

extracted material from alcohol-water. Thus, when 10 mg of DL-Bz-Leu-Gly-OEt was added to 1.00 g of the L isomer, 30% of the DL form was readily recovered by this procedure.

Application of this technique to the reaction product of 1 equiv of L-Bz-Leu-OH and 1 equiv of N-methylmorpholine with 5% excess isobutyl chloroformate in THF at  $-15^{\circ}$  for 4 min followed by 5% excess H-Gly-OEt showed that no racemate was formed. A 93% yield of pure L-Bz-Leu-Gly-OEt, mp  $157-158^{\circ}$ , was found. (From several experiments, we have found  $[\alpha]^{25D} -32.5 \pm 0.5^{\circ}$  ( $c$  3, EtOH) for this product; further recrystallization did not give the  $-34^{\circ}$  reported by Williams and Young. A differential thermal analysis gave a single endotherm at  $159^{\circ}$ .) A similar experiment with 2 equiv of N-methylmorpholine gave a 16% yield of racemate and a 50% yield of L isomer. By older procedures, Williams and Young found crude yields of 85-88% with estimated L isomer 18-22%.

On the basis of our present evidence, steric factors appear to be particularly important for the complete formation of the mixed anhydride. Racemization *via* oxazolones seems likely.

Although N-methylmorpholine is the safer amine to use in the mixed anhydride procedure, the fact that good results were obtained with proper use of the strong racemizer trimethylamine is made even more striking by the following experiment. Z-Gly-Phe-N<sub>3</sub> (L) was made from the corresponding hydrazide (20 mmoles) at  $-5^{\circ}$  in ethyl acetate-1 *N* hydrochloric acid by treatment with sodium nitrite. The ethyl acetate solution was washed with aqueous potassium bicarbonate to remove excess acid, dried over sodium

sulfate a few minutes while chilling, then divided into two equal portions. A solution of 10 mmoles of trimethylamine in THF was added to one, and both were kept for 12 min in an ice-salt bath. Then 10 mmoles of ethyl glycinate was added to each. After refrigeration ( $-3^{\circ}$ ) overnight, each was worked up to yield 3.14 g of product, mp  $\sim 83-92^{\circ}$ . Thin layer chromatography (silica gel, chloroform-methanol 2:1) showed spots at  $R_f$  0.8 (Z-Gly-Phe-Gly-OEt) and 0.65 (Z-Gly-Phe-NH<sub>2</sub>). Fractional crystallizations from 2% solutions in ethanol gave a 1.6% yield of DL tripeptide from the reaction done with trimethylamine and none from the control. Yields of L tripeptide were 19 and 24%, respectively. Concentration of the alcohol solutions remaining and recrystallization of products from ethyl acetate yielded 18% of pure Z-Gly-Phe-NH<sub>2</sub>, mp  $143-144^{\circ}$ ,  $[\alpha]^{25D} +9.74^{\circ}$  ( $c$  2, EtOH), from the trimethylamine reaction and 9%, mp  $143-144^{\circ}$ ,  $[\alpha]^{25D} +10.8^{\circ}$  ( $c$  2, EtOH) from the control. Authentic Z-Gly-Phe-NH<sub>2</sub> (L), made by reaction of NH<sub>3</sub> with the mixed anhydride from Z-Gly-Phe-OH (L) and isobutyl chloroformate, had  $[\alpha]^{25D} +9.5^{\circ}$  ( $c$  2, EtOH). *Anal.* Calcd for C<sub>19</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>: C, 64.21; H, 5.96; N, 11.83. Found: C, 64.66; H, 6.21; N, 11.88 for the product from the control peptide synthesis. The isolation of the DL tripeptide provides the first example of racemization by the azide method, to our knowledge.

George W. Anderson, Joan E. Zimmerman  
Francis M. Callahan

Organic Chemical Research Section, Lederle Laboratories  
American Cyanamid Co., Pearl River, New York

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## Book Reviews

**Oxidation and Combustion Reviews.** Volume 1. Edited by C. F. H. TIPPER, Ph.D., D.Sc., Senior Lecturer in the Department of Inorganic, Physical, and Industrial Chemistry, University of Liverpool. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1965. 344 pp. 16 × 23 cm. \$14.50.

The study of combustion and oxidation must have started before recorded history, and because of the complexity of the subject it is likely to be studied for a similar period of time in the future. The titles of the papers given at the 1964 International Combustion Symposium (over 1400 pages in small print) reveal a tremendous range of topics varying from experimental fires to reaction kinetics. Dr. Tipper envisages that the series of "Oxidation and Combustion Reviews," of which the first volume has recently been published, should cover a similarly wide field including, in later volumes, the more physical and the engineering aspects of the subject.

Judging by the first volume, it is intended that each volume should contain a wide range of topics. The first volume concentrates on the chemistry of the oxidation process in both gaseous and solid oxidations. There are six chapters, each written by different authors in differing styles with differing degrees of success. Therefore it is best to review each chapter separately.

The first chapter by Ben-Ain and Lucquin deals with the branched-chain process in slow combustion and in cool flames. Judging by the dates of the references given, this subject has not progressed

much recently and the authors may be criticized for a rather complacent acceptance of some unsubstantiated theories. Thus they accept that consumption of reactants competing with chain branching causes a slow combustion reaction to reach a maximum rate.

The chapter on oxidation reactions induced by ionizing radiation is little more than a very useful list of references with a brief summary of the results obtained in this field.

Gas-phase photooxidation reactions are described by McMillan and Calvert in a well-argued account which begins by detailing some effects (*e.g.*, quenching) associated with electronically excited molecules. This is followed by a good account of the reactions of alkyl, acyl, peracyl, and alkoxy radicals. The reactions are each considered separately in preference to a separate treatment of the photooxidation of each parent compound.

The chapter by J. H. Thomas on oxidation reactions involving nitrogen dioxide deals, by contrast, in considerable detail with the kinetics of the reactions between nitrogen dioxide and (a) hydrogen, (b) hydrocarbons, (c) halogen-containing compounds, and (d) formaldehyde and formic acid. This is a good review.

Oxidative degradation of high polymers is ably dealt with by W. L. Hawkins in a more descriptive account of the environmental factors which in practice are responsible for the oxidation of polymers in general use. A description of the natural degradation is followed by an account of laboratory experiments designed to give some idea of the reaction mechanisms involved and the products obtained.

The heterogeneous selective oxidation of hydrocarbons is described in a chapter by Sampson and Shooter. They detail the ways in which the yields of required oxidation products can be increased by varying the nature of the surfaces which act as catalysts or catalyst supports. This is rather a long chapter dealing in considerable detail with the oxidation of ethylene (12 pages) and propylene (20 pages) and also with the oxidation of  $C_4$  and aromatic hydrocarbons.

The volume is therefore a mixture of pure and applied research with a considerable variation in the sophistication of the work involved. Taken as a whole, it is an interesting volume for those concerned with the chemistry of combustion processes.

D. E. Hoare

Chemistry Department, Queen's College  
Dundee, Scotland

**Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry.** By PIERRE CRABBÉ, Syntex, S.A., and Iberoamerican University, Mexico. Holden-Day, Inc., 728 Montgomery St., San Francisco, Calif. 1965. xv + 378 pp. 19.5 × 26 cm. \$11.75.

The use of optical rotatory dispersion (ORD) and circular dichroism (CD) measurements in organic chemistry has developed dramatically during the last 10 years. Together these two techniques constitute a unique method for studying the chirality or "handedness" of molecules. The techniques are perhaps chiefly of value to the natural product chemist or biochemist, since nearly all naturally occurring organic compounds are dissymmetric; however, they are of potential value to chemists working with any type of dissymmetric structures.

Two standard books on these methods have previously appeared (Djerassi, "Optical Rotatory Dispersion," 1960; Velluz, Legrand, and Grosjean, "Optical Circular Dichroism," 1964). Dr. Pierre Crabbé has now produced an excellent over-all picture of both techniques. This book extends and brings up to date the treatment in the two previous volumes and is presented from the point of view of a structural organic chemist.

The first four chapters of the book give a brief theoretical and technical treatment and an outline of the types of problem to

which the methods can be applied, including the study of *absolute* and *relative* configurations, location of functional groups, and conformational studies.

The chromophores which have optically active absorption bands, and therefore give rise to Cotton effects, can be divided into two classes, *viz.*, symmetrical, but perturbed chromophores, and inherently dissymmetric chromophores. Chapters 6 and 7 of Dr. Crabbé's book (108 pp) deal in great detail with the saturated carbonyl group, which has been studied most intensively and most profitably. Chapter 11 (66 pp) considers the other perturbed chromophores; some of these (carboxyl, aromatic rings, and nitro groups) have been studied intensively during the few months since this book was published.

The inherently dissymmetric or twisted chromophores are dealt with in Chapters 8, 9, and 10. Biaryls and conjugated dienes are discussed briefly, and then an extensive treatment (53 pp) of unsaturated ketones is given; up to the present, these compounds come next in importance to the saturated carbonyl compounds.

Chapter 12 deals with biopolymers (polypeptides, proteins, and nucleic acids). This is a field of great and growing importance, and the ORD and CD techniques are particularly valuable for the study of helical forms. A final Appendix treats the automatic processing of data for circular dichroism curves.

The book contains full references and is well printed with excellent formulas and diagrams; these are essential for a book dealing with any aspect of stereochemistry. Each chapter contains carefully planned tables, which illustrate the value of the techniques in structural problems. All concerned are to be congratulated on the *speed* with which the book was produced.

This subject is developing rapidly at present, and the next few years will certainly see great extensions to the scope of these techniques. Dr. Crabbé has written a well-balanced account, with emphasis on those aspects which are important to the natural product chemist. His book can be heartily recommended to anyone wishing to enter the field and to see how these relatively new techniques may help his own research. Those working in the field will certainly have the book already and will no doubt thank Dr. Crabbé for providing such a compact and encyclopedic picture of the present situation.

W. Klyne

Westfield College  
London, N.W.3, England