

These compounds yielded on pyrolysis isomeric hydrocarbons of the composition $C_{21}H_{16}$ (m. p. 119 and 270°, respectively), indicating that the method of synthesis is practical and that pyrolysis proceeds without migration of the aroyl group in the naphthalene nucleus. The ketone I was then synthesized as follows: *p*-bromotoluene was converted by the Blanc reaction into a mixture of the two chloromethyl derivatives; this was treated with sodium malonic ester and the product was hydrolyzed and decarboxylated. Ring closure through the acid chloride mixture gave an easily separated mixture of two methylbromohydrindones (m. p. 154 and 95°) which on reduction by the Clemmensen method yielded the same hydrindene (b. p. 265–267°). The Grignard reagent from this hydrindene on reaction with α -naphthoyl chloride gave the ketone I (liquid) and on pyrolysis of I there was obtained a yellow hydrocarbon (*Anal.* Calcd. for $C_{21}H_{16}$: C, 93.98; H, 6.02. Found: C, 94.11, 94.18; H, 6.26, 5.96) which when purified through the picrate formed yellow needles melting at 176.5–177.5°; picrate 180–181°. No depression in the melting points was observed on admixture with samples of methylcholanthrene (m. p. 176–177°) and its picrate (m. p. 178–179°) prepared from desoxycholic acid.

This synthesis of a bile acid degradation product having 21 of the 24 original carbon atoms and all four of the original rings serves to confirm the accepted structures and it opens the way to the preparation of other hydrocarbons of interest in the study of carcinogenic activity. Further work in this direction is in progress. Before reporting the details of the above synthesis we are attempting to establish the structures of the intermediates obtained in the preparation of the ketone I, although this is not essential to a knowledge of the structure of the latter compound.

CONVERSE MEMORIAL LABORATORY LOUIS F. FIESER
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RECEIVED DECEMBER 17, 1934

THE PREPARATION OF GLUCOSIDODI-HYDROXYACETONE PENTAACETATE

Sir:

It has been pointed out by Evans and Hockett [THIS JOURNAL, 53, 4384 (1931)] that in the alkaline degradation of gentiobiose (6-glucosidoglucose) to lactic acid, 3-glucosido-glyceric aldehyde is a theoretically possible intermediate com-

pound. Under such alkaline conditions it is possible for this derivative of glyceric aldehyde to undergo the well-known Lobry de Bruyn and van Ekenstein rearrangement to give glucosidodihydroxyacetone. It was furthermore pointed out that the alkaline degradation of melibiose (6-galactosidoglucose) should yield 3-galactosido-glyceric aldehyde as an intermediate stage in the reaction.

Through the Koenig and Knorr reaction, with powdered "Drierite" as a desiccant in the chloroform, we have recently synthesized the glucosidodihydroxyacetone pentaacetate in good yields by the use of bromoacetoglucose tetraacetate and dihydroxyacetone monoacetate reported by Fischer, Baer and Feldmann [*Ber.*, 63, 1732 (1930)]. This compound crystallized from ether, having m. p. 103° (corr.); $[\alpha]_D^{18} -25.2^\circ$ ($CHCl_3$); an acetyl number equivalent to 10.81 cc. of 0.1 *N* NaOH per 0.10 g. (calcd., 10.82). Its *p*-nitrophenylhydrazone crystallizes from alcohol as a yellow derivative with m. p. 187° (corr.); $[\alpha]_D^{19} -129.8^\circ$ ($CHCl_3$); an acetyl number equivalent to 8.37 cc. of 0.1 *N* NaOH per 0.10 g. (calcd., 8.37).

The study of the behavior of glucosidodihydroxyacetone pentaacetate toward deacetylation reagents as well as potassium hydroxide after the manner of Evans and Hockett (*loc. cit.*) is now in progress in this Laboratory. The syntheses of the corresponding galactosido compounds as well as the corresponding hexosido-glyceric aldehyde ones are also being studied.

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STRUCTURE OF VITAMIN B

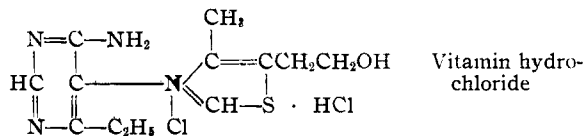
Sir:

On treatment with sulfite the vitamin is quantitatively split into $C_6H_9N_3SO_3$ (I) and C_6H_9NSO (II). (I) on the basis of ultraviolet absorption and chemical evidence is a 6-aminopyrimidine sulfonic acid. We provisionally allocate $-SO_3H$ to position 5 and $-C_2H_5$ to position 4.

The second cleavage product has been submitted to Dr. H. T. Clarke for examination. He has proposed a thiazole ring nucleus, which finding is confirmed by ultraviolet absorption studies. This base contains a free $-OH$ group also present in the vitamin, gives a negative iodo-

form reaction and on oxidation yields $C_5H_5NSO_2$. Windaus [*Z. physiol. Chem.*, **288**, 27 (1934)] also obtained this compound by direct oxidation of the vitamin but did not recognize it as a thiazole derivative. Present evidence indicates that it is 4-methylthiazole-5-carboxylic acid [*Ann.*, **259**, 299 (1890)].

The facts justify considering the vitamin as a quaternary base. Such a formulation best explains the chemical properties of the vitamin, notably the action of alkali and of sulfite as well as certain physical characteristics such as the solubility of the base and its hydrochloride. We regard the following as the most probable configuration



Studies are in progress to secure additional evidence on the proposed structure and to ascertain to what extent the sulfite cleavage is a general reaction of quaternary ammonium bases. A fuller account will appear shortly in a series of papers under the authorship of the various collaborators.

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY
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R. R. WILLIAMS

RECEIVED DECEMBER 24, 1934

NEW BOOKS

Handbuch der anorganischen Chemie. (Handbook of Inorganic Chemistry.) Edited by DR. R. ABEGG, DR. FR. AUERBACH and DR. I. KOPPEL. Fourth Volume, third division, second part B, section 3. Iron. Verlag von S. Hirzel, Königstrasse 3, Leipzig, Germany, 1934. xxvi + 201 pp. 198 figs. 18 × 25.5 cm. Price, RM. 28.

This latest instalment of Volume IV of the Abegg *Handbook* is of unusually wide interest. The first section of 92 pages, by E. Roehrich and E. Einecke, is entitled "Catalysis by Iron and Compounds of Iron." It gives an account of the many instances of great theoretical interest where these substances are active as inductors or catalysts, not only in homogeneous systems but also in a number of heterogeneous systems of great industrial importance, such as those involved in the synthesis of ammonia and in the oxidation of ammonia, hydrogen, carbon monoxide, etc. This section also includes a valuable chapter by A. Reid, entitled "The Importance of Iron in the Living World."

The second section of 20 pages, by A. Bondi and A. Kurtenacker, is devoted to the analytical chemistry of iron.

The final section of 88 pages, by D. Deutsch, I. Koppel, G. Lindau and W. Heller, is entitled "Colloidal Compounds of Iron." This section contains a full account of the preparation and chemical properties of sols of ferric oxide and also an unusually careful discussion of their physical properties.

It can be seen from the above that this volume is of great interest not only to the inorganic chemist, but also to the physical chemist, the organic chemist, the industrial chemist and the analyst.

ARTHUR B. LAMB

Conductometric Analysis. Principles, Technique, Applications. By HUBERT T. S. BRITTON, D.Sc., B.Sc., D.I.C., F.I.C., Lecturer in Physical and Inorganic Chemistry, University College of the South-West of England, Exeter. D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, 1934. xi + 178 pp. 49 figs. 14 × 22 cm. Price, \$5.00.

Although two monographs on conductimetric titrations have been written in German, no similar reference book was available in English. Britton, who in recent years has made valuable contributions to the subject and is the author of the well-known text "Hydrogen Ions," has filled a gap by publishing this excellent text on "Conductometric Analysis." The style is clear and concise and the treatment of the theoretical part is adequate for the particular purpose. Still, the use of the "degree of dissociation" of solutions of strong electrolytes in the classical sense might be changed to a more modern discussion in a future edition. In the first 20 pages a general introduction and theoretical discussion is given. This is followed by a review of conductimetric titration apparatus. In the next 100 pages the author describes the application of conductimetric methods to volumetric analysis, including a chapter on "abnormal acids" (molybdates, tungstates, vanadates). In this connection something might have been said about the system silicate-acid which is not mentioned in the book. An interesting chapter of 13 pages is devoted to the application of conductimetric titrations to research. In this chapter the author might have suggested that the organic chemist make more use of the information obtainable from conductimetric work. In addition the author should have mentioned the important application of conductimetric methods to the physico-chemical analysis of sols (Pauli, Rabinowitsch). A short chapter on industrial