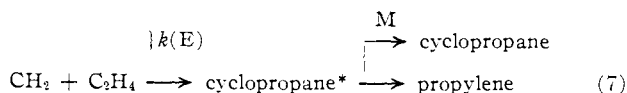
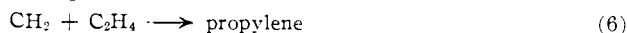


The experiments involve the determination of the rates of allylic and vinylic carbon-hydrogen and carbon-deuterium bond insertion (eq. 2 and 4) relative to carbon-carbon double bond addition (eq. 3 and 5) for *cis*-butene-2 and *cis*-butene-2-*d*₈, respectively. Ketene-butene mixtures (1:20) were photolyzed for up to 1 hr. in Pyrex reaction vessels with the filtered (~3200 Å.) radiation of a G.E. AH-6 mercury lamp. Product analyses were done by standard gas chromatographic techniques. All gas handling was done in a conventional vacuum system. The relative rates were obtained from the limiting high pressure ratios of each of the various pentenes to the corresponding dimethylcyclopropane, as determined from product composition curves measured over the range of total pressures from 0.3-1500 mm. at 25°, and in the high pressure region at -30°. The relative rates of addition to the carbon-carbon double bond of *cis*-butene-2 and of *cis*-butene-2-*d*₈ were in turn determined by an internal comparison of each butene separately with ethylene, in known mixtures (1:1 butene-ethylene) at ~15 cm. total pressure.



The results are shown in Table I. As seen from Table I, the isotope effects for methylene radical insertion into allylic and vinylic carbon-hydrogen bonds, compared to carbon-deuterium bonds, are factors of

1.96 and 1.55, respectively, *i.e.*, larger than the classical reduced mass factor for carbon-hydrogen and carbon-deuterium isotopes, ~1.37. The observed increases in the isotopic ratio for *k*_i and *k*_a in going from 25° to -30°, if not simply the result of experimental error, are small. The secondary isotope effect for double bond addition is small (6-9%).

TABLE I
RATE CONSTANT RATIOS FOR THE REACTION OF METHYLENE WITH *cis*-BUTENE-2 AND *cis*-BUTENE-2-*d*₈

	25°	-30°	Average
<i>k</i> _i (H)/ <i>k</i> _d (H) ^a	1.35	1.5 ^b	
<i>k</i> _i (D)/ <i>k</i> _d (D) ^a	0.80	0.9 ^b	
[<i>k</i> _i (H)/ <i>k</i> _d (H)]/[<i>k</i> _i (D)/ <i>k</i> _d (D)]	1.68	1.69	
<i>k</i> _a (H)/ <i>k</i> (E) ^c	1.01	0.92	
<i>k</i> _a (D)/ <i>k</i> (E) ^c	0.94	0.84	
<i>k</i> _a (H)/ <i>k</i> _a (D)	1.07	1.09	1.08
<i>k</i> _i (H)/ <i>k</i> _i (D)	1.80	1.84	1.82
<i>k</i> _v (H)/ <i>k</i> _a (H) (per bond)	-	-	1.21
<i>k</i> _v (D)/ <i>k</i> _a (D) (per bond)	-	-	1.52
<i>k</i> _a (H)/ <i>k</i> _a (D)	-	-	1.96
<i>k</i> _v (H)/ <i>k</i> _v (D)	-	-	1.55

^a *k*_i = 6*k*_a + 2*k*_v. ^b Ratios containing some extrapolation errors due in large part to presence of minor fraction of triplet methylenes, such that the ratio of the ratios in line 3 is more accurate. ^c Each comparison with ethylene was made in duplicate. The ratio of the ratios given in line 6 is more accurate than these individual values for the same reason as in footnote *b*.

That the last effect is close to unity seems quite reasonable in view of the very low or zero activation energy for the addition reaction.^{6,7} A very small secondary isotope effect has also been reported recently for H addition to the double bond of propylene-*d*₆.⁷ For the somewhat slower insertion reactions, the two primary isotope effects are appropriately higher and both are consistent with the idea that C-H bond extension is important in the activated complex; unfortunately, the energetics of this methylene radical system are still somewhat uncertain.

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RECEIVED FEBRUARY 9, 1963

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(6) W. B. Demore, H. O. Pritchard and N. Davidson, *ibid.*, **81**, 5874 (1959).
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(8) General Electric predoctoral fellow.

BOOK REVIEWS

Regular Solutions. By JOEL H. HILDEBRAND, Professor of Chemistry, Emeritus, University of California, Berkeley, and ROBERT L. SCOTT, Professor of Chemistry, University of California, Los Angeles. Prentice-Hall, Inc., Englewood Cliffs, New Jersey. 1962. x + 180 pp. 15.5 × 23.5 cm. Price, \$7.00.

Hildebrand's first paper on solutions appeared in 1909, "The Color of Iodine Solutions," including of course the violet of the royal family of regular solutions, although they were not christened as regular until twenty years later. In 1961, he published a review article, "Solubility," in *This Journal*, and the first edition (206 pages) of the book with this title appeared in 1924. The second edition (203 pages), which came out in 1936, omitted an unimportant chapter on electrolytes. The third edition (488 pages), "Solubility of Nonelectrolytes," in 1950 has Scott as co-author. Now in 1962 they publish, "Regular Solutions" (180 pages). Although it is about on schedule for a fourth edition, it is more a sublimation. Scott's contribution to the third edition is obvious and important, but it is hard to detect any

further contributions to the current book. It seems to be pure Hildebrand.

The chapters and appendices are titled: Preface, The Regular Solution Concept, Thermodynamic Relations, Entropy of Mixing, Regular Solutions of Gases in Liquids, The Liquid State, Intermolecular Forces, Heat of Mixing, Volume Changes on Mixing, Regular Solutions of Solids, Liquid-Liquid Mixtures, Summary and Critique; List of Symbols, The Acentric Factor and Critical Data, Solubility of Gases and Entropy of Solution, Solubility of Iodine and Its Dependence on Temperature at 25°C., Solubility Parameters.

Anyone interested in solutions, and every chemist must be, should read this book. One should go from the preface and first chapter immediately to the tenth—"Summary and Critique." The intervening chapters may be read in any order.

We cannot give a better picture of this book than the first two "conclusions" of the summary.

"1. A pure liquid, if composed of non-polar, symmetrical, compact molecules, has a structure of maximum randomness, as

represented by the radial distribution function. There is no quasi-crystalline or lattice structure; there are no "holes" of definite size or shape, no discrete molecular frequencies or velocities, and no distinguishable "gas-like" and "solid-like" molecules."

"2. The molecules of homogeneous solutions of two non-polar, non-reacting, molecular species may be regarded, for practical purposes, as mixed with maximum randomness except in the immediate neighborhood of their liquid-liquid critical point."

DEPARTMENT OF CHEMISTRY
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cis-trans Isomeric Carotenoids, Vitamins A and Arylpolyenes. By L. ZECHMEISTER, California Institute of Technology, Pasadena, California. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1962. xiv + 251 pp. 61 × 23.5 cm. Price, \$10.00.

Between 1927 and 1940, while at the University of Pécs, Hungary, L. Zechmeister reported numerous investigations of the carotenoid pigments. At the early stages of this work, only about a half-dozen, yellow, fat-soluble, carotene-like substances were known. All these pigments were found to be highly unsaturated with 10 to 13 double bonds, most of which occur alternately with single bonds in conjugated systems. With carbon skeletons constructed of isoprenic units, these pigments owe their color to the number and arrangement of the double bonds.

Although many unsaturated substances occur naturally as spatial isomers, each carotenoid pigment was presumed to exist in but one spatial form. Zechmeister and a few others observed, however, that carotenoid pigments are altered when their solutions are heated. This alteration is revealed by a shift of the absorption maxima to shorter wave lengths and by the formation of several interconvertible isomers that may be isolated by chromatography.

Moving to the California Institute of Technology in 1940, Zechmeister studied the several isomers obtained from each carotenoid pigment. This field was rendered even more complex by the discovery of many additional carotenoids, some of which could be readily converted to the more common stable forms. Through his ingenious applications of the chromatographic adsorption method, Zechmeister isolated many of the labile isomers of each carotenoid and determined their properties, particularly their spectral absorption characteristics. In this way he found that the common, most stable isomeric form of each pigment was the "all-trans" form with *trans* arrangement of the groups at the doubly bonded carbon atoms. The less stable isomers contained *cis* arrangements at some of the double bonds. Eventually, the spatial structure of each isomeric pigment was established.

This monograph summarizes the investigations carried out at Cal. Tech. It also correlates this work with that done elsewhere. It is a monument to careful, persistent and imaginative investigation. It illustrates the importance of chemical investigation for the elucidation of molecular biology. It provides a basic framework for even more complicated future studies as, for example, the biosynthesis of the carotenoids and the role of the carotenoids in photosynthesis. Everyone interested in the carotenoid pigments and in related polyene compounds will find this an indispensable book.

ARGONNE NATIONAL LABORATORY
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Les Méthodes Analytiques des Lipides Simples. By C. PAQUOT, Directeur du Laboratoire de Lipochimie, C.N.R.S., Mlle. J. MERCIER, Ingénieur, C.N.R.S., D. LEFORT, Chargé de Recherches, C.N.R.S., A. MATHIEU, Ingénieur, C.N.R.S., and R. PERRON, Sous-directeur du Laboratoire de Lipochimie, C.N.R.S. Centre National de La Recherche Scientifique, 71, Boulevard Péreire, Paris 17, France. 1962. 281 pp. Price, 18 NF.

The book presents a complete and excellent treatment of the physical and chemical methods required for the characterization and analysis of lipid substances.

From the physical standpoint, the author includes the latest techniques available such as methods for index of refraction, specific weight, rotatory power, viscosity, melting and solidification temperature, boiling points, visible, ultraviolet and infrared analysis and X-ray diffraction, including a reasonably good treatment of the theory.

Besides the conventional chemical methods, the author has included the latest developments in the application of column, paper and gas phase chromatography to lipid chemistry. Also included are detailed procedures for the identification and de-

termination of chlorophylls, sterols, gossypol, sesamolene, sesamine and antioxidants.

The volume is thoroughly cross-referenced to other standard methods work such as those of the International Union of Pure and Applied Chemistry, the French, German and British Standards organizations as well as the American Oil Chemists' Society methods.

All in all, the book has been presented as a good reference analytical text for investigators in the field of lipid chemistry.

GENERAL FOODS CORPORATION
TECHNICAL CENTER B. F. DAUBERT
WHITE PLAINS, NEW YORK

The Radiochemical Manual. Part One. Physical Data. A Collection of Data for Users of Radioisotopes. Compiled by the Radiochemical Centre, Amersham, Buckinghamshire, England. British Information Services, 45 Rockefeller Plaza, New York 20, N. Y. 1962. 102 pp. 21 × 26.5 cm. Price, \$3.00.

"There is now an astonishing diversity of radioactive materials at the disposal of those who use them in medicine, research and industry. More than 150 different radioisotopes are offered commercially, many of them 'off the shelf' and in quantities ranging from microcuries to megacuries. Superimposed on this range of isotopic species is an almost unlimited number of variants of chemical and physical forms." So begins this manual of the physical (radioactive) properties of radioisotopes and their availability through the U. K. Radiochemical Centre at Amersham. The format is different from a catalogue issued by the Oak Ridge National Laboratory but has the same objective of acquainting habitual and potential users of radioisotopes with the array of substances at their command. This manual makes reference to a 'catalogue of radioactive chemicals and radiation sources' (also issued by the Radiochemical Centre) for current prices and fuller information.

The expansion of the uses of radioisotopes, labeled compounds and special sources has been accompanied by an expansion of the numbers of suppliers. In the United States much of the specialized service, e.g., synthesis of C¹⁴-labeled organic compounds, has been taken over by private companies. In the U. K. these functions have apparently remained with the Radiochemical Centre. It behooves the would-be user of radioisotopes to study all sources of supply because the services offered by different suppliers are not necessarily identical. One may be able to furnish the radioisotope in exactly the desired form, another may have produced his material for a different purpose. One of the features of the Radiochemical Centre which one can glean from their manual is that many of their products are furnished with absolutely standardized disintegration rates.

In addition to the central table, the manual has other listings classified in terms of: beta energies and gamma energies vis-a-vis half-lives, approximate minimum activities for detection, sources for radiography and thickness gaging, etc.

DEPARTMENT OF CHEMISTRY
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Paramagnetic Resonance. An Introductory Monograph. By G. E. PAKE, Washington University, Saint Louis, Mo. W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1962. xv + 205 pp. 15 × 23 cm. Price, paperbound, \$4.95; cloth-bound, \$6.95.

Professor Pake's monograph will be welcomed by many students and researchers in paramagnetic resonance. The book is a refinement and enlargement of lecture notes for a course in EPR given at Stanford University. It presumes one year of quantum mechanics as a background. This book is perhaps the first unified treatment of EPR by an author concerned chiefly with teaching the subject in an orderly way.

The book opens with a basic description of the cause of the resonance signal, a brief history of research in paramagnetism, and a classification of paramagnetic materials. The next chapter covers rotating coordinates, the Bloch equations, rapid passage and saturation effects; and it outlines experimental techniques. Separate chapters are devoted to the effects of crystal electric fields, dipolar and exchange interactions between electrons, ions and radicals dissolved in liquids, and spin-lattice relaxation. A short chapter introduces more sophisticated theories of line shapes and relaxation, based mostly on Kubo and Tomita. A final chapter is devoted to specialties: ferromagnetic and conduction-electron resonance, masers and double resonance. An appendix of 20 pages lists observed EPR constants for various crystals.

Professor Pake presents all topics both verbally and mathematically, often with considerable skill. The description of precession in the rotating frame is unusually good. Rapid pas-