atom concerned has the α-configuration. In an α-D-fructopyranose the 2-OH is in the α-orientation and the 2-CH$_2$OH in the β-orientation. The carbon centers in α-D-glucose, as shown in formula I, are: 1α, 2α, 3β, 4α, 5β.

In the Fischer–Rosanoff system of nomenclature as defined by Hudson,[6] the enantiomer of α-D-glucose of formula II is called α-L-glucose, but the true meaning is conveyed more accurately by the designation "α"-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 α-D-glucose is the exact optical opposite at all centers, including C_1, and is properly described as: 1β, 2β, 3α, 4β, 5α.

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 α or β. Thus I is 1α-D-glucose (or 1α-D-glucopyranose); II is 1β-L-glucose; methyl α-D-fructopyranoside is more specifically described as methyl 2α-D-fructopyranoside. For purposes of discussion it may be convenient to state that 1α-D-mannopyranose is the 2β-epimer of 1α-D-glucopyranose, or that methyl 1α-L-idopyranoside is the 5α-epimer of methyl 1α-D-glucopyranoside. The important relationship discovered by Hudson[1] can be so stated that one rule is applicable to all types of cyclic sugars of both the D- and L-series: in a pair of glycosidic epimers, the isomer with the glycosidic hydroxyl or alkoxyl group in the α-orientation is invariably more dextrorotatory than the β-epimer. A relationship discovered by Isbell[7] can be stated as follows: a 1α-D-pyranose, in which C_1 and C_5 are α and β, respectively, or *trans*, is oxidized much more slowly than the 1β-epimer in which they are β and β, 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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Polytetramethylene Sebacate: Pyrophoric Lead as an Ester Interchange Catalyst

BY C. S. MARVEL* AND JOHN H. JOHNSON[1]

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 appeared to be finely divided lead. As a result, pyrophoric lead[2] 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[3] but no mention was made of pyrophoric lead.

The polyesters were prepared in an apparatus similar to that described by Hardy[4] 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.

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° and atmospheric pressure, then three hours at 0.1 mm.; $[\eta]$ 0.55.

Anal. Calcd. 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°.

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* Editorial Board 1943–.

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

(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).

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Preparation of Naphthyl Acid Phosphates[1]

BY ORRIE M. FRIEDMAN* AND ARNOLD M. SELIGMAN†

Methods for the histochemical demonstration of alkaline phosphatase[2] and acid phosphatase[3] have been developed utilizing as substrates the calcium salts of α- and β-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[2,3] their poor solubility in water requires their use in a fine suspension for

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(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).

the histochemical methods. The phosphoric acid esters, on the other hand, dissolve readily in buffered solutions, and were found to be more satisfactory for both the histochemical methods and for serum phosphatase determinations.[4]

The preparation of α-naphthylphosphoryl dichloride as described by Kunz[5] was repeated with difficulty and gave poor yields. Good yields were obtained of both alpha and beta isomers by treatment of an equimolar mixture of naphthol and phosphorus oxychloride in dry benzene with one equivalent of pyridine. Di-α-naphthylphosphoryl chloride was similarly prepared from the appropriate amounts of naphthol, phosphorus oxychloride and pyridine.

The hydrolysis of the naphthylphosphoryl dichlorides to the corresponding naphthyl acid phosphates was effected quantitatively by exposure of the acid chlorides to a moist atmosphere over aqueous alkali in an evacuated desiccator. β-Naphthyl acid phosphate was obtained also by solution of the dichloride in water. Kunz[5] reported the preparation of α-naphthyl acid phosphate (m. p. 142°) by hydrolysis of the dichloride with cold water but gave no analysis. The melting point of the product obtained by moist air hydrolysis is twelve degrees higher than that given by Kunz.[5] Hydrolysis of di-α-naphthylphosphoryl chloride to the acid phosphate could not be effected with moist air and was accomplished either with acetone and water or with pyridine and water. With the latter procedure the product was isolated as the pyridinium salt.

Experimental Part[6]

α-Naphthylphosphoryl Dichloride.—A solution of 25 g. of crude α-naphthol and 26.5 g. (15.5 cc.) of phosphorus oxychloride in 90 cc. of dry benzene heated under reflux was treated with 13.7 g. of dry pyridine by slow addition over a period of thirty minutes. During the addition a precipitate of pyridine hydrochloride began to form. The mixture was heated for an additional fifteen minutes, and after cooling, a voluminous precipitate of pyridine hydrochloride was removed by filtration. The solvent was distilled and the residue on distillation gave a fraction, b. p. 195–205°, 70 mm., which on redistillation was obtained as a clear colorless sirup, b. p. 199–201°, 20 mm., n^{27}_D 1.596, 34 g. (93%).

α-Naphthyl Acid Phosphate.—When a sample of α-naphthylphosphoryl dichloride as a thin layer (2–3 mm.) was stored in a shallow dish in a partially evacuated desiccator for two days over aqueous potassium hydroxide there occurred a quantitative conversion to α-naphthyl acid phosphate obtained as a white crystalline solid, m. p. 155–157°.

Anal. Calcd. for $C_{10}H_9PO_4$: C, 53.56; H, 4.05. Found: C, 53.72; H, 3.96.

A convenient method for carrying out this transformation in amounts up to 150 g. was provided by the use of large Petri dishes stacked in a vacuum desiccator. Longer periods of five to six days were required for completion of the reaction. The *monosodium salt* was precipitated from a solution of the acid phosphate in methanol by addition of an equivalent of sodium methoxide in methanol.

Di-α-naphthylphosphoryl Chloride.—To a solution of 23.2 g. of crude α-naphthol in 80 cc. of refluxing dry benzene was added at once 7.2 cc. of phosphorus oxychloride and then over a period of thirty minutes a solution of 12.8 cc. of dry pyridine in 20 cc. of dry benzene was added. A precipitate of pyridine hydrochloride formed part way through the addition. Heating was continued for an additional hour. After the mixture cooled, the pyridine hydrochloride was separated on a filter, the solvent was distilled and the residue fractionated at reduced pressure. After separation of the sublimate in the fore-run the fraction, b. p. 250–265°, 0.3 mm., was obtained as a yellow sirup which immediately began to crystallize, 12.5 g. (41%). The product crystallized from benzene-benzin as fine needles, m. p. 88–90°.

Anal. Calcd. for $C_{20}H_{14}PO_3Cl$: C, 65.13; H, 3.83. Found: C, 64.50; H, 3.93.

Di-α-naphthylphosphate. (a) From Di-α-naphthylphosphoryl Chloride in Acetone with Water.—A solution of 1.0 g. of the dichloride in 10 cc. of acetone to which 5 cc. of water was added, was heated on the steam-cone until precipitation of an oil occurred. The oil crystallized after standing for several hours and was obtained as a fine white powder, m. p. 134–137°, 0.9 g. (94%). The product was recrystallized from methanol-water as fine needles, m. p. 137–139°.

Anal. Calcd. for $C_{20}H_{15}PO_4$: C, 68.65; H, 4.28. Found: C, 68.75; H, 4.46.

(b) In Pyridine with Water.—A solution of 0.5 g. of di-α-naphthylphosphoryl chloride in two cc. of warm pyridine diluted with 10 cc. of water was heated on the steam-bath for ten minutes and then further diluted to a volume of 50 cc. After standing in the cold the resulting milky suspension precipitated fine shining white flakes. The product which proved to be a pyridinium salt was filtered and after treatment with Norit in hot benzene crystallized as fine fluffy white needles, 0.4 g. (89%), m. p. 105–106°. This material gave a strong odor of pyridine when treated with aqueous alkali.

Anal. Calcd. for $C_{20}H_{15}PO_4 \cdot C_5H_5N$: C, 69.92; H, 4.69. Found: C, 70.47; H, 5.17.

β-Naphthylphosphoryl Dichloride.—The procedure followed was identical to that described for the preparation of α-naphthylphosphoryl dichloride. There was obtained 31 g. of crude product b. p. 145–155°, 1 mm., which on redistillation gave 27 g. (75%) of a water-white sirup b. p. 150–155°, 1 mm. The product crystallized on standing as a solid mass, m. p. 34–35°.

Anal. Calcd. for $C_{10}H_7PO_2Cl_2$: C, 45.97; H, 2.68. Found: C, 45.91; H, 2.61.

β-Naphthyl Acid Phosphate.—A quantitative hydrolysis of β-naphthylphosphoryl dichloride was accomplished in identical manner to that described for the alpha isomer; the product m. p. 176–177°. The identical product was obtained when 2.6 g. of the phosphoryl dichloride was dissolved by warming in 10 cc. of water. On cooling there precipitated 2.0 g. (83%) of granular product, m. p. 176–177°.

Anal. Calcd. for $C_{10}H_9PO_4$: C, 53.56; H, 4.05. Found: C, 53.36; H, 4.24.

The monosodium salt was precipitated from a solution of the acid phosphate in methanol by addition of an equivalent of sodium methoxide in methanol.

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[4] Seligman, Chauncey, Manheimer and Nachlas, unpublished results.

[5] Kunz, *Ber.*, **27**, 2559 (1894).

[6] Analyses by Shirley R. Golden all melting points corrected.

Dehydration Products of α- and β-Amyrin

BY C. R. NOLLER* AND P. J. HEARST

α- and β-amyrin are triterpene alcohols having the empirical formula $C_{30}H_{50}O$. Three different

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