We have reported the conversion of IIa through IIb of m.p. 81° (67°[5]) and IIIb into IIIc, which took up two moles of hydrogen in dilute ammonia over palladium.[7] The reduction product, IIId, was not reported because the analyses were variable; from dilute ammonia with acetic acid, it formed stable colorless needles[5] (82%), m.p. *ca.* 233° (dec.) (*Anal.* Calcd. for $C_{11}H_{14}N_2O_6$: C, 48.89; H, 5.22; N, 10.36. Found: *e.g.*, C, 48.21, 47.72; H, 5.92, 5.83; N, 10.28).

The same product, IIId, has now been obtained from IIb by these reactions in different orders: through IIc (85%), colorless needles, m.p. 86° (58°[5]) (*Anal.* Calcd. for $C_{17}H_{24}N_2O_7$: C, 55.42; H, 6.56; N, 7.61. Found: C, 55.47; H, 6.33; N, 7.26), and either IIIc,[7] the *hydrochloride* of IId, or the lactam IVa (80%). We have not encountered the free base IId.[5] The oxime IIc is reduced over palladium in ethanolic hydrochloric acid to the hydrochloride of IId (90%), colorless needles, m.p. 195–196° (*Anal.* Calcd. for $C_{17}H_{28}N_2O_6 \cdot HCl$: C, 52.37; H, 6.72; Cl, 9.07; N, 7.18. Found: C, 52.36; H, 6.90; Cl, 8.97; N, 7.41). In ethanolic ammonia IIc is similarly reduced to the lactam IVa (80%), colorless needles, m.p. 235–236° (decomp.), also obtained from the above hydrochloride with alkali (*Anal.* Calcd. for $C_{15}H_{20}N_2O_5$: C, 58.41; H, 6.54; N, 9.09; OEt, 29.20. Found: C, 58.76; H, 6.57; N, 9.33; OEt, 28.92).

However synthesized, the infrared spectra of IIId in Nujol mull showed inconsistent and minor differences, and the analyses were variable, though better on the monohydrate. Its nature and purity are no longer doubted because all specimens show identical X-ray powder photographs and chromatographic behavior. Also with aqueous pyridine and acetic anhydride, they give the lactam IVb (60%), colorless plates decomposing above 325° (*Anal.* Calcd. for $C_{11}H_{12}N_2O_5$: C, 52.38; H, 4.80; N, 11.11. Found: C, 52.10; H, 4.65; N, 11.00).

The lactam IVb is much more easily decarboxylated than is IIId. We have not yet been able to isolate porphobilinogen after heating IIId, either in 2*N* hydrochloric acid or better in aqueous pyridine with copper acetate[4], although paper chromatography does show its presence. On boiling with water, IVb gave porphobilinogen lactam, IVc, (80%), colorless plates, m.p. 282–284° (dec.) (*Anal.* Calcd. for $C_{10}H_{12}O_3N_2$: C, 57.68; H, 5.81; N, 13.46. Found: C, 57.55; H, 5.80; N, 13.19). Its identity with material of natural origin[2] was confirmed by mixed m.p., paper chromatography, infrared spectra in Nujol mull, X-ray powder photographs, and by the m.p., 248–250°,[2] and analysis of its methyl ester.

Porphobilinogen, I, was obtained from IVc with a slight excess of 2*N* sodium hydroxide at 100°. The removal of about 10% of unchanged IVc by repeated treatment with lead and mercuric acetates then recrystallization,[2] reduced the yield from 80 to 25%. It formed slightly pink micro-prisms, m.p. 172–175° (dec.) (*Anal.* Calcd. for $C_{10}H_{14}N_2O_4 \cdot H_2O$: C, 49.17; H, 6.60; N, 11.47. Found: C, 49.29, 49.15; H, 6.63, 6.56; N, 11.23). Its purity and identity were established by paper chromatography, and by the infrared spectra in Nujol mull and the X-ray powder photographs, of the natural and synthetic porphobilinogens and also of their hydrochlorides.

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(7) D. M. MacDonald and S. F. MacDonald, *Canad. J. Chem.*, **33**, 573 (1955).

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A SYNTHESIS OF α-D-RIBOFURANOSE-1-PHOSPHATE

Sir:

The synthesis of β-D-ribofuranose-1-phosphate recently has been reported from this laboratory.[1] The purpose of the present communication is to record the synthesis of the anomeric compound (I) which is identical in chemical properties with the enzymatically-prepared samples of ribose-1-phosphate[2,3] and is fully active as a substrate for the fish muscle purine nucleoside phosphorylase.[3]

The importance of "neighbouring group participation" in the synthesis of nucleosides,[4] as well as β-D-ribofuranose-1-phosphate,[1] using acylfuranoside-1-halides has become clear. Thus, in most of the syntheses reported products having a C_1-C_2 *trans*-configuration are obtained.[4] Our basic aim, therefore, in approaching the problem of the synthesis of α-D-ribofuranose-1-phosphate was to prepare a suitably protected ribofuranosyl-1-halide in which the blocking group at C_2 would not exercise the important neighboring group influence in the replacement reaction at C_1, and which would, at the same time, be readily removed at a later step in the synthesis. The synthesis of a D-ribofuranose 2,3-cyclic carbonate, which meets the above requirements, was undertaken.

Methyl-2,3-isopropylidene-5-benzyl-D-ribofuranoside[5] (II) was converted quantitatively to the oily methyl 5-benzyl-D-ribofuranoside (III) (b.p. 140° (0.02 mm.)) by treatment with aqueous methanolic sulfuric acid.[6]

The glycol (III) was then brought into reaction with phosgene in a mixture of pyridine and dioxane, and the product, methyl 5-benzyl-ribofuranoside 2,3-cyclic carbonate (IV), was obtained, again in excellent yield, as an oil distilling at bath temperature up to 190° (0.01 mm.). This product gave no reaction with periodic acid. On storage at low temperature, an aqueous methanolic solution of the product, which presumably is a mixture of the α- and β-anomers, deposited crystals in 40% yield; m.p., after recrystallization from ether–petroleum

(1) R. S. Wright and H. G. Khorana, THIS JOURNAL, **77**, 3423 (1955), and in press.

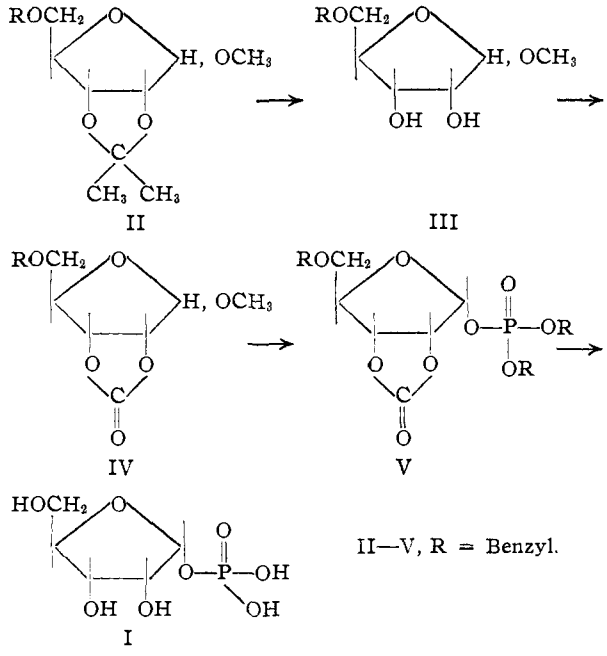
(2) H. M. Kalckar, *J. Biol. Chem.*, **167**, 477 (1947).

(3) H. L. A. Tarr, *Fed. Proc.*, **14**, 291 (1955). We are grateful to Dr. Tarr for the enzymatic tests on the synthetic sample of D-ribose-1-phosphate.

(4) See *e.g.* B. R. Baker, *et al.*, *J. Org. Chem.*, **18**, 1786 (1954).

(5) P. A. Levene and E. T. Stiller, *J. Biol. Chem.*, **104**, 299 (1934); G. W. Kenner, C. W. Taylor and A. R. Todd, *J. Chem. Soc.*, 1620 (1949).

(6) *Cf.* C. H. Shunk, J. B. Lavigne and K. Folkers, THIS JOURNAL, **77**, 2210 (1955).



II—V, R = Benzyl.

ether, 59°, $[\alpha]^{20}D$ −54.5° (*c* 1.06 in ethyl alcohol) *Anal.* Calcd. for $C_{14}H_{16}O_6$; C, 59.5; H, 5.7. Found: C, 59.9; H, 5.8. The crystalline product was converted by treatment with hydrogen bromide–acetic acid to an oily bromide which was directly treated in benzene with one equivalent of triethylammonium dibenzylphosphate to give presumably V. Hydrogenolysis of this product in the presence of palladium-charcoal catalyst, followed by mild alkaline treatment, gave α-D-ribofuranose-1-phosphate which was isolated as the barium salt in 60% yield (based on the crystalline carbonate, IV). The dicyclohexylammonium salt, prepared by passing a solution of the barium salt through a column of Amberlite IR-120-cyclohexylammonium form, was crystallized from a methyl alcohol–ether mixture. *Anal.* Calcd. for $C_{17}H_{37}O_8N_2P \cdot H_2O$: C, 45.74; H, 8.81; P, 6.94. Found: C, 45.38; H, 8.82; P, 7.4; $[\alpha]^{20}D$ +40.3° (*c* 2.37 in water).[7] In lability to acid, behavior on paper chromatograms and reaction with dicyclohexylcarbodiimide,[1] the synthetic sample was identical with the enzymatically-prepared samples of ribose-1-phosphate. Incubation of the synthetic sample with fish muscle phosphorylase in the presence of hypoxanthine gave rise to the corresponding riboside, inosine.

It is clear that the crystalline methyl 5-benzylribofuranoside 2,3-cyclic carbonate offers a promising route to the synthesis of α-D-ribonucleosides as well as other ribose phosphates.[8,9] These synthetic possibilities are under investigation.

We wish to thank the National Research Council of Canada, Ottawa, for the financial support of this work and Dr. D. R. Idler for the microanalyses.

(7) Dr. D. H. Hayes in a private communication stated that a crystalline sample of dicyclohexylammonium ribose-1-phosphate prepared enzymatically had $[\alpha]^{22}D$ +53° (*c* 0.519 in water). We are grateful to Drs. Hayes and Kalckar for a sample of their material.

(8) H. Klenow, *Arch. Biochem. Biophysics*, **46**, 186 (1953).

(9) A. Kornberg, I. Lieberman and E. S. Simms, *J. Biol. Chem.*, **215**, 389 (1955).

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BOOK REVIEWS

Some Aspects of the Crystallization of High Polymers. BY G. SCHUUR, Member of the Staff of the Rubber-Stichting. Rubber-Stichting, Oostsingel 178, Delft, The Netherlands. 1955. 82 pp. 15.5 × 24 cm. Price, Five Dutch florins.

This short book (82 pages) is essentially a review paper of certain aspects of crystallization phenomena in high polymeric systems. The five chapters are concerned with: a general introduction; formation, structure and melting of spherulites; mechanism of crystallization; continuity of the crystal lattice, particularly in oriented and stretched polymers; rate phenomena and the melting range. The author refers frequently to papers published up to and including 1954, making this booklet quite up to date.

In addition to a thorough discussion of the published work on those topics selected, this book contains an appreciable amount of original material by the author. It is well organized and written. This reviewer was particularly taken by the beautiful microphotographs of spherulites taken with polarized light. The diagrams showing the growth of these spherulites are unusually clear.

This book is recommended to the attention of those interested in the crystal properties of high polymers. It is not at all complete, since the author addressed himself only to "some aspects," particularly those dealing with the natural rubber systems. For example, there is not a detailed discussion of the excellent, recent work on the crystalline high polymers. Therefore, within the limits which the author has set for himself, he has done an excellent job.

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Dielectric Behavior and Structure. Dielectric Constant and Loss, Dipole Moment and Molecular Structure. BY CHARLES PHELPS SMYTH, Professor of Chemistry, Princeton University. International Chemical Series, Louis P. Hammett, Ph.D., Consulting Editor. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y. 1955, x + 441 pp. 16.5 × 23.5 cm. Price $9.00.

In 1931, Professor Smyth gave us a book on dielectric constant and molecular structure, which provided a very timely and useful survey of a rapidly growing field of work. Since then there has been great progress in which he and his pupils have taken a leading part. He has now placed us further in his debt by writing a completely new book covering not only the original topic but also several others which have developed collaterally and concurrently.

It is now possible to write a more or less definitive book. Basic theory is not likely to develop very rapidly. The methods of applying dipole moment measurements to the elucidation of chemical problems are now standard; and much the same is true of the methods of using other properties