mole); *n*-butyric acid, 55.9% (0.0034 mole); *n*-butyl *n*-butyrate, 27.5% (0.0010 mole); *n*-butanol, 3.7%; *n*-butyraldehyde, 0.8%; propionic acid, 0.9%; *n*-butyl propionate and *n*-propyl *n*-butyrate, traces; and an unknown hydroxy (?) acid, 1.3%. The analysis of the major component was confirmed by conventional chemical separation and identification.

We wish to thank the California Research Corporation for support which made this investigation possible.

DEPT. OF CHEMISTRY AND CHEMICAL ENGINEERING
STANFORD UNIVERSITY HARRY S. MOSHER
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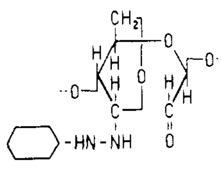
RECEIVED SEPTEMBER 6, 1955

THE FORMAZAN REACTION IN PROVING THE STRUCTURE OF PERIODATE OXIDIZED POLYSACCHARIDES

Sir:

We have reported[1] that the *aldehydo*-phenylhydrazones of sugars couple with diazo compounds to build *formazans*, but that the phenylhydrazones of ring structures derived from the hemiacetal form do not. We now propose to make use of this observation in a study of the precise structures of polysaccharides oxidized with periodic acid and of the phenylhydrazones obtainable from them.[2,3]

As with polysaccharides oxidized with periodic acid, each individual oxidized monosaccharide reacts with only *one* mole of aromatic amine, *e.g.*, of phenylhydrazine.[4,5] In the literature the following three formulas are suggested for the monosaccharides,[6,7] and their phenylhydrazones,[8,9] respectively.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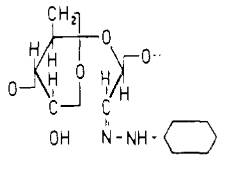
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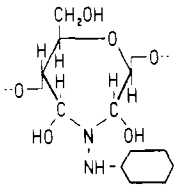
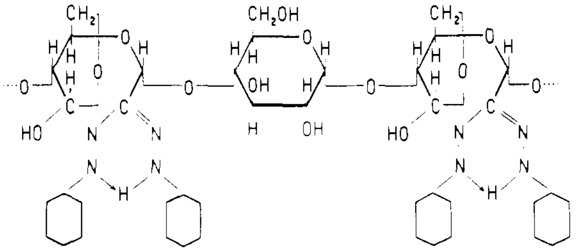

III

(I) is an aldehyde-hemiacetalphenylhydrazone, II, a hemiacetal-aldehydo-phenylhydrazone, and III, a "hemialdal" structure. Of these, only II contains an aldehydo-phenylhydrazone structure suitable for yielding a formazan.

On coupling with diazotized aniline in ice-cold pyridine solution, the phenylhydrazones of several polysaccharides (cellulose, starch, inulin, xylan and dextrin) oxidized wirh periodic acid, we obtained bright-red *diphenyl-formazans*, and thereby obtained unambiguous proof of the presence of structure II in these compounds.

On this basis, we suggest this formula for the structure of formazans obtained from polysaccharides, *e.g.*, from starch, oxidized with periodic acid



Procedure.—The polysaccharide samples were oxidized at room temperature with 3 to 5% sodium metaperiodate for 24 and 48, and in the case of insoluble polysaccharides (*e.g.*, cellulose or xylan) for 120 hours, respectively. The corresponding phenylhydrazones were prepared as described by Barry and Mitchell.[4] The bright yellow phenylhydrazones were then dissolved or suspended in pyridine or a 1:1 mixture of pyridine and ethanol. Dropwise addition with ice-cooling, of a diazotized aniline solution led to coupling to give the formazan. The vividly red solution or suspension was poured into ice water, and the polysaccharide formazans separated. With concentrated sulfuric acid they yielded the dark-blue color-reaction characteristic of the formazans.

By regulating the rate of oxidation it is possible to determine how many formazan groups form per monosaccharide group. For instance, if a *cellulose* wad is oxidized for 120 hours as described by Jayme and Sätre,[3] it will contain only one formazan group to three monosaccharides, and retain its original fibrous structure.

Anal. Calcd. for the phenylhydrazone $(C_{24}H_{34}O_{14}N_2)_x$: N, 4.88. Found: N, 5.04. Calcd. for the formazan $(C_{30}H_{38}O_{14}N_4)_x$: N, 8.26. Found: N, 7.42.

If *potato starch* is oxidized with 5% sodium metaperiodate for 24 hours, or *inulin* with 4% sodium metaperiodate for 48 hours, the resulting product will contain two formazan groups to three monosaccharides.

Anal. Calcd. for the phenylhydrazone $(C_{30}H_{38}N_4O_{13})_x$: N, 8.46. Found: N for starch, 8.31; for inulin 8.40. Calcd. for the formazan $(C_{42}H_{46}N_8O_{13})_x$: N, 12.87. Found: N for starch, 11.80; for inulin, 12.50.

A *xylan* sample oxidized with 3% periodate solution for 120 hours and a *dextrin* sample oxidized for 48 hours applying the above-described procedure likewise yielded the corresponding polysaccharide formazans. (Found: N for xylan 11.19; N for dextrin, 12.05).

This new reaction, yielding sparingly soluble formazans of vivid red color and high nitrogen content, will facilitate establishing as yet undecided structures of polysaccharides.

Experiments to form new active groups (tetrazoliums, thioaldonic-acid-phenylhyrazides, metallic complexes) in the molecule of polysaccharides by

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[1] L. Mester and A. Major, THIS JOURNAL, **77**, 4297 (1955).

[2] E. L. Jackson and C. S. Hudson, *ibid.*, **59**, 2049 (1937).

[3] G. Jayme and M. Sätre, *Ber.*, **77**, 242, 248 (1944).

[4] V. C. Barry and P. W. D. Mitchell, *J. Chem. Soc.*, 4020 (1954).

[5] V. C. Barry, J. E. McCormick and P. W. D. Mitchell, *ibid.*, 3692 (1954).

[6] J. H. Mitchell and C. B. Purves, THIS JOURNAL, **64**, 589 (1942).

[7] J. W. Rowell, F. H. Forziati and R. E. Reeves, *ibid.*, **73**, 4484 (1951).

[8] Z. A. Rogovin, A. G. Jasunskaja and B. M. Bogoslovskij, *J. Prikladnoi Chimiji*, **23**, 631 (1950).

[9] V. C. Barry and P. W. D. Mitchell, *J. Chem. Soc.*, 3631 (1953).

way of transformation of formazan groups,[10, 11] are in progress.

Thanks are due to Prof. G. Zemplén for valuable advice given and to E. Moczar for assisting in the experiments.

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RECEIVED JUNE 16, 1955

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[10] V. C. Barry, *Nature*, **152**, 537 (1943).

[11] V. C. Barry, T. Dillon and W. McGottrick, *J. Chem. Soc.*, 183 (1942).

BOOK REVIEWS

Synthetic Methods of Organic Chemistry. An Annual Survey. Volume 9. By W. THEILHEIMER. Interscience Publishers, Inc., 250 Fifth Avenue, New York, N. Y. 1955. xvi + 491 pp. 16.5 × 23.5 cm. Price $18.90.

Nine years ago this reviewer had the privilege of commenting on the first volume of Theilheimer's "Synthetic Methods." Now the ninth volume has appeared, covering the years 1952–1954: the author is to be complimented upon having kept abreast of the ever-swelling tide of research results and upon having done so with adherence to the high principles formulated at the outset.

An added feature, presented beginning with Volume VIII, consists in a few introductory pages of "Trends in Organic Chemistry" in which the author presents a condensed survey of synthetic methods recently introduced, perfected, modified, or disinterred, that appear to be of broad significance and applicability; there is, *e.g.*, a paragraph devoted to methods of peptide syntheses.

The series has, to all intents and purposes, become one of the standard resources of every research library, and this reviewer feels that any further discussion of the collection, including the good-natured controversy over the system of symbols, would be redundant if it were to go beyond an expression of gratification at the successful continuation of a very worthwhile enterprise.

RESEARCH DEPARTMENT
CIBA PHARMACEUTICAL PRODUCTS, INC.
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HANS HEYMANN

Physical Chemistry. A Series of Monographs. Edited by ERIC HUTCHINSON, Stanford University, California. Volume III. **Degradation of Vinyl Polymers.** By H. H. G. JELLINEK, Senior Lecturer in Physical and Inorganic Chemistry, University of Adelaide, South Australia. Academic Press Inc., Publishers, 125 East 23rd Street, New York 10, N. Y. 1955. 329 pp. 15.5 × 23 cm. Price, $8.50.

The author states, and the reader will concur, that the book should be of interest to the polymer chemist concerned with fundamental aspects of degradation reactions and also to the polymer chemist in the applied field. The latter may be somewhat dismayed by the montage of differential equations confronting him in the first chapter. If he will begin at page 31, he can avoid much of the mathematical derivations and will find the ideas and experimental data just as interesting.

The author demonstrates an excellent familiarity with the whole field of polymer degradation. The book is admittedly written from the standpoint of reaction kinetics and is a theoretical treatise of mechanisms of polymer degradation. However, considerable experimental data are presented, much of it the work of the author himself. Chapters 2, 3 and 4 will be of especial interest to the applied chemist in the field of polymers. Since this chemist is interested in the degradation of polymers from the standpoint of being able to prevent that degradation, he will find fruitful suggestions and ideas coming into his mind while digesting the author's suggested mechanisms. He will, however, be disappointed that the very important field of photodegradation of polymers is relegated to one paragraph each in the chapters on "Degradation in Solution and Bulk Degradation *in vacuo*." The chemist interested in fundamental studies will find quoted many of the postulated mechanisms of chemical reaction such as oxidation, hydrolysis, pyrolysis. Though it is unthinkable that he would agree with all of the mechanisms presented, they represent the latest published hypotheses.

The presentation is factual; the editing, excellent. Errors are at a minimum. For the kineticist it is recommended reading; for the applied polymer chemist it should be a required course.

PLASTICS DIVISION RESEARCH DEPT.
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O. V. LUKE, JR.

Solubilization and Related Phenomena. Physical Chemistry. A Series of Monographs. Volume IV. By MARY EVELYN LAING MCBAIN AND ERIC HUTCHINSON, Department of Chemistry, Stanford University, Stanford, California. Academic Press, Inc., Publishers, 125 East 23rd Street, New York 10, N. Y. 1955. xv + 259 pp. 15.5 × 23.5 cm. Price, $7.00.

Although dedicated to the memory of J. W. McBain and introduced by a selection from his writing, this book is not a compilation of contributions from the Colloid Chemistry Group at Stanford University, but an attempt to organize the voluminous literature on solubilization and to proceed as far as the state of knowledge permits toward a theoretical treatment of the subject. The fact that the concepts the authors advance in the light of recent work on colloidal electrolytes are sometimes at variance with those supported by Professor McBain during his active research in the field does not disturb them and would probably not have troubled McBain, who had a thorough respect for the logic of experiment.

The phenomena of solubilization by strictly micellar systems are presented in a brief but excellent historical chapter and in a longer chapter bearing the noncommittal title, "Data and Facts of Solubilization." The latter, which occupies nearly half the book, is in fact a well organized and readable survey into which the authors have introduced a considerable body of stimulating discussion based on their view of solubilization as a partition between the solvent proper and a micellar pseudo-phase. The chapter opens with a summary of the experimental methods available for the study of solubilization. This is brief, in keeping with the condensation characterizing most of the volume; it is regrettable that the scale of the work does not permit a more detailed and critical consideration of the experimental procedures and the assumptions implicit in their use. The remainder of the chapter is devoted to the effect of such variables as constitution, extraneous solutes, temperature and mixed micelle formation, with specific sections on emulsion polymerization, solubilization in non-aqueous systems and solubilization phenomena in two-phase systems. In the effort to compress a large volume of information into small compass it is perhaps inevitable that minor inaccuracies should appear; those noted do not affect the major conclusions drawn and will not be listed here.

There is a relatively detailed preliminary chapter on the formal thermodynamics of micellar systems and on the methods for measuring the critical micelle concentration.