use of heavy print. If the use of offset is not noticed early on, then confusion reigns, since there is no indication on the reproduced spectra. However, these are relatively minor points in a first-class exposition. Dr. Elvidge is to be congratulated on his section.

The second section was well written by four contributors (J. K. Brown, K. J. Morgan, C. J. Timmons, and D. Whiffen). They have succeeded in presenting useful applications of infrared spectroscopy while avoiding the common fault of several texts in that they stress more clearly than usual the very definite limitations of the method. The latter point is apparent from the nine examples chosen and from the six unknowns. The tentative nature of many assignments is commendably indicated, though one would still like to see a positive statement that the dependence of the organic chemist upon infrared spectroscopic structural analysis has been reduced by the advent of nmr. This is particularly true for any functional group containing a proton. Students need to be clearly told that a complete structure is seldom arrived at from infrared spectroscopy alone.