(m. p. 135°) and a **dipicrate** (m. p. 206-207°) of *dl*-sparteine, which they obtained from naturally occurring *dl*-lupanine. As a further proof of identity, our *dl*-sparteine was converted to *dl*oxysparteine, m. p. 110-111°, by treatment with alkaline potassium ferricyanide. The melting point of *dl*-oxysparteine has been reported as 110-111°, <sup>5</sup> 112-113°, <sup>4</sup> 113°.<sup>7</sup> Finally, the infrared absorption spectra of our synthetic *dl*-sparteine dipicrate and an authentic sample of *l*-sparteine dipicrate (m. p. 208°) were found to be identical in solution.<sup>8</sup>

We are aware of the desirability of resolving *dl*sparteine and of isolating the other two racemates of I. We also foresee the applicability of our method to the synthesis of other bases related to sparteine.

(8) The authors are indebted to Mrs. James L. Johnson for determination of the infrared absorption spectra.

THE NOVES CHEMICAL LABORATORY

UNIVERSITY OF ILLINOIS URBANA, ILLINOIS Nelson J. Leonard Roger E. Beyler

## A CRYSTALLINE FACTOR FUNCTIONALLY RELATED TO FOLIC ACID

Sir:

In a systematic study of factors functionally related to *p*-aminobenzoic acid and folic acid and occurring in liver extracts used for the treatment of pernicious anemia, a factor was discovered which prevented the toxic action of methylfolic acid<sup>1</sup> upon the growth of *Leuconostoc mesenteroides* 8293. In a medium previously described<sup>2</sup> but supplemented with 300  $\gamma$  of thymine per 10 cc., the ratio of methylfolic acid to folic acid just necessary for maximum inhibition was 3,000. The addition of this factor in adequate amounts (equivalent to 0.01–0.03  $\gamma$  of crystalline material per 10 cc.) increases the antibacterial index about tenfold.

A medium suitable for quantitative assay was obtained by the addition of 0.03  $\gamma$  of folic acid and 200  $\gamma$  of methylfolic acid per 10 cc. to the above medium. Under these conditions increasing concentrations of the factor resulted in increasing growth levels.

Employing this assay, a principle has been isolated from hog liver in crystalline form. Recrystallized from isopropyl alcohol, this principle appears as fine, colorless prisms, m. p. 189–190°. Under the testing conditions, the factor is several times as active as folic acid in promoting a halfmaximum growth response.

Extracts prepared from either liver, hog duodenal mucosa, or grass are highly active, but milk, muscle tissue and yeast extract are relatively poor sources of active material. Liver extracts used in

(1) Crude mixture from the condensation of  $\alpha,\beta$ -dibromobutyraldehyde, 2,4,5-triamino-6-hydroxypyrimidine and p-aminobenzoylglutamic acid obtained from Dr. E. L. R. Stokstad [Franklin. et al., J. Biol. Chem., 169, 427 (1947)].

(2) Snell, et al., ibid., 148, 519 (1942).

treatment of pernicious anemia are relatively potent, and some experimental extracts of high potency (determined clinically) assayed by the above method appear to contain as much as 1%of this factor.

Preliminary investigation of the structure of the compound indicated that it was thymidine<sup>3</sup> or a structurally related compound.

We acknowledge our indebtedness to Eli Lilly and Company for their coöperation. Particular thanks are due Drs. Ewald Rohrmann and Edward D. Campbell for their coöperation in furnishing experimental extracts and analytical facilities.

(3) Since this paper was submitted, we have obtained a sample of thymidine originally isolated from desoxyribonucleic acid by Levene and London (J. Biol. Chem., 83, 793 (1929)). The X-ray diffraction pattern and the biological properties of this sample are identical with those of the isolated factor.

THE BIOCHEMICAL INSTITUTE AND<br/>THE DEPARTMENT OF CHEMISTRY<br/>THE UNIVERSITY OF TEXAS, AND<br/>THE CLAYTON FOUNDATION FOR<br/>Research, AUSTIN, TEXASWILLIAM SHIVE<br/>ROBERT E. EAKIN<br/>W. M. HARDING<br/>JOANNE M. RAVEL<br/>RUDIN E. SUTHERLAND<br/>RECEIVED APRIL 16, 1948

## THE KINETICS OF THE POLYMERIZATION OF CARBONIC ANHYDRIDES

Sir:

Carothers (Chem. Rev., 8, 353 (1931)) has divided polymerizations into two types, "addition" and "condensation." In the former type, initiation, propagation, transfer and termination reactions are involved (cf. Bamford and Dewar, Proc. Roy. Soc. (London), 192, 309 (1948)), but in condensation polymerizations only chain-growth occurs, and in this reaction every species reacts with every other. There is, however, a third type of polymerization in which there are only two reactions, initiation, and a propagation reaction where the polymers do not react with each other, but only with the monomer. The polymerizations of carbonic anhydrides (e. g., I) appear to belong to this third type, and are also important since they can be used to synthesize polypeptides of some complexity. The reactions involved are

$$M + A \longrightarrow X + CO_2 \quad (k_1) \qquad (1)$$
  
$$M + X \longrightarrow X + CO_2 \quad (k_2) \qquad (2)$$

where M denotes the carbonic anhydride, X any polymer species, and A the initiator which may be a hydroxylic or amino compound.



Although a complete formal solution of the kinetic equations is impossible, the following methods are available for the absolute determina-

$$k_2/k_1 = (M_0 - A_0 + A_\infty)/(A_0 \log (A_0/A_\infty) - A_0 + A_\infty)$$
(3)

Since end-group estimation gives  $A_0 - A_{\infty}$ , this equation enables  $k_2/k_1$  to be evaluated.

The experimental conditions can be adjusted so that the concentration of initiator (A) is approximately constant, when it can be shown that there is a maximum rate given by

$$[d(M)/dt]_{max.}^{2} = \frac{1}{27} k_{1}k_{2}A_{0}(2M_{0} + k_{1}A_{0}/k_{2})^{3} \quad (4)$$

A simpler procedure, however, is to use the preformed polymer to initiate the polymerization, so that the second step (equation (2)) is isolated. The molar concentration of polymer  $(X_0)$ , is thus constant, and the rate of disappearance of carbonic anhydride is given by

$$-d(M)/dt = k_2 X_0(M)$$
<sup>(5)</sup>

The kinetics of the polymerization of sarcosine

carbonic anhydride (I) is being investigated. The polymer (II) used for initiating is obtained as a colorless, hygroscopic solid by the action of dimethylamine on the anhydride (I) in dioxane.

The polymerization in nitrobenzene is followed manometrically by the evolution of carbon dioxide. In accordance with equation (10) the reaction shows first-order dependence on (M); this confirms the assumption that  $k_2$  is independent of the molecular weight of the polymer, for molecular weights between about 500 and 5000. Preliminary measurements indicate that the velocity constant,  $k_2$ , can be expressed by the equation

$$k_2 = 1600e^{-5.800/RT}$$
 liters mole<sup>-1</sup> sec.<sup>-1</sup>

The low value of the frequency factor is noteworthy.

We hope to extend this investigation to other carbonic anhydrides and to co-polymerizations.

Courtaulds, Limited Maidenhead, Berks. England	S. G. Waley J. Watson
RECEIVED APRIL 20, 1948	÷

## NEW BOOKS

Chemical Insect Attractants and Repellents. By VINCENT G. DETHIER, A.M., Ph.D., Professor of Zoology and Entomology, The Ohio State University; formerly Entomologist, Inter-Allied Malaria Control Commission, Gold Coast, B. W. A. The Blakiston Company, Philadelphia, Pennsylvania, 1947. xv + 298 pp. Illustrated.  $15.5 \times 23.5$  cm. \$5.00.

The manner in which various chemicals attract or repel insects is of considerable interest to both chemists and entomologists working in economic entomology, to students of insect ecology and to others. The subject has also intrigued biologists not so well acquainted with the peculiarly specialized behavior of the insect world. Although the literature on attractants and repellents is extensive, most of the effort has been expended on research by the trial-and-error method, with not enough consideration of the chemical, physical, physiological and botanical factors involved. In an effort to remedy the situation and to impart a greater impetus to research in this field, Dr. Dethier has undertaken the difficult task of assembling and correlating the widely scattered literature. In this respect he has done a commendable piece of work.

respect he has done a commendable piece of work. The text is not a compilation of formulas of attractant and repellent substances. Rather it represents a theoretical approach to the study of the subject. The book is divided into ten chapters. An introductory chapter is followed by six that deal specificially with attractants, one with repellents, and two that are devoted to a more general discussion. There are approximately 750 literature citations.

Although the importance of research on insect repellents, especially for those insects that transmit disease, such as malaria-carrying mosquitoes, is pointed out, no mention is made of the extensive studies carried on during the recent war by the Bureau of Entomology and Plant Quarantine, United States Department of Agriculture; neither are the excellent fundamental studies on repellents by DeLong at the Ohio State University, nor is adequate treatment given the work of Granett at Rutgers University. The important subject of mothproofing warrants more than a brief paragraph. The book contains numerous errors in chemical nomenclature and in the structural formulas of compounds. These errors might have been avoided if the manuscript had been submitted to an organic chemist for review. Nevertheless the book is a valuable one and meets a definite need for both the chemist and the entomologist.

H. L. HALLER

Fundamentals of Photographic Theory. By T. H. JAMES, Ph.D., and GEORGE C. HIGGINS, Ph.D., Research Laboratories of Eastman Kodak Company. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y., 1948. vii + 286 pp. 14 × 22 cm. Price, \$3.50.

The recognized standing of the authors, not to mention coöperation by members of the Eastman staff, arouses in the reader expectations which are not disappointed. By concentrating upon black and white photography, exclusive of cameras or accessories, a coverage of the central theme admirable from physical, chemical and psychophysical standpoints is achieved. Consistent use of the sensitivity-speck basis for the latent image, together with the Gurney-Mott hypotheses, resolves in plausible fashion a great variety of complicated or at first sight contradictory phenomena. The chemistry of essential dark-room procedures is set forth in detail, but some will regret the omission of intensification, reduction and toning. Conflicting theories are critically examined in the light of data and of physico-chemical generalizations. Objective evaluations of photographic images are