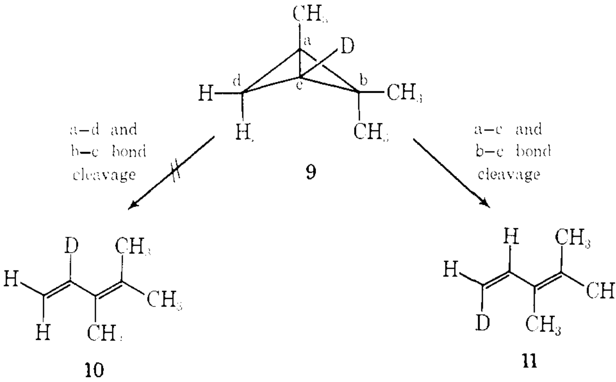
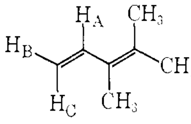
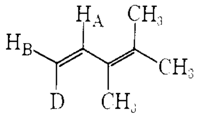
a–d and b–c bonds of **1**, in a manner similar to the thermal reaction, or *via* cleavage of the a–c and b–c bonds of **1**. In order to distinguish between these two possibilities we subjected **9**[6,8] to our catalytic conditions. If the catalytic reaction involved cleavage of the a–d and b–c bonds of **9** in a manner similar to the thermal reaction, the deuterium at position c of **9** would end up at C-2 as represented by the formation of **10**. However, if bonds a–c and b–c were opened, 1-deuterio-3,4-dimethyl-1,3-pentadiene would be expected. In fact, the transition metal catalyzed rearrangement was found to be amazingly stereospecific in that the only diene formed was **11** which had the deuterium at C-1 in a cis configuration.



The structure of **11** was readily established by nmr spectroscopy through comparison of the nmr spectra of **2** and **11**. The nmr spectrum of **2** consisted of two overlapping singlets at τ 8.26 and 8.22 (9 H) for the three methyl groups, a one-proton doublet (H_B) at τ 5.10 (J_{AB} = 11 cps), a one-proton doublet (H_C) at τ 4.95 (J_{AC} = 17 cps),[9] and a one-proton doublet of doublets (H_A) at τ 3.20. The nmr of **11** showed no change in the pattern for the methyl groups. However, H_A now appeared as a well-defined doublet of triplets at τ 3.20 (J_{AB} = 11 cps, J_{H-D} = 2.8 cps[10]), H_B appeared as a one-proton doublet at τ 5.10 (J_{AB} = 11 cps), and H_C, which had been replaced to the extent of *ca.* 80% with deuterium, appeared as a doublet at τ 4.95 with only 18% of its former intensity. Thus, the structure of our diene was firmly established as being that shown by **11**.

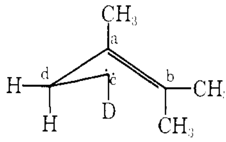


2



11

The presence of deuterium on only the terminal carbon indicated that the transition metal catalyzed opening of **1** resulted in cleavage of the a–c and b–c bonds in contrast to the thermal cleavage which cleaves the a–d and c–b bonds. In addition the presence of the deuterium cis to the rest of the carbon chain indicated an amazing degree of stereospecificity in the reaction. Formally, cleavage of the a–c and b–c bonds of **9** would result in the formation of **12** (neglecting the presence of the transition metal catalysis). Stereospecific transfer of a hydrogen from C_d to C_c would then give **11**. Overall, this reaction can be formally envisaged as a transition metal catalyzed[11] retrocarbene addition.



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We are continuing to investigate the mechanism and scope of the metal-catalyzed isomerizations of strained ring systems.

Acknowledgment. We are indebted to the National Science Foundation and to the Alfred P. Sloan Foundation for funds which supported this investigation.

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(8) Nmr analysis indicated that **9** was *ca.* 80% monodeuterated.

(9) Normal ranges for J_{AB}, J_{AC}, and J_{BC} are 6–14 cps, 11–18 cps, and 0–3.5 cps, respectively (L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p 85).

(10) H. J. Bernstein and N. Sheppard (*J. Chem. Phys.*, 37, 3012 (1962)) have shown that $J_{HH} \cong 6.55 J_{HD}$. On the basis of the J_{H-H} of 17 cps, a value of 2.6 cps would have been predicted for J_{HD} in our system.

(11) This reaction is not limited to the rhodium dicarbonyl chloride dimer catalyst. Dichlorotricarbonylruthenium dimer decomposed **1** to give 46% **2** and 22% **3**.

(12) Alfred P. Sloan Research Fellow, 1967–1969.

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Received October 21, 1970

Book Reviews

Chemical Energetics and the Curriculum. Edited by Professor D. J. Millen, Ph.D., D.Sc., F.R.I.C. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1970. 192 pp. 14 × 22 cm. $6.50.

Collect eleven lectures by as many distinguished English chemists and chemical educators who participated in a course at University College London on Modern Trends in Chemistry and the Sixth Form dedicated to the proposition that in chemical education energetic considerations constitute a desirable, integrating theme—because "the trend today in science education is towards programmes which try to develop in the student the desire to investigate, to ask why and to seek understanding in place of the former emphasis on rote memory of a large number of facts...[and this approach] demands that students be provided, as early as possible, with guiding general principles"—add an editor and a willing publisher, and one sends forth to an unspecified audience (presumably chiefly teachers of high-level general chemistry courses) eleven workmanlike yet readable, introductory and nonmathematical, snapshot-like, nonhistorical, expository, ten- to twenty-page essays on energetics, and the atom and education (Nyholm), bond energies (Ross), endothermic reactions (Heslop), equilibrium (Ashmore), ionic crystals and solutions (Tobe), kinetics (Sykes), radiation (Walmsley), statistics (Millen), volatility (Maccoll), structure (Raitt), and, again, equilibria (E. H. Coulson), together with five separate elementary discussions of the NO_2–N_2O_4 equilibrium; four sketchy plausibility arguments for the relation $\Delta G = \Delta H - T\Delta S$ (everyone wants to get to this equation); several endorsements of the view that ΔH represents the "total energy push," $T\Delta S$ the "probability energy push" behind chemical reactions; three introductory discussions of the Born–Haber cycle, with several interesting applications to nonexistent compounds; two identical treatments of C–C and C–H bond energies; numerous citations, yet no intellectually satisfying discussion, of the equation $dS = dq_{rev}/T$ (What I tell you three—or five—times is true.); frequent implications that thermodynamics is a source (rather than a summary) of data, in such remarks as "equilibrium constants are dependent upon the thermodynamic quantities" (though often the inverse statement is true); a brief, one-page index, with no citations to chemical compounds (not even nitrogen dioxide); and some regrettable typographical errors (*e.g.*, "[metal] oxides are stable in a normal atmosphere as long as $K_p = PO_2$ [sic] > 0.2 atm.") culminating in this unexpected, here's-the-answer-what's-the-question puzzle:

$$= \frac{\mathrm{dSC^{p}dT}}{\mathrm{T}}$$

While, to avoid future shock in the chemical profession, diversity in chemical education should probably be encouraged, I am troubled by a style that, like the older descriptive chemistry, force-feeds students material that seems important but that, at the moment, cannot be (or is not) strongly intertwined with other facts and ideas with which the students are already thoroughly familiar.

If students cannot reason critically about the expression $\Delta G < 0$, if they are merely told that "It may be shown that...," "We have that...," and "a research chemist...accepts as founded on sound principles" the equation $\Delta G° = -RT \ln K_p$, what can they do? They can memorize the equation; they can learn to substitute numbers into it by rote; or, perhaps, they may decide that some other field might be more understandable, more interesting, and intellectually more challenging.

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The Systematic Identification of Flavonoids. By T. J. Mabry, K. R. Markham, and M. B. Thomas. Springer-Verlag, New York, Inc., 175 Fifth Ave., New York, N. Y. 1970. xi + 354 pp. 20 × 27.5 cm. $27.00.

The determination of the structure of a new flavonoid compound, or the identification of one already known, can frequently be accomplished solely with the aid of spectral measurements, often with no more of the compound than can be eluted from a band on a paper chromatogram. The use of reagents to detect and locate nuclear hydroxyl groups and to determine their capacity for chelate formation permits extensive structure analysis with a few milliliters of solution, all of the manipulations being carried out in the sample cuvette. The authors of this book have described the methods used in spectroscopic analysis of this kind and, happily, have provided explicit descriptions of many of the experimental procedures used. The book gives clear, step-by-step directions, and documents the discussions with the actual ultraviolet spectra of 175 flavonoid compounds of nearly all of the known classes. Anthocyanins and their glycosides are omitted.

The book consists of three major divisions: (1) the isolation, purification, and partial characterization of flavonoid compounds, which deals principally with the use of chromatographic methods; (2) the analysis of flavonoid structure by the use of ultraviolet spectroscopy; and (3) the use of nuclear magnetic resonance spectroscopy in structure analysis and identification. The use of infrared spectroscopy, which is of limited value in flavonoid chemistry, is properly omitted.

The use of nmr in flavonoid structure analysis is described in detail, and the complete nmr spectra of 128 flavones, flavanones, isoflavones, chalcones, aurones, and many of their glycosides are reproduced. The use of trimethylsilyl ethers of chloroform-insoluble compounds has expanded the range of usefulness of nmr spectroscopy in flavonoid chemistry, and special attention is given to the details of the procedures used. A proton-by-proton analysis of the signal characteristics of flavonoid compounds, including the sugar residues of their glycosides, is a valuable feature of this section.

It is to be regretted that in a treatment otherwise so complete little or no attention has been paid to the more conventional properties of these compounds. Many flavonoid compounds crystallize well, have useful melting points in a convenient range, and are easily converted into crystalline acetates and methyl ethers. Since the isolation of compounds in sufficient quantity and purity for nmr study would permit (or require) the determination of a melting point, it seems pointless to omit the inclusion of these data. Not only are most O-acetylated aglycons derivatives with excellent physical characteristics, but they are usually suitable for nmr study. The authors allude briefly to the effect of acetylation of hydroxyl groups upon the chemical shift of ring protons, but few examples of this often illuminating observation are given.

The book is relatively free from errors. Some inconsistencies in nomenclature appear; for example, "7-rhamnoglucoside" and "7-O-rhamnoglucoside" are both used. The name 7-hydroxypentamethoxyquercetagetin (p 30) is improper for 7-hydroxy-3,3′,4′,5,6-pentamethoxyflavone, or quercetagetin 3,3′,4′,5,6-pentamethyl ether. "Quercetin-3′,4′,5,6,7-pentamethyl ether" is found in the Index.

Despite these few shortcomings, this book will doubtless prove to be a valuable handbook in the practical problems of flavonoid structure proof. It is unfortunate that its high price will diminish its availability to individual investigators, for it is a book that deserves to be read rather than referred to.

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Theoretical Biochemistry. Physico-Chemical Principles of Vital Processes. By Hans Netter, Professor of Physiological Chemistry at the University of Kiel. Wiley-Interscience Division, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1969. xx + 928 pp. 17 × 26.5 cm. $39.50.

The German edition of this book was published in 1958, this English translation in 1969. In a foreword one of the editors of the translation writes that so many parts were revised before and during translating that this English version is in effect the Second Edition. In my opinion the book should not be purchased on the supposition that it is therefore approximately up-to-date.

An obvious aspect of the revisionary process has been the addition of more recent references. Nevertheless, I note roughly a ten-to-one dominance by references from the fifties over those from the sixties, nearly all of the latter being for the years 1960 to 1963. At the textual level the revision has still left the book badly outdated in my estimation. Whether the reader looks under apolar bonding, studies of globular proteins by X-ray diffraction, membrane transport, or the function of flavoproteins or hemoglobin, I think he will find causes for this dissatisfaction.

Had the author not had the courage to mingle the less changeable knowledge of theoretical chemistry with the more rapidly changing biological information, this otherwise impressive work would no doubt have tolerated better the delays to be expected from translation.

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