Synthesis of Bis(4-hydroxy-2-butenyl) Ether and Two Ester Derivatives

William J. Bailey* and Joseph Di Pietro

Department of Chemistry, University of Maryland, College Park, Maryland 20742

Bis(4-hydroxy-2-butenyl) ether was synthesized by acid treatment of commercially available 2-butene-1,4-diol in a 32% conversion or a 59% yield based on unrecovered starting materials. Treatment of the dihydroxy ether with acetic anhydride produced the corresponding bis(4-acetoxy-2-butenyl) ether in a 91% yield. In a similar reaction treatment of the dihydroxy ether with methyl chloroformate and pyridine produced an 84% yield of the bis(4-hydroxy-2-butenyl) ether bis(methyl carbonate).

The commercial availability of 2-butene-1,4-diol (I) suggested that this material would be a convenient and inexpensive starting material for the preparation of a series of highly functional compounds. One derivative that appeared of interest for producing unsaturated polyesters and as a possible starting material for the production of bis dienes was bis(4-hydroxy-2-butenyl) ether (II). By the general method of Pratt and Draper (*4*) for producing benzyl and allyl ethers, 2-butene-1,4-diol (I) was heated under reflux in the presence of *p*-toluenesulfonic acid in a benzene solution and the liberated water was collected in a Dean Stark trap. The reaction was interupted after slightly over half of the theoretical amount of water had been collected in order to minimize the formation of higher ethers and yet maximize the yield of II. This treatment resulted in a 32% conversion of the diol I to the bis(4-hydroxy-2-butenyl) ether (II). Since 46% of the starting material was also recovered, the yield of dihydroxy ether II, based on unrecovered starting material, was 59%. The material was characterized by analysis and infrared spectrum which showed the absence of an isomer which would have resulted from an isomerization of the double bond or an allylic rearrangement during the ether formation. Since this work was completed, Arino, Camps, and Serratosa (*1*) reported the preparation of the ether by the lithium aluminum hydride reduction of a crude explosive sample of bis(4-hydroxy-2-butynyl) ether in a 32% yield. They reported a boiling point but no analysis. However, they did convert it to a 9% yield of a solid hexaacetate derivative (*1*). When the dihydroxy ether II was heated under reflux with acetic anhydride, a 91% yield of the bis(4-acetoxy-2-butenyl) ether (III) was obtained. This diester III was characterized by analysis and an infrared spectrum. In a very similar manner the bis(4-hydroxy-2-butenyl) ether (II) was treated with methyl chloroformate and pyridine in a chloroform solution to give an 84% yield of the bis(4-hydroxy-2-butenyl) ether bis(methyl carbonate) (IV).

$$\underset{\text{I}}{\mathrm{HOCH_2CH{=}CHCH_2OH}} \xrightarrow[\substack{\text{benzene}\\ \text{reflux}\\ 59\%}]{\mathrm{CH_3PhSO_3H}} \underset{\text{II}}{\mathrm{HOCH_2CH{=}CHCH_2OCH_2CH{=}CHCH_2OH}} \tag{1}$$

$$\text{II} \xrightarrow[91\%]{\mathrm{Ac_2O}} \underset{\text{III}}{\mathrm{AcOCH_2CH{=}CHCH_2OCH_2CH{=}CHCH_2OAc}} \tag{2}$$

$$\text{II} \xrightarrow[\substack{\text{pyridine}\\ \mathrm{CCl_3H}\\ 84\%}]{\mathrm{CH_3OC({=}O)Cl}} \underset{\text{IV}}{\mathrm{CH_3OC({=}O)OCH_2CH{=}CHCH_2OCH_2CH{=}CHCH_2OC({=}O)OCH_3}} \tag{3}$$

Pyrolysis of the two esters produced the expected acetic acid and carbon dioxide, respectively, but no butadienyl ethers could be isolated.

Experimental Section

Bis(4-hydroxy-2-butenyl) Ether (II). A 5-L flask was fitted with a Dean Stark trap, graduated in 1.0-mL divisions to a total volume of 20 mL and connected to a reflux condenser to the top of which was attached a calcium chloride tube. To a solution of 2.5 L of benzene and 1000 g (11.36 mol) of 2-butene-1,4-diol (I) (General Aniline, technical grade), bp 97–102 °C (0.8–1.0 mm), $n^{27}{}_D$ 1.4750 [reported (*2*) bp 232–235 °C, $n^{25}{}_D$ 1.4768], heated under reflux, was added 2.5 g (0.013 mol) of *p*-toluenesulfonic acid monohydrate (Eastman Kodak reagent). After the reaction was heated under reflux for a period of approximately 45 h in order to collect 108 g (6.0 mol) of water, the benzene solution was then neutralized with solid sodium bicarbonate. The mixture was filtered, the excess benzene was removed from the filtrate by distillation, and the brown residue (765 g) was subjected to a slow fractionation through an 18-in. Vigreux column to yield 460 g (5.22 mol) of starting material, 2-butene-1,4-diol (I) and 290 g (32%) of bis(4-hydroxy-2-butenyl) ether (II), bp 136–138 °C (0.4 mm), $n^{29}{}_D$ 1.4930 [reported (*1*) bp 133 °C (0.02 mm), no analysis]. Anal. Calcd for $C_8H_{14}O_3$: C, 60.75; H, 8.87. Found: C, 60.89; H, 8.99. The infrared spectrum of bis(4-hydroxy-2-butenyl) ether (II) gave strong wide peaks at 1033, 1885, 1420, 2880, and 3400 cm^{-1}. These peaks indicated the presence of an aliphatic ether bond, a double bond, and a hydroxyl group, respectively. The absence of a peak at the 900-cm^{-1} region from the infrared spectrum of the sample was taken as definite evidence that an isomer possessing a terminal methylene group was not present in the sample of the prepared ether.

Bis(4-acetoxy-2-butenyl) Ether (III). To a mixture of 280 g (2.75 mol) of acetic anhydride and 5 g (0.08 mol) of acetic acid in a 1-L, three-necked flask fitted with a stirrer, a reflux condenser, and a dropping funnel was added 100 g (0.63 mol) of bis(4-hydroxy-2-butenyl) ether (II) over a period of 85 min while the mixture was heated under reflux. After the excess acetic anhydride and acetic acid were removed by vacuum distillation, the remainder of the solution was fractionally distilled through a 10-in. column packed with glass helices to yield 139 g (91%) of bis(4-acetoxy-2-butenyl) ether (III), bp 106–107 °C (0.2 mm), $n^{24}{}_D$ 1.4615. Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.45; H, 7.49. Found: C, 59.14; H, 7.77.

An infrared spectrum of the bis(4-acetoxy-2-butenyl) ether (III) showed strong absorption bands at 1033, 1250, 1400, and 1755 cm^{-1} indicative of the presence of an aliphatic ether, a double bond, and an ester.

Bis(4-hydroxy-2-butenyl) Ether Bis(methyl carbonate) (IV). Into a 1-L, three-necked flask placed in an efficient hood fitted with a large dry ice condenser, a stirrer, and a dropping funnel fitted with a calcium sulfate drying tube was condensed 400 g (4.04 mol) of phosgene while the mixture was cooled by

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an ice-salt mixture. After 128 g (4.00 mol) of absolute methanol had been added dropwise through the dropping funnel, the reaction mixture was allowed to stir overnight to ensure evaporation of all the excess phosgene. The crude methyl chloroformate was washed with two 50-mL portions of ice water and dried over anhydrous sodium sulfate and calcium carbonate for 1 day. Distillation at atmospheric pressure yielded 280 g (75%) of methyl chloroformate, bp 70-72 °C (reported (*2*) bp 71.5 °C).

A 2-L, three-necked flask fitted with a water condenser, a dropping funnel, and a stirrer was charged with 120 g (0.76 mol) of bis(4-hydroxy-2-butenyl) ether (II), 400 mL of dry chloroform, and 200 g (2.5 mol) of dry pyridine. To the reaction flask cooled at 0 °C was added 235 g (2.5 mol) of freshly distilled methyl chloroformate over a period of 8 h. The reaction mixture was washed successively with 200 mL of water, 100 mL of 5% hydrochloric acid, and 100 mL of a saturated sodium bicarbonate solution. After the chloroform solution was dried over anhydrous magnesium sulfate overnight, the chloroform was removed by distillation under reduced pressure, and the residue was fractionally distilled through a 12-in., helix-packed column to yield 175 g (84%) of bis(4-hydroxy-2-butenyl) ether bis(methyl carbonate) (IV), bp 155-157 °C (0.8 mm), $n^{30}{}_{D}$ 1.4564. Anal. Calcd for $C_{12}H_{18}O_7$: C, 52.55; H, 6.56. Found: C, 52.74; H, 6.73.

An infrared spectrum analysis of bis(4-hydroxy-2-butenyl) ether bis(methyl carbonate) (IV) showed strong absorption bands at 958, 1100, 1275, 1450, 1760, and 3000 cm^{-1} indicative of the presence of an aliphatic ether, a covalent carbonate, and a double bond.

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Synthesis and Fluorescence Spectra of 1,4-Bis(phenylethynyl)anthracene

Ronald A. Henry, Dan E. Bliss, and Carl A. Heller*
Chemistry Division, Code 385, Naval Weapons Center, China Lake, California 93555

The synthesis of the title compound, 1,4-BPEA, was accomplished in the same manner as for 9,10-BPEA, but with lower yield due to a side reaction. The compound is a fair fluorescer with 60% quantum yield in benzene. The emission peaks are at 449 and 478 nm in benzene—blue-shifted from 9,10-BPEA—but still red-shifted from 9,10-diphenylanthracene. Ethanol solutions peak at 443 and 472 nm with the same quantum yield.

Introduction

In a recent paper (*3*) we gave the fluorescence spectra of several substituted 9,10-bis(phenylethynyl)anthracenes. We have now synthesized a related fluorescer, 1,4-BPEA, measured the fluorescence and quantum yield, and noted how these are affected by this change in the position of the phenylethynyl groups.

Syntheses of 1,4-Bis(phenylethynyl)anthracene and 2-Phenylethynyl-1,4-dihydroxyanthracene

1,4-Anthraquinone (6.3 g, 0.0303 mol; mp 221-224 °C, reported (*2*)) was reacted with lithiophenylacetylide (6.8 g of phenylacetylene, 1.5 g of lithium amide, 85 mL of dry dioxane) in the same manner (*1*) used with 9,10-anthraquinone. The dark tarry product obtained when the reaction mixture was quenched with 4 g of ammonium chloride in 100 mL of water was separated from the liquid phase by decanting the latter. The crude product was triturated several times with pentane to remove excess phenylacetylene and then with water; after drying, the crude product was boiled with 100 mL of benzene and chilled overnight at 5 °C, and the solid (1.8 g) was removed and saved (A). When the benzene solution was diluted with 75 mL of *n*-hexane and further cooled, 3.6 g of olive green solid separated. The latter was filtered and redissolved in 25 mL of acetone and the solution chilled at −15 °C for 3 days, 0.14 g of solid (mp >320 °C; same IR spectrum as that for the following by-product) was removed. This acetone solution was diluted with 20 mL of acetone and added dropwise with stirring to 5.5 g of stannous chloride in 50 mL of 50% aqueous acetic acid. After overnight stirring at 25 °C, the mixture was diluted with 100 mL of water, slurried with some Celite, and centrifuged. The supernatant was discarded. The cake was resuspended in water and centrifuged, and the washings were discarded; this process was repeated twice more. After drying the cake, it was extracted with one 50-mL and two 25-mL portions of boiling benzene. The combined extracts were diluted with 250 mL of cyclohexane and 100 mL of *n*-hexane and chilled at -15 °C for several days; the supernatant was decanted from the dark resinous material, which had separated, and evaporated to leave 0.8 g of dark yellow 1,4-bis(phenylethynyl)anthracene. Sublimation at pump limit and a pot temperature of 160-170 °C gave felted yellow needles of 1,4-BPEA, mp 164-165 °C. Carbonyl absorptions were absent in the IR spectrum.

By fractionally crystallizing the solid A from benzene there was isolated a small amount of greenish yellow solid, mp >320 °C, whose infrared spectrum showed a CO absorption at 1680 cm^{-1}. Although this evidence might suggest a 1,4-anthraquinone derivative, the ^1H NMR spectrum is more consistent with the assumption that this material is the keto tautomer of 2-