219. *2-Butyne-1 : 4-diol. Part II. Reactions involving the Triple Bond.*

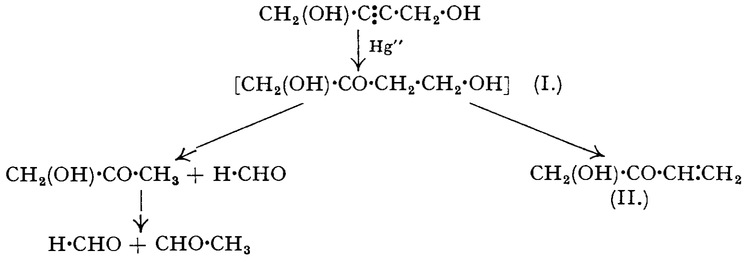
By A. W. Johnson.

Hydrogenation of 2-butyne-1 : 4-diol yields either *cis*-2-butene-1 : 4-diol or butane-1 : 4-diol. Hydration in the presence of acid solutions of mercuric salts gives a variety of products derived from butane-1 : 4-diol-2-one. Addition of hydrogen chloride in the presence of cuprous chloride and ammonium chloride yields 2 : 2-*dichlorobutane*-1 : 4-*diol*, and addition of iodine yields 2 : 3-*di-iodo-2-butene*-1 : 4-*diol*. The action of hydrogen chloride at 100° or of 48% hydrobromic acid at room temperature gives the corresponding 2(3) : 4-dihalogeno-2-buten-1-ols.

The reactions of 2-butyne-1 : 4-diol involving the triple bond are mainly additions. Partial reduction to *cis*-2-butene-1 : 4-diol is known to be effected either by zinc and aqueous sodium hydroxide (I.G. Farbenind., B.P. 508,543) or by hydrogenation over partly poisoned catalysts (I.G. Farbenind., F.P. 853,148; General Aniline and Film Corp., U.S.P. 2,300,598). The *cis*-diol has now been prepared in excellent yield by hydrogenation at atmospheric pressure over 0·5% palladium–calcium carbonate or Raney nickel by taking advantage of the distinct change in the rate of hydrogenation after the absorption of one equivalent of hydrogen. This change of rate was not obtained with platinum catalysts in accordance with the observation of Lespieau (*Compt. rend.*, 1910, **150**, 1761). The identification of the ethylenic compound as the *cis*-isomer depended on the observation that its *dibenzoyl* derivative differed from that of the *trans*-diol, prepared by Prévost (*Compt. rend.*, 1926, **183**, 1292; 1928, **186**, 1209; *Ann. Chim.*, 1928, **10**, 400) by hydrolysis of *trans*-1 : 4-dibromo-2-butene.

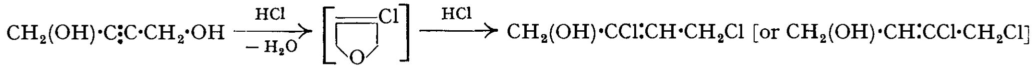
Complete hydrogenation of 2-butyne-1 : 4-diol can be effected over a variety of catalysts, *e.g.*, nickel on pumice (I.G. Farbenind., U.S.P. 2,222,302; G.P. 721,004); copper (General Aniline and Film Corp., U.S.P. 2,335,795); platinum (Lespieau, *loc. cit.*); nickel, cobalt, copper, or silver (I.G. Farbenind., B.P. 508,944; U.S.P. 2,319,707). Butane-1 : 4-diol has also been obtained by hydrogenation of succinic ester (*inter al.*, Muller, *Monatsh.*, 1928, **49**, 28) and by hydrolysis of 1 : 4-diacetoxybutane (derived from tetrahydrofuran) by calcium oxide (Bennett and Heathcote, *J.*, 1929, 268). It has been shown that a more convenient method of hydrolysis of 1 : 4-diacetoxybutane is by the action of concentrated hydrochloric acid, but this method is unsatisfactory on a large scale. Hydrogenation of 2-butyne-1 : 4-diol over Raney nickel at elevated pressure has been repeated and this is undoubtedly the best laboratory method for preparing butane-1 : 4-diol which is an important industrial intermediate; dehydration yields tetrahydrofuran or 1 : 3-butadiene and halogenation yields the 1 : 4-dihalogenobutanes which may be converted into 1 : 4-dicyanobutane by the action of sodium cyanide (General Aniline and Film Corp., U.S.P. 2,222,302).

The hydration of the triple bond of 2-butyne-1 : 4-diol was first attempted by Dupont (*Ann. Chim.*, 1913, **30**, 485) with Denigès's solution (acid mercuric sulphate) but no product was isolated and the reagent was reduced to metallic mercury. The probable primary product of this hydration, butane-1 : 4-diol-2-one (I), has been reported to be unstable by Charlton and Kenner (*J.*, 1932, 750) who were unable to isolate the ketone or the corresponding oxime, but succeeded in isolating the phenylosazone. Although a neutral solution of mercuric chloride was reduced to mercurous chloride on warming with 2-butyne-1 : 4-diol, it has been found that, when Denigès's solution was used below 25°, acetaldehyde and formaldehyde could be isolated from the product as the corresponding 2 : 4-dinitrophenylhydrazones. Acetol, as the 3 : 5-*dinitrobenzoate*, and a ketone as its yellow 2 : 4-dinitrophenylhydrazone, $C_{10}H_{10}O_5N_4$, m. p. 111—115°, were also obtained. When the reaction mixture was warmed for a short time at 100°, a further product, probably 3-buten-1-ol-2-one (II), was isolated as its red 2 : 4-*dinitrophenylhydrazone*, m. p. 232—234°. All these products were obtained in only very small yields.



Since the above work was carried out, Lozach (*Bull. Soc. chim.*, 1944, **11**, 514) has reported that hydration of 2-butyne-1 : 4-diol in the presence of aqueous mercuric sulphate gives a polymeric substance probably formed by dehydration of (I) to (II) followed by polymerisation by sulphuric acid formed by hydrolysis of the mercuric sulphate. In boiling acetic acid in the presence of mercuric acetate, the diacetate of 2-butyne-1 : 4-diol was converted into 1 : 4-diacetoxy-2-butanone and 1-acetoxy-3-buten-2-one.

Hydrogen chloride has been added to 2-butyne-1 : 4-diol in the presence of cuprous chloride and ammonium chloride to yield 2 : 2-*dichlorobutane*-1 : 4-*diol*. The action of gaseous hydrogen chloride on 2-butyne-1 : 4-diol at 100° gave a small amount of 1 : 4-dichloro-2-butyne (Part I, preceding paper) together with 2(3) : 4-*dichloro*-2-*buten*-1-*ol* (*phenylurethane*). The mechanism of this reaction is uncertain but it is possible that 3-chloro-2 : 5-dihydrofuran is an intermediate.



Hydrolysis of 2(3) : 4-dichloro-2-buten-1-ol with an aqueous suspension of calcium carbonate gave 2-*chloro*-2-*butene*-1 : 4-*diol* [*bis*-(3 : 5-*dinitrobenzoate*)], and interaction with β-naphthol in alcoholic potassium hydroxide gave 2(3)-*chloro*-4-β-*naphthoxy*-2-*buten*-1-*ol*.

On dissolving 2-butyne-1 : 4-diol in 48% hydrobromic acid and keeping at room temperature for several days, the principal product was 2(3) : 4-*dibromo*-2-*buten*-1-*ol* which on treatment with β-naphthol in alcoholic alkali gave 2(3)-*bromo*-4-β-*naphthoxy*-2-*buten*-1-*ol*.

On warming 2-butyne-1 : 4-diol with a solution of iodine in aqueous potassium iodide, 2 : 3-*di-iodo*-2-*butene*-1 : 4-*diol* was formed; the dibromo-analogue was readily obtained by adding bromine to a benzene suspension of 2-butyne-1 : 4-diol (Lespieau, *Ann. Chim.*, 1912, **27**, 137; 1914, **2**, 280; *Compt. rend.*, 1914, **158**, 707). No definite product was isolated from the action of chlorine on 2-butyne-1 : 4-diol, a reaction which is known to be complex with 2 : 5-dimethyl-3-hexyne-2 : 5-diol (Hennion and Wolf, *J. Amer. Chem. Soc.*, 1940, **62**, 1368). An attempt to prepare 2 : 3-dichloro-2-butene-1 : 4-diol from the dibromo-analogue by heating with an alcoholic solution of mercuric chloride also yielded a complex mixture of products.

It was not possible to add aniline to the triple bond of 2-butyne-1 : 4-diol; in the presence of mercuric chloride the diol was largely unchanged, and with sulphuric acid and mercuric sulphate hydration of the triple bond occurred. An attempted addition of hydroxylamine also failed. Addition products of certain amino-anthraquinones and 2-butyne-1 : 4-diol have been claimed (I.G. Farbenind., F.P. 828,581/50,208).

No Diels–Alder adduct of 2-butyne-1 : 4-diol and *cyclo*pentadiene could be obtained under the conditions recommended for the addition of 2-butene-1 : 4-diol, *viz.*, heating at 180° in an autoclave for 7 hours (I.G. Farbenind., F.P. 857,937). Acetylenic compounds are known to be often more reluctant than the corresponding ethylenic compounds to undergo Diels–Alder additions (Johnson, *J.*, 1945, 715). No formation of pyrazole derivatives was observed on allowing 2-butyne-1 : 4-diol to stand for two weeks in contact with excess of diazomethane in acetone.

Other reactions of 2-butyne-1 : 4-diol reported in the literature include addition of sodium hydrogen sulphite to give sodium butane-1 : 4-diol-2 : 3-disulphonate (I.G. Farbenind., F.P. 858,185); conversion into 4-hydroxybutaldehyde by passing an aqueous solution over a palladium–pumice catalyst at 105° in an atmosphere of hydrogen (I.G. Farbenind., U.S.P. 2,333,216); formation of pyrroles by passing the diol with ammonia or a primary amine over a heated catalyst (I.G. Farbenind., G.P. 701,825); and catalytic oxidation to maleic anhydride (I.G. Farbenind., F.P. 721,763/49,921).

EXPERIMENTAL.

M. ps. are uncorrected. Micro-analyses were carried out by Mr. E. S. Morton.

Hydrogenation.—(a) 2-*Butene*-1 : 4-*diol*. 2-Butyne-1 : 4-diol (20 g.) was dissolved in methanol (350 c.c.) and hydrogenated in the presence of 0·5% palladium–calcium carbonate (2·0 g.). After 24 hours, one equivalent of hydrogen (5650 c.c.) had been absorbed. The catalyst was then separated and the filtrate distilled, giving *cis*-2-butene-1 : 4-diol as a colourless oil (15·7 g.; 77%), b. p. 134—135°/15 mm., $n_D^{25^\circ}$ 1·4716 (General Aniline and Film Corp., U.S.P. 2,300,598, give b. p. 129—130°/13 mm. for *cis*-2-butene-1 : 4-diol). The *dibenzoate* formed prisms from aqueous methanol, m. p. 69—70° (Prévost and Lutz, *Compt. rend.*, 1934, **198**, 2264, give m. p. 101° for the dibenzoate of *trans*-2-butene-1 : 4-diol) (Found : C, 72·85; H, 5·45. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%). The *bis*-(3 : 5-*dinitrobenzoate*) formed pale yellow plates from 2-ethoxyethanol, m. p. 171—172° (Found: C, 45·1; H, 2·75; N, 12·3. $C_{18}H_{12}O_{12}N_4$ requires C, 45·4; H, 2·6; N, 11·75%).

(b) *Butane*-1 : 4-*diol.* (i) 2-Butyne-1 : 4-diol (250 g.) in methanol (300 c.c.) was rotated in an autoclave at 150 atmospheres hydrogen pressure at room temperature with Raney nickel (50 g.) (I.G. Farbenind., B.P. 508,944). The reaction was very rapid (30 mins.) and external cooling was required. After removal of the catalyst the product was distilled to give butane-1 : 4-diol (230 g.; 92%) as a colourless oil, b. p. 128—129°/23 mm.

(ii) 1 : 4-Diacetoxybutane (44 g.) (Paul, *Compt. rend.*, 1929, **208**, 587) in ethanol (25 c.c.) was refluxed with concentrated hydrochloric acid (12·5 c.c.) and the solvent then removed on the steam-bath. The residue was distilled giving butane-1 : 4-diol, b. p. 125—126°/20 mm. (16·6 g.; 73%). Repetition of this experiment on a larger scale gave lower yields owing to the formation of some tetrahydrofuran.

Hydration.—2-Butyne-1 : 4-diol (20 g.) was added with stirring during 30 minutes to Denigès's solution (50 c.c.) [prepared by dissolving mercuric oxide (5 g.) in hot 27% sulphuric acid (140 g.)] with ice cooling. The solution rapidly darkened and mercury was precipitated (cf. Dupont, *loc. cit.*). After being stirred for a further hour, the solution was heated for ½ hour on the steam-bath; some tar had then formed. The cooled product was extracted with ether overnight in a continuous extractor, and the extract dried and distilled. The main fraction, b. p. 100—150°/15 mm. (1·3 g.), warmed with aqueous 2 : 4-dinitrophenylhydrazine hydrochloride, gave a 2 : 4-*dinitrophenylhydrazone* which was dried and purified by chromatography of a benzene solution on alumina. The product, isolated by removal of benzene from the eluate, was obtained as red needles (from ethyl acetate), m. p. 232—234° (Found: C, 45·6; H, 3·4. $C_{10}H_{10}O_5N_4$ requires C, 45·2; H, 3·75%). Light absorption: The 2 : 4-dinitrophenylhydrazone in chloroform showed a main maximum at 3950—4000 A., $\epsilon = 21{,}300$, indicating that the compound is a derivative of an $\alpha\beta$-unsaturated ketone (cf. Braude and Jones, *J.*, 1945, 498). The experiment was repeated but without heating the reaction product at 100°. The ether distillate had a strong odour of acetaldehyde and on shaking with excess of aqueous 2 : 4-dinitrophenylhydrazine hydrochloride yielded acetaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 145—146° (alone or mixed with an authentic specimen) and formaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 164—166° (alone or mixed with an authentic specimen), separated by crystallisation from alcohol. A portion of the crude residue from the ether distillation was treated with aqueous 2 : 4-dinitrophenylhydrazine hydrochloride solution, and the precipitate separated, dried, and crystallised from ethyl acetate–light petroleum (b. p. 60—80°) yielding a 2 : 4-*dinitrophenylhydrazone* as a yellow solid, m. p. 111—115° (Found: C, 45·5; H, 3·75. $C_{10}H_{10}O_5N_4$ requires C, 45·2; H, 3·75%).

Treatment of a further portion of the crude residue from the ether distillation with 3 : 5-dinitrobenzoyl chloride and pyridine gave a small quantity of *acetol* 3 : 5-*dinitrobenzoate*, m. p. 92—93°, slender needles from aqueous methanol (Found: C, 45·0; H, 3·35; *M* (micro), 284. $C_{10}H_8O_7N_2$ requires C, 44·7; H, 3·0%; *M*, 268).

Addition of Hydrogen Chloride.—2 : 2-*Dichlorobutane*-1 : 4-*diol.* 2-Butyne-1 : 4-diol (20 g.) was stirred with a mixture of concentrated hydrochloric acid (78 c.c.), cuprous chloride (10 g.), and ammonium chloride (4 g.) at room temperature for 4 days. Most of the excess of hydrochloric acid was removed by aeration, precipitated salts were separated, and the filtrate was distilled. The main fraction, 2 : 2-*dichlorobutane*-1 : 4-*diol* (7·4 g.; 20%), b. p. 145—160°/15 mm., solidified on cooling and crystallised from benzene as colourless needles, m. p. 80—81° (Found: C, 30·5; H, 4·1; Cl, 44·3. $C_4H_8O_2Cl_2$ requires C, 30·2; H, 3·8; Cl, 44·6%).

Addition of Halogens.—(a) 2 : 3-*Di-iodo-2-butene*-1 : 4-*diol.* 2-Butyne-1 : 4-diol (2 g.) was warmed on the steam-bath for ½ hour with a solution of iodine (6 g.) and potassium iodide (8 g.) in water (70 c.c.). The precipitate, 2 : 3-*di-iodo-2-butene*-1 : 4-*diol*, was separated and washed; it crystallised from water (500 c.c.) as short colourless rods, m. p. 179—181° (with liberation of iodine) (Found: C, 14·6; H, 2·1; I, 74·2. $C_4H_6O_2I_2$ requires C, 14·1; H, 1·8; I, 74·7%).

(b) 2 : 3-*Dibromo-2-butene*-1 : 4-*diol* (Lespieau, *Ann. Chim.*, 1914, **2**, 280). Colourless needles (from benzene), m. p. 116—117°.

(c) *Addition of chlorine to 2-butyne*-1 : 4-*diol.* 2-Butyne-1 : 4-diol (10·5 g.) was stirred with a solution of chlorine (8·6 g.) in carbon tetrachloride (20 c.c.), at 5—10° for 2 hours. A black oil formed on the surface of the carbon tetrachloride. This oil was separated by decantation, washed, and distilled, but proved to be a complex mixture of labile products each of which, on exposure to air, blackened within a few minutes. No definite compound was identified apart from a small quantity of unchanged 2-butyne-1 : 4-diol.

Action of Hydrogen Chloride.—(a) Dry hydrogen chloride was passed into a stirred solution of 2-butyne-1 : 4-diol (20 g.) and acetic acid (1 g.) at 100—110° for 4 hours. The black oily product was distilled and the following fractions collected: (*A*) up to 50°/20 mm. (1·5 g.) which separated into 2 layers the upper one of which was water. (*B*) B. p. 102—122°/15 mm. (17 g.). (*C*) Residue. Fraction (*A*) was extracted with ether (3 × 5 c.c.) and the combined extracts were washed and dried. Removal of the solvent gave 1 : 4-dichloro-2-butyne (Part I, preceding paper) (0·7 g.; 2·4%), identified by conversion into 1 : 4-dipiperidino-2-butyne and thence into the corresponding dipicrate, m. p. 198—201° (decomp.) alone and m. p. 201—202° (decomp.) on admixture with an authentic specimen. Fraction (*B*) was re-distilled and yielded 2(3) : 4-*dichloro-2-buten*-1-*ol*, b. p. 106°/15 mm., $n_D^{20°}$ 1·5042, as a colourless oil, almost insoluble in water but soluble in the common organic solvents (Found: C, 34·4; H, 4·3; Cl, 50·0. $C_4H_6OCl_2$ requires C, 34·0; H, 4·3; Cl, 50·3%). The *phenylurethane* had m. p. 64—65° from light petroleum (b. p. 40—60°) (Found: C, 50·6; H, 4·3. $C_{11}H_{11}O_2NCl_2$ requires C, 50·8; H, 4·2%).

2(3) : 4-Dichloro-2-buten-1-ol (1·05 g.) was dissolved in a solution of β-naphthol (3 g.) in N/2-alcoholic potassium hydroxide (42 c.c.) and refluxed for 1 hour. The solution was poured into water (250 c.c.) and the precipitated 2(3)-*chloro*-4-β-*naphthoxy-2-buten*-1-*ol* collected, washed, and crystallised from aqueous ethanol; colourless plates, m. p. 95—96° (Found: C, 67·35; H, 5·1. $C_{14}H_{13}O_2Cl$ requires C, 67·6; H, 5·2%).

2(3) : 4-Dichloro-2-buten-1-ol (6 g.) was refluxed with a suspension of calcium carbonate (12 g.) in water (60 c.c.) for 2 hours. The excess of calcium carbonate was separated from the residue and the filtrate evaporated and distilled giving 2-*chloro-2-butene*-1 : 4-*diol* as a colourless water-soluble oil (1·9 g.), b. p. 141—142°/14 mm., $n_D^{20°}$ 1·4955 (Found: Cl, 28·5. $C_4H_7O_2Cl$ requires Cl, 28·9%). The *bis*-(3 : 5-*dinitrobenzoate*) formed pale yellow plates from 2-ethoxyethanol, m. p. 189—190° (Found: N, 10·9. $C_{18}H_{11}O_{12}N_4Cl$ requires N, 11·0%).

(b) 2-Butyne-1 : 4-diol was unaffected by a saturated aqueous solution of hydrogen chloride at 0° or by concentrated hydrochloric acid at room temperature. On refluxing with concentrated hydrochloric acid in the presence of zinc chloride, complete decomposition occurred with the formation of a black coke-like product.

Action of Hydrogen Bromide.—A solution of 2-butyne-1 : 4-diol (10 g.) in 48% hydrobromic acid (100 c.c.) was kept at room temperature for 7 days. The mixture, which rapidly darkened, was extracted with ether (3 × 100 c.c.) and the combined extracts were washed, dried, and distilled, and the following fractions collected; (*A*) b. p. 60°/0·05 mm. (14·6 g.), pale yellow oil; (*B*) b. p. 86°/0·05 mm. (2·6 g.), dark green oil. Fraction (*B*) has not been further investigated. Fraction (*A*) was 2(3) : 4-*dibromo-2-buten*-1-*ol* [Found: C, 21·2; H, 2·6; Br, 69·4; OH (Zerewitinoff), 6·3. $C_4H_6OBr_2$ requires C, 20·9; H, 2·6; Br, 69·55; OH, 7·4%]. On treatment of the product with piperidine a vigorous reaction occurred, showing the presence of the active bromine atom.

2(3) : 4-Dibromo-2-buten-1-ol (1 g.) was dissolved in a solution of β-naphthol (1·5 g.) in N/2-alcoholic potassium hydroxide (21 c.c.) and refluxed for 1 hour. The solution was poured into water (150 c.c.) and the precipitated

2(3)-*bromo*-4-*β*-*naphthoxy*-2-*buten*-1-*ol* collected and crystallised from 80% aqueous 2-ethoxyethanol (carbon clarification); colourless plates, m. p. 153—154° (Found: Br, 26·9. $C_{14}H_{13}O_2Br$ requires Br, 27·3%).

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