218. *2-Butyne-1 : 4-diol. Part I. Reactions of the Hydroxyl Groups.*

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Esters, halides,* and ethers of 2-butyne-1 : 4-diol are described. 1 : 4-*Dibromo-2-butyne* and 1 : 4-*di-iodo-2-butyne* undergo anionotropic rearrangements on standing to the corresponding 2 : 3-dihalogeno-1 : 3-butadienes. 1-Ethoxy-1-buten-3-yne instead of the expected 1 : 4-diethoxy-2-butyne is obtained by the action of alcoholic sodium ethoxide on 1 : 4-*dichloro-2-butyne*. Substituted 1 : 4-diamino-2-butynes are prepared by the action of the appropriate amines on the 1 : 4-dihalogeno-2-butynes.* Malonic ester and ethylmagnesium bromide react normally with the 1 : 4-dihalogeno-2-butynes yielding 3-hexyne-1 : 1 : 6 : 6-tetracarboxylic ester and 4-octyne respectively. 2-Butyne-1 : 4-diol is converted to propargyl alcohol on heating with mild alkalis. Attempts to prepare 1 : 4-dicyano-2-butyne and to oxidise the carbinol groups of 2-butyne-1 : 4-diol have failed.

2-Butyne-1 : 4-diol was first obtained by Iotsitch (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 252) and later by Lespieau (*Ann. Chim.*, 1912, **27**, 137) and Dupont (*ibid.*, 1913, **30**, 485) by the interaction of acetylenedimagnesium bromide and formaldehyde or paraform. Lespieau (*ibid.*, 1914, **2**, 280; *Compt. rend.*, 1914, **158**, 707) has also obtained 2-butyne-1 : 4-diol by the action of zinc on 2 : 3-dibromo-2-butene-1 : 4-diol :

$$\left.\begin{array}{l} BrMgC{:}CMgBr + 2H{\cdot}CHO \\ CH_2(OH){\cdot}CBr{:}CBr{\cdot}CH_2{\cdot}OH \end{array}\right\} \xrightarrow[\text{hydrolysis}]{\text{after}\ \ Zn} CH_2(OH){\cdot}C{:}C{\cdot}CH_2{\cdot}OH.$$

The compound was not further investigated until 1938; I.G. Farbenind. then claimed a new method for its preparation, by the interaction of acetylene with formaldehyde at an elevated temperature and pressure in the presence of a catalyst such as copper or silver acetylide on silica. The reaction can be carried out either as a continuous process (Swiss P. 220,204; Brit. Appl. 5810/40) or as a batch process (B.P. 508,062; General Aniline and Film Corp., U.S.P. 2,222,302). Later patents (U.S.P. 2,300,969) indicate that the presence of a cuprene inhibitor, *e.g.*, bismuth salts, is also desirable. Propargyl alcohol, a by-product in the manufacture of 2-butyne-1 : 4-diol, reacts with formaldehyde in the presence of a copper acetylide catalyst to give 2-butyne-1 : 4-diol (General Aniline and Film Corp., U.S.P. 2,238,471).†

Few of the reactions of 2-butyne-1 : 4-diol have been described in the literature. The possible reactions of this readily available intermediate may be divided into three types : (*a*) reactions involving the hydroxyl groups, (*b*) reactions involving the triple bond, and (*c*) reactions involving the hydroxyl groups and the triple bond. This paper is devoted to reactions of type (*a*). Reactions of types (*b*) and (*c*) will be described in Part II (following paper).

The following esters of 2-butyne-1 : 4-diol have been prepared : *diacetate*; *dibenzoate*; *bis*-(3 : 5-*dinitrobenzoate*); *bisphenylurethane*. 1 : 4-*Dichloro-2-butyne* was obtained in 90% yield by the action of thionyl chloride on the diol in the presence of pyridine; yields were poorer in benzene solution or using phosphorus trichloride, oxychloride, or pentachloride in benzene. 1 : 4-*Dibromo-2-butyne* was obtained in excellent yield by the action of phosphorus tribromide on a suspension of 2-butyne-1 : 4-diol in benzene, and 1 : 4-*di-iodo-2-butyne* was prepared from 1 : 4-dichloro-2-butyne by refluxing with a solution of potassium iodide in acetone. 2-Butyne-1 : 4-diol and thionyl bromide in pyridine solution yielded 1 : 2 : 2 : 4-*tetrabromobutane*, m. p. 72—73°, as a result of addition of hydrogen bromide to the triple bond. A liquid product described as possibly being 1 : 2 : 2 : 4-tetrabromobutane has been obtained by Demjanov and Dojarenko (*Ber.*, 1923, **56**, 2210) by the action of bromine on methylene*cyclo*propane. The action of piperidine on 1 : 2 : 2 : 4-tetrabromobutane gave a product, m. p. 98—99°, of undetermined structure.

1 : 4-Dibromo-2-butyne when freshly distilled showed a broad flat maximum at 2200—2250 A., $E^{1\%}_{1\ cm.}$ 186, $\epsilon_{max.}$ 3940. After exposure of the compound to air for five months this absorption rose to $E^{1\%}_{1\ cm.}$ 230, $\epsilon_{max.}$ 4900, indicating a slow irreversible change to 2 : 3-dibromo-1 : 3-butadiene. This change was accelerated by warming with benzoyl peroxide, the mixture becoming increasingly viscous and finally solidifying giving a pale yellow product, probably a polymer of dibromobutadiene, the bromine of which was only slightly attacked by

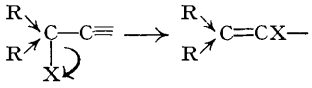
* Patent application pending.

† A review of the German work on 2-butyne-1 : 4-diol is contained in a translation of a paper by Reppe (" New Technical Applications of Acetylene," H.M. Stationery Office, 1946).

boiling sodium hydroxide. 1 : 4-Dibromo-2-butyne was largely unchanged by refluxing with iodine in acetone, or by heating for 4 hours in air; on heating at 170° for 1 hour in air it was converted into a black tar.

1 : 4-Di-iodo-2-butyne, even if freshly distilled, showed a maximum at 2400 A., $E^{1\%}_{1\,cm.}$ 324, $\epsilon_{max.}$ 9900, indicative of partial isomerisation to 2 : 3-di-iodo-1 : 3-butadiene. On exposure to air it rapidly precipitated a solid polymer, a change which could be retarded by addition of quinol and accelerated by warming with a little benzoyl peroxide. This polymer was insoluble in all common solvents, did not decolourise bromine in carbon tetrachloride, reduced neutral permanganate slowly, and was only slightly hydrolysed on boiling with 2N-sodium hydroxide.

1 : 4-Dichloro-2-butyne could not be induced to undergo this type of anionotropic rearrangement. There are several examples in the literature of analogous rearrangements of the dihalides of ditertiary acetylenic diols (Krestinsky *et al.*, *Ber.*, 1926, **59**, 1930; *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 1691; Zal'kind *et al.*, *ibid.*, 1926, **58**, 1044; 1927, **59**, 283; 1929, **61**, 803; 1930, **62**, 1022; Wieland and Kloss, *Annalen*, 1929, **470**, 201) which are more facile than the rearrangement of the acetylenic diprimary dihalides owing to the inductive effect of the additional alkyl groups which facilitate the separation of the anionic halogen atoms :



(X = halogen)

The structure of the 1 : 4-dihalogeno-2-butynes was proved by hydrolysis to 2-butyne-1 : 4-diol by refluxing with an aqueous suspension of calcium carbonate or silver oxide. The activity of the halogen atoms of the 1 : 4-dihalogeno-2-butynes was of the same order as that of the halogen atoms in the allyl halides and the 1 : 4-dihalogeno-2-butenes. As in the case of the allyl halides, a useful test for the 1 : 4-dihalogeno-2-butynes was the strongly exothermic reaction with piperidine or *cyclo*hexylamine, a reaction not shown by vinyl or alkyl halides (cf. Ziegler *et al.*, *Annalen*, 1942, **551**, 80).

In the presence of suitable diluents, 1 : 4-dihalogeno-2-butynes readily reacted with amines to yield the corresponding acetylenic diamines. The following have been prepared : 1 : 4-*diamino*- (hydrogenated over platinum to putrescine), 1 : 4-*di*(*methylamino*)-, 1 : 4-*di*(*butylamino*)-, 1 : 4-*di*(cyclo*hexylamino*)-, 1 : 4-*di*(*acetanilido*)-, 1 : 4-bis(dimethylamino)-, 1 : 4-*dipiperidino*-, and 1 : 4-*di*-(N-*methylanilino*)-2-*butyne*. No reaction occurred between 1 : 4-dichloro-2-butyne and diphenylamine. The manufacture of 1 : 4-bis(dimethylamino)-2-butyne has been described by I.G. Farbenind. (B.P. 510,904) by condensation of formaldehyde, dimethylamine, and acetylene over a copper acetylide catalyst. An attempt to prepare 1 : 4-dipiperidino-2-butyne by interaction of 2-butyne-1 : 4-diol and piperidine was unsuccessful, the reactants being recovered unchanged. It is therefore clear that the intermediate product in the direct synthesis from *sec.*-amine, formaldehyde, and acetylene is the hydroxy-methylamine and not 2-butyne-1 : 4-diol. With triethylamine, 1 : 4-dichloro-2-butyne formed 2-butyne-1 : 4-bis(triethylammonium chloride), characterised as the *dipicrate*. No pure product could be isolated from the corresponding reaction with pyridine. Attempts to hydrate 1 : 4-bis(dimethylamino)-2-butyne or 1 : 4-dipiperidino-2-butyne to the corresponding substituted 1 : 4-diamino-2-butanones by heating with Denigès's reagent (acid mercuric sulphate) were unsuccessful.

The aliphatic ethers of 2-butyne-1 : 4-diol can be obtained by the action of chloromethyl alkyl ethers on acetylenedimagnesium bromide (Gauthier, *Ann. Chim.*, 1909, **16**, 289; Lespieau, *ibid.*, 1912, **27**, 137; Dupont, *ibid.*, 1913, **30**, 485) :

$$(\vdots CMgBr)_2 + 2CH_2Cl\cdot OR \longrightarrow (\vdots C\cdot CH_2\cdot OR)_2 + 2MgClBr$$

1 : 4-Diethoxy-2-butyne has been prepared by this method. Kranzfelder and Vogt (*J. Amer. Chem. Soc.*, 1938, **60**, 1714) have prepared the dipropyl ether of 2-butyne-1 : 4-diol by the action of acetylenedimagnesium bromide on propylal :

$$2CH_2(OPr)_2 + (\vdots CMgBr)_2 \longrightarrow (\vdots C\cdot CH_2\cdot OPr)_2$$

Attempts to prepare ethers directly from 2-butyne-1 : 4-diol by the action of the appropriate alcohol in the presence of sulphuric acid have failed.* The action of an alcoholic solution of sodium ethoxide on 1 : 4-dichloro-2-butyne yielded, not the expected 1 : 4-ethoxy-2-butyne, but 1-ethoxy-1-buten-3-yne, presumably with the intermediate formation of diacetylene (cf. G.P. 601,322).

$$CH_2Cl\cdot C\vdots C\cdot CH_2Cl \xrightarrow{KOH} [HC\vdots C\cdot C\vdots CH] \xrightarrow{EtOH} HC\vdots C\cdot CH{:}CH\cdot OEt.$$

The action of methyl alcoholic potassium hydroxide on 1 : 4-dibromo-2-butene did not proceed analogously, but yielded 1 : 4-*dimethoxy*-2-*butene*. Petrov (*J. Gen. Chem. Russia*, 1943, **13**, 108) has prepared 1 : 4-diethoxy-2-butene by this method and mentioned that a little 1-bromo-1 : 3-butadiene was obtained as a by-product, thus indicating that dehydrohalogenation occurs to a slight extent.†

The following aryl ethers of 2-butyne-1 : 4-diol have been prepared by the action of the sodium derivatives of the appropriate phenol on 1 : 4-dichloro-2-butyne : 1 : 4-*diphenoxy*-, 1 : 4-*di*-β-*naphthoxy*-, 1 : 4-*di*-(p-

* I.G. Farbenind. (G.P. 742,650) have since claimed the preparation of aliphatic ethers of 2-butyne-1 : 4-diol by the action of alkyl sulphates in the presence of aqueous alkali.

† Since this work was carried out, details of a German patent (I.G. Farbenind., G.P. 740,637) have appeared whereby diacetylene is prepared by the action of alkalis on 1 : 4-dichloro-2-butyne. This claim has been confirmed (author), and undoubtedly represents the most convenient laboratory method of preparation of diacetylene.

anilinophenoxy)-, and 1 : 4-*di*-(p-*acetamidophenoxy*)-2-*butyne*. 1 : 4-Diphenoxy-2-butyne, like the propargyl ethers (Tarbel, *Chem. Reviews*, 1940, **27**, 540), did not undergo a Claisen rearrangement to 1 : 4-di-(*o*-hydroxyphenyl)-2-butyne on heating.

1 : 4-Dichloro-2-butyne with ethyl sodiomalonate in toluene solution (alcohol is an unsatisfactory solvent) yielded a crude tetracarboxylic ester, hydrolysed to the corresponding acid which was then decarboxylated directly. The product was re-esterified with methyl alcohol and then fractionated to yield *methyl* 3-*hexyne*-1 : 6-*dicarboxylate* and *methyl* 3-*hexyne*-1 : 1 : 6-*tricarboxylate*. Hydrolysis of the former yielded 3-*hexyne*-1 : 6-*dicarboxylic acid* which gave suberic acid on hydrogenation with a platinum catalyst. The formation of the tricarboxylic acid in the decarboxylation of the tetracarboxylic acid can be avoided if the experiment is carried out on a small scale (approx. 5 g.). The structure of methyl 3-hexyne-1 : 1 : 6-tricarboxylate was proved by hydrogenation over platinum to *methyl hexane*-1 : 1 : 6-*tricarboxylate*, hydrolysis and decarboxylation of which gave suberic acid.

1 : 4-Dibromo-2-butyne with ethylmagnesium bromide yielded 4-octyne, the structure of which was proved by hydration to 4-octanone. Attempts to prepare 1 : 4-dicyano-2-butyne from the corresponding dihalides by the action of alkali metal cyanides or cuprous cyanide in various solvents were unsuccessful; either the dihalide was recovered unchanged, or extensive decomposition occurred. 1 : 4-Dichloro-2-butyne is largely unaffected by the action of potassium cyanide in boiling 2-ethoxyethanol, conditions which have been described by du Pont (U.S.P. 2,342,101) for the preparation of 1 : 4-dicyano-2-butene from the corresponding dichloride. 1 : 4-Dithiocyano-2-butyne was obtained by the action of an acetone solution of ammonium thiocyanate on 1 : 4-dichloro-2-butyne, but the crude product decomposed violently on attempted distillation. von Braun and Lemke (*Ber.*, 1922, **55**, 3536) have described a similar conversion of 1 : 4-dibromo-2-butene into the corresponding dithiocyanate. No reaction could be induced between 1 : 4-dichloro-2-butyne and magnesium in ether; with dibromobutyne, the reaction proceeded steadily at first but was eventually terminated by deposition of an insoluble substance on the magnesium. The solution gave a faint positive colour reaction for $-CH_2MgX$ (Gilman *et al.*, *J. Amer. Chem. Soc.*, 1925, **47**, 2002).

2-Butyne-1 : 4-diol has been converted into propargyl alcohol on heating with mild alkalis. Optimum conditions were obtained by heating the diol at 140° with 5% of its weight of potassium carbonate; a higher proportion of potassium carbonate caused the reaction to become too violent. Considerable tar formation accompanies the reaction and the yield of pure propargyl alcohol (estimated as the mercury derivative) is only 15—20%. 2-Butyne-1 : 4-diol is slowly decomposed on boiling with aqueous potassium hydroxide solutions to give formaldehyde (converted into potassium formate) and acetylene.

Attempts to oxidise the carbinol groups of the diol with chromic acid or with aluminium *iso*propoxide in the presence of acetone (cf. Heilbron, Johnson, and Jones, *J.*, 1939, 1560) were unsuccessful.

Reference is made in the experimental part to the vesicant and lachrymatory effects of some of the compounds described.

Experimental.

M. ps. are uncorrected. The microanalyses were carried out by Mr. E. S. Morton and the absorption spectra by Dr. F. R. Cropper.

2-Butyne-1 : 4-diol.—This was prepared by the interaction of acetylene and formaldehyde in the presence of a copper–silver acetylide on silica catalyst using bismuth oxyiodide as a cuprene inhibitor according to a modification of the method of I.G. Farbenind. (U.S.P. 2,300,969). The product, b. p. 145°/15 mm., m. p. 55°, crystallised in colourless plates from ethyl acetate. Small quantities are more conveniently crystallised from benzene. The diol is readily soluble in water, alcohols, and hot ethyl acetate; moderately soluble in cold ethyl acetate; sparingly soluble in benzene, chloroform, and ether; and almost insoluble in ligroin. It is odourless and non-explosive. There is some evidence that the solid has a slight vesicant action.

Esters of 2-Butyne-1 : 4-diol.—The *diacetate* was a colourless oil, b. p. 122—123°/10 mm., $n_D^{20°}$ 1·4611 (Found : C, 56·4; H, 6·2. $C_8H_{10}O_4$ requires C, 56·5; H, 5·9%). The *dibenzoate* formed prisms from methanol, m. p. 76—77° (Found : C, 73·3; H, 5·0. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·8%). The *bis*-(3 : 5-*dinitrobenzoate*) formed pale yellow plates from 2-ethoxyethanol, m. p. 189—191° (Found : C, 45·7; H, 2·4; N, 11·85. $C_{18}H_{10}O_{12}N_4$ requires C, 45·6; H, 2·1; N, 11·8%). The *bisphenylurethane* formed plates from benzene, m. p. 130—132° (Found : C, 66·2; H, 4·8; N, 8·9. $C_{18}H_{16}O_4N_2$ requires C, 66·7; H, 4·9; N, 8·6%).

1 : 4-Dihalogeno-2-butynes.—*1 : 4-Dichloro-2-butyne.* 2-Butyne-1 : 4-diol (100 g.; 1 mol.) was dissolved in dry pyridine (170 c.c.), and thionyl chloride (201 c.c.; 2·4 mols.) was added dropwise during 6 hours with stirring and cooling, the temperature being kept between 10° and 20°. The mixture was allowed to warm to room temperature, stirred overnight, and treated with crushed ice. The product was extracted with ether (3 × 200 c.c.), and the combined extracts were washed with sodium bicarbonate solution, dried, and fractionated to give 1 : 4-*dichloro*-2-*butyne* (118·7 g.; 83%) as a colourless oil, b. p. 68—69°/17 mm., 73°/24 mm., 165—166°/760 mm. (slight decomp.); $n_D^{20°}$ 1·5072; $d_4^{20°}$ 1·258. It exhibited no absorption of appreciable intensity in the range 2200—4000 A. (Found : C, 39·15; H, 3·4. $C_4H_4Cl_2$ requires C, 39·0; H, 3·3%). 1 : 4-Dichloro-2-butyne is a vesicant and a weak lachrymator. It was mainly unchanged (slight darkening) on refluxing with benzoyl peroxide, iodine, aluminium chloride, or zinc chloride.

1 : 4-Dibromo-2-butyne. 2-Butyne-1 : 4-diol (5 g.; 1 mol.) was suspended in benzene (40 c.c.) and phosphorus tribromide (13·7 g.; 2·4 mol.) added dropwise at room temperature with stirring; only a very slight temperature rise occurred and the stirring was continued overnight. Iced water was added and the mixture extracted with ether (3 × 50 c.c.); the combined extracts were washed with sodium bicarbonate solution, dried, and fractionated to give 1 : 4-*dibromo*-2-*butyne* (10·7 g.; 87%) as a pale yellow oil which darkened in air, b. p. 60°/0·07 mm., $n_D^{19°}$ 1·5927 (Found : Br, 75·9. $C_4H_4Br_2$ requires Br, 75·5%). 1 : 4-Dibromo-2-butyne is a powerful vesicant and lachrymator. On warming 1 : 4-dibromo-2-butyne with a small quantity of benzoyl peroxide the mixture became more viscous and finally solidified. The product was washed with hot ethanol and dried in a vacuum; it then formed a pale yellow solid (cf. Lespieau and Prévost, *Compt. rend.*, 1925, **180**, 675) giving a strong positive test for bromine. On heating, the polymer darkened at 120°, blackened at 170°, and completely decomposed at 200°.

1 : 2 : 2 : 4-*Tetrabromobutane*. 2-Butyne-1 : 4-diol (9 g.; 1 mol.) was dissolved in pyridine (18 c.c.; 1·1 mol.) and thionyl bromide (19 c.c.; 1·15 mol.; Hibbert and Pullman, *Inorg. Synth.*, 1939, **1**, 113) added dropwise (3 hours), the temperature of the reaction being kept at 15—20°. After 48 hours at room temperature, the mixture was decomposed with ice and extracted with ether (3 × 100 c.c.). The combined ethereal extracts were washed and dried and the solvent was removed; on cooling, the lachrymatory residue (15 g.) partly solidified and was crystallised from light petroleum (b. p. 40—60°) yielding 1 : 2 : 2 : 4-*tetrabromobutane* as colourless needles, m. p. 72—73° (Found : C, 13·1; H, 1·7; Br, 85·6. $C_4H_6Br_4$ requires C, 12·8; H, 1·6; Br, 85·6%).

1 : 4-*Di-iodo-2-butyne*. 1 : 4-Dichloro-2-butyne (5 g.) in dry acetone (50 c.c.) was refluxed overnight with powdered potassium iodide (20 g.). The black solution was poured into water and extracted with ether (3 × 100 c.c.); the combined extracts were washed with sodium thiosulphate solution until free from iodine, dried, and the solvent removed. Quinol (0·05 g.) was added and the residue distilled giving 1 : 4-*di-iodo-2-butyne* (6·5 g.; 52%) as a pale yellow oil, b. p. 70—72°/0·1 mm. (Found : C, 16·1; H, 1·45. $C_4H_4I_2$ requires C, 15·7; H, 1·3%). The product rapidly decolorised a solution of bromine in carbon tetrachloride and reduced neutral permanganate. In the absence of a stabilising agent (quinol), 1 : 4-di-iodo-2-butyne rapidly solidified; this change, which was complete after 6 hours at room temperature, was accelerated by warming, especially in the presence of a small quantity of benzoyl peroxide. In the presence of a small amount of quinol, rearrangement and polymerisation were not complete until after about 10 days. The solid polymer was washed with warm alcohol to remove iodine and dried in a vacuum (Found : C, 16·6; H, 2·1. $C_4H_4I_2$ requires C, 15·7; H, 1·3%). On heating, the polymer darkened at 150° and evolved iodine at a slightly higher temperature without melting.

Reactions of the 1 : 4-*Dihalogeno-2-butynes*.—(a) *Hydrolysis*. 1 : 4-Dichloro-2-butyne (1 g.) was refluxed overnight with a suspension of calcium carbonate (3 g.) in water (10 c.c.). The excess of calcium carbonate was separated and the filtrate evaporated to dryness on the steam-bath. The solid residue (3·8 g.) was distilled and the distillate, b. p. 140—150°/16 mm., which solidified on cooling was crystallised from ethyl acetate (carbon) giving 2-butyne-1 : 4-diol, m. p. 53—54°, alone and mixed with an authentic specimen. Hydrolysis was also effected by refluxing with an aqueous suspension of silver oxide, but the yield of 2-butyne-1 : 4-diol was lower.

(b) *Reaction with alcoholic sodium ethoxide*. 1 : 4-Dichloro-2-butyne (15 g.) was added to a solution of sodium ethoxide (from 6 g. of sodium) in ethanol (100 c.c.) and the mixture refluxed for 1 hour. The product was poured into water (600 c.c.) and extracted with ether (3 × 100 c.c.); the combined extracts were washed, dried, and distilled to give 1-ethoxy-1-buten-3-yne as a colourless oil (5·25 g.), b. p. 42°/15 mm., 71°/53 mm.; $n_D^{19°}$ 1·4759 (Viguier, *Compt. rend.*, 1912, **154**, 218; *Ann. Chim.*, 1913, **28**, 515, gives b. p. 29—33°/16 mm.; 126—130°/760 mm.; $n_D^{19.5°}$ 1·462. I.G. Farbenind., G.P. 601,822, give b. p. 46°/20 mm.) (Found : C, 74·7; H, 8·2. Calc. for C_6H_8O : C, 75·0; H, 8·3%). The product rapidly darkened in air and with an ammoniacal solution of silver nitrate gave an insoluble silver salt which exploded on rapid heating.

(c) *Reactions with alkali metal phenoxides*. The following general method was used. 1 : 4-Dichloro-2-butyne (1 mol.) and the appropriate phenol (2·5 mols.) in N/2-alcoholic potassium hydroxide (2·5 mols.) were refluxed overnight and the resulting ethers isolated either by direct filtration or by pouring into water and extraction with ether. The following 1 : 4-diaryloxy-2-butynes were obtained : *diphenoxy-*, colourless oil, b. p. 168°/3 mm. (Found : C, 80·1; H, 6·25. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%); *di-β-naphthoxy-*, m. p. 124—125° (from 80% aqueous 2-ethoxyethanol) (Found : C, 85·05; H, 5·3. $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·3%); *di*-p-*anilinophenoxy-*, m. p. 88—89° (from light petroleum, b. p. 60—80°) (Found : C, 79·8; H, 5·2. $C_{28}H_{24}O_2N_2$ requires C, 80·0; H, 5·7%); *di*-p-*acetamidophenoxy-*, m. p. 218—220° (from ethanol) (Found : C, 67·85; H, 5·75; N, 7·85. $C_{20}H_{20}O_4N_2$ requires C, 68·2; H, 5·7; N, 8·0%).

(d) 1 : 4-*Diamino-2-butyne*. 1 : 4-Dichloro-2-butyne (5·12 g.) was stirred overnight with concentrated ammonia solution (*d* 0·880; 200 c.c.) at room temperature; the mixture rapidly became homogeneous. The excess of ammonia was removed on the steam-bath and the remaining solution acidified to Congo-red with hydrochloric acid. The acid solution was evaporated almost to dryness on the steam-bath, the residue made alkaline to Clayton-yellow with 10N-sodium hydroxide and extracted overnight with ether in a continuous extractor. Removal of the ether gave a dark brown oil which was distilled to give a main fraction (1·2 g.; 34%), b. p. 60—80°/11 mm., which on cooling solidified to a colourless crystalline mass of 1 : 4-diamino-2-butyne, m. p. 42—46°. The base readily absorbed carbon dioxide from the atmosphere, and was soluble in water and alcohols. The *dipicrate* formed yellow needles from water, m. p. 230—232° (decomp., with darkening at 160° and blackening at 200°) (Found : C, 35·1; H, 2·9; N, 20·1. $C_{16}H_{14}O_{14}N_8$ requires C, 35·4; H, 2·6; N, 20·6%).

1 : 4-Diamino-2-butyne (1·0 g.) in water (5·0 c.c.) was hydrogenated over Adams's platinum catalyst (0·1 g.) until no more hydrogen was absorbed (20 hours). After removal of the catalyst the aqueous solution of putrescine was converted directly into derivatives. Dibenzoyl derivative, colourless plates from aqueous methanol, m. p. 176—177° (*lit.* 177°). Dipicrate, yellow plates from water, m. p. 256° (decomp.) (*lit.* m. p. 250—255°). Attempts to prepare 1 : 4-diamino-2-butyne from 1 : 4-dichloro-2-butyne by the action of alcoholic ammonia yielded mainly a polymer, m. p. >330°, presumably $(NH{\cdot}CH_2{\cdot}C{\equiv}C{\cdot}CH_2)_n$. The action of liquid ammonia at −35° for five hours on 1 : 4-dichloro-2-butyne formed a small amount (25%) of the above polymer but the main portion (64%) was unchanged 1 : 4-dichloro-2-butyne.

(e) *Reactions with primary amines*. (i) 1 : 4-Dichloro-2-butyne (5 g.) was stirred with 22% aqueous solution of methylamine (290 g.) at room temperature for 16 hours; the solution was completely homogeneous after one hour. The product was treated similarly to the ammonia experiment (above) and the final alkaline solution extracted overnight with ether in a continuous extractor. Removal of solvent gave a brown oil which was dried over sodium and distilled to yield 1 : 4-*di*(*methylamino*)-2-*butyne*, b. p. 72°/20 mm. (1·5 g.), as a colourless oil (Found : N, 24·8. $C_6H_{12}N_2$ requires N, 25·0%). *Dipicrate*, yellow needles from water, m. p. 213—215° (decomp., with darkening at 180°) (Found : C, 38·2; H, 3·5; N, 19·0. $C_{18}H_{18}O_{14}N_8$ requires C, 37·9; H, 3·2; N, 19·6%).

(ii) 1 : 4-Dichloro-2-butyne (25 g.) and butylamine (86 c.c.) in benzene (240 c.c.) were refluxed for 3 hours. The product was cooled, treated with excess of 2N-sodium hydroxide, and the benzene layer washed and dried. After removal of the solvent the residue was distilled giving 1 : 4-*di*(*butylamino*)-2-*butyne* as a colourless liquid, b. p. 105—115°/0·2 mm., which very quickly darkened in air. A satisfactory analysis could not be obtained, probably because of this very rapid deterioration. *Dipicrate*, yellow needles from water, m. p. 206—207° (decomp.) (Found : C, 44·2; H, 4·7; N, 17·0. $C_{24}H_{30}N_8O_{14}$ requires C, 44·05; H, 4·6; N, 17·1%).

(iii) 1 : 4-Dichloro-2-butyne (5 g.) and *cyclo*hexylamine (17 g.) in benzene (25 c.c.) were heated under reflux for 3 hours. The benzene was then removed on the steam-bath and the residue distilled. The fraction, b. p. >150°/0·1 mm. (2·5 g.), solidified and was crystallised from light petroleum (b. p. 60—80°) giving 1 : 4-*di*(cyclo*hexylamino*)-2-*butyne* as colourless needles, m. p. 83—84° (Found : C, 77·5; H, 10·9; N, 11·4. $C_{16}H_{28}N_2$ requires C, 77·4; H, 11·3; N, 11·3%).

(iv) 1 : 4-Dichloro-2-butyne (5·2 g.) and aniline (17 c.c.) in *n*-butanol (30 c.c.) were heated under reflux for 5 hours. The product was basified to Clayton-yellow with 2N-sodium hydroxide and distilled in steam to remove aniline and butanol. The residue was acidified to Congo-red with 2N-hydrochloric acid, clarified with carbon, cooled, and basified with 2N-sodium hydroxide; the base was then precipitated as a low-melting oil. This was extracted with ether (3 × 100 c.c.) and the combined ethereal extracts were washed and dried and the solvent was removed. The residue

of 1 : 4-dianilino-2-butyne was converted into the diacetyl derivative by boiling for 5 minutes with excess of acetic anhydride (20 c.c.). The product was poured into water and basified; the oil which separated rapidly solidified on cooling and was crystallised first from aqueous methanol and then from ligroin (b. p. 60—80°)–benzene yielding 1 : 4-*di*(*acetanilido*)-2-*butyne* as colourless needles, m. p. 99—100° (Found : C, 75·5; H, 6·1; N, 8·85. $C_{20}H_{20}O_2N_2$ requires C, 75·0; H, 6·25; N, 8·75%).

(f) *Reactions with secondary amines.* (i) 1 : 4-Dichloro-2-butyne (5·4 g.) in benzene (50 c.c.) was mixed with piperidine (14·9 g.). A vigorous reaction occurred and external cooling was necessary. After the initial reaction had subsided, the mixture was heated under reflux for 1 hour, cooled, and washed with excess of 2N-sodium hydroxide. The benzene layer was washed, dried, and distilled, giving 1 : 4-*dipiperidino*-2-*butyne* (4·8 g.; 57%) as a pale yellow oil, b. p. 124°/3 mm., $n_D^{19°}$ 1·5040 (Found : N, 12·6. $C_{14}H_{24}N_2$ requires N, 12·7%). *Dipicrate*, yellow needles from water, m. p. 204—205° (Found : C, 46·3; H, 4·9; N, 16·6. $C_{26}H_{30}O_{14}N_8$ requires C, 46·0; H, 4·4; N, 16·5%). 1 : 4-Dipiperidino-2-butyne was also obtained by the action of a benzene solution of piperidine on 1 : 4-dibromo-2-butyne or on freshly prepared 1 : 4-di-iodo-2-butyne, and was identified in each case as the dipicrate, m. p. 204—205°.

(ii) 1 : 4-Dichloro-2-butyne (10 g.) was added dropwise to a 21% aqueous solution of dimethylamine (100 g.) with stirring. Reaction occurred rapidly and the temperature rose to 50°. The mixture was stirred overnight at room temperature and then heated at 50° for 1 hour. After cooling, the solution was made alkaline to Clayton-yellow with 2N-sodium hydroxide and extracted overnight with ether in a continuous extractor. After removal of the ether, the residue was distilled and two fractions obtained : (*A*) b. p. 66°/54 mm., 54°/25 mm.; $n_D^{19°}$ 1·3888 (6·15 g.). (*B*) b. p. 92°/31 mm.; $n_D^{20°}$ 1·4561 (3·55 g.). Fraction (*B*) was 1 : 4-bis(dimethylamino)-2-butyne (I.G. Farbenind., B.P., 510,904, give b. p. 180°) and was converted into the *dipicrate*, yellow needles from water, m. p. 240—242° (decomp.) (Found : C, 40·1; H, 3·8; N, 18·55. $C_{20}H_{22}O_{14}N_8$ requires C, 40·1; H, 3·7; N, 18·7%). Fraction (*A*) was a constant-boiling mixture of water and 1 : 4-bis(dimethylamino)-2-butyne. It formed a dipicrate, m. p. 240—242°, identical with that obtained from the pure material.

(iii) 1 : 4-Dichloro-2-butyne (5 g.) and methylaniline (18 c.c.) in *n*-butanol (30 c.c.) were heated under reflux for 5 hours. The product was basified to Clayton-yellow with 2N-sodium hydroxide, and distilled in steam to remove methylaniline and *n*-butanol. The residue was acidified (Congo-red) with 2N-hydrochloric acid, clarified with carbon, cooled, and basified with 2N-sodium hydroxide. The colourless precipitate was collected, washed, and dried; m. p. 58—64° (8·0 g.). Crystallisation from light petroleum (b. p. 60—80°) gave 1 : 4-*di*-N-*methylanilino*-2-*butyne* as colourless needles, m. p. 63—64° (Found : C, 81·4; H, 7·4; N, 11·2. $C_{18}H_{20}N_2$ requires C, 81·8; H, 7·6; N, 10·6%).

(g) *Reactions with tertiary amines.* (i) A mixture of 1 : 4-dichloro-2-butyne (1 g.) and triethylamine (2·6 g.) in dry acetone (10 c.c.) was kept at room temperature overnight; a brown oil separated which slowly solidified to a grey crystalline mass of 2-butyne-1 : 4-bis(triethylammonium chloride). This was collected and washed with acetone; it was exceedingly deliquescent and was converted into the *dipicrate*, yellow plates from water, m. p. 229—231° (decomp., with previous darkening) (Found : C, 47·2; H, 5·3; N, 15·75. $C_{28}H_{40}O_{14}N_8$ requires C, 47·2; H, 5·6; N, 15·4%).

(ii) Interaction of 1 : 4-dichloro-2-butyne and pyridine in dry acetone yielded a black solid which could not be purified. It contained ionisable chlorine, and was very soluble in water and alcohol and sparingly soluble in acetone and petrol.

(h) *Reaction with ethyl malonate.* Ethyl malonate (215 c.c.) was added dropwise over ½ hour with stirring at 50° to powdered sodium (25 g.) in toluene (1200 c.c.) and then stirred at 50° for a further 4 hours. 1 : 4-Dichloro-2-butyne (50 g.) was added dropwise and the mixture heated at 80° with stirring overnight. The product was cooled and washed with excess of 2N-sulphuric acid and with water. Estimation of chloride ion in the combined aqueous washings indicated that the conversion of the 1 : 4-dichloro-2-butyne had been quantitative. The toluene layer was dried and the solvent removed under reduced pressure, leaving the crude tetracarboxylic ester which did not solidify on cooling. Potassium hydroxide solution (170 g. of potassium hydroxide in 950 c.c. of water) was added to the oil and the mixture heated on the steam-bath for 3 hours. The solution was acidified to Congo-red with concentrated hydrochloric acid and evaporated until a saturated solution was obtained which was cooled and extracted overnight with ether in a continuous extractor. Removal of the ether gave the crude tetracarboxylic acid which was divided into 3 portions, each of which was heated at 170—180° until evolution of carbon dioxide had ceased (1 hour). The combined products were dissolved in a mixture of methanol (500 c.c.) and sulphuric acid (20 c.c.) and refluxed for 3 hours, poured into water, and extracted with ether (3 × 200 c.c.). The combined extracts were washed, dried, and distilled, the following fractions being obtained. (*A*) b. p. 96°/0·2 mm. (5·7 g.), $n_D^{24°}$ 1·4600. (*B*) Intermediate : b. p. 97—130°/0·2 mm. (3·95 g.), $n_D^{19°}$ 1·4597. (*C*) b. p. 140—142°/0·1 mm. (37·6 g.), $n_D^{19°}$ 1·4625. (*D*) Residue. Fraction (*A*), *methyl* 3-*hexyne*-1 : 6-*dicarboxylate*, on cooling formed colourless crystals, m. p. 30—32° (Found : C, 60·3; H, 7·15. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%). Hydrolysis of the ester with aqueous potassium hydroxide gave 3-*hexyne*-1 : 6-*dicarboxylic acid* as colourless plates (from water), m. p. 208—209° (Found : C, 56·8; H, 5·9; equiv., 85·5. $C_8H_{10}O_4$ requires C, 56·5; H, 5·9%; equiv., 85·0). Complete hydrogenation of an aqueous solution of 3-hexyne-1 : 6-dicarboxylic acid in the presence of Adams's platinum catalyst at room temperature yielded suberic acid, m. p. alone and mixed with an authentic specimen 140—141°. Fraction (*C*), a colourless unsaturated viscous liquid, was *methyl* 3-*hexyne*-1 : 1 : 6-*tricarboxylate* (Found : C, 55·9; H, 6·5; equiv., 83. $C_{12}H_{16}O_6$ requires C, 56·2; H, 6·3%; equiv., 85·3). The tricarboxylic ester (4·5 g.) was completely hydrogenated in methanol (30 c.c.) in the presence of Adams's platinum catalyst. When no more hydrogen was absorbed (25 mins.), the catalyst was separated and the solvent removed. Distillation of the residue gave *methyl hexane*-1 : 1 : 6-*tricarboxylate* as a colourless oil, b. p. 154°/3 mm.; $n_D^{27°}$ 1·4426 (Found : C, 55·6; H, 7·65. $C_{12}H_{30}O_6$ requires C, 55·4; H, 7·7%). Hydrolysis of this ester with alcoholic potassium hydroxide yielded a brown oil (crude tricarboxylic acid) which was decarboxylated by heating at 180—190° for ½ hour until carbon dioxide evolution had ceased. On cooling, the product solidified and, after crystallisation from water, suberic acid, m. p. and mixed m. p. with an authentic specimen 140—141°, was identified.

Hydrolysis of methyl 3-hexyne-1 : 1 : 6-tricarboxylate with methyl alcoholic potassium hydroxide gave crude 3-hexyne-1 : 1 : 6-tricarboxylic acid. Attempts to decarboxylate this acid to 3-hexyne-1 : 6-dicarboxylic acid by heating alone at 190°, heating with copper bronze at 190°, or heating under reflux with acetic anhydride, were unsuccessful.

(i) *Reaction with ethylmagnesium bromide.* A solution of 1 : 4-dibromo-2-butyne (4 g.) in dry ether (10 c.c.) was added dropwise to an ethereal solution of ethylmagnesium bromide (from 1·4 g. of magnesium) during ½ hour with stirring. The pale yellow solution was refluxed overnight, cooled, and decomposed with excess of 2N-hydrochloric acid. The ethereal layer was removed and the aqueous layer extracted with ether (2 × 100 c.c.). The combined ethereal extracts were washed, dried, and distilled, giving a main fraction, b. p. 120—140° (1·2 g.) (Vaughn *et al.*, *J. Org. Chem.*, 1937, **2**, 1, give b. p. 130·5°/745 mm. for 4-octyne). This product was refluxed with Denigès's solution (20 c.c.) for 3 hours and the cooled product extracted with ether (3 × 50 c.c.), and the combined ethereal extracts were washed, dried, and distilled giving a main fraction, b. p. 50—70°/20 mm. (0·5 g.) (Tiffeneau and Deux, *Compt. rend.*, 1941, **212**, 105, give b. p. 70°/26 mm. for 4-octanone). The semicarbazone formed colourless plates from aqueous methanol, m. p. 98—99° alone and mixed with an authentic specimen (Bouveault and Locquin, *Bull. Soc. chim.*, 1906, **35**, 648, give m. p. 98—99°).

Propargyl Alcohol.—2-Butyne-1 : 4-diol (10 g.) was heated with potassium carbonate (0·5 g.) at 140—150° and the distillate collected in a cooled receiver. The yield of crude propargyl alcohol was 50—60% and of pure propargyl alcohol, 15—20% (estimated as the mercury derivative, m. p. 203—204°, colourless needles from 2-ethoxyethanol). On heating the diol with equal quantities of potassium carbonate, magnesium oxide, barium oxide, calcium carbide, calcium hydroxide, or sodium carbonate, the reaction was difficult to control and at well-defined temperatures violent decomposition occurred with formation of considerable amounts of acetylene. Below these temperatures, decomposition to propargyl alcohol and formaldehyde occurred smoothly.

1 : 4-*Dimethoxy-2-butene.*—1 : 4-Dibromo-2-butene (100 g.; Farmer, Lawrence, and Thorpe, *J.*, 1928, 729) was added to a solution of potassium hydroxide (58 g.) in methanol (750 c.c.) and the mixture refluxed for 1 hour. The precipitated potassium bromide was separated and most of the methanol removed from the filtrate by distillation through an 8-inch Widmer column. The residue was poured into water (500 c.c.) and extracted with ether (3 × 150 c.c.), and the combined ethereal extracts were washed, dried, and distilled to yield 1 : 4-*dimethoxy-2-butene* as a main fraction (42·5 g.), b. p. 77°/36 mm., $n_D^{20°}$ 1·4220 (Found : C, 63·0; H, 8·9. $C_6H_{10}O_2$ requires C, 63·2; H, 8·8%).

1 : 4-*Diethoxy-2-butyne.*—By the condensation of chloromethyl ethyl ether and acetylenedimagnesium bromide (Gauthier, *Ann. Chim.*, 1909, **16**, 289), 1 : 4-diethoxy-2-butyne was obtained in 70% yield as a colourless liquid, b. p. 82°/17 mm., 97—99°/38 mm.; $n_D^{20°}$ 1·4360 (Gauthier, *loc. cit.*, gives b. p. 179—180°/730 mm.; $n_D^{22°}$ 1·435), which rapidly darkened in air. This darkening could be delayed by the addition of a trace of quinol.

The author thanks Mr. J. D. Rose for his advice and encouragement throughout this work. He is also indebted to Dr. P. V. Youle and Dr. R. G. A. New who collaborated in the preparation of 2-butyne-1 : 4-diol.

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Research Laboratories, Blackley, Manchester, 9. [*Received, March 6th*, 1946.]