

dropwise while the mixture was stirred and the temperature maintained at 5–10°. The mixture was stirred for three hours at 5–10° and three hours at 25°. It was then washed with water and distilled under reduced pressure to give 74 g. of bromoform and 7 g. of product, b. p. 126–128° (6 mm.), which solidified in the receiver. Upon recrystallization from petroleum ether the  $\gamma$ -tribromobutyronitrile formed colorless needles melting at 98° (uncor.).

*Anal.* Calcd. for  $C_4H_4Br_3N$ : C, 15.71; H, 1.31; Br, 78.41; N, 4.58. Found: C, 15.80; H, 1.38; Br, 77.90; N, 4.65.

The compound is soluble in alcohol, ether, acetone, benzene, and ethylene dichloride, and is slightly soluble in cold petroleum ether.

**$\gamma$ -Tribromobutyramide.**—A mixture of 13 g. of 30% hydrogen peroxide, 25 g. of water, 0.2 g. of sodium hydroxide and 5 g. of  $\gamma$ -tribromobutyronitrile was stirred at 40–45° for five hours and allowed to stand overnight. The white solid material (3 g.) was filtered off, dried and recrystallized from petroleum ether. It formed colorless crystals, m. p. 102–103° (uncor.). *Anal.* Calcd. for  $C_4H_6Br_3NO$ : C, 14.82; H, 1.87; Br, 74.04; N, 4.32. Found: C, 15.00; H, 1.90; Br, 73.70; N, 4.21.

**$\gamma$ -Tribromobutyric Acid.**—A mixture of 7 g. of  $\gamma$ -tribromobutyronitrile and 40 g. of concentrated hydrochloric acid was heated at 60–65° for six hours with rapid stirring. The mixture was allowed to stand overnight. The crystalline product consisting of a mixture of the amide and the acid was washed with water and shaken with a 10% sodium carbonate solution to extract the acid, leaving 2 g. of the insoluble amide. The sodium carbonate extract was acidified with hydrochloric acid to yield 3 g. of  $\gamma$ -tribromobutyric acid which separated in the form of colorless crystals. The analytical sample upon recrystallization from petroleum ether melted at 94–95°. *Anal.* Calcd. for  $C_4H_5Br_3O_2$ : C, 14.78; H, 1.55; Br, 73.82. Found: C, 14.90; H, 1.60; Br, 73.50.

**Reaction of Iodoform with Acrylonitrile.**—Five grams of aqueous 40% trimethylbenzylammonium hydroxide was added at 20° to a solution of 39.4 g. of iodoform in 50 g. of dioxane. Acrylonitrile (11 g.) was added dropwise while the mixture was stirred at 18–23°. After stirring for twenty-four hours the product was filtered and the yellow solid (6 g.) recrystallized first from nitromethane and then from alcohol to give yellow needles m. p. 132–133°. It is only slightly soluble in benzene, alcohol and acetone. The product is an addition compound  $C_6H_5-CH_2N(CH_3)_3I-CHI_3$  instead of  $\gamma$ -tri-iodobutyronitrile. *Anal.* Calcd. for  $C_{11}H_{17}NI_4$ : C, 19.68; H, 2.56; N, 2.09; I, 75.67. Found: C, 19.80; H, 2.64; N, 2.05; I, 75.70. The filtrate did not yield  $\gamma$ -tri-iodobutyronitrile.

The same addition product can be obtained by mixing alcoholic solutions of iodoform and trimethylbenzylammonium iodide.

**Acknowledgment.**—The analyses of the above compounds were made by Mr. C. W. Nash of these laboratories.

### Summary

1. Acrylonitrile reacts in the presence of alkaline catalysts with chloroform and with bromoform to yield  $\gamma$ -trihalo-butyronitriles,  $\begin{matrix} X \\ X \\ X \end{matrix} \text{C}-CH_2CH_2CN$ . Iodoform did not react with acrylonitrile under the same conditions.

2. From  $\gamma$ -trichlorobutyronitrile and  $\gamma$ -tribromobutyronitrile the corresponding  $\gamma$ -trihalo-butyramides and  $\gamma$ -trihalo-butyric acids were prepared.

PHILADELPHIA, PA.

RECEIVED DECEMBER 30, 1944

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

## 2,4:3,5-Dimethylene-L-Iditol and Some of its Derivatives

BY RAYMOND M. HANN AND C. S. HUDSON

There is an uncertainty in the literature concerning formaldehyde acetals of iditol. Lobry de Bruyn and Alberda van Ekenstein<sup>1</sup> prepared from L-iditol,<sup>2</sup> formalin and concentrated hydrochloric acid a crystalline acetal which was first designated (p. 8) a trimethylene-L-iditol and later (p. 180) shown to be a dimethylene-iditol; its melting point was 262° and they reported that it was sufficiently soluble in chloroform to permit a reading of its rotation, which was  $[\alpha]_D -8^\circ$  (c, 0.2). They also prepared the enantiomorphous dimethylene-D-iditol. Six years later Bertrand and Lanzenberg<sup>3</sup> prepared an acetal which they reported to be a trimethylene-D-iditol by heating D-iditol, formaldehyde and fuming hydrochloric acid in a sealed tube at 100°; it was not sufficiently soluble in chloroform to permit a read-

ing of its rotation, but the value in glacial acetic acid was "about  $-35^\circ$ ." It began to sublime on the "bloc Maquenne" at 250° and the crystals hardly melted until about 300–305° ("les cristaux ne fondant guère que vers 300–305°"). It is evident from their statements on p. 1079 that they were not acquainted with Lobry de Bruyn and Alberda van Ekenstein's analysis (p. 180 of reference 1) which showed the composition of a dimethylene acetal of iditol, because they regarded their substance as identical with the "trimethylene" acetal which those workers had made. We have recently had occasion to study the formation of an acetal from L-iditol, 37% aqueous formaldehyde and concentrated hydrochloric acid under various conditions of temperature. Only one acetal has been found and it is readily produced in high yield. The best conditions seem to be slow evaporation of the reactants at room temperature; the yield was 97%. Its melting point is 264–266° in a capillary tube and its  $[\alpha]_D^{20}$  in glacial acetic acid is  $+37^\circ$ ; in water the  $[\alpha]_D^{20}$  value is  $+39.2^\circ$ . Its solubility in

(1) Lobry de Bruyn and Alberda van Ekenstein, *Rec. trav. chim.*, **19**, 8, 180 (1900).

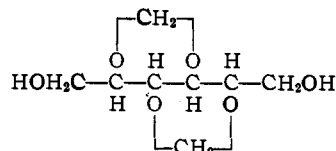
(2) Rosanoff's D and L nomenclature for the iditols is used throughout this article; the letters are the reverse of those used in references 1 and 3.

(3) Bertrand and Lanzenberg, *Bull. soc. chim.*, [3] **35**, 1078 (1906).

chloroform, namely, 0.002% at 20°, is not sufficient to permit a reading of its rotation. Analysis proves that it is a dimethylene-iditol and this conclusion is confirmed by the analyses of several derivatives from it. We believe that this dimethylene-iditol is the substance that the previous investigators had in hand in the enantiomorphous forms, even though Bertrand and Lanzenberg reported analytical data which conform with the composition of a trimethylene-iditol; we have repeated their precise directions (starting with crystalline L-iditol) and have obtained the dimethylene-iditol in 74% yield as the sole crystalline product of the reaction. As previously mentioned, its rotation in glacial acetic acid is near the value which Bertrand and Lanzenberg reported for its enantiomorph and is of the opposite sign; its melting point agrees with the data of Lobry de Bruyn and Alberda van Ekenstein. The older data concerning this dimethylene-iditol having now become clarified, there remains the problem of determining the structure of the substance.

Dimethylene-L-iditol forms a ditosyl derivative which readily exchanges both tosyloxy groups for iodine when it is heated with a solution of sodium iodide in acetylacetone<sup>4</sup>; this is good evidence by the Oldham-Rutherford rule<sup>5</sup> that the tosyl groups are attached to the terminal carbon atoms. If such be indeed the case the diacetal is 2,3,4,5-dimethylene-L-iditol. When the diacetal reacts with a 2% sulfuric acid acetylizing solution there results in 88% yield a diacetyl-dimethylene-L-iditol, but no acetoxymethyl derivative could be found; this is confirmatory evidence that the two acetal rings involve only secondary hydroxyls,<sup>6</sup> in agreement with the 2,3,4,5-dimethylene structure. Finally, conclusive proof that the structure is 2,4:3,5-dimethylene-L-iditol was obtained through oxidation of the substance in glacial acetic acid solution with chromic anhydride. The oxidation product is a dimethylene-idosaccharic acid which proves to be identical with the dimethylene-L-idosaccharic acid which Haworth, Jones, Stacey and Wiggins<sup>7</sup> obtained by the inversion, at carbon atom 5, of their dimethylene-D-glucosaccharic acid. The latter acid was obtained by Haworth and Wiggins<sup>8</sup> through oxidation of a 2,3,4,5-dimethylene-D-sorbitol which has since been shown<sup>9</sup> to possess the definitive 2,4:3,5 structure. This structure therefore applies to dimethylene-iditol and the diacetal from L-iditol is 2,4:3,5-dimethylene-L-iditol (I).

In a recent article<sup>10</sup> we have shown that this structure conforms with the generalizations that were there proposed concerning the relationship between the configurations of polyhydroxy alco-



2,4:3,5-Dimethylene-L-iditol (I)

hols and the corresponding structures of their usual formaldehyde and benzaldehyde acetals.

We express our appreciation to Dr. A. T. Ness for performing the analyses and to Dr. Alice T. Merrill and Mr. Harry W. Diehl for assistance in the preparation of some of the derivatives.

### Experimental

**Hexaacetyl-L-iditol from L-Sorbose.**—A solution of 50 g. of L-sorbose in 350 cc. of water was agitated at 100° for six hours with 10 g. of Raney nickel and hydrogen under a pressure of 133 atmospheres. The catalyst was separated by filtration and the filtrate was concentrated *in vacuo* to a sirup which was dried by the successive addition and evaporation of two 100-cc. portions of absolute alcohol; the solid was then heated for thirty minutes on the steam-bath with 10 g. of fused sodium acetate and 200 cc. of acetic anhydride. The cooled solution was poured upon crushed ice and the mixture of hexaacetates of D-sorbitol and L-iditol which precipitated was separated by filtration. The yield was 94 g. (78%). The mixed hexaacetates were dissolved in 10 parts of hot alcohol and after crystallization had progressed for eighteen hours at 23° the almost pure hexaacetyl-L-iditol (m. p. 120–122°;  $[\alpha]^{20}_D$  in chloroform  $-23.4^\circ$ ) which had deposited, was collected. The yield was 42.5 g. (35%). One recrystallization from 10 parts of alcohol gave a product which melted at 121–122° and rotated  $[\alpha]^{20}_D -25.5^\circ$  in chloroform (*c.* 3.36); these constants are in good agreement with those of 121.5° and  $[\alpha]^{16}_D -25.5^\circ$ , respectively, recorded by Bertrand.<sup>11</sup> Jones and Wiggins<sup>12</sup> reported values of 122° and  $-24.8^\circ$  in chloroform (*c.* 5.63), respectively, for hexaacetyl-L-iditol.

**L-Iditol from Hexaacetyl-L-iditol.**—Fifty grams of the hexaacetate readily dissolved in 200 cc. of methyl alcohol containing 5 cc. of *N* sodium methylate during agitation for ten minutes. After the solution had stood overnight it was evaporated to sirupy consistency and it slowly crystallized in the form of hard prisms. After one recrystallization from methyl alcohol the L-iditol melted at 73–74° and rotated  $[\alpha]^{20}_D -3.5^\circ$  in aqueous solution (*c.* 9.95), in agreement with the data of Bertrand<sup>11</sup>; the yield of crystalline hexitol was 16 g. (76%). L-Iditol may be recrystallized also from two and a half parts of ethylene glycol monomethyl ether ("methyl cellosolve") as clear prisms, with many faces developed.

**2,4:3,5-Dimethylene-L-iditol.**—A solution of 21.0 g. of sirupy L-iditol, from the deacetylation of 50 g. of hexaacetyl-L-iditol, in a mixture of 60 cc. of 37% aqueous formaldehyde and 60 cc. of concentrated hydrochloric acid was allowed to concentrate slowly at 25° in an evacuated desiccator containing small beakers of concentrated sulfuric acid and sodium hydroxide pellets. The initial deposition of crystalline material occurred in two days and after one week the precipitate (12.2 g.) was separated by filtration; the mother liquor was returned to the desiccator and as concentration progressed further crops of 4.6, 4.9 and 1.3 g. of crystals were obtained. The various fractions were recrystallized separately from 40 parts of hot water and proved to be a single product, namely, the dimethylene-L-iditol. The yield of 23.0 g. is therefore 97%. We found no evidence of the presence of a trimethylene-L-iditol. Dimethylene-L-iditol crystallizes from its solution in 40 parts of boiling water in the form of elongated thin plates;

(11) Bertrand, *Bull. soc. chim.*, [3] **33**, 166 (1905).

(12) Jones and Wiggins, *J. Chem. Soc.*, 363 (1944).

(4) Murray and Purves, *This Journal*, **62**, 3195 (1940).

(5) Oldham and Rutherford, *ibid.*, **54**, 366 (1932).

(6) Ness, Hann and Hudson, *ibid.*, **65**, 2215 (1943).

(7) Haworth, Jones, Stacey and Wiggins, *J. Chem. Soc.*, 61 (1944).

(8) Haworth and Wiggins, *ibid.*, 58 (1944).

(9) (a) Jones and Wiggins, *J. Chem. Soc.*, 364 (1944); (b) Hann, Wolfe and Hudson, *This Journal*, **66**, 1898 (1944).

(10) Hann and Hudson, *ibid.*, **66**, 1909 (1944).

it is only slightly soluble in boiling methyl and ethyl alcohols and its solubility in U. S. P. chloroform at 20° is only 0.002%. It is soluble in hot glacial acetic acid to the extent of 1-2%; at 20° a saturated solution of the compound in this solvent contains 0.09% and it shows a specific rotation  $[\alpha]^{20D} +37^\circ$ ; because of the low concentration this figure is uncertain in the second digit, but it approximates in value and is opposite in sign to the rotation of  $-35^\circ$  recorded by Bertrand and Lanzenberg<sup>3</sup> for their trimethylene-D-itol. In aqueous solution (*c*, 0.4) the specific rotation  $[\alpha]^{20D}$  is  $+39.2^\circ$ . Upon rapid heating in a capillary tube the diacetal decomposes at 264-266°; when the tube is introduced into the bath at 250° and the rate of heating is about 2° per minute the compound decomposes at 260-262°; Lobry de Bruyn and Alberda van Ekenstein<sup>1</sup> reported a melting point of 262°. In an effort to obtain a trimethylene-L-itol such as Bertrand and Lanzenberg<sup>3</sup> believed their acetal to be, we conducted a methylenation of L-itol according to their directions, namely, by heating a solution of 2.0 g. of crystalline-L-itol in a mixture of 2.5 cc. of 37% aqueous formaldehyde and 5 cc. of fuming hydrochloric acid in a sealed tube at 100° for one hour. The only crystalline reaction product which could be isolated was the above described dimethylene-L-itol and it was obtained in a yield of 1.7 g. (74%).

*Anal.* Calcd. for  $C_8H_{14}O_8$ : C, 46.60; H, 6.84. Found: C, 46.45; H, 6.81.

**1,6-Diacetyl-2,4:3,5-dimethylene-L-itol.**—To a stirred ice-cold acetylating solution, prepared by adding 1 cc. of concentrated sulfuric acid dropwise to a mixture of 35 cc. of acetic anhydride and 15 cc. of acetic acid, 5.0 g. of finely powdered dimethylene-L-itol was added. The diacetal dissolved and after five minutes a crystalline precipitate separated from the solution. The reaction mixture was poured upon 200 g. of crushed ice and when the ice had melted the precipitate (4.7 g.) was separated by filtration. The filtrate was neutralized with sodium bicarbonate and extracted with chloroform in the usual manner; evaporation of the washed extract yielded a further 1.5 g. of reaction product to give a total yield of 6.2 g. (88%). The diacetal diacetate was recrystallized from 100 parts of alcohol or 75 parts of water as glistening needles which melted at 219-220° and rotated  $[\alpha]^{20D} -3.9^\circ$  in chloroform (*c*, 2.01). It is also soluble in methyl alcohol, acetone, pyridine and acetic acid. The same product was obtained by the acetylation of the diacetal with acetic anhydride and sodium acetate. Upon deacetylation it gave a quantitative yield of 2,4:3,5-dimethylene-L-itol.

*Anal.* Calcd. for  $C_{12}H_{18}O_8$ : C, 49.65; H, 6.25;  $CH_3CO$ , 29.7. Found: C, 49.69; H, 6.30;  $CH_3CO$ , 29.7.

**1,6-Dibenzoyl-2,4:3,5-dimethylene-L-itol.**—To a suspension of 2.0 g. of finely powdered 2,4:3,5-dimethylene-L-itol in 20 cc. of ice-cold pyridine 2.5 cc. (2.2 molecular equivalents) of benzoyl chloride was added dropwise; the reaction mixture was allowed to stand at 25° for twenty-four hours during which time almost all of the diacetal dissolved. The precipitate (3.4 g.) which was obtained by pouring the mixture upon crushed ice was collected and suspended in 40 parts of cold chloroform; the small amount of diacetal which had not reacted was separated by filtration and the filtrate was evaporated to recover the diacetal dibenzoate. The yield was 3.2 g. (80%). The compound, upon recrystallization from 160 parts of acetone, formed cottony needles which melted at 242-243° and rotated  $[\alpha]^{20D} +38.6^\circ$  in chloroform (*c*, 0.78). It is readily soluble in chloroform and pyridine, difficultly soluble in hot methyl and ethyl alcohols and insoluble in cold water.

*Anal.* Calcd. for  $C_{22}H_{22}O_8$ : C, 63.76; H, 5.35;  $C_6H_5CO$ , 50.7. Found: C, 63.72; H, 5.41;  $C_6H_5CO$ , 50.6.

**1,6-Ditosyl-2,4:3,5-dimethylene-L-itol.**—A mixture of 5.0 g. of finely powdered 2,4:3,5-dimethylene-L-itol and 11.2 g. (3.3 molecular equivalents) of *p*-toluenesulfonyl chloride in 50 cc. of pyridine was allowed to stand at 50° for forty-eight hours. Some undissolved diacetal (1.5 g.) was separated by filtration and the filtrate was poured into

ice-cold water; the precipitated ditosylate (8.3 g.) was recrystallized by solution in 10 parts of hot acetone and the addition of 50 parts of hot methyl alcohol. The compound (yield, 7.5 g. or 86%), which melted at 187-188° and rotated  $[\alpha]^{20D} +9.0^\circ$  in chloroform (*c*, 0.81), crystallized in the form of small glistening rods. It is readily soluble in dioxane, toluene and ethyl acetate, sparingly soluble in methyl and ethyl alcohols and nearly insoluble in water.

*Anal.* Calcd. for  $C_{22}H_{26}O_{10}S_2$ : C, 51.35; H, 5.09; S, 12.46. Found: C, 51.39; H, 5.02; S, 12.30.

**1,6-Didesoxy-1,6-di-iodo-2,4:3,5-dimethylene-L-itol.**—Upon heating an acetone solution (25 cc.) of 1,6-ditosyl-2,4:3,5-dimethylene-L-itol (1.0 g.) and sodium iodide (1.0 g.) at 100° for two hours only 0.07 g. of sodium tosylate (theory, 0.75 g.) was obtained, indicating that the halogenation was about 10% complete under the usual conditions employed for testing of the applicability of the Oldham-Rutherford rule.<sup>6</sup> Using 25 cc. of acetylacetone as a solvent and a heating period of twenty-four hours at 110°, there were obtained 0.73 g. (97%) of sodium tosylate and 0.79 g. (95%) of 1,6-didesoxy-1,6-di-iodo-2,4:3,5-dimethylene-L-itol. For preparations on a larger scale it was found convenient to reflux a mixture of 5.0 g. of ditosylate, 5.0 g. of sodium iodide and 75 cc. of acetic anhydride for ninety minutes; the cooled reaction mixture was poured into cold water and the precipitated di-halogenated acetal, which was sufficiently pure for use in further syntheses, was separated by filtration. The yield was 4.0 g. (98%). The compound, recrystallized from 115 parts of alcohol, formed glistening platelets which melted at 224-225° and rotated  $[\alpha]^{20D} +43.5^\circ$  in chloroform; it is soluble in cold acetone, ethyl acetate, benzene and dioxane and in warm methyl and ethyl alcohols and insoluble in water.

*Anal.* Calcd. for  $C_8H_{12}O_4I_2$ : C, 22.55; H, 2.84; I, 59.58. Found: C, 22.71; H, 2.86; I, 59.42.

**1,6-Didesoxy-2,4:3,5-dimethylene-L-itol.**—A suspension of 4.0 g. of 1,6-didesoxy-1,6-di-iodo-2,4:3,5-dimethylene-L-itol and 2.0 g. of Raney nickel in a mixture of 150 cc. of methyl alcohol and 6.2 cc. of 20% methyl alcoholic potassium hydroxide solution (2.2 molecular equivalents) was agitated in a glass bottle under a slight positive pressure of hydrogen. In twenty minutes the calculated amount of hydrogen (462 cc. at 27° and 756 mm.) was taken up and no further absorption was noted in an additional forty minutes. The catalyst was separated by filtration and the filtrate was combined with a similar one obtained through the reduction of 4.1 g. of dihalogenated diacetal. The combined filtrates were evaporated to dryness, the crystalline residue was extracted with 5 cc. of ice-cold water to remove soluble salts, and the didesoxy derivative was separated by filtration. The yield was 3.1 g. (94%). The compound was recrystallized from 10 parts of acetone; it formed plates which melted at 203-205° and rotated  $[\alpha]^{20D} +38.4^\circ$  in chloroform (*c*, 0.81). It is soluble in methyl and ethyl alcohols, dioxane and benzene and nearly insoluble in ether and petroleum ether.

*Anal.* Calcd. for  $C_8H_{14}O_4$ : C, 55.16; H, 8.10. Found: C, 55.08; H, 8.21.

**2,4:3,5-Dimethylene-L-idosaccharic Acid from 2,4:3,5-Dimethylene-L-itol.**—To a cold solution of 1.5 g. of chromic anhydride in 200 cc. of glacial acetic acid 1.0 g. of finely powdered 2,4:3,5-dimethylene-L-itol was added and the mixture was agitated on a shaking machine at 25° for twenty-four hours. The solution of the diacetal was incomplete; an additional 1.5 g. of chromic anhydride was added and the shaking was resumed for an additional twenty-four hours. Two such oxidation mixtures were combined and concentrated *in vacuo* to dryness. The dry green residue was dissolved in 150 cc. of cold water and the chromium was precipitated by the addition of 600 cc. of cold 5% aqueous barium hydroxide octahydrate solution. After one hour the precipitate was filtered on a Büchner funnel precoated with a little Filtercel. The gelatinous precipitate was washed with 100 cc. of cold water and then extracted with 200 cc. of boiling water.

The barium was precipitated from the combined filtrates by sulfuric acid and the barium-free solution was concentrated *in vacuo* to dryness. The residue was recrystallized from about 50 parts of ethyl alcohol and then from 20 parts of methyl alcohol. The yield was 1.5 g. (65%). The 2,4:3,5-dimethylene-L-idosaccharic acid rotated  $[\alpha]^{20D} +76.3$  in aqueous solution ( $c$ , 0.83) in agreement with the specific rotation  $[\alpha]^{20D} +76.4^\circ$  for a sample of acid prepared by the epimerization of dimethyl 2,4:3,5-dimethylene-D-glucosaccharate as described in the following section. The melting point of the compound was determined by Dr. C. P. Saylor of the National Bureau of Standards in a microscope furnace of the type designed by Stadnichenko<sup>13</sup> and found to be 298.5–299.0°; in the same apparatus the melting point of the acid which was prepared by epimerization was found to be 297.8°. Dr. Saylor also found that the products prepared by each procedure showed the same crystallographic and optical properties. The compound belongs to the monoclinic system and crystallizes as rectangular plates which are greatly flattened parallel to the base and bounded by clino- and orthopinacoids; nearly all individuals are complexly twinned parallel to the base. The refractive indices  $n^{20D}$  are  $\alpha = 1.526$ ,  $\beta = 1.534$  and  $\gamma = 1.581$  (all  $\pm 0.001$ ). The crystals are biaxial and positive in sign, the optical axial angle being about 40°, but variable, and the plane of the optic axis is normal to the long direction.

*Anal.* Calcd. for  $C_8H_{10}O_8$ : C, 41.03; H, 4.30; neutralization equivalent, 234. Found: C, 40.96; H, 4.21; neutralization equivalent, 237.

**2,4:3,5-Dimethylene-L-idosaccharic Acid from Dimethyl 2,4:3,5-Dimethylene-D-glucosaccharate.**—The epimerization was conducted essentially by the procedure of Haworth, Jones, Stacey and Wiggins.<sup>7</sup> The dimethyl 2,4:3,5-dimethylene-D-glucosaccharate, which was obtained in a yield of 15% by the methylenation of potassium hydrogen glucosaccharate, melted at 156–157° in agreement with their value of 157.5°. It was recrystallized from 18 parts of methyl alcohol and showed a specific rotation  $[\alpha]^{20D} +34.9^\circ$  in chloroform solution ( $c$ , 0.99). A solution of 10 g. of the ester and 20 g. of barium hydroxide octahydrate in 300 cc. of water was refluxed for six hours; the barium ions were balanced out by *N* sulfuric acid, the barium sulfate was separated by filtration and the filtrate was concentrated *in vacuo* to dryness. The dry residue was extracted with warm acetone to remove some impurities, and the insoluble portion was recrystallized from 3

parts of water or 20 parts of methyl alcohol. The acid showed a specific rotation  $[\alpha]^{20D} +76.4^\circ$  in aqueous solution ( $c$ , 1.3) and crystallographic optical examination showed it to be identical with the acid obtained by oxidation of dimethylene-L-iditol. The yield was 5.1 g. (57%). Haworth, Jones, Stacey and Wiggins<sup>7</sup> reported a specific rotation  $[\alpha]^{16D} +73.7$  in water ( $c$ , 1.817) and a melting point of 292° (dec.) for this compound.

**Dimethyl 2,4:3,5-Dimethylene-L-idosaccharate.**—One-gram samples of 2,4:3,5-dimethylene-L-idosaccharic acid, prepared in one case by oxidation of the 2,4:3,5-dimethylene-L-iditol and in the other by epimerization of 2,4:3,5-dimethylene-D-glucosaccharic acid, were esterified by the method of Haworth, Jones, Stacey and Wiggins.<sup>7</sup> The reaction products (1.0 g., 91%) were recrystallized from about 200 parts of boiling water and submitted to Mr. J. J. Fahey, of the United States Geological Survey, for comparison as to identity. He reported that the esters from the two sources were identical. The compound crystallizes in the monoclinic system; its refractive indices  $n^{20D}$  are  $\alpha = 1.508$ ,  $\beta = 1.511$  and  $\gamma = 1.515$ , all  $\pm 0.001$ ; the optic axial angle is about 60° and the dispersion of violet is greater than red. A saturated aqueous solution of the compound at 20° ( $c = 0.064$ ) showed a rotation  $[\alpha]^{20D} +80 \pm 2^\circ$ . A saturated solution in methyl cellosolve at 20° ( $c = 0.043$ ) also showed  $[\alpha]^{20D} +80 \pm 2^\circ$ . The ester also has been prepared recently by the condensation of paraformaldehyde with calcium L-idosaccharate under the catalytic action of warm sulfuric acid.<sup>12</sup>

### Summary

The dimethylene-L-iditol that is obtained in nearly quantitative yield by slow evaporation of a mixture of L-iditol, aqueous formaldehyde and concentrated hydrochloric acid has been shown to be 2,4:3,5-dimethylene-L-iditol. This is the structure which is to be expected in the case of iditol by applying to its configuration the generalizations that we published recently.

A number of derivatives of the diacetal are described.

Evidence is presented which shows that this dimethylene-L-iditol is in all probability the acetal which Lobry de Bruyn and Alberda van Ekenstein, and later Bertrand and Lanzenberg, described in its enantiomorphous forms.

BETHESDA, MARYLAND

RECEIVED JANUARY 11, 1945

[CONTRIBUTION FROM THE ESSO LABORATORIES, CHEMICAL DIVISION, THE STANDARD OIL DEVELOPMENT COMPANY]

## Oxidation of N-Phenyl-2-naphthylamine

BY JOHN REHNER, JR., FRED W. BANES AND SAMUEL B. ROBISON

In the course of some work on oxidation in synthetic rubbers it was found desirable to investigate the nature of the oxidation products of N-phenyl-2-naphthylamine. Kinetic schemes that have been proposed<sup>1</sup> in attempts to explain the rate of oxidation of rubber have left unanswered the specific nature of the product into which the added antioxidant is transformed in the presumed chain termination reactions.

(1) Morgan and Naunton, *Proc. Rubber Techn. Conf.* London, 1938, p. 599. The Bibliography given by Dufrasse in Davis and Blake, "Chemistry and Technology of Rubber," Reinhold Publ. Corp., New York, N. Y., 1937, p. 440, contains references to earlier chain reaction theories of antioxidant behavior.

As one of the most effective<sup>2</sup> and widely used members of the group of secondary arylamines displaying considerable antioxidant activity in various hydrocarbons and oils N-phenyl-2-naphthylamine possesses an industrial importance in notable contrast to the scanty literature on its oxidation products. Graebe and Knecht<sup>3</sup> found that when the amine is passed through a red-hot tube 5-benzo[b]carbazole is formed, in addition to ammonia, hydrogen cyanide, and other substances. Streiff<sup>4</sup> found that phthalic acid is

(2) Jones and Craig, *Ind. Eng. Chem.*, **23**, 23 (1931).

(3) Graebe and Knecht, *Ann.*, **202**, 1 (1880).

(4) Streiff, *ibid.*, **209**, 151 (1881).