Derivatives of Butanediol-1,3

Several derivatives of butanediol-1,3 (*dl*-butylene glycol) were prepared by us, as we required some 1-mono derivatives of this glycol for synthetical purposes in a project which was supported by the United Hospital Fund of New York. Synthetic butanediol-1,3 was obtained from the Carbide and Carbon Chemicals Corporation.

Except for the monobenzyl ether, no mono derivative could be obtained. Partial acetylation of the diol and partial saponification of the di-acetate were of no avail for the preparation of a monoacetate.

A mono-benzyl ether of butanediol-1,3 was prepared as follows: one mole of butanediol (90 g.) and one mole of sodium methylate (54 g.) were heated in 150 ml. of dry toluene under nitrogen on the boiling water-bath; after most of the methanol had been distilled off, 1 mole of benzyl chloride (127 g.) was added dropwise. When about one half had been added, a vigorous reaction set in and sodium chloride precipitated; the reaction was completed with stirring for another three hours. The reaction product was poured on ice, the toluene layer, plus several toluene extracts of the neutralized aqueous layer, was washed and dried; after removal of the toluene, the product was distilled *in vacuo*. The main fraction (yield, 30%) distilled at 110–112° under 1–2 mm. pressure and 113–116° under 2–3 mm. pressure; d^{25}_4 1.016; $n^{25}\text{D}$ 1.5042.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.52; H, 9.12.

This mono-ether, presumably the 1-ether, formed neither a phenylurethan nor a benzoyl derivative and could not be further benzylated to the di-benzyl ether.

As the trityl ether was considered more promising for our purposes than a benzyl derivative, we studied the tritylation of butanediol. Tritylation of polyhydroxy derivatives usually remains confined to the primary hydroxyl groups. However, butanediol, when treated with an equimolecular amount of triphenylmethyl chloride in two equivalents of pyridine for six hours on the boiling water-bath, yielded the crystalline **di-trityl ether of butanediol-1,3**. Modifications of the procedure, including lower temperatures, varying reaction times, absence of pyridine or use of sodium methylate, yielded mixtures of varying composition.

In all these experiments the crystals formed were freed from the adhering sirup and pyridine by treatment with glacial acetic acid, ether and xylene. The crystals, after several recrystallizations from absolute ethanol, melted at 142–143°.

Anal. Calcd. for $C_{42}H_{38}O_2$: C, 87.77; H, 6.66. Found: C, 87.57; H, 6.81.

The **bis-phenyl urethan of butanediol-1,3** was prepared by heating one part of the diol with three parts of phenyl isocyanate for forty-five minutes at 100°. The reaction mixture crystallized on standing overnight; after several washings with petrolic ether, the product was recrystallized five times from 80% ethanol, whereupon it melted at 118.5–119°.

Anal. Calcd. for $C_{18}H_{20}O_4N_2$: C, 65.84; H, 6.14; N, 8.53. Found: C, 65.46; H, 6.11; N, 8.73.

The optically active D-form of this compound had been described by Levene and Haller[1]; it melts at 122–123°.

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[1] Levene and Haller, *J. Biol. Chem.*, **69**, 574 (1926).

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Some Substituted Veratroles

4-(1′-Hydroxypentadecyl)-veratrole (I).—Thirty-three grams (0.2 mole) of veratric aldehyde was treated with the Grignard reagent from 82.5 g. of *n*-tetradecyl bromide in 100 cc. of dry ether and 7.3 g. of magnesium turnings following the method of Backer and Haack.[1] After hydrolysis with 2 *N* sulfuric acid, a white solid crystallized from the washed and dried ethereal solution on cooling. The product was recrystallized from petroleum ether three times to yield 61 g. (83.5% yield) of the desired veratrole derivative, m. p. 72–73.5°. A sample for analysis was recrystallized six more times from petroleum ether as white hair-like needles, m. p. 73–73.5°.

Anal. Calcd. for $C_{23}H_{40}O_3$: C, 75.8; H, 11.1. Found: C, 75.9; H, 11.2.

4-(1′-Pentadecenyl)-veratrole (II).—To 60 g. (0.17 mole) of (I) dissolved in 100 cc. of dry xylene in a Spitzkolbe flask set up for vacuum distillation using a Wood's metal-bath, 4 g. of dry powdered potassium bisulfate was added and the bath was heated to 200° (atmospheric pressure). At this temperature the xylene and water formed in the dehydration reaction slowly distilled over, and the bath was maintained at 200° for ten minutes after the last visible traces of water had been removed. The residue was then distilled at 222–232° at 2.5 mm. (bath at 285–295°). A yield of 41.3 g. (72.5%) of white solid melting at 45.5–47° was obtained. A sample recrystallized six times from 95% ethanol and twice from petroleum ether as white fern leafed needles melted at 49–50°.

Anal. Calcd. for $C_{23}H_{38}O_2$: C, 79.7; H, 11.1. Found: C, 79.9; H, 11.2.

3-(1′-Pentadecenyl)-benzyloxybenzene (III).—The same procedure as used for the preparation of (I) was employed to convert 23 g. (0.12 mole) of *m*-benzyloxybenzaldehyde to the corresponding hydroxypentadecyl derivative of phenol benzyl ether using 45.2 g. of myristyl bromide and 3.96 g. of magnesium. After hydrolysis with 2 *N* sulfuric acid the ether layer was separated, washed, dried and evaporated. The white residue which remained was dissolved in 200 cc. of 95% ethanol. Upon cooling to 0°, 4 g. of crude octacosane precipitated and was removed by filtration. The alcoholic filtrate was evaporated to dryness to yield 41 g. of crude *m*-benzyloxy-(1′-hydroxypentadecyl)-benzene melting at 36–38°. Without further purification, a 36-g. sample was converted to *m*-benzyloxypentadecenyl-1′-benzene with powdered fused potassium bisulfate using the same procedure as described for the preparation of (II). A yield of 28.4 g. of unsaturated compound boiling at 242–252° (0.4 mm.) (Wood's metal-bath at 300–340°) was obtained. A middle fraction redistilled at 248–252° (0.7 mm.) (bath at 268–285°) melted at 34–35° and was taken for analysis:

Anal. Calcd. for $C_{28}H_{40}O$: C, 85.6; H, 10.3. Found: C, 85.4; H, 10.4.

***m*-Benzyloxypentadecylbenzene (IV).**—This ether was obtained by reducing 6.3 g. of (III) in 100 cc. of pure toluene using 2 g. of 5% palladium on carbon and 1 atm. of hydrogen. The crystalline product melted at 39.5–40.5° after two recrystallizations from a 75% alcohol–25% acetone mixed solvent. A 1:2 mixture of compounds III and IV melted at 31–34°.

Anal. Calcd. for $C_{28}H_{42}O$: C, 85.2; H, 10.7. Found: C, 84.9; H, 10.7.

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[1] Backer and Haack, *Rec. trav. chim.*, **60**, 661 (1941).

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3-(*o*-Methylbenzyloxy)-1,2-propanediol and 2,2-Dimethyl-4-(*o*-methylbenzyloxymethyl)-1,3-dioxolane[1]

To a suspension of 3.2 g. of sodamide in 150 ml. of toluene there was added with stirring 8.0 g. of 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane.[2] As soon as the

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[1] Aided by a grant from the National Foundation for Infantile Paralysis, Inc.

[2] Irvine, Macdonald and Soutar, *J. Chem. Soc.*, **107**, 337 (1915).