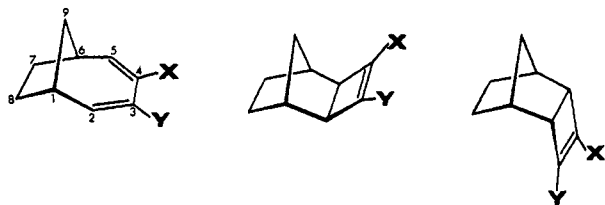


cided by those factors which are responsible for determining the preferred conformations of molecules in their ground states. Thus, the ratio of **2** to **3** should constitute a reliable index of the relative steric hindrances encountered on the exo and endo sides of norbornene. In order to confirm the generality of the reaction the photochemical experiment was carried out not only with the parent diene **1**, but also with its monochloro and dichloro derivatives **4** and **7**, respectively.⁸



1 X=Y=H	2 X=Y=H	3 X=Y=H
4 X=Cl, Y=H	5 X=Cl, Y=H	6 X=Cl, Y=H
7 X=Y=Cl	8 X=Y=Cl	9 X=Y=Cl

Solutions of **1**, **4**, and **7** (1.67, 1.3, and 0.53 mmol, respectively) in *n*-hexane (10 ml) under nitrogen were stirred and irradiated with an unfiltered 200-W Hanovia lamp at 25°. Periodically, samples were extracted and monitored by vapor-phase chromatography (5% SE-30 on Chromosorb G, column temperature of 100°, for the products from compound **1**, and 25% Apiezon L on Chromosorb W, column temperature of 120°, for the products from compounds **5** and **8**). Analysis revealed two major products which were the expected exo and endo cyclobutene derivatives.^{9a} The parent compound **1** reacted smoothly, whereas the chloro derivatives **4** and **7** were more sluggish. After irradiation for 6 hr conversions to ring-closed products were 92, 42, and 17%, respectively.^{9b} Compounds **1**, **4**, and **7** gave, respectively and reproducibly, the exo and endo

(8) Compounds **1**, **4**, and **7** were prepared starting from the reaction of dichlorocarbene with bicyclo[3.2.1]octene-2 and its chloro derivatives. For the general method, see C. W. Jefford, J. Gunsher, D. T. Hill, P. Brun, J. Le Gras, and B. Waegell, *Org. Syn.*, **51**, 60 (1971), and C. W. Jefford, S. Mahajan, R. T. Medary, W. Wojnarowski, B. Waegell, and K. C. Ramey, *Chem. Commun.*, 310 (1967). Details of these syntheses will be published elsewhere (work of F. Delay).

(9) (a) For related cyclizations see H. M. Frey, J. Metcalfe, and J. M. Brown, *J. Chem. Soc. B*, 1586 (1970). (b) Minor products (~20%) resulted mainly from polymerization of starting material and to a lesser extent from further reaction of the primary photoproducts. Percentage conversions were corrected to account for loss of starting material by polymerization.

cyclobutenes, **2** plus **3**, **5** plus **6**, and **8** plus **9** in percentage ratios of 30:70, 53:47, and 60:40 which were essentially invariant with time. The pair of isomers **8** and **9** had very similar retention times, but the other pairs (**2** and **3**, **5** and **6**) were easily separated and identified by nmr analysis.¹⁰ The exo isomer in all cases had the shorter retention times. The essential feature which differentiated the exo from the endo isomers was the coupling of 4.5–5.0 Hz between the bridgehead protons (C-1 and C-2) which is characteristic of an exo disposition of the C-2 proton on the norbornane skeleton.^{11,12}

These findings permit several observations and conclusions pertinent to the norbornene problem. The origin of these exo–endo preferences cannot reside in torsional interactions; indeed the direction of closure is the opposite of that predicted.^{4a} A reasonable explanation is that in the transition state for cyclization a delicate balance of attractive and repulsive forces exists between the nascent double bond moiety at C-3–C-4 and the methylene or ethylene bridges. For the parent hydrocarbon **1** the endo side appears to be the least encumbered; however, the fact that peripheral substitution by chlorine brings about a displacement of the double bond moiety to the exo side could be ascribed to steering by attractive forces between the polarizable chlorine atom and the methylene bridge.^{5a}

Lastly, it can be inferred for the hypothetical photochemical [2 + 2] cycloaddition of acetylene to norbornene that, in the absence of stereoelectronic control, the endo approach would be more navigable than the exo. Chloroacetylene would experience more or less equal steric difficulties on the two sides of the molecule, whereas dichloroacetylene would be directed to the exo side.

Acknowledgments. We thank Dr. U. Burger for the nmr spectra and the decoupling experiments. We are grateful to Firmenich & Cie and the P. Chuit Foundation for the provision of funds with which the Varian Model XL-100 spectrometer was purchased.

(10) Spectral analysis was carried out on a Varian Associates Model XL-100 spectrometer. The coupling constants were typically those found in cyclobutyl and norbornyl derivatives (ref 11 and 12).

(11) I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967).

(12) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

C. W. Jefford,* F. Delay

Department of Organic Chemistry, University of Geneva
1211 Geneva 4, Switzerland

Received March 17, 1972

Book Reviews*

Microbiology. 1971. Edited by P. HEPPLÉ. Applied Science Publishers Ltd., Barking, Essex. 1971. v + 114 pp. £ 3.60.

This book contains the proceedings of a conference held in London and organized by the Institute of Petroleum. There are eight contributed chapters plus an opening address, panel discussion, and a summary. There is a considerable amount of chemistry included, as indicated by such representative titles as "Hydrocarbons as Carbon Substrates," "Microbial Degradation of Crude Oil," and "Enzymes as Industrial Catalysts."

* Unsigned book reviews are by the Book Review Editor.

Reagents for Organic Synthesis. Volume 3. By MARY FIESER and LOUIS F. FIESER (Harvard University). Wiley-Interscience, New York, N. Y. 1972. 401 pp. \$16.95.

The latest volume to this useful series is divided between new information on previously listed reagents (about two-thirds) and reagents treated for the first time (about one-third). The term "reagent" is interpreted surprisingly broadly, for the book has entries for substances used only as solvents (e.g., hexamethylphosphoramide). Many of the entries are for special applications of

common reagents, such as sulfur, sodium bicarbonate, or silver nitrate. The newly listed reagents have in many instances been reported only once, perhaps only briefly, and their usefulness and importance have yet to be explored. Nevertheless, it is valuable to have them listed in this convenient form, which will undoubtedly hasten their general examination.

As in the previous volumes, this one is well indexed, not only for authors and subjects, but also for type of reaction. A particularly useful feature is the list of suppliers from whom many of the reagents can be obtained. The references to new publications extend through 1970.

Organic Reaction Mechanisms. 1970. Edited by B. CAPON (University of Glasgow) and C. W. REES (University of Liverpool). Wiley-Interscience, New York, N. Y. 1972. viii + 689 pp. \$34.50.

The increasing number of organic chemists who have come to depend on this valuable aid to current awareness will be pleased to find that it is still being brought out with special promptness. The approximately 4400 references cited are to publications that appeared from December 1969 through November 1970. The material is grouped into fourteen chapters by twelve British chemists and is arranged according to reactive intermediate or type of mechanism (sample headings: Carbonium Ions; Radical Reactions). The most important contributions are discussed in the usual critical yet remarkably concise manner, and the others are listed. Structural formulas are used freely. A 54-page author index is a valuable help in finding what one is interested in, although the subject index is also substantial.

Organic Electronic Spectral Data. Volume 7. Edited by J. P. PHILLIPS (University of Louisville), J. C. DACONS (U. S. Naval Ordnance Laboratory), and R. G. RICE (W. R. Grace and Co.). Wiley-Interscience, New York, N. Y. 1971. xv + 1318 pp.

The newest volume of this important reference work covers the years 1964 and 1965 and presents in tabular form all of the ultraviolet-visible spectra of organic compounds published in those years. As always, the entries are arranged in formula-index fashion, with names, usually in *Chemical Abstracts* style, following the formula. The data reported are confined to absorption maxima and intensity, with the solvent used and the literature reference code. Volume VIII is slated to be in preparation, and further volumes are contemplated.

Selective Organic Transformations. Volume 2. Edited by B. S. THYAGARAJAN (University of Idaho). Wiley-Interscience, New York, N. Y. 1972. ix + 352 pp. \$19.95.

This second book of what is evidently envisaged as an on-going series consists of six chapters by eight contributors. Two of them deal with the direction of opening of three-membered rings (epoxides, cyclopropanes); two deal with lead tetraacetate oxidations (alcohols, olefins), and two deal with stereochemistry (vinyl radicals, Hofmann eliminations). The emphasis is on understanding the mechanisms and the basis for the selectivity; there are thus lots of structures and diagrams, but few tables (although there are extensive bibliographies). The topics chosen are timely, and their treatment is competent, but the index (4 pages) is perhaps rather short for a work of such reference value.

Structural Analysis of Organic Compounds by Spectroscopic Methods. By WILHELM SIMON and THOMAS CLERC (E. T. H., Zurich). American Elsevier, New York, N. Y., and MacDonald, London. 1971. iv + 195 pp. £ 3.50.

This book is essentially a collection of tables embodying information of practical use in interpreting spectra. The first 36 pages present a combined table, arranged according to structural type, giving for each the essential features of ir, uv, nmr, and mass spectra. This is followed by separate tables giving greater detail for each of the four types of spectra. The section on nmr, for example, gives the usual tables of chemical shifts, coupling constants, and correlation factors, and has in addition a useful tabulation of chemical shifts in various aromatic compounds and in heterocycles. There are no references, but there are useful reading lists of textbooks and monographs at the end of each section. The last half of the book is

devoted to problems: fifty compounds, for which ir, uv, nmr, and mass spectra are given (the answers are listed on the last page).

This compact volume is a most useful reference book for ordinary spectroscopic interpretation and is very convenient to use. It could be quite a suitable textbook for courses in which the teacher is prepared to provide all the pedagogy. For self-teaching, the book would be insufficient unless the student already had a basic acquaintance with the origin and instrumentation of the spectroscopy.

Quantum Theory and Beyond. Edited by TED BASTIN (Cambridge Language Research Unit). Cambridge University Press, London. 1971. viii + 345 pp. \$16.00.

This book is a collection of 24 essays and discussions that arose from an informal colloquium that was held in July 1968 at Cambridge University, England. The colloquium was organized so that difficulties in the current formulations and interpretations of quantum theory could be discussed and critically examined, as well as possible alternative approaches.

The account of the colloquium is organized into six sections. First, an Introduction is presented, in which some of the main difficulties of current formulations of quantum theory are given. The main problem, according to T. Bastin, is that quantum theory is intended to provide comprehension to a class of phenomena which were necessarily incomprehensible in terms of classical concepts, and yet it retains only classical concepts to describe these quantum events. The other difficulty that is singled out of the "main-stream" dogma of quantum theory arises from the "complementarity" principle of Bohr, and its implications to the interpretation of experiments. The remaining sections (II. Neils Bohr and Complementarity; III. The Measurement Problem; IV. New Directions Within Quantum Theory; V. A Fresh Start?; VI. Philosophical Papers) discuss in detail the background of Bohr's thinking, how to incorporate the measurement process properly within the deductive structure of quantum theory, what is the range of applicability of the existing mathematical structure of quantum theory, what are some of the alternative formulations (regardless of how radical) that are available, and general comments of a philosophical nature regarding the quantum theory problem.

The overall impression given by the various articles is that there are serious questions remaining in the current formulations of quantum theory. However, as admitted by T. Bastin in an editorial article, the "Quantum Theory and Beyond" colloquium did not give rise to a new view of quantum theory that is satisfactory. As implied by the nature of the questions that were discussed, this book is not one that will provide easy reading for most chemists, although some of the articles (*e.g.*, the article concerning the role of hidden variables by D. Bohm) give particularly clear and readable expositions. On the whole, it appears as a book that is written by experts, and the ideas presented there will, in the main, be of interest primarily to other experts in this area.

Ralph E. Christoffersen, *University of Kansas*

Chemisorption and Reactions on Metallic Films (2 Volumes). Edited by J. R. ANDERSON (University of Melbourne). Academic Press, New York, N. Y. 1971. ix + 878 pp. \$21.00.

This two-volume work is a collection of ten independent contributions on the subject of adsorption and catalysis on metal film surfaces. Five of the ten chapters comprise an excellent up-to-date review of adsorption, including treatments of kinetics, surface structure, bonding, catalysis, and methods for evaluating surfaces. About one-third of a sixth chapter on alloy films is concerned with catalytic activity, and a seventh chapter describes the various influences of adsorbed species on electrical and mechanical properties of films. The remaining chapters describe phenomena of film deposition, growth and structure, and methods for evaluating structure and techniques of film deposition.

This work suffers the drawbacks of most edited volumes of this type in that the redundancy level is high and treatment of the subjects is uneven regarding scholarship, both within chapters and comparing chapters with each other. Aside from this criticism, these volumes present current phenomena, models and methods in the area of adsorption and catalysis, and should serve as a useful reference work as well as text to graduate students and workers in the field.

Robert B. Marcus, *Bell Laboratories*