Synthesis and Reactions of 3-Butyne-1,2-diol

BY V. A. ENGELHARDT AND J. E. CASTLE

RECEIVED NOVEMBER 13, 1952

It has been found that 3-butyne-1,2-diol can be prepared from monovinylacetylene by the hydroxylation procedure of Swern and co-workers[1] using hydrogen peroxide in formic acid. This method offers a more direct route to the acetylenic glycol than an earlier four-step synthesis based on acetaldehyde.[2] The preferential attack of hydroxylating agents on the olefinic portion of a conjugated eneyne compound has been previously demonstrated in the oxidation of 2-pentene-4-yne-1-ol to 4-pentyne-1,2,3-triol by performic acid[3] and in the hydroxylation of 1-phenyl-3-ene-1-yne type compounds by peracetic acid.[4]

Derivatives of 3-butyne-1,2-diol such as the diacetate, dibenzoate, dicarbanilate and 3,5-octadiyne-1,2,7,8-tetrol have been prepared. The tetrol was prepared by oxidative coupling of 3-butyne-1,2-diol diacetate followed by methanolysis. An attempt to prepare the tetrol by oxidative coupling of 3-butyne-1,2-diol was unsuccessful due to the difficulty in isolating the water-soluble tetrol from an aqueous solution of ammonium and copper salts.

Experimental

3-Butyne-1,2-diol.—Formic acid (98–100%, 150 ml.), aqueous 30% hydrogen peroxide (151 g., 0.45 mole) and monovinylacetylene (15.6 g., 0.3 mole) were charged into each of nine pressure bottles at 0°. These bottles were capped and then placed in a rocker bath at 40° for 25 hours. It is necessary to carry out this reaction in a properly shielded water-bath, for a bottle that was allowed to stand at room temperature in the open air exploded within a short time. The combined products were passed through a steam-jacketed stripping still under 80 mm. pressure to remove the bulk of the formic acid. Distillation of the residual oil gave 119 g. of the monoformate, b.p. 70–115° (0.5–0.9 mm.), which distilled mainly at 71° (0.6 mm.). The distillate (119 g.) was placed in an ice-bath and aqueous 33% sodium hydroxide (77 ml.) was added portionwise with swirling to keep the temperature below 40°. After two hours at room temperature, water was removed from the solution at 70° (10 mm.). The residue was mixed with acetone (250 ml.) and filtered from sodium formate. After distillation of acetone, the residual oil was distilled to give 67.7 g. (29% over-all yield) of 3-butyne-1,2-diol, b.p. 64–66° (0.2 mm.), $n^{25}\text{D}$ 1.4723.

A sample of the glycol was recrystallized from an equal volume of absolute ether to give hygroscopic crystals which melted at 37.5–38.5°. A melting point of 39.5–40° was reported by Lespieau.[2]

Anal. Calcd. for $C_4H_6O_2$: C, 55.80; H, 7.02; mol. wt., 86; quant. hydrogenation, g. H_2/g., 0.0468. Found: C, 56.14; H, 7.15; mol. wt. (ebullioscopic in ethanol), 90; quant. hydrogenation, g. H_2/g., 0.0469.

3-Butyne-1,2-diol Dicarbanilate.—This compound, m.p. 134–135°, was prepared according to the directions of Lespieau.[2]

Anal. Calcd. for $C_{18}H_{16}O_4N_2$: C, 66.66; H, 4.97; N, 8.64. Found: C, 66.81; H, 5.20; N, 8.60.

3-Butyne-1,2-diol Dibenzoate.—3-Butyne-1,2-diol (0.7 g., 0.008 mole) and benzoyl chloride (2.0 g., 0.014 mole) were dissolved in pyridine (10 ml.). After the initial reaction had subsided, the solution was boiled for one minute and then poured into water (30 ml.). Decantation of the aqueous layer left an oil which was then triturated with water several times. After standing for two days, the oil crystallized. The solid was washed with aqueous 5% sodium bicarbonate and then recrystallized twice from ethanol to give 0.7 g. of product, m.p. 74–75°.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79. Found: C, 73.62; H, 4.90.

The presence of a terminal acetylenic group in this compound was shown by the formation of a precipitate with potassium mercuric iodide reagent.[5]

3-Butyne-1,2-diol Diacetate.—3-Butyne-1,2-diol (50 g., 0.58 mole) and freshly fused sodium acetate (25.9 g.) were dissolved in acetic anhydride (259 ml.). This solution was heated on a steam-bath for two hours and then poured with stirring into ice-water (1.7 l.). The aqueous mixture was neutralized with sodium carbonate (300 g.) and then extracted several times with ether. The combined ethereal extracts were washed with aqueous 5% sodium bicarbonate and then dried over magnesium sulfate. Evaporation of the ether left an oil which on distillation gave 86.0 g. (87% yield) of the diacetate, b.p. 54.5–55.5° (0.2 mm.), $n^{25}\text{D}$ 1.4351.

Anal. Calcd. for $C_8H_{10}O_4$: C, 56.46; H, 5.92; sapn. equiv., 85. Found: C, 56.96; H, 6.08; sapn. equiv., 85.

Although this diacetate failed to give a positive test for a terminal acetylene group with potassium mercuric iodide reagent,[5] the presence of such a group was indicated by infrared absorption bands at 3.04 and 4.70 μ and by formation of a white precipitate with ammoniacal aqueous 5% silver nitrate.

3,5-Octadiyne-1,2,7,8-tetrol.—3-Butyne-1,2-diol diacetate was oxidatively coupled using a procedure developed for the coupling of acetylenic alcohols.[6] The diacetate (48 g., 0.28 mole), cuprous chloride (55.5 g., 0.28 mole), ammonium chloride (90 g., 1.68 moles), ethanol (12 ml.), hydrochloric acid (0.6 ml.) and water (305 ml.) were stirred and heated at 55–60° for 6.5 hours while air was bubbled through the solution. After standing overnight the mixture was extracted with ether. The combined extracts were dried with magnesium sulfate, evaporated on the steam-bath, and heated at 126° (0.2 mm.), to give a residue of viscous oil (48 g.). A portion of this crude tetraacetate (14 g., 0.041 mole) was dissolved in absolute methanol (140 ml.) containing sodium (0.1 g.). This solution was allowed to stand overnight and was then refluxed for 3.5 hours. Volatile material was removed at 40° (2 mm.) leaving a tan, waxy solid. This was dissolved in hot ethanol and the solution was decolorized with Darco, diluted with an equal volume of benzene, and cooled to give 4.4 g. (62% yield) of a cream colored solid. The product was evidently a mixture of diastereoisomers for it melted over the range of 116–121° after repeated recrystallizations.

Anal. Calcd. for $C_8H_{10}O_4$: C, 56.46; H, 5.92; quant. hydrogenation, g. H_2/g., 0.0474; mol. wt., 170. Found: C, 55.89; H, 5.94; quant. hydrogenation, g. H_2/g., 0.0470; mol. wt. (thermoelectric method in water[7]), 166.

The ultraviolet spectrum of 3,5-octadiyne-1,2,7,8-tetrol is analogous to those of closely related diacetylenes[8] as shown in Table I.

TABLE I

Compound	Maximum I		Maximum II		Maximum III	
	λ, Å.	ε	λ, Å.	ε	λ, Å.	ε
3,5-Octadiyne-1,2,7,8-tetrol	2310	390	2430	392	2570	255
2,4-Hexadiyne-1,6-diol	2315	410	2440	440	2580	250
3,5-Octadiyne-1,8-diol	2285	450	2395	490	2540	330

CONTRIBUTION NO. 318, CHEMICAL DEPARTMENT
EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & CO.
WILMINGTON 98, DELAWARE

---

[1] D. Swern, G. N. Billen, T. W. Findley and J. T. Scanlan, THIS JOURNAL, **67**, 1786 (1945).

[2] R. Lespieau, *Bull. soc. chim.*, [4] **43**, 199 (1928).

[3] R. A. Raphael, *J. Chem. Soc.*, S-44 (1949).

[4] N. M. Malenok, *J. Gen. Chem. U.S.S.R.*, **9**, 1947 (1939); N. M. Malenok and J. V. Sologub, *ibid.*, **6**, 1904 (1936); **9**, 1947 (1939); **11**, 983 (1941).

[5] J. R. Johnson and W. L. McEwen, THIS JOURNAL, **48**, 469 (1926).

[6] K. Bowden, I. Heilbron, E. R. H. Jones and K. H. Sargent, *J. Chem. Soc.*, 1579 (1947).

[7] G. B. Taylor and M. B. Hall, *Anal. Chem.*, **23**, 947 (1951).

[8] J. B. Armitage and M. C. Whiting, *J. Chem. Soc.*, 2005 (1952).