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}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).

reaction with sodamide was complete, 7.0 g. of *o*-methylbenzyl chloride[3] was added dropwise. This reaction mixture was boiled under reflux for two hours, cooled, and washed several times with water. After removal of the toluene *in vacuo*, the residual oil was distilled yielding 7.1 g. (60%) of a colorless oil; b. p. 116–117° at 1.2 mm.; $n^{21}D$ 1.4984.

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.15; H, 8.65. Found: C, 71.25; H, 8.74.

Hydrolysis of a sample of 2,2-dimethyl-4-(*o*-methylbenzyloxymethyl)-1,3-dioxolane (2.0 g.) was accomplished by boiling it for one hour with a solution containing 14 ml. of alcohol, 5 ml. of water and 0.2 ml. of concentrated sulfuric acid. The mixture was neutralized with sodium carbonate, and the organic layer was separated and distilled. There was obtained 0.75 g. (45%) of a colorless oil; b. p. 149–151° at 0.4 mm.; $n^{21}D$ 1.5330.

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.52; H, 8.11.

Attempts to prepare 3-(*o*-methylbenzyloxy)-1,2-propanediol by the reaction of the sodium salt of *o*-methylbenzyl alcohol with epichlorohydrin or glycerol α-monochlorohydrin were unsuccessful.

Since 3-(*o*-methylbenzyloxy)-1,2-propanediol is an analog of myanesin (3-(*o*-toloxy)-1,2-propanediol), it was tested for physiological action by intraperitoneal injection into mice.[4] It was found that even at lethal dosages muscular paralysis was incomplete.

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(3) Newman, THIS JOURNAL, **62**, 2295 (1940).

(4) Physiological tests were made by F. M. Berger, M.D., Department of Pediatrics, University of Rochester School of Medicine, Rochester, New York.

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Five New Tertiary Carbinols and Four New Aliphatic Hydrocarbons

In the course of work on the mechanism of anomalous Grignard reactions,[1] five tertiary carbinols were obtained, which are believed to be new. Four of these were converted to the corresponding hydrocarbons.

Compound	B. p.[a] °C.	B. p.[a] Mm.	$n^{20}D$	Yield, %	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2,4,5-Trimethylheptan-4-ol[b]	54–55	3	1.4382	15	$C_{10}H_{22}O$	75.9	76.3	13.9	13.9
3,4-Dimethyloctan-4-ol[c]	64–65	3	1.4418	20	$C_{10}H_{22}O$	75.9	75.8	13.9	14.0
3,4-Dimethylnonan-4-ol[d]	68–69	2	1.4430	15	$C_{11}H_{24}O$	76.7	76.2	13.9	14.1
2,6-Dimethyl-4-isopropylheptan-4-ol[e]	48–49	1	1.4448	20	$C_{12}H_{26}O$	77.4	77.6	14.0	13.9
2,6-Dimethyl-4-isobutylheptan-4-ol[f]	72–73	2	1.4390	15	$C_{13}H_{28}O$	78.0	77.6	14.0	13.9
2,4,5-Trimethylheptane[g]	49.5	18	1.4160		$C_{10}H_{22}$	84.5	84.6	15.5	15.1
3,4-Dimethyloctane[g]	58.0–58.4	20	1.4182		$C_{10}H_{22}$	84.5	84.6	15.5	15.0
3,4-Dimethylnonane[g]	75.0–75.2	18	1.4223		$C_{11}H_{24}$	84.8	84.9	15.2	14.8
2,6-Dimethyl-4-isobutylheptane	81.9–82.5	20	1.4238		$C_{13}H_{28}$	84.6	84.3	15.4	15.0

[a] Uncorrected. By the interaction of *s*-BuMgBr and MeCOBu-*i*. [c] By the interaction of *s*-BuMgBr and MeCOBu-*n*. [d] By the interaction of *s*-BuMgBr and MeCOAm-*n*. [e] By the interaction of *i*-PrMgBr and *i*-BuCOBu-*i*. [f] By the interaction of *i*-BuMgBr and *i*-BuCOBu-*i*. Skraup and Freundlich, *Ber.*, **55**, 1080 (1922), report that they made this by the action of *i*-BuMgBr on isovaleric ester, but say that the pure carbinol could not be obtained, since it decomposed when distilling in a high vacuum. No physical constants were given. [g] Calculations of the physical constants of this are given by Francis, *Ind. Eng. Chem.*, **35**, 442–448 (1943).

In the conversion of the carbinols to the hydrocarbons, the former were dehydrated to the olefins with naphthalene-2-sulfonic acid, and the olefins were fractionated, the column used being packed to a length of 12 inches with Fenske helices, and fitted with a total-reflux-variable-take-off still head. They were then reduced in glacial acetic acid with Adams catalyst and hydrogen at 50 p. s. i. pressure until no unsaturation could be detected with a solution of bromine in carbon tetrachloride. The hydrocarbons were fractionated through the column described above.

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(1) Shine and Turner, "The Anomalous Reactions of Grignard Reagents (I)," submitted for publication in THIS JOURNAL.

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COMMUNICATIONS TO THE EDITOR

EXCHANGE REACTIONS BETWEEN CERIUM(III) AND CERIUM(IV) AND BETWEEN IRON(II) AND IRON(III)

Sir:

We have studied the exchange reaction between cerium(III) and cerium(IV) in perchloric acid and in sulfuric acid solutions. Using electrical migration methods to partially separate the reactants we have found no evidence that the exchange is measurably slow. The 30-day Ce^{141} used as cerium(III) tracer was obtained from the Clinton Laboratories on allocation from the U. S. Atomic Energy Commission. It was purified by precipitation of cerium(III) fluoride and ammonium hexanitratocerate(IV). The Ce^{141} content of solutions was determined by gamma-counting. Cerium was determined by titration with iron(II) sulfate. In sulfuric acid solutions cerium(IV) migrated toward the anode, cerium(III) toward the cathode. In perchloric acid solutions both ions migrated toward the cathode, cerium(III) being the more mobile. Samples enriched in each