Jan., 1950

The last of these is the model proposed by Dr. Price, with

Al-B	2.19 Å.	В–Ң′	1. <b>2</b> 9 Å.
B–H°	1.20	B–B	3.79

The qualitative appearance of the computed intensity curves of these does not agree as well with the visual pattern as does the original model proposed by Beach and Bauer (type  $\alpha$ ); however, A and B are nevertheless admissible; C, D and E are definitely eliminated.

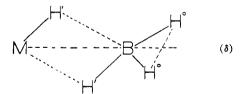
Models  $F \cdots J$  are of the  $\gamma \angle$  type; the common distances are

			H 1.18Å.	
F 🖌	A1BH' =	69.5° A	1-H' = 2.20  Å.	B-H' = 1.66  Å
G		55.8	1.80	1.54
н		<b>3</b> 6	1.30	1.53
J		45	1.51	1.51

In this group, the qualitative appearance of F and G are compatible with the experimental data.

We may therefore conclude that the available electron diffraction data are compatible with  $\gamma$ type models for Al(BH<sub>4</sub>)<sub>8</sub>, wherein: Al-B, 2.15 Å.; B-H' 1.28; Al-H', 2.1 Å.; B-H°, 1.21;  $\angle$  AlBH', 60°. The  $\gamma_{\perp}$  are preferable to the  $\gamma_{\angle}$ configurations.

We thus find that the original conclusion that symmetrical bridge structures are inadmissible has been confirmed; however, the BH<sub>4</sub> tetrahedra may be oriented with a twofold axis ( $\gamma$ ) rather than a threefold axis ( $\alpha$ ) along the M-B bond. Were larger amounts of material available so that sector photographs, and diffraction patterns covering a large angular range, could be prepared, an unambiguous decision between these two might be made. Indeed, then it would be worthwhile to test configurations of the type



However, one conclusion is pertinent—on the basis of either the  $\alpha$  or  $\gamma$  model, the boron atom is surrounded by four hydrogens situated approximately at the corners of a tetrahedron, as in LiBH<sub>4</sub>, etc. According to Harris and Meibohm,<sup>3</sup> in lithium borohydride the Li<sup>+</sup> ions are actually surrounded by rough tetrahedra of H atoms, but each hydrogen comes from a different BH<sub>4</sub><sup>-</sup> group.

**Acknowledgment.**—The author wishes to thank the Office of Naval Research which provided funds for computers and draftsmen, under contract number N6-ori-213, Task 1, and Harvard University for its hospitality.

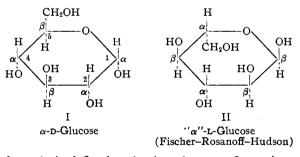
DEPARTMENT OF CHEMISTRY CORNELL UNIVERSITY ITHACA, NEW YORK

RECEIVED MAY 27, 1949

## Nomenclature of the Sugars

## By LOUIS F. FIESER\*

In 1909 Hudson<sup>1</sup> pointed out certain numerical relations in the optical rotations of glycosidic epimers of the ring forms of sugars and their glycosides, deduced a set of empirical rules, and applied these rules to definition of his familiar rules of nomenclature. After many years of search for evidence on the question of whether or not the  $\alpha$ - and  $\beta$ -allocations deduced from rotatory relations are really correct, an unequivocal experimental method of determining the configurations was found in application of the elegant method of periodate oxidation of methyl glycosides,<sup>2</sup> and the results confirmed in all respects the allocations previously deduced through rotatory relations.<sup>3</sup> Thus in the Dseries, the originally trivial prefix " $\alpha$ " now stands for a rigorously established configuration of the glycosidic carbon atom and has the same significance in defining an orientation relative to the rest of the molecule as the prefix  $\alpha$  does in the sterol series.<sup>4</sup> When the Haworth perspective formula<sup>5</sup> for  $\alpha$ -D-glucose is oriented with the oxidic oxygen at the top or rear and  $C_1$  to the right, the C<sub>1</sub>-hydrogen projects up or to the front (full line) and the C1-hydroxyl projects down or to the rear (dotted line). If  $C_1$  in this



formula is defined as having the  $\alpha$ -configuration, or if the 1-hydroxyl group is defined as  $\alpha$ -oriented, then by logical extension the same scheme can be applied to the other four asymmetric centers: if a hydroxyl, alkyl or other substituent besides hydrogen projects down or to the rear, the carbon

\* Harvard University Ph.D. 1924; Faculty 1930-.

(1) C. S. Hudson, This Journal, 31, 66 (1909).

(2) B. L. Jackson and C. S. Hudson, *ibid.*, **58**, 378 (1936); **59**, 994 (1937).

(3) Claude S. Hudson, "Collected Papers," II, Academic Press, New York, N. Y., 1948, pp. 1125-1182.

(4) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1949.

(5) W. N. Haworth, "The Constitution of the Sugars." Edward Arnold and Co., London, 1929.

atom concerned has the  $\alpha$ -configuration. In an  $\alpha$ -D-fructopyranose the 2-OH is in the  $\alpha$ -orientation and the 2-CH<sub>2</sub>OH in the  $\beta$ -orientation. The carbon centers in  $\alpha$ -D-glucose, as shown in formula I, are:  $1\alpha$ ,  $2\alpha$ ,  $3\beta$ ,  $4\alpha$ ,  $5\beta$ .

In the Fischer-Rosanoff system of nomenclature as defined by Hudson,<sup>6</sup> the enantiomer of  $\alpha$ -D-glucose of formula II is called  $\alpha$ -L-glucose, but the true meaning is conveyed more accurately by the designation " $\alpha$ "-L-glucose, for the prefix is used merely in a trivial sense and does not bear the connotation of configuration. Since the actual configurations are established with certainty, it would seem rational to abandon the trivial designations in favor of prefixes that have configurational significance. The enantiomer of  $\alpha$ -D-glucose is the exact optical opposite at all centers, including C<sub>1</sub>, and is properly described as:  $1\beta$ ,  $2\beta$ ,  $3\alpha$ ,  $4\beta$ ,  $5\alpha$ .

The proposed system can be distinguished from that in current use by including in the name a number indicating the carbon atom whose configuration is defined by  $\alpha$  or  $\beta$ . Thus I is  $1\alpha$ -Dglucose (or  $1\alpha$ -D-glucopyranose); II is  $1\beta$ -L-glucose; methyl  $\alpha$ -D-fructopyranoside is more specifically described as methyl  $2\alpha$ -D-fructopyranoside. For purposes of discussion it may be convenient to state that  $1\alpha$ -D-mannopyranose is the  $2\beta$ -epimer of  $1\alpha$ -D-glucopyranose, or that methyl  $1\alpha$ -L-idopyranoside is the  $5\alpha$ -epimer of methyl  $1\alpha$ -D-glucopyra-The important relationship discovered by noside. Hudson<sup>1</sup> can be so stated that one rule is applicable to all types of cyclic sugars of both the D- and Lseries: in a pair of glycosidic epimers, the isomer with the glycosidic hydroxyl or alkoxyl group in the  $\alpha$ -orientation is invariably more dextrorotatory than the  $\beta$ -epimer. A relationship discovered by Isbell<sup>7</sup> can be stated as follows: a 1 $\alpha$ -D-pyranose, in which C<sub>1</sub> and C<sub>5</sub> are  $\alpha$  and  $\beta$ , respectively, or *trans*, is oxidized much more slowly than the  $1\beta$ -epimer in which they are  $\beta$ and  $\hat{\beta}$ , or cis.

(6) C. S. Hudson, "Historical Aspects of Emil Fischer's Fundamental Conventions for Writing Stereo-Formulas in a Plane," *Adv. in Carbohydrate Chem.*, **3**, 1 (1948).

(7) H. S. Isbell, J. Research Natl. Bur. Standards, 18, 505 (1937), RP 990; H. S. Isbell and W. W. Pigman, *ibid.*, 18, 141 (1937) RP 969; H. S. Isbell, J. Chem. Educ., 12, 96 (1935).

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**Received October 8, 1949** 

## Polytetramethylene Sebacate: Pyrophoric Lead as an Ester Interchange Catalyst

By C. S. MARVEL\* AND JOHN H. JOHNSON<sup>1</sup>

In preparing polytetramethylene sebacate from butane-1,4-diol and dimethyl sebacate with a litharge catalyst, one run gave a better grade of polyester than had been obtained before. In this polyester sample there was a black deposit that

\* Editorial Board 1943-.

(1) Allied Chemical and Dye Corporation Fellow, 1948-1949.

appeared to be finely divided lead. As a result, pyrophoric lead<sup>2</sup> was tried as a catalyst in this interchange reaction and found to work well. The use of a wide variety of finely divided metals as catalysts for the preparation of polyethylene terephthalate from ethylene glycol and dimethyl terephthalate has been described<sup>8</sup> but no mention was made of pyrophoric lead.

The polyesters were prepared in an apparatus similar to that described by Hardy<sup>4</sup> from 11.8 g. of dimethyl sebacate and 5.0 g. of butane-1,4-diol. The charges were heated with the 0.1 g. of catalyst under varying conditions and then the polyesters were purified by solution in chloroform, filtration and reprecipitation with acetone. The following cases seem sufficient to indicate that pyrophoric lead is a satisfactory catalyst in this type of reaction. The yields are essentially quantitative.

**Run No. 1:** 0.1 g. of litharge as catalyst; reaction mixture heated for two hours at 183° and atmospheric pressure, then for one hour at 259° and 0.1 mm. pressure. The polymer was isolated and the intrinsic viscosity taken in 0.4% solution in chloroform at 25.5°;  $[\eta]$  0.61.

in 0.4% solution in chloroform at 25.5°;  $[\eta]$  0.61. **Run No.** 2: Same catalyst as No. 1; reaction mixture heated three hours at 155° and atmospheric pressure and one hour at 155° and 0.03 mm. pressure;  $[\eta]$  0.33.

**Run No. 3:** 0.1 g. of pyrophoric lead; reaction mixture heated two hours at 172° and atmospheric pressure and six hours longer at 1 mm;  $[\eta]$  0.98.

**Run No. 4**: Same catalyst as No. 3; reaction mixture heated three hours at  $172^{\circ}$  and atmospheric pressure, then three hours at 0.1 mm.;  $[\eta] 0.55$ .

Anal. Caled. for  $C_{14}H_{24}O_4$ : C, 65.60; H, 9.44. Found: C, 65.45; H, 9.63.

The polyesters obtained with pyrophoric lead were whiter than those from the litharge runs. The polymers all melted at  $64-64.5^{\circ}$ .

(2) King, "Inorganic Preparations," D. Van Nostrand Company, New York, N. Y., 1936, p. 24.

(3) British Patent, 578,079.

(4) Hardy, J. Soc. Chem. Ind., 67, 426 (1948).

NOYES CHEMICAL LABORATORY

UNIVERSITY OF ILLINOIS

URBANA, ILLINOIS RECEIVED SEPTEMBER 19, 1949

## Preparation of Naphthyl Acid Phosphates<sup>1</sup>

By Orrie M. Friedman\* and Arnold M. Seligman<sup>†</sup>

Methods for the histochemical demonstration of alkaline phosphatase<sup>2</sup> and acid phosphatase<sup>3</sup> have been developed utilizing as substrates the calcium salts of  $\alpha$ - and  $\beta$ -naphthyl acid phosphates. Following enzymatic hydrolysis of these substrates, coupling with a suitable diazonium compound, results in the deposition of an insoluble azo dye at the site of enzymatic activity.

Although the calcium salts of these phosphoric esters are readily prepared<sup>2,3</sup> their poor solubility in water requires their use in a fine suspension for

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† Harvard Upiversity Assistant Professor of Surgery, Medical School.

(1) This investigation was supported by a research grant from the National Cancer Institute of the National Institutes of Health, Public Health Service.

(2) (a) Menten, Junge and Green, J. Biol. Chem., 153, 471 (1944).
(b) Manheimer and Seligman, J. Nat. Cancer Instit., 9, 181 (1948).

(3) Seligman and Manheimer, ibid., 9, 427 (1949).