[Contribution from the Chemical Laboratory of the University of Notre Dame]

SOME REACTIONS OF 2-BUTYNE-1,4-DIOL[1, 2]

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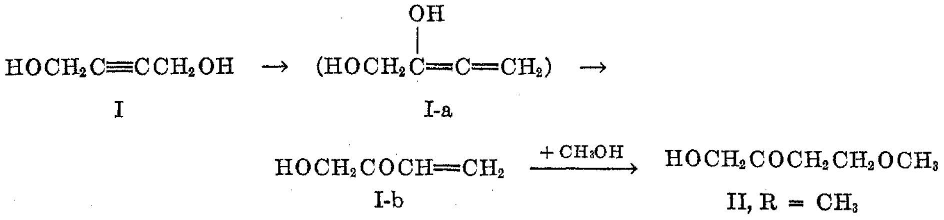
2-Butyne-1,4-diol (I), a white crystalline solid, m.p. 57.5°, was first prepared in 1906 by the action of acetylenedimagnesium bromide on formaldehyde (1). It aroused little interest until about 1940 when the direct synthesis from acetylene and aqueous formaldehyde was revealed (2). Subsequently butynediol became an exceedingly important commodity in the German chemical industry of the World War II period (3).

Since this interesting acetylene is one of the few commercially available in this country, it was decided to study some of its reactions as part of our general program of research on higher acetylenes, especially since much of our knowledge of it comes only from patents, O. P. B. reports, and reviews (3).

One of the very typical reactions of acetylenes, the addition of alcohols, is described clearly in the case of I and methanol by Nazarov (4) and Yurev (5) who stated the product to be 1-hydroxy-4-methoxy-2-butanone (II, R = CH_3). Henshall (6) claimed that ethanol added across the triple bond to produce 2-ethoxy-2-butene-1,4-diol. In order to resolve this serious disagreement, the reaction of I with methyl, ethyl, *n*-propyl, and isobutyl alcohols was studied. All were found to yield products of type II. This raises the question of the mechanism of the reaction. Yurev (5) postulated the following steps, the first of which resembles the Meyer-Schuster rearrangement (7). Butynediol can indeed be rearranged to hydroxymethyl vinyl ketone (I-b) but it is significant that mercuric, cupric, or silver salts of strong acids are required catalysts (3). This suggests that a typical acetylene addition reaction is involved in the mechanism, which we prefer to picture as follows.



$$\underset{\text{I}}{HOCH_2C{\equiv}CCH_2OH} \rightarrow \underset{\text{I-a}}{(HOCH_2\overset{OH}{\overset{|}{C}}{=}C{=}CH_2)} \rightarrow$$

$$\underset{\text{I-b}}{HOCH_2COCH{=}CH_2} \xrightarrow{+CH_3OH} \underset{\text{II, R = CH}_3}{HOCH_2COCH_2CH_2OCH_3}$$

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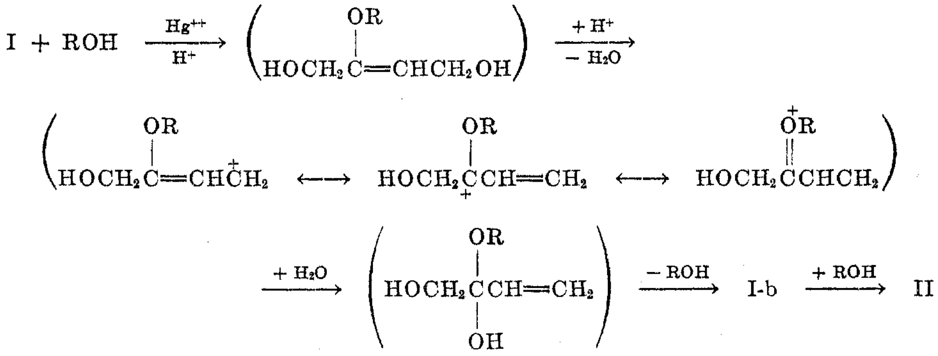
[1] Abstracted from the Ph.D. Dissertation of Floyd P. Kupiecki, University of Notre Dame, 1953.

[2] Paper LX on substituted acetylenes; previous paper, *J. Am. Chem. Soc.*, **75**, 4297 (1953).

[3] General Aniline and Film Corporation Fellow, 1951–1953.

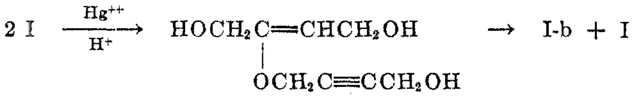


$$\mathrm{I} + \mathrm{ROH} \xrightarrow[\mathrm{H^+}]{\mathrm{Hg^{++}}} \left(\mathrm{HOCH_2\overset{\overset{OR}{|}}{C}{=}CHCH_2OH}\right) \xrightarrow[-\mathrm{H_2O}]{+\mathrm{H^+}}$$

$$\left(\mathrm{HOCH_2\overset{\overset{OR}{|}}{C}{=}CH\overset{+}{C}H_2} \longleftrightarrow \mathrm{HOCH_2\underset{+}{\overset{\overset{OR}{|}}{C}}CH{=}CH_2} \longleftrightarrow \mathrm{HOCH_2\overset{\overset{\overset{+}{O}R}{\|}}{C}CHCH_2}\right)$$

$$\xrightarrow{+\mathrm{H_2O}} \left(\mathrm{HOCH_2\underset{\underset{OH}{|}}{\overset{\overset{OR}{|}}{C}}CH{=}CH_2}\right) \xrightarrow{-\mathrm{ROH}} \text{I-b} \xrightarrow{+\mathrm{ROH}} \mathrm{II}$$

In defense of this proposal, it may be pointed out that the isomerization of I to I-b (in inert solvents) may proceed in exactly the same manner, I also serving in place of ROH.



$$2\ \mathrm{I} \xrightarrow[\mathrm{H^+}]{\mathrm{Hg^{++}}} \mathrm{HOCH_2\underset{\underset{OCH_2C\equiv CCH_2OH}{|}}{C}{=}CHCH_2OH} \longrightarrow \text{I-b} + \mathrm{I}$$

Also, this mechanism indicates that addition of small amounts of water to the reaction mixture should be beneficial, as was observed to be the case.

The structures of the four compounds (II, R = CH_3, C_2H_5, n-C_3H_7, and $(CH_3)_2CHCH_2$, respectively) were proved by oxidation with periodic acid and by examination of the infrared (IR) spectra. Special interest attached to the ethoxy compound, in view of Henshall's claim (6). Oxidation gave the known β-ethoxypropionic acid (III, R = C_2H_5), whose p-bromphenacyl ester (IV) had the correct m.p., not depressed by admixture with an authentic sample (8). The IR spectrum of II (R = C_2H_5) showed the typical hydroxyl band at 2.9μ and the carbonyl at 5.8μ.

The four products (II) are described in Table I.

In view of the isomerization in the reaction of I with alcohols, the same reaction was studied in the case of the dimethyl ether (V) and methanol. The methyl and ethyl ethers were readily prepared by alkylation with sulfates in alkaline solution. Using the procedure previously described (9), the butynediol dimethyl ether-methanol reaction gave the anticipated ketal (VI) in good yield. Rearrangement, as in the case of the diol (I), discussed above, would have yielded 1,4-dimethoxy-2-butanone (VII); the latter was prepared independently both by hydrolysis of VI and by direct hydration of V.

The dimethyl ether (V) is reported (10) to yield 1,2,4-trimethoxy-2-butene (VIII) by heating with sodium methoxide in methanol. This was confirmed.

The butynediol diethers (V, R = CH_3 and C_2H_5) were hydrated readily to the ketones (VII). The reaction with the dimethyl ether was carried out by dropwise addition of a methanol solution to a catalyst composed of mercuric oxide and sulfuric acid in aqueous methanol. When the diethyl ether (V, R = C_2H_5) was treated in the same way, the product was chiefly 1-ethoxy-4-methoxy-2-butanone, indicating a facile replacement of the 4-ethoxy group. This difficulty was circumvented by using aqueous ethanol for the hydration of the diethyl ether.

Since three 1,4-dialkoxy-2-butanones (VII) were thus available, each was treated with sodium acetylide in liquid ammonia to produce the ethynyl carbinols (IX). These substances were sought since they are alkoxy substitution products of 2-ethynyl-2-butanol, recently announced as a hypnotic (11). Our compounds, 1,4-dimethoxy-2-ethynyl-2-butanol and the 1,4-diethoxy and 1-ethoxy-4-methoxy analogs (IX), showed sedative and hypnotic action by oral administration to rats only in very large doses (*ca.* 400–900 mg./kg.).[4]

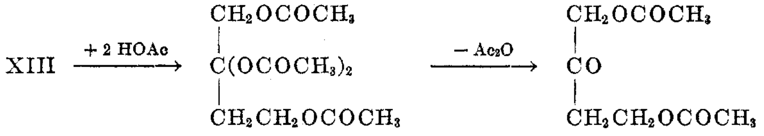
The replacement of ethoxy by methoxy in the hydration of V, discussed above, suggested other reactions of a similar type. When 1,4-dimethoxy-2-butanone (VII, R = CH_3) was heated with piperidine under a fractionating column, methanol was removed by distillation and 1-methoxy-4-piperidino-2-butanone (X) was formed. Another experiment, using *n*-amylamine, proved unsuccessful. On the other hand, reaction of VII (R = CH_3) with nitromethane in the presence of a little piperidine or diethylamine involved only the carbonyl group, producing XI in good yield. Dehydration of the latter was studied also; best results were obtained by the use of thionyl chloride and pyridine. That the product (XII) had the double bond as shown was proved by examination of the IR and UV spectra.

TABLE I

Physical Constants of 1-Hydroxy-4-alkoxy-2-butanones, $HOCH_2COCH_2CH_2OR$

R	B.P., °C.	MM.	n_D^{25}	d^{25}	YIELD, %
CH_3	63–64	4	1.4370	1.0865	61
C_2H_5	68	2.5	1.4356	1.0378	54
n-C_3H_7	77	2.2	1.4360	1.0118	55
$(CH_3)_2CHCH_2$	59	0.6	1.4340	0.9827	46

Butynediol diacetate (XIII) was prepared in order to study its hydration, accomplished by addition to acetic acid containing mercuric oxide and sulfuric acid in small amounts. The following transformations were envisaged.



$$\mathrm{XIII} \xrightarrow{+2\ \mathrm{HOAc}} \begin{array}{l} CH_2OCOCH_3 \\ | \\ C(OCOCH_3)_2 \\ | \\ CH_2CH_2OCOCH_3 \end{array} \xrightarrow{-\mathrm{Ac_2O}} \begin{array}{l} CH_2OCOCH_3 \\ | \\ CO \\ | \\ CH_2CH_2OCOCH_3 \end{array}$$

(XIII-a) (XIII-b)

The product was not XIII-b, but rather acetoxymethyl vinyl ketone (XIV) previously reported (12, 13). The mechanism of its formation can be pictured as above, assuming 3,4-elimination of acetic acid under the highly acidic conditions existing in the reaction mixture. It was observed that XIV is an unusually active

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[4] The hypnotic tests were performed in the Lilly Research Laboratories, Indianapolis, Indiana. Grateful acknowledgment of this assistance is made.

vinyl monomer; when a sample was allowed to stand in a closed container overnight, it was completely polymerized. The preparation of XIV from II suggested itself as further evidence for the structure of each. The transformation was achieved by heating II with acetic anhydride containing a little camphorsulfonic acid.

The reactions and products enumerated above are diagrammed in the accompanying Chart I. It should be mentioned that various other reactions of butynediol have been described recently by A. W. Johnson (14).

EXPERIMENTAL

2-Butyne-1,4-diol (I) was supplied by the General Aniline and Film Corporation[5] as a 35% aqueous solution and in the crystalline form. The aqueous material was used without purification. The solid was stored in a desiccator over calcium chloride; solutions in appropriate solvents were prepared as needed and filtered before use.

1-Hydroxy-4-ethoxy-2-butanone (II, R = C_2H_5). Crystalline butynediol (30 g.) in 75 ml. of 95% ethanol was added slowly with stirring to 2 g. of mercuric oxide, 1.5 g. of conc'd sulfuric acid, and 5 g. of water in 25 ml. of 95% ethanol. The addition (5 hours) was regulated to maintain a temperature of 35–40°. Additional mercuric oxide was added in three 0.5-g. portions at intervals of about 1 hour. When addition was complete, the stirring was continued for an hour. Anhydrous sodium carbonate (7 g.) was then added with stirring. The mixture was filtered with suction and distilled, retaining the portion boiling at 68–70° at 2 mm.; yield 25 g. (54%). A sample redistilled for analysis had b.p. 68° at 2.5 mm.; n_D^{25} 1.4356; d^{25} 1.0378.

Anal.[6] Calc'd for $C_6H_{12}O_3$: C, 54.53; H, 9.15.
Found: C, 54.77; H, 9.33.

1-Hydroxy-4-methoxy-2-butanone (II, R = CH_3) was prepared in substantially the same way from 50 g. of I, 200 g. of methanol, and 18 g. of water. Distillation gave 42 g. (61%), b.p. 71° at 3.6 mm. The physical properties (see Table I) agreed well with the literature (4) values: b.p. 85° at 9 mm.; n_D^{20} 1.4395; d^{20} 1.0920.

1-Hydroxy-4-propoxy-2-butanone (II, R = C_3H_7) was similarly made from 30 g. of I, 125 g. of *n*-propanol, and 10 g. of water. The yield was 28 g. (55%).

Anal. Calc'd for $C_7H_{14}O_3$: C, 57.51; H, 9.65.
Found: C, 57.35; H, 9.80.

1-Hydroxy-4-isobutoxy-2-butanone (II, R = $(CH_3)_2CHCH_2$). Compound I (30 g.), 125 g. of isobutyl alcohol, and 15 g. of water gave 25 g. of product (46% yield).

Anal. Calc'd for $C_8H_{16}O_3$: C, 59.97; H, 10.07.
Found: C, 59.87; H, 10.15.

Oxidation of 1-hydroxy-4-ethoxy-2-butanone. The compound (2 g.) was dissolved in 35 ml. of water followed by 4.5 g. of trisodium dihydrogen paraperiodate. Conc'd sulfuric acid (2.3 g.) was then added and the mixture was allowed to stand over-night. It was then extracted with three 10-ml. portions of ether and the ether was evaporated. One-half gram of the residue was used to prepare the *p-bromophenacyl ester*; yield, 0.4 g.; m.p. 55–56°, not depressed by mixing with an authentic sample made from β-ethoxypropionic acid.

The other 1-hydroxy-4-alkoxy-2-butanones were oxidized in the same general way. The β-alkoxypropionic acids were converted to their *p-bromophenacyl esters*. M.ps., β-methoxy, 69–70°; β-propoxy, 59–60°; β-isobutoxy, 60–61°; these values are in reasonable agreement with the literature (8).

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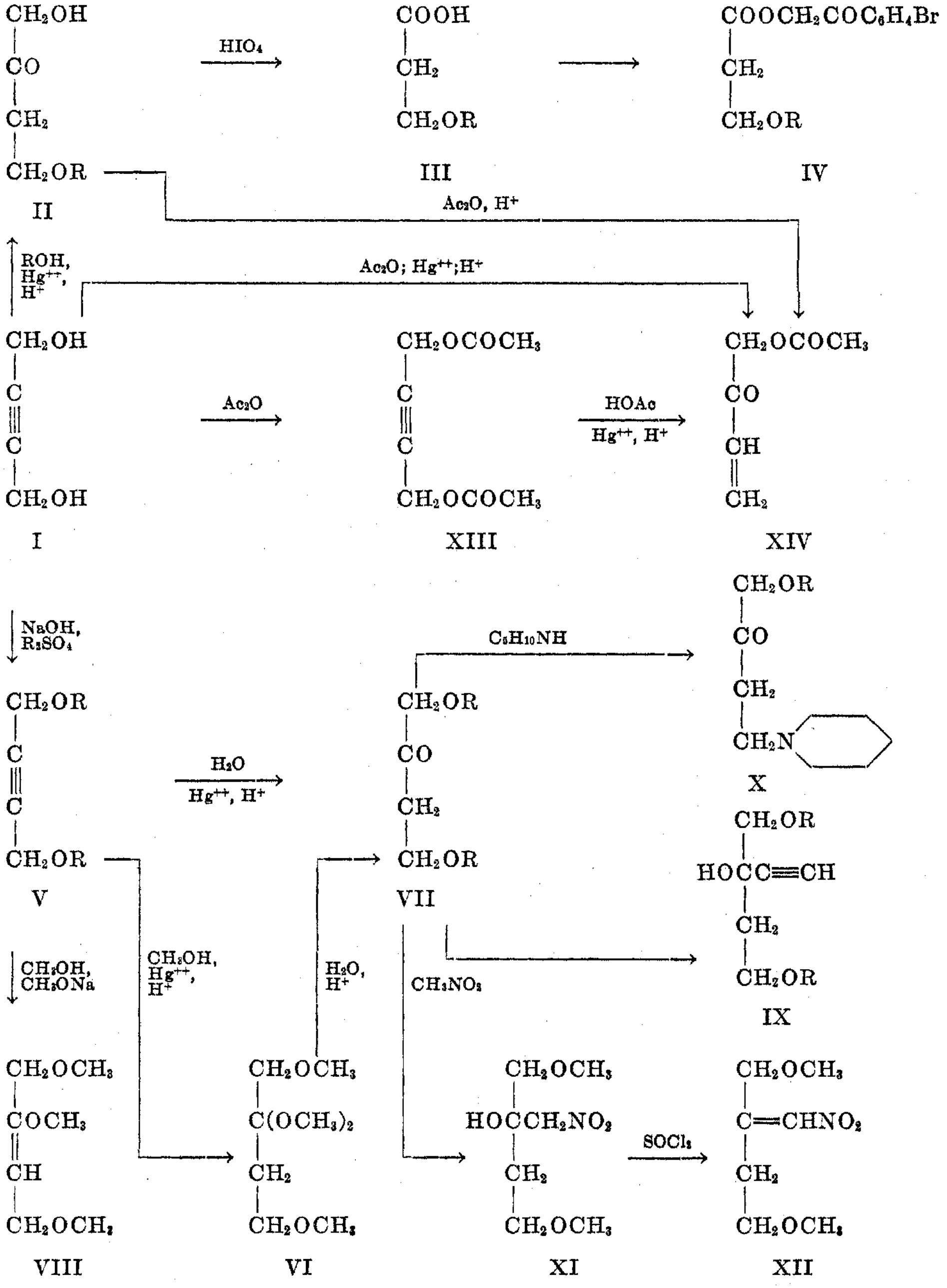
[5] General Aniline and Film Corporation, Commercial Development Department, 435 Hudson Street, New York 14, New York.

[6] Analyses were performed by Micro-Tech Laboratories, Skokie, Illinois, through the courtesy of Mr. Charles W. Beazley.

CHART I



Butynediol dimethyl ether (V, R = CH_3). Two moles of I (492 g. of 35% solution) were placed in a three-neck three-liter flask equipped with stirrer and dropping-funnel. The flask was immersed in an ice-bath and sodium hydroxide pellets were added to the butynediol in 20-g. portions. Meanwhile dimethyl sulfate was added dropwise with stirring. A total of 200 g. of sodium hydroxide and 630 g. of dimethyl sulfate were used, the additions requiring 4 hours. The dropping-funnel was then replaced with a reflux condenser and the mixture was heated over a water-bath for 2 hours. After cooling to room temperature, 200 ml. of water was added to dissolve the precipitated salts. The upper layer was separated and the aqueous layer was extracted three times with 100-ml. portions of ether. The ethereal extracts were combined with the upper layer and the whole was dried over potassium carbonate. Distillation gave 200 g. of product (88% yield), b.p. 69–73° at 28–30 mm. A portion was redistilled, b.p. 72–73° at 30 mm.; 57–58° at 15 mm.; n_D^{25} 1.4321; d^{25} 0.9437. Literature values (10) are b.p. 158° at 730 mm.; n_D^{22} 1.437; d^{22} 0.9576.

Butynediol monomethyl ether. When 246 g. of 35% aqueous butynediol solution (1 mole) was treated with 45 g. (1.1 moles) of sodium hydroxide and 139 g. (1.1 moles) of dimethyl sulfate the mono- and di-methyl ethers were formed in poor yields. Using the procedure described above, distillation gave 35 g. of dimethyl ether, b.p. 80–95° at 32 mm. and 26 g. (26% yield) of the monomethyl ether. The latter had b.p. 114° at 30 mm.; 85° at 6 mm.; n_D^{25} 1.4573; d^{25} 1.0279.

Anal. Calc'd for $C_5H_8O_2$: C, 59.98; H, 8.05.

Found; C, 59.15; H, 8.10.

Butynediol diethyl ether (V, R = C_2H_5) was prepared in a similar way except that 492 g. of 35% butynediol solution, 200 g. of sodium hydroxide, and 740 g. of diethyl sulfate were mixed initially at 25–35°. When mixed in the cold, as described above, a violent reaction occurred early in the subsequent heating. The yield was 239 g. (84%), b.p. 84° at 18 mm.; n_D^{25} 1.4323; d^{25} 0.9090. [Lit. (10), b.p. 179–180° at 730 mm.; n_D^{22} 1.435; d^{22} 0.9156.]

1,2,2,4-Tetramethoxybutane (VI). A 300-ml. three-necked flask provided with stirrer, reflux condenser, and dropping-funnel was charged with 6 g. of red mercuric oxide, 4 ml. of boron trifluoride etherate, and 4 ml. of methanol. The mixture was warmed for a minute to dissolve a little of the mercuric oxide and 40 g. of methanol was added. Then 114 g. (1.0 mole) of butynediol dimethyl ether diluted with 40 g. of methanol was admitted dropwise with stirring during two hours. The temperature was maintained at 40–50° (exothermic reaction) by occasional cooling. Three 0.5-g. portions of mercuric oxide were added in successive 30-minute intervals after the first hour. When addition was complete, the mixture was stirred for an additional two hours and 7 g. of anhydrous powdered potassium carbonate added to neutrality. The solids were filtered off and the filtrate was distilled. The yield of VI was 143 g. (80%), b.p. 91° at 16 mm.; n_D^{25} 1.4187; d^{25} 0.9935.

Anal. Calc'd for $C_8H_{18}O_4$: C, 53.91; H, 10.18.

Found: C, 54.18; H, 10.29.

1,2,4-Trimethyoxy-2-butene (VIII). Sodium (27 g.) was dissolved in 290 g. of absolute methanol contained in a one-liter three-neck flask equipped with a reflux condenser protected with a calcium chloride drying-tube. Butynediol dimethyl ether (68.4 g., 0.6 mole) was then added and the mixture was refluxed for 16 hours. The solution was then transferred to a distilling flask and most of the excess methanol was distilled. Water (275 ml.) was added and the layers were separated. The aqueous layer was extracted with three 75-ml. portions of ether and the extracts were combined with the organic layer. After drying over potassium carbonate, distillation yielded 28 g. (33% yield) of VIII, b.p. 86–87° at 30 mm. A middle fraction had n_D^{25} 1.4313; d^{25} 0.9667. [Lit. (10) b.p. 179–180° at 730 mm.]

Anal. Calc'd for $C_7H_{14}O_3$: C, 57.51; H, 9.65.

Found: C, 57.58; H, 9.92.

1,4-Dimethoxy-2-butanone (VII, R = CH_3). A solution of 97 g. of butynediol dimethyl ether in 50 g. of methanol was added dropwise to a well-stirred mixture of 3 g. of red mercuric oxide, 3 g. of conc'd sulfuric acid, and 150 ml. of 70% aqueous methanol. The temperature rose slowly to 50° and was maintained near this point by occasional cooling. When mixing was complete an additional 1 g. of mercuric oxide was added and the stirring was continued until the mixture cooled to room temperature. Then 5.5 g. of powdered anhydrous sodium acetate was added with good stirring and the solids were allowed to settle overnight. The liquid was decanted and most of the methanol and water were distilled under a vacuum. Meanwhile some sodium sulfate crystallized from the reaction product. This was filtered off and the distillation was resumed at 20 mm. yielding 81.5 g. (73% yield), b.p. 80–82°/20 mm. Redistillation gave 76 g., b.p. 84–85° at 19 mm.; n_D^{25} 1.4198; d^{25} 1.0049.

The product was also prepared from 71 g. (0.4 mole) of 1,2,2,4-tetramethoxybutane (VI) by addition of 1 ml. of conc'd hydrochloric acid diluted to 10 ml. with water. The solution was heated for 30 minutes and then was distilled without neutralization. The yield was 45.5 g. (87%), b.p. 84–85° at 20 mm.; n_D^{25} 1.4201.

1-Ethoxy-4-methoxy-2-butanone was the major product when the above procedure was used with 146 g. of butynediol diethyl ether, 150 g. of methanol, and 50 g. of water. The second distillation gave three fractions: (a) 48.2 g., b.p. 96–100° at 21 mm.; n_D^{25} 1.4199; (b) 17.2 g., b.p. 100° at 21 mm.; n_D^{25} 1.4197; (c) 44.6 g., b.p. 100° at 21 mm.; n_D^{25} 1.4194. Fraction (b) was analyzed.

Anal. Calc'd for $C_7H_{14}O_3$: C, 57.51; H, 9.65.
Found: C, 56.64; H, 9.52.

1,4-Diethoxy-2-butanone (VII, R = C_2H_5). The procedure described above was employed with 140 g. of butynediol diethyl ether, 4 g. of mercuric oxide, 3 g. of conc'd sulfuric acid, 150 g. of 95% ethanol, and 50 g. of water. Two distillations yielded 79 g. (50% yield), b.p. 96° at 15 mm.; n_D^{25} 1.4195; d^{25} 0.9478.

Anal. Calc'd for $C_8H_{16}O_3$: C, 59.97; H, 10.07.
Found: C, 60.10; H, 10.16.

1,4-Dimethoxy-4-ethynyl-2-butanol (IX, R = CH_3). Sodium acetylide was prepared from 29 g. (1.25 g.-atoms) of sodium in 1.5 liters of liquid ammonia in the usual way. One mole (132 g.) of 1,4-dimethoxy-2-butanone diluted with three volumes of anhydrous ether was added dropwise with good stirring. Slow admission of acetylene was continued during the addition and throughout the subsequent 7-hour stirring period. When most of the ammonia had evaporated 70 g. of ammonium chloride was added cautiously in small portions followed by 250 g. of chopped ice and 100 ml. of ether. The ethereal layer was separated and the aqueous layer was extracted three times with 50-ml. portions of ether. The combined ethereal extract was washed twice with 100 ml. of saturated brine, once with 80 ml. of 5% acetic acid in brine, and finally with 80 ml. of brine. After drying with magnesium sulfate, distillation gave 90 g. of product (57% yield), b.p. 63–65° at 1.8 mm. Redistillation afforded 81.7 g., b.p. 63° at 1.7 mm.; n_D^{25} 1.4471; d^{25} 1.0108.

Anal. Calc'd for $C_8H_{14}O_3$: C, 60.73; H, 8.92.
Found: C, 60.52; H, 8.83.

1-Ethoxy-4-methoxy-2-ethynyl-2-butanol was prepared in the same way from 90 g. of 1-ethoxy-4-methoxy-2-butanone, 16 g. of sodium, and excess acetylene. The yield was 46 g. (44%); b.p. 78–79° at 2.6 mm.; n_D^{25} 1.4430; d^{25} 0.9751.

Anal. Calc'd for $C_9H_{16}O_3$: C, 62.70; H, 9.36.
Found: C, 62.51; H, 9.35.

1,4-Diethoxy-2-ethynyl-2-butanol was similarly made from 77 g. of 1,4-diethoxy-2-butanone, 13 g. of sodium, and excess acetylene. The yield was 44 g. (49%), b.p. 83° at 3 mm., n_D^{25} 1.4408; d^{25} 0.9548.

Anal. Calc'd for $C_{10}H_{18}O_3$: C, 64.48; H, 9.74.
Found: C, 64.37; H, 9.85.

1-Methoxy-4-piperidino-2-butanone (X, R = CH_3). 1,4-Dimethoxy-2-butanone (33 g.) was added to 23 g. of piperidine contained in a 100-ml. round bottom flask. The flask was attached to a short fractionating column (22 × 1.2 cm.) and slow distillation of methanol was achieved by heating with an oil-bath. Methanol first appeared in the column head at a bath temperature of 140°. By raising the bath temperature slowly to 165° a total of 6 g. of methanol was collected, b.p. 64–68°. Subsequent distillation of the residue *in vacuo* gave 22 g. of product (48% yield), b.p. 77–82° at 1.7 mm. When redistilled, the b.p. was 83–84° at 2 mm.; n_D^{25} 1.4648; d^{25} 0.9852.

Anal. Calc'd for $C_{10}H_{19}NO_2$: C, 64.82; H, 10.33.
Found: C, 63.58; H, 10.31.

1,4-Dimethoxy-2-nitromethyl-2-butanol (XI). A mixture of 1,4-dimethoxy-2-butanone (51 g., 0.39 mole), excess nitromethane (91.5 g., 1.5 moles), and diethylamine (7 g.) was allowed to stand at room temperature for 5 days. The red solution was then distilled under reduced pressure. There were recovered 28 g. of unreacted 1,4-dimethoxy-2-butanone and 31 g. of product, b.p. 109–111° at 3 mm.; n_D^{25} 1.4495. Combined material from several runs was redistilled, b.p. 107° at 2.2 mm.; n_D^{25} 1.4500; d^{25} 1.1543.

Anal. Calc'd for $C_7H_{15}NO_5$: C, 43.51; H, 7.82.

Found: C, 43.16; H, 7.80.

1-Nitro-2-methoxymethyl-4-methoxy-1-butene (XII). 1,4-Dimethoxy-2-nitromethyl-2-butanol (XI) (27 g.) dissolved in 25 g. of pyridine was cooled in an ice-bath and 20 g. of thionyl chloride was added dropwise with stirring. The mixture was allowed to warm to room temperature with stirring and the product was recovered by three extractions with 50-ml. portions of ether. The ethereal solution was washed with aqueous sodium bicarbonate and then with water. After drying with magnesium sulfate, distillation gave 12 g. of product (49% yield), b.p. 93–94° at 1.8 mm.; n_D^{25} 1.4682; d^{25} 1.1030.

Anal. Calc'd for $C_7H_{13}NO_4$: C, 47.99; H, 7.48.

Found: C, 48.45; H, 7.66.

The infrared spectrum showed strong bands at 6.05 μ and 6.5 μ, indicating conjugate olefinic and nitro groups, respectively. Further support of the assigned structure (XII) was obtained from the exaltation of molecular refraction (MR calc'd 42.97; found 44.16) and from the ultraviolet absorption spectrum (λ_{max} 245; ϵ_{max} 4800).

Butynediol diacetate (XIII). A solution of 34.4 g. of crystalline butynediol in 92 g. of acetic anhydride heated for 2 hours at 95–100° gave by distillation 67 g. of diacetate, b.p. 91–93° at 2 mm. Redistillation yielded 60 g. (88% yield), b.p. 135° at 17 mm.; n_D^{25} 1.4512; d^{25} 1.1223. Johnson (14) reports b.p. 122–123° at 10 mm.; n_D^{20} 1.4611.

Acetoxymethyl vinyl ketone (XIV). One-fourth mole (21.5 g.) of butynediol was converted to the diacetate (not isolated) as described above. The entire product was added dropwise with stirring to a mixture of 1 g. of red mercuric oxide, 0.5 g. of conc'd sulfuric acid, and 10 ml. of glacial acetic acid. The reaction was notably exothermic and a temperature of 50–60° was maintained throughout the reaction by occasional cooling as needed. An additional 0.5 g. of mercuric oxide was added when mixing was complete and the stirring was continued for 30 minutes. The sulfuric acid was then neutralized by addition of 2 g. of anhydrous sodium acetate. The solids were filtered off (suction) and the filtrate was distilled under reduced pressure. The acetic acid and acetic anhydride were removed at 49–60° at 25–30 mm. and the pressure was then reduced to 4 mm. to distill the product; b.p. 70–71° at 4 mm.; yield, 23.5 g. (73%). After redistillation the physical constants were b.p. 70° at 4 mm.; n_D^{25} 1.4355; d^{25} 1.0788. [Lit. (12), b.p. 83° at 14 mm.; n_D^{15} 1.4455.)

Acetoxymethyl vinyl ketone was also prepared by heating 10 g. of 1-hydroxy-4-methoxy-2-butanone with 18 g. of acetic anhydride and 0.5 g. of camphorsulfonic acid. The product was collected at 81–83° at 13 mm.; yield, 7.5 g. (69%).

SUMMARY

A number of ethers, esters, carbinols, and ketones have been prepared from 2-butyne-1,4-diol.

NOTRE DAME, INDIANA

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