BOOK REVIEWS

Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry. By L. M. Jackman, Lecturer in Organic Chemistry, Imperial College of Science and Technology, London. Pergamon Press, Inc., 122 East 55th Street, New York 22, N. Y. 1959. xii + 134 pp. 17 × 24.5 cm. Price, $5.50.

Of the four published books on nuclear magnetic resonance (NMR) spectroscopy of particular interest to chemists, the present volume is clearly the best for a practicing organic chemist to use when confronted with the problem of interpreting a NMR spectrum of one of his products. The coverage of chemical shifts and representative spin–spin coupling situations is about as thorough as could possibly be expected in 80 pages and is clearly and interestingly presented. A considerable number of typical and important spectral problems are analyzed. The presentations of the underlying physical principles are generally brief and may not provide a novice in the field with much understanding of the basic nature of NMR phenomena.

In the opinion of the reviewer, a definitive exposition of spin–spin splitting for organic chemists is yet to be published. The fundamental contribution to the analysis of spin–spin multiplets made by McConnell, MacLean and Reilly [*J. Chem. Phys.*, **23**, 1152 (1955)] was directed to specialists in molecular spectroscopy, and later restatements by others are similarly beyond the grasp of the average organic chemist. The discussion in the present volume is based on the notation and procedures of Pople, Schneider and Bernstein (collected and summarized in "High-Resolution Nuclear Magnetic Resonance," McGraw–Hill Book Co., Inc., 1959) and is purely descriptive, no effort being made to show the mathematical relationships between coupling constants, magnetic shieldings, transition energies and transition probabilities. This can be unfortunate, as in the discussion of the ABX case on pp. 90–91, where it is going to be hard to see how A can ever appear to split X if J_{AX} is negligibly small. Matters might have been helped considerably by noting that (when $\delta_A \sim \delta_B$) if A and B are more tightly coupled to each other than each is to X, then A and B act as though they are equally coupled to X even if $J_{BX} >> J_{AX}$. Hopefully, a treatise on spin–spin splitting will some time be written for organic chemists using reasonably familiar words and mathematics which will give a clear understanding of how transition energies and probabilities can be calculated.

The present volume is very attractively printed and illustrated, but contains a fair number of typographical errors. It is highly recommended to organic chemists interested in the qualitative interpretation of NMR spectra.

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Toxic Aliphatic Fluorine Compounds. By F. L. M. Pattison, M. A., Ph.D., F.R.I.C., F.C.I.C., Professor and Head, Department of Chemistry, University of Western Ontario, London, Ontario, Canada. D. Van Nostrand Company, Inc., 120 Alexander Street, Princeton, New Jersey. 1959. xi + 227 pp. 13 × 19 cm. Price, $3.50.

This valuable little book begins with the familiar quotations, "Mordre wol out," and "In poison there is physic." In the past the naturally occurring ω-fluoroacetates and derivatives were perfect poisons. They were stable, inoffensive and had a delayed action, but finally caused convulsions, paralysis and death, with no known antidote available, leaving behind no identifiable residue. However, modern research has clearly revealed the mode of action of these poisons, antidotes have been found, and accurate methods for determining fluorine have become available. It has also been found possible to use these poisons as tags in animals to verify or predict metabolic pathways, knowledge which may ultimately benefit humans.

The first chapter presents a broad survey of the material to be considered later on. Most important, perhaps, is the description of the alternating toxicities of the ω-fluorocarboxylic acids on ascending the homologous series, indicating that they are degraded *in vivo* by β-oxidation. Only the even numbered members of the series can be thus degraded to monofluoroacetic acid, which is therefore the actual toxic species in all cases.

The second chapter gives in detail the history, preparation, properties, toxicology, pharmacology, biochemistry and medical aspects of the simple monofluoroacetates and derivatives. It has been found that monofluoroacetic acid mimics acetic acid in the animal organism by combining with coenzyme A and so entering into the tricarboxylic acid cycle to form fluorocitric acid, which then inhibits the enzyme aconitase, thus effectively blocking the oxidative cycle. This results in loss of energy, accumulation of citric acid in the tissues and ultimate death.

Next we find a similar description of the occurrence, chemistry and toxicology of the long chain ω-fluorocarboxylic acids and derivatives, and their degradation by β-oxidation. Incidentally, an African plant containing ω-fluoro-oleic acid was long used by the natives to poison both their enemies and animals (ratsbane), thus anticipating the modern commercial use of sodium fluoroacetate as a rodenticide.

Then there are listed series of ω-fluoro alkanes, alkenes, alkynes, alcohols, aldehydes, ketones, nitriles, and many others, all showing alternating toxicities, some even greater than that of fluoroacetic acid. These alternating toxicities may be used as a tag to determine the fate of a functional group *in vivo*. Nitriles containing an odd number of carbon atoms are toxic, thus confirming the known theory that nitriles *in vivo* do not yield corresponding carboxylic acids, but undergo α-oxidation with the loss of hydrogen cyanide. Also, many polyfluoro alkenes are highly toxic, and even the vapor from overheated Teflon can be dangerous.

The final chapter discusses potential uses and applications. Of these the use of sodium fluoroacetate (compound 1080) as a rodenticide, fluothane ($CF_3CHClBr$) as a non-explosive anesthetic, and fluoroacetamide as a systemic insecticide for non-edible plants, are the most important. Many other possible uses are described.

This volume, the first of a forthcoming series, is well organized (6 figures, 31 tables, some extensive), well documented (over 400 references), and well printed with a minimum of errors. It also contains a succinct summary and four appendices, dealing with chemical properties, preparations, first-aid treatment and a special bibliography of informative articles.

This valuable reference book by a competent author should be on the active reading list of every fluorine chemist, either in research or production: in the best interests of safety, and of a better understanding of biological problems.

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Chromatographic Reviews. Progress in Chromatography, Electrophoresis and Related Methods. Volume 2. Edited by Michael Lederer, Institut du Radium, Arcueil (Seine), France. D. Van Nostrand Company, Inc., 120 Alexander Street, Princeton, New Jersey. 1960. viii + 195 pp. 17 × 24 cm. Price, $9.00.

Last year M. Lederer, the editor of the "Journal of Chromatography," introduced the practice of republishing the review articles from his periodical in book form. The summaries in French and German were translated into English. This publication represents a continuation of that policy. It contains six articles, amply illustrated and documented by experienced investigators, plus a subject index. Gas–liquid chromatography is reviewed by C. J. Hardy and F. H. Pollard (43 pp., 619 refs.); starch block electrophoresis by H. Bloemendahl (16 pp., 62 refs.); paper chromatography of dinitrophenylamino acids by G. Biserte, J. W. Holleman, J. Holleman-Dehove and P. Sautiere (46 pp., 104 refs.); chromatography of flavanoid pigments by J. B. Harbourne (24 pp., 91 refs.); separation of different types of human haemoglobin by H. K. Prins (42 pp. 84 refs.); inorganic adsorption and precipitation chromatography by E. Hayek (20 pp., 211 refs.).

This publication will be extremely useful to everyone whose interests lie in its fields. But for material that is already available in the "Journal of Chromatography," the price is very high.

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Zeitschrift für Elektrochemie. Band 64, Nr. 1. **Bericht über das Internationale Kolloquium über schnelle Reaktionen in Lösungen in Hahnenklee/Harz vom 14. bis 17 September, 1959.** Edited by M. EIGEN, Göttingen. Verlag Chemie, G.m.b.H., Pappelallee 3, Weinheim/Bergstr., Germany. March 1960. 204 pp. 21 × 29.5 cm. Price, DM. 13.—.

In September, 1959, about a hundred persons met for four intensive days at Hahnenklee in the Harz Mountains near Göttingen. The conference was devoted to the study of fast reactions in solution, and it was beyond question the most exciting meeting this reviewer has ever attended. The papers and much of the discussion have now been collected in a single issue of the "Zeitschrift für Elektrochemie." The issue cannot pack the excitement of the conference itself, but it can give readers a lot of valuable information and provide an inkling of what it was like to be there.

The kinetic study of solution reactions was long confined almost entirely to organic processes because the limitations of human reflexes made it impossible to study the large number of inorganic reactions that went to completion in less than a few seconds. In fact, rapidity of reaction was grafted upon the theory of ionic dissociation, and Walther Nernst of Göttingen hurled verbal thunderbolts at any who dared to question that ionic reactions were "infinitely" fast. By a peculiar quirk of fate, Göttingen has again become Olympus for those interested in the rates of ionic reactions. There Dr. Manfred Eigen has been the key figure in the development of techniques that now permit us to measure rate constants for reactions that seem to reach equilibrium instantaneously.

Techniques certainly provided the dominant theme of the conference, and the discussion was repeatedly directed toward establishing the attainable limits for different methods. The possible ranges of these methods overlap to provide a continuum such that in principle any lifetime greater than 10^{-9} second can already be measured for some reactions. Since not all methods are applicable to all reactions of interest, the practice falls somewhat short of universality, but the measurements already accomplished are impressive in the extreme.

The conference was initiated by Dr. F. J. W. Roughton of Cambridge who told how the study of fast reactions started with his 1923 experiments on flow systems. Rapid mixing has shortened the times accessible by such methods, but the present limit is a few tenths of a millisecond with little prospect of decreasing it by many powers of ten.

The other methods must use previously mixed solutions. When delivery of ions to an electrode becomes a limiting factor in electrochemical measurements, the rates of fast homogeneous reactions can be followed; but discussion pointed up the difficulties of a rigorous interpretation of the data. Resonance methods involve a periodic disturbance of the system at a frequency corresponding to some process of interest; techniques were reported with ultrasound and with nuclear and electronic spin changes. Flash photolysis procedures have been described previously, and the attention of the conference was directed chiefly toward establishing the minimum times attainable for study.

Undoubtedly Dr. Eigen's relaxation techniques created the greatest interest. If an existing equilibrium is perturbed by a small amount, the rate at which the new equilibrium is established is proportional to the displacement from the final state, and the appropriate time constant can be measured for both single and periodic perturbations. Temperature, pressure and electric field all have been used as perturbing influences, and the limits are expected to be reached at times of the order of 10^{-11} second. While such a time is still much longer than the period of a molecular vibration, it is sobering to realize that light travels only about 3 mm. during this interval!

About half of the papers are classified under the heading Reaction Mechanisms, but many of these are concerned with methods as much as with results. The time scales of chemical kinetics have suddenly been extended by several powers of ten, and the first experiments have been chiefly exploratory. As the methods become standardized, we can expect the accumulation of a large body of data to be followed by the understanding that comes with interpretation. These developments are only beginning.

Any collection of symposium papers inevitably suffers from a lack of uniformity, and the effect is somewhat heightened here by the approximately equal division of the contributions into English and German. An organized treatise by a very few authors would make a better reference work than this rather amorphous accumulation, but there is no treatise in the field and this collection will be a useful source of information in the meantime.

The Deutschen Bunsen-Gesellschaft für physikalische Chemie is to be commended for this method of presenting the papers. Many libraries now feel that they must purchase every technical book that appears, and we have reached the frightening situation where almost *any* volume can be produced at a profit. Publishers have succumbed to the temptation and are producing hard backed collections of symposium papers that merely duplicate material already in the journals. The Hahnenklee symposium has been published instead as a single issue of the Zeitschrift für Elektrochemie. No library need buy this in addition to its regular subscription, but any chemist interested in solution reactions will be glad to spend $3 to have this paperback on his own desk.

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Absorption Spectra in the Ultraviolet and Visible Region. Volume I. Edited by Dr. L. LANG, Dr. J. SZOKE, Dr. G. VARSANYI and M. VIZESY, Collaborators. Publishing House of the Hungarian Academy of Sciences, Alkotmany u. 21, Budapest V., Hungary. 1959. Text volume, 80 pp.; Volume I, 414 pp. 24.5 × 19.5 cm. Price, $18.00.

This volume contains a compilation of 172 ultraviolet and visible spectra, including 13 vapor phase spectra, recorded in Hungarian research institutes, and consists of detailed spectral data some of which have been briefly reported in Hungarian or other less common journals. It is intended that future volumes will also contain data recorded in other laboratories.

The authors report data which are not already recorded in similar compilations and deal with such varied compounds as cobalt complexes (8), carotenoids (15), substituted salicylic acids (8), benzanils and related compounds (20), sulfonilamides (7), glucosyl derivatives of benzoic acid and thiazoles (14), diphenyl sulfides (6), phenanthrenes (11), furyl compounds (7), flavones and isoflavones (32), purines (9) and alkaloids (14). The vapor spectra (13) are of benzene and simple halogen derivatives. A compound index and formula index are provided to facilitate in locating substances. The spectra are recorded from *ca.* 200 up to 400 or 600 mμ, many in different solvents or at different *p*H, and are given as graphs of absorbancy with a table of readings at every 5 mμ or less on the reverse side, the various graphs being bound in a ring file. The original literature reference or laboratory reporting the data are also given.

The compilation is clearly printed on gloss paper, but the ring binder is of poor quality, and although a large number of different compounds are dealt with the inclusion of both hydroxycarotenoids and their palmitates and of such uncommon substances as 2-carboxyphenylselenoglycolic acid seems unnecessary. The tables seem reasonably free from errors, although the c^4 is missing from the table on page 100, and the data for N-3-hydroxybenzylidine aniline in I *M* sodium hydroxide record a dip at 238 mμ, not shown in the graph, which gives an absorbancy value more like 1.38 instead of the reported 1.08. No discussion of the spectra