diazo compounds *in situ* which decompose carbenically to products[2b] is frequently of limited preparative value. The yields may be poor, the system must be aprotic,[2b] and the hydrocarbons may be difficult to separate from the solvent, particularly in small-scale experiments.[7] It has been found that pyrolysis of dry salts of *p*-tosylhydrazones at reduced pressures (100–760 mm.) in distillation equipment is often of real advantage in effecting their carbenic decomposition to intramolecular products. At appropriate pressures and thermolytic temperatures, the diazo compounds formed *in situ* decompose in the liquid and/or gaseous states to give products in good yields. The techniques are simple, rapid, free of many complications, and adaptable to small-scale experimentation. The method has been satisfactorily extended to injection in gas chromatographs of salts of tosylhydrazones as a dry powder or in suspension in a hydrocarbon; thermolysis is subsequently effected in a clean, heated injector unit and the products are separated, analyzed, and collected by usual techniques.

(7) (a) Metal alcoholates may cause complication in that the alcohols generated in formation of salts of the *p*-tosylhydrazones can lead to cationic decomposition of the intermediate diazo compounds. N-Methylpyrrolidone as a solvent when using metal alcoholates as bases frequently allows decomposition of the *p*-tosylhydrazones to intermediate alkyl *p*-tolylsulfinates which are saponified or transesterified to alcohols. (b) Similar observations have been made by J. W. Wilt and C. A. Schneider, *Chem. Ind.* (London), 865 (1963).

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# *Book Reviews*

**Spectra–Structure Correlation.** By JOHN P. PHILLIPS, Department of Chemistry, University of Louisville, Louisville, Ky. Academic Press, Inc., 111 Fifth Ave., New York 3, N. Y. 1964. ix + 172 pp. 16 × 26 cm. Price, $6.00.

As stated by the author in his preface, "The principal novelty of this book is its attempt to present a balanced survey of the data of absorption spectroscopy for organic compounds in all regions of the spectrum from far ultraviolet to far infrared." I believe that this is an excellent idea and it is indeed astonishing that until 1964 nobody seems to have undertaken the writing of a book of this type. The other surprising fact about this book is that it is so short. There is the other great merit of the author: he recognized the fact that, where analytical or other diagnostic work in spectroscopy is concerned, only relatively few correlations can be used for actual structure determination, the great majority of available data having little more than fingerprint value.

The reader whom this book will interest is clearly the chemist who uses the spectra as a tool, not the theoretically minded spectroscopist. It covers the spectra from 175 mμ to 35 μ, the range which is readily accessible to commercial instruments. The book is written in a vigorous personal style; nowhere does it become dull as so many other scientific books do.

The extreme brevity of the text (at places it is almost telegrammatic) has not only advantages. Certain concepts such as the oscillator strength or "the cross-sectional area of the absorbing species" are literally parachuted into the text. On page 3, the inexperienced reader may get the impression that sodium chloride prisms can be used in the 16–18 μ area. On page 11, one may be led to believe that cumulative systems have stretching bands above 2000 cm.$^{-1}$ only. On page 12, symmetric and asymmetric bending frequencies are mentioned in relation with nonlinear $XY_2$-type molecules while there is only one bending (scissoring) vibration in this case. The out-of-plane bending vibrations of olefins are really treated too shortly (p. 40).

Even at such places, however, the work remains highly informative. Even though many things are not explained, almost every thing is at least mentioned, and good entries to the literature are given. On pages 13 to 19, a highly useful list of books and review papers is given. Many of the latter are not widely known. Only the absence of a somewhat larger number of "old" references in the text may be regretted. Concerning units, it would have been good, in the reviewer's opinion, to give both μ (or mμ) and cm.$^{-1}$ in characterizing the spectral location of bands. This may be cumbersome, but it is probably the only satisfactory solution in the present confused situation. It is somewhat unpleasant to be given the spectral location of a fundamental in cm.$^{-1}$ but that of its overtones in μ.

Summing up, it is rather nice to have spectral information for most typical organic compounds in only 160 pages covering the ultraviolet–visible, the near infrared, and the infrared, and even part of the far ultraviolet and the far infrared. I think that Dr. Phillips succeeded in writing something that will be useful for many. It may even encourage someone to write a book which will cover n.m.r. as well.

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**The Cyanine Dyes and Related Compounds.** By FRANCES M. HAMER, Formerly Research Chemist, Kodak Ltd., London, and Honorary Lecturer, Imperial College of Science and Technology, London. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1964. xxxvi + 790 pp. 16 × 23.5 cm. Price, $45.00.

A considerable body of work dealing with the cyanine and related dyes, including hundreds if not thousands of patent specifications, has issued over the years, particularly during the last three decades.

The cyanines are of special interest for several reasons. More than most dyes, they lend themselves to almost limitless structural variation, as a result of which they present by far the most diverse assemblage of absorption spectra (and hence of colors) of any known dye series. They are polymethine dyes, and in the symmetrical benzothiazole series $A=\overset{|}{C}(-\overset{|}{C}=\overset{|}{C})_n-A$, where A represents the appropriate forms of the benzothiazole ring, dyes have been prepared where $n$ = 0, 1, 2, 3, 4, 5, and 6. Since each successive increase in $n$ has the effect of shifting the absorption maximum by about 100 mμ toward longer wave lengths, the extraordinary range of absorptions of this one series can be imagined.

On the practical side, the cyanines, with certain exceptions, are generally too fugitive to be useful in the dyeing of textiles, but happily this deficiency is balanced by their outstanding usefulness as color sensitizers in photography. For this purpose they are dyes of choice, and it is not too much to say that the elaborate edifice of photography could not exist without them in anything like the form in which we know it today.

The appearance of the present volume, the first to deal exclusively with these dyes, has accordingly been awaited with great interest, not only by the relatively small number of chemists actively working in the field but by the many others who would welcome an opportunity to become familiar with the main features of the

cyanines without the burdensome necessity of consulting original sources.

In a preface the author states that "emphasis has been laid on the preparative methods rather than on the theoretical aspects of the subject." The cyanine specialist will find this is indeed the case, for Dr. Hamer, a distinguished contributor to the subject over many years, has chosen to include all the considerable number of dye types in a manner reminiscent of Beilstein. The book is thus of great value as a reference source.

For a presentation of the "theoretical aspects" of the subject, the book cannot be recommended, however, as the author indicated, for although many separate themes are presented, little attempt has been made to combine them into a coherent whole.

A generous vote of thanks is owed to Dr. Hamer by the cyanine and heterocyclic fraternity for the accomplishment of a useful but formidable task undertaken at the close of a long and active career in the laboratory. The book will be of less interest to the general reader, however, for whom a lucid and concise account of these interesting dyes has still to appear.

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**Identification of Materials via Physical Properties, Chemical Tests, and Microscopy.** By A. A. BENEDETTI-PICHLER, Queens College of the University of the City of New York. Academic Press, Inc., 111 Fifth Ave., New York 3, N. Y. 1964. xi + 492 pp. 17 × 25 cm. Price, $18.00.

The practice of modern chemistry frequently requires the identification of unknown materials ranging from sediment in pharmaceutical preparations to matter under the fingernails of a corpse. The book under discussion describes techniques, both macro and micro, for the systematic investigation of specimens and emphasizes the necessity for acute reasoning that continuously weighs all accumulating evidence. The content of the book is heavily weighted toward micro procedures—a well-justified arrangement.

Following a general introduction which outlines principles and limitations, there is a section on the use of the chemical microscope with its polarizing attachments (45 pp.). Then there is a detailed description of the techniques employable for handling samples on the gram, centigram, milligram, and microgram scales (160 pp.). At this point the author outlines various approaches which may be used in deriving maximum information with minimum destruction of material and the development of leads which will determine the further course of the investigation. Both organic and inorganic materials are treated (96 pp.).

The last major section of the book is devoted to descriptions of confirmatory tests for various elements and a systematic scheme for the detection of cations and anions (103 pp.). The Appendix contains useful tables of such things as melting points of inorganic materials in order of increasing temperatures; crystal systems of certain substances; compounds which sublime, explode with heat, ignite with heat, etc. An extensive bibliography is furnished at the end of the book.

This book is designed for self-instruction of readers and as possibly the basis for a laboratory course. It contains many illustrative experiments. The author's 40 years of experience are of great advantage in the accumulation of such great detail as is presented in this volume.

The most prominent deficiency of the book lies in the section on the use of the microscope. The discussion of the immersion method for determination of index of refraction of solids (pp. 39–41) makes no mention of the fact that most solids display more than one refractive index and that the method described would only apply to isotropic crystals. The section devoted to polarized light is so concentrated and heavily written as to be essentially useless to a beginner. The use of terms such as pleochroism, goniometer, slow component, $\alpha$, $\beta$, $\gamma$ (indices), Ramsden disk, etc., without any definitions, can only frustrate the reader. In the discussion on polarization colors, it would be helpful to include a statement to the effect that the end of each color order is located at the higher-order edge of the red band. To attempt to gather useful information from the observation of interference figures without knowledge of orientation (p. 62) would be foolhardy. The important phenomenon of polymorphism is mentioned briefly on pages 64 and 271 but not called by name.

The other sections of the book cover their subjects quite well, and the techniques described should be extremely useful to the laboratory chemist even though he may not be working strictly on unknown materials.

There are a number of areas where the editor might well have produced a more tidy book. He should have corrected such oversights as "Fusions perform in crucibles of..., etc." (p. 70), "vertical" instead of "perpendicular" (pp. 60 and 75), "...the latter is fused while observing through the microscope" (p. 205), "with the raser of a pencil" (p. 151), etc. Manuscript notations appear at the bottom of the first and second pages of each signature of the book.

There is certainly a wealth of useful information in the volume under discussion, and it is worthy of high recommendation if the uninitiated reader will refer to other sources for a more useful introduction to the polarizing microscope.

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**Infrared Spectroscopy of High Polymers.** By RUDOLF ZBINDEN, Pioneering Research Division, Textile Fibers Dept., E. I. du Pont de Nemours and Co., Inc., Wilmington, Del. Academic Press, Inc., 111 Fifth Ave., New York 3, N. Y. 1964. xii + 264 pp. 16 × 24 cm. Price, $9.50.

This book is recommended to those who like to use infrared spectroscopy as one of their tools for polymer research. The material is also suited for discussion in an introductory course on molecular spectroscopy.

In Chapter II the group theory and its application to polymer spectra were discussed. The description is brief but it is enough to illustrate how the observed spectrum of a crystalline polymer can be analyzed. Two examples were given in this chapter. It is no doubt that polyethylene should be chosen as the first example. The second example, the spectrum of polyhydroxymethylene, is new and interesting. Since both of the polymers have a planar zig-zag backbone, it would be helpful if another example on the spectrum of helical polymer were given.

In Chapter V the important topic on the polarized spectra of oriented polymers was discussed. There are several review papers on this topic, but the present chapter gives the problem a much more detailed and systematical consideration. Some experimental problems and sources for errors in dichroic ratio measurements were discussed first, and then the expected dichroic ratios for various types of orientation were calculated. Examples on quantitative measurements were given. This chapter will be helpful to everyone interested in using polarized infrared radiation.

Other topics discussed in the book are as follows. In the discussions of crystallinity and analytical applications given in Chapter I, pertinent examples were given. Some figures in this part may be improved if the book is going to be printed again. The skeletal vibrations and the vibrational interaction in chain molecules, discussed, respectively, in Chapters III and IV, are of fundamental interest. Since the calculations were based on rather simplified models, the calculated frequencies may not be used for analytical purpose without caution. Those who are interested in normal coordinate analysis of high polymers may wish to see skeletal vibrations of helical polymers and somewhat detailed treatment on polyethylene to be included in the book.

In the appendix, the guide to the literature of individual polymers is listed. The list is quite complete and it is certainly a helpful collection. From the large number of references listed, it is indicated that there is room for additional chapters to the present book, or another volume to review and to make detailed discussions on the spectra of individual polymers or groups of polymers.

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