sample and the picrates and 2,4,7-trinitrofluorenone complexes on admixture gave no depression in melting point.

### Experimental[3]

**$\gamma$-(*p*-Tolyl)-valeric Acid** (III).—To 120 ml. of toluene and 40 g. (0.4 mole) of $\gamma$-valerolactone was added with stirring over ten minutes 52.3 g. (0.4 mole) of aluminum chloride. The temperature rose from 25 to 75° as a pea-green complex formed. The mixture was stirred at 90° for one hour, decomposed in the usual fashion and distilled to give 50.1 g. (65%) of the acid as a clear, colorless oil, b.p. 133–134° (0.8 mm.), $n^{23}_{\mathrm{D}}$ 1.5138.

*Anal.* Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.84; H, 8.26.

The yield of acid was 60% when the reaction temperature was maintained at 25°. When the amount of aluminum chloride was increased to two equivalents, about 20% of the tetralone (IV) was obtained as a forerun, b.p. 106–108° (0.8 mm.) and the yield of acid dropped a corresponding amount (to *ca.* 45%).

Oxidation of the acid in aqueous permanganate followed by esterification of the product gave a 76% yield of dimethyl terephthalate, m.p. 137–138°, identical in all respects with an authentic sample, m.p. 137.5–138.5°.

**4,7-Dimethyl-1-tetralone** (IV).—A mixture of 19.0 g. (0.1 mole) of $\gamma$-(*p*-tolyl)-valeric acid and 200 g. of polyphosphoric acid[5] was heated to 100° with stirring for two hours. The olive-green complex was allowed to stand overnight, poured into cold water and extracted with ether. The ether extracts were then shaken with carbonate solution, dried and distilled to give 15.7 g. (91%) of the ketone as a clear colorless liquid, b.p. 106.5–108° (0.8 mm.), $n^{25}_{\mathrm{D}}$ 1.5567; $d^{20}_{4}$ 1.049.

*Anal.* Calcd. for $C_{12}H_{14}O$: C, 82.74; H, 8.10. Found: C, 83.09; H, 8.03.

The **semicarbazone** crystallized as colorless needles from ethanol, m.p. 193–195°; lit.[6] m.p. 194–195°.

**1,6-Dimethyl-1,2,3,4-tetrahydronaphthalene** (V).—A solution of 14.7 g. (0.084 mole) of tetralone (IV) in 50 ml. of diethylene glycol containing 10 ml. of 85% hydrazine hydrate was heated under reflux for 2.5 hours. To the pale yellow solution was added 11 g. of 85% potassium hydroxide and the mixture was heated without condenser to 190° where it was held for four hours. The usual workup gave on distillation 9.2 g. (68%) of the tetralin, b.p. 108.5–110° (11 mm.), $n^{25}_{\mathrm{D}}$ 1.5320, $d^{20}_{4}$ 0.946.

*Anal.* Calcd. for $C_{12}H_{16}$: C, 89.92; H, 10.08. Found: C, 90.25; H, 9.96.

**1,6-Dimethylnaphthalene** (VI).—A mixture of 3.15 g. (0.02 mole) of tetralin (V) and 0.5 g. of 10% palladium–charcoal catalyst was heated under reflux (250–270°) for three hours. The crude product was taken up in ethanol, filtered and added to a saturated solution of picric acid from which there precipitated 4.8 g. (63%) of an orange picrate, m.p. 111–14°. When crystallized from a saturated solution of picric acid, the picrate formed orange needles, m.p. 113–134°, undepressed on admixture with an authentic sample, m.p. 113–134°.[7]

By chromatography of the picrate on alumina, a pure sample of 1,6-dimethylnaphthalene (b.p. 253–254°, $n^{25}_{\mathrm{D}}$ 1.6055) was obtained and its infrared absorption spectrum was superimposable on that of an authentic specimen. This material was used to prepare the **2,4,7-trinitrofluorenone complex**, orange needles from acetic acid, m.p. 138–140°.

*Anal.* Calcd. for $C_{25}H_{17}N_3O_7$: C, 63.70; H, 3.64; N, 8.91. Found: C, 63.90; H, 3.82; N, 8.81.

The authentic trinitrofluorenone complex was also prepared, orange needles from acetic acid, m.p. 139–140°; mixed m.p. 138–140°.

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[3] Melting points are corrected; boiling points are uncorrected. Infrared absorption spectra were determined on a Perkin–Elmer model 21 spectrophotometer. Distillations were carried out with a 30-cm. Podbielniak type column with partial reflux head.[4] Analyses are by Geller Labs., Hackensack, N. J.

[4] J. Cason and H. Rapoport, "Laboratory Experiments in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 237.

[5] H. R. Snyder and F. X. Werber, THIS JOURNAL, **72**, 2965 (1950).

[6] H. Rupe and F. Schütz, *Helv. Chim. Acta*, **9**, 992 (1926).

[7] The recorded m.p. for the picrate of 1,6-dimethylnaphthalene is 114° (F. B. Kipping and F. Wild, *J. Chem. Soc.*, 1239 (1940)), whereas the picrate of 1,7-dimethylnaphthalene is reported as lemon-yellow needles, m.p. 123–124° (G. Darzens and A. Heinz, *Compt. rend.*, **184**, 33 (1927)).

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## The Preparation and Proof of Structure of 1,4-Bis-*O*-*p*-nitrobenzoylerythritol[1]

BY F. SMITH AND J. W. VAN CLEVE

RECEIVED FEBRUARY 28, 1955

In studies on a new procedure for the correlation of the structure of glycosides[2] it was shown that D′- and L′-methoxydiethylene glycol, obtained from methyl $\alpha$- and from methyl $\beta$-D-(and L)-pentopyranosides, gave upon hydrolysis ethylene glycol and glycolic aldehyde.[3] The former was characterized readily but the identification of the glycolic aldehyde as such in small quantities presented difficulty since the usual aldehyde reagents, the aromatic hydrazines, do not distinguish glycolic aldehyde from glyoxal. Both give bis-hydrazones of glyoxal.[4,5]

To avoid ambiguity the bis-*O*-*p*-nitrobenzoate of D′- and L′-methoxydiethylene glycol was hydrolyzed so that the glycolic aldehyde would appear as a mono-*O*-*p*-nitrobenzoate, since the *O*-benzoate of glycolic aldehyde[6] had been shown previously to react normally to give a 2,4-dinitrophenylhydrazone[7] and it was anticipated that the *p*-nitrobenzoate would behave similarly. This, proving to be the case, necessitated the synthesis of an authentic specimen of the 2,4-dinitrophenylhydrazone of *O*-*p*-nitrobenzoylglycolic aldehyde.

When erythritol was esterified with two molecular proportions of *p*-nitrobenzoyl chloride the principal product was a bis-*p*-nitrobenzoate. Of the possible structures for such a diester only the 1,4- and 1,2-diesters can react with lead tetraacetate. The 1,4-diester I should consume one mole of lead tetraacetate to yield two moles of glycolic aldehyde *O*-*p*-nitrobenzoate; in the case of the 1,2-diester II,[8] one mole of lead tetraacetate would be consumed with the formation of one mole of glyceraldehyde bis-*O*-*p*-nitrobenzoate and one mole of formaldehyde.

The bis-*p*-nitrobenzoate which had been prepared consumed one mole of lead tetraacetate without the formation of formaldehyde. Hence its structure must be represented by I. The *O*-*p*-nitro-

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[1] From a thesis submitted to the graduate faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy by John W. Van Cleve, 1951. Paper No. 3107, Scientific Journal Series, Minnesota Agricultural Experiment Station.

[2] M. Abdel-Akher, J. E. Cadotte, Bertha A. Lewis, R. Montgomery, F. Smith, and J. W. Van Cleve, *Nature*, **171**, 474 (1953).

[3] F. Smith and J. W. Van Cleve, THIS JOURNAL, **77**, 3091 (1955).

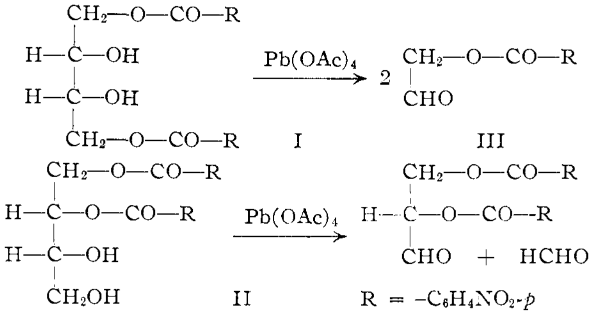
[4] A. Wohl and C. Neuberg, *Ber.*, **33**, 3095 (1900).

[5] E. Fisher and K. Landsteiner, *ibid.*, **25**, 2549 (1892).

[6] L. Palfray, H. Halasz and S. Rovira, *Comp. rend.*, **210**, 765 (1940).

[7] H. Ohle and G. A. Melkonian, *Ber.*, **74**, 291 (1941).

[8] There are two theoretically possible 1,2-diesters, only one of which (II) is shown, which should be optically active thus forming an enantiomorphic pair.



benzoylglycolic aldehyde (III) thus produced was characterized by the formation of its crystalline 2,4-dinitrophenylhydrazone.

## Experimental

**Preparation of 1,4-Bis-*O*-*p*-nitrobenzoylerythritol.**[9]—To a solution of erythritol (1.525 g.) in pyridine (30 ml.), well cooled in an ice-bath, a solution of *p*-nitrobenzoyl chloride (4.635 g.) in pyridine (30 ml.) was added slowly with vigorous stirring. After the addition had been completed, the reaction mixture was allowed to come slowly to room temperature by standing in the melting ice-bath overnight. After removing most of the pyridine by distillation *in vacuo*, the residual thin sirup was poured, with stirring, into ice-water (1000 ml.) containing sodium bicarbonate (4.0 g.). The precipitated ester was filtered, washed free of pyridine with water and dried on a porous plate. The dried product (1.49 g.) was dissolved in boiling 95% ethanol (300 ml.) and the resulting solution was filtered hot in order to separate a small amount of insoluble residue. The clear filtrate was allowed to evaporate in an open beaker for 4 days at room temperature. The compact clusters of small needles thus formed (1.05 g.) gave upon recrystallization from absolute ethanol (250 ml.) 1,4-bis-*O*-*p*-nitrobenzoylerythritol, m.p. 202–203°.

*Anal.* Calcd. for $C_{18}H_{16}O_{10}N_2$: C, 51.4; H, 3.8; N, 6.7. Found: C, 51.5; H, 3.9; N, 6.8.

**Oxidation with Lead Tetraacetate.**—To a solution of 1,4-bis-*O*-*p*-nitrobenzoylerythritol (84 mg., 0.0002 mole) in glacial acetic acid (25 ml.) was added 0.1033 *N* lead tetraacetate in glacial acetic acid (15 ml.). The mixture was adjusted to a volume of 50 ml. with glacial acetic acid and then heated on the water-bath at 85° for 1.5 hours. At the end of this time an aliquot of the reaction mixture was added to an aqueous sodium acetate–potassium iodide buffer solution and the liberated iodine was titrated with a standard sodium thiosulfate solution.[10] This titration showed that 0.97 mole of lead tetraacetate had been consumed per mole of 1,4-bis-*O*-*p*-nitrobenzoylerythritol.

**Test for the Presence of Formaldehyde in the Oxidation Product.**—An aliquot (30 ml.) of the reaction mixture from the previous experiment was treated with 60 ml. of aqueous sodium acetate–potassium iodide buffer solution[10] and the liberated iodine was reduced with sodium thiosulfate solution. The resulting solution was distilled *in vacuo* on the water-bath (40–50°). The first few ml. of aqueous distillate gave a negative Schiff test.

For the purpose of comparison, a 30-ml. aliquot of a solution of formaldehyde (0.0002 mole, corresponding to 0.0002 mole of 1,4-bis-*O*-*p*-nitrobenzoylerythritol) in 50 ml. of glacial acetic acid which had been heated on the water-bath at 85° for 1.5 hours, was treated with 60 ml. of the aqueous sodium acetate–potassium iodide buffer solution[10] and distilled *in vacuo* (bath, 40–50°). The first few ml. of distillate gave a positive Schiff test.

**Preparation of *O*-*p*-Nitrobenzoylglycolic Aldehyde 2,4-Dinitrophenylhydrazone.**—To a suspension of 1,4-bis-*O*-*p*-nitrobenzoylerythritol (0.5 g.) in benzene (30 ml.) was added one molecular equivalent of lead tetraacetate (0.4294 g.). The mixture was refluxed for 1.5 hours during which time the crystals of the ester disappeared and white lead acetate separated. The cool solution was filtered to remove the lead acetate and shaken with saturated sodium bicarbonate solution to remove acetic acid. The benzene solution was dried over anhydrous calcium chloride and evaporated *in vacuo* to give a white crystalline residue (0.3758 g.) which gave a positive Schiff test. The crystalline material, which was not purified further since it decomposed slowly on standing, was insoluble in water but suspended particles of it turned a deep violet with Schiff reagent. It did not reduce boiling Fehling solution.

To a solution of the crystalline material (0.3008 g.) in 95% ethanol (30 ml.) was added glacial acetic acid (3 ml.) followed by 2,4-dinitrophenylhydrazine (0.3 g.). The reaction mixture was agitated, occasionally, over a period of about 30 min. during which time the red crystals of 2,4-dinitrophenylhydrazine dissolved and bright yellow crystals separated. The reaction was completed by refluxing for 15–20 min. After allowing the reaction mixture to cool to room temperature, the 2,4-dinitrophenylhydrazone of glycolic aldehyde *O*-*p*-nitrobenzoate was filtered off and washed with 95% ethanol (yield 0.4487 g.). It was recrystallized from boiling 86% (v./v.) aqueous acetic acid (35 ml.). Upon standing, large orange needles separated followed by canary-yellow fluffy crystal masses. By suspending the combined crystals in ether it was possible to decant, almost quantitatively, the suspended yellow crystals from the heavier orange crystals. The orange crystals and the yellow crystals had the same melting point, 189.5–190.5°, and a mixed melting point gave no depression. When the orange crystals were recrystallized from chloroform–petroleum ether, only yellow crystals were formed.

*Anal.* Calcd. for $C_{15}H_{11}O_8N_5$: C, 46.3; H, 2.9; N, 18.00. Found (for orange crystals): C, 46.3; H, 3.3; N, 17.9. Found (for yellow crystals): C, 46.7; H, 3.3; N, 18.1.

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[9] *Cf.* A. Einhorn and F. Hollandt, *Ann.*, **301**, 95 (1898).

[10] R. C. Hockett and W. S. McClenahan, THIS JOURNAL, **61**, 1670 (1939).

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## Reactions of Vanillin and its Derived Compounds. XXV.[1] Hydrazides of Vanillic and Related Acids[2]

BY IRWIN A. PEARL AND DONALD L. BEYER

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During the course of our studies on lignin model compounds and on vanillin derivatives we had occasion to prepare many carboxylic acids related to vanillic acid. Recent developments in the pharmaceutical field indicated that hydrazides of these acids might have activity against certain microorganisms. Accordingly, the methyl or ethyl ester of acids previously reported in our vanillin and lignin studies was treated in ethanol with an excess of hydrazine hydrate. In most cases the desired hydrazide was obtained. Data for these hydrazides are found in Table I.

In some reactions anomalous products were formed. Reaction of ethyl orthovanillate with hydrazine hydrate in the regular manner yielded the hydrazine salt of orthovanillic acid hydrazide. If the solution was acidified with sulfuric acid after reaction, the hemisulfate hydrate of orthovanillic acid hydrazide was obtained. The hydrazine salt of orthovanillic acid hydrazide also was obtained if the methyl or ethyl ester of orthovanillic acid allyl ether was treated in the same manner with hydrazine hydrate. The cleavage of the allyl group in these compounds by the hydrazinolysis reaction and lack of cleavage of the allyl group in the case of

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[1] For paper XXIV of this series, see THIS JOURNAL, **77**, 757 (1955); XXVI, *ibid.*, **77**, 2826 (1955).

[2] The results reported here are from a research program at this Institute, sponsored by the Sulphite Pulp Manufacturers' Research League. Acknowledgment is made for their permission to publish these results.