9. *Researches on Acetylenic Compounds. Part XXVIII. A New Route to Diacetylene and its Symmetrical Derivatives.*

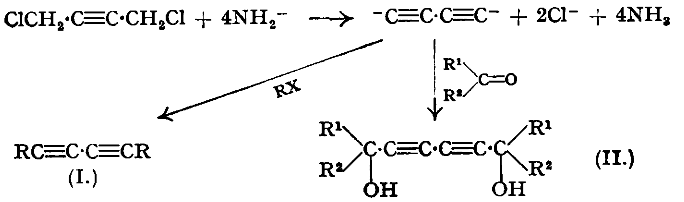
By J. B. ARMITAGE, E. R. H. JONES, and M. C. WHITING.

Treatment of the readily available 1 : 4-dichlorobut-2-yne with aqueous sodium hydroxide gives diacetylene in good yield. When the dehydrohalogenation is effected with sodamide in liquid ammonia the disodium salt can be prepared, and this can then react *in situ* with alkyl halides or with carbonyl compounds to give symmetrical conjugated diacetylenic hydrocarbons or glycols.

ALTHOUGH diacetylene has been hnown for many years (Baeyer, *Ber.*, 1885, **18**, 674, 2269) and although its potential applications in organic synthesis are numerous and important, its wide spread use has been precluded by the difficulty of preparing it in quantity. Many methods of synthesis have been investigated. Baeyer (*loc. cit.*) obtained it by decarboxylation of the corresponding dicarboxylic acid; Zalkind and Aizikovich (*J. Gen. Chem. Russia*, 1937, **7**, 227; *Chem. Abs.*, 1937, **31**, 4283) observed its formation in the alkaline decomposition of 2 : 7-dimethylocta-3 : 5-diyne-2 : 7-diol. Numerous examples of its formation in very small yields in pyrolytic decompositions have been recorded, and its isolation from the by-product of the arc process for acetylene synthesis, as operated just before and during the war in Germany (see Copenhaver and Bigelow, " Acetylene and Carbon Monoxide Chemistry," Reinhold, New York, 1949, p. 300), probably made possible the only well-known instance of its use on a comparatively large scale (Kuhn and Wallenfells, *Ber.*, 1938, **71**, 1889). The most useful techniques for the laboratory preparation of diacetylene hitherto described, however, have involved the oxidation of metallic derivatives of acetylene. That of Strauss and Kolleck (*Ber.*, 1926, **59**, 1664), employing cupric chloride and cuprous acetylide, has furnished the small quantities necessary for several physical investigations whilst very recently Schlubach and Wolf (*Annalen*, 1950, **568**, 141) have described an elegant method whereby sodium acetylide is oxidised by potassium permanganate in liquid ammonia, giving a 35% yield of diacetylene.

Amongst the methods previously employed, the only route which appeared to offer possibilities of development into a convenient synthesis for use on a moderately large scale was that discovered by Keyssner and Eichler (G.P., 740,637; *Chem. Abs.*, 1946, **40**, 586) and confirmed by Johnson (*J.*, 1946, 1009). This involves treatment of 1 : 4-dichlorobut-2-yne—easily prepared from the corresponding glycol, which is now commercially available—with " alkaline reagents." Our investigations have shown that the nature of the alkaline reagent is critical; thus with potassium hydroxide in ethanol or 2-ethoxyethanol, reaction occurred at room temperature, but the solvent retained diacetylene so strongly that its removal, before subsequent alkali-catalysed addition of alcohol to give a 1-alkoxybut-1-en-3-yne (see Copenhaver and Bigelow, *op. cit.*, p. 305; Johnson, *loc. cit.*), proved impracticable. On stirring the chloride with aqueous alkalis it was found that calcium hydroxide, potassium carbonate, and trisodium phosphate failed to give any diacetylene even at 100°, whilst 10% sodium hydroxide gave a good (60%) yield. When stronger solutions of sodium hydroxide were used more polymeric material was formed and the yield fell; on the other hand, the addition of 10% of dioxan proved beneficial. Diacetylene was readily isolated in a graduated trap at $-25°$. Although it has not as yet been necessary to prepare more than 15 g. in one experiment, there seems no reason to doubt that many times this quantity could be obtained without difficulty. Numerous experiments involving the preparation and redistillation of diacetylene have been carried out without mishap, but it should be remembered that potentially this is a dangerously explosive substance (see Copenhaver and Bigelow, *op. cit.*, p. 303). Diacetylene rapidly decomposes at temperatures near its boiling-point, giving explosive polymers, and for that reason it was invariably kept at $-25°$ or below until used. It was characterised by condensation with acetone through its Grignard derivative, whereby the crystalline 2 : 7-dimethylocta-3 : 5-diyne-2 : 7-diol was obtained in 62% yield.

When 1 : 4-dichlorobut-2-yne was treated with sodamide in liquid ammonia rapid dehydrohalogenation ensued; indeed when after one minute the excess of sodamide was decomposed by ammonium nitrate, and the ammonia evaporated, titration of the resulting sodium chloride showed that at least 95% of the theoretical quantity had been formed. A control experiment in the absence of sodamide showed that no appreciable liberation of chloride ions from 1 : 4-dichlorobut-2-yne occurs in 30 minutes (*cf.* Johnson, *loc. cit.*). When four molecular proportions of sodamide were employed the disodium salt of diacetylene was apparently formed, since addition of methyl iodide then gave dimethyldiacetylene (hexa-2 : 4-diyne) in 65% yield.



This crystalline hydrocarbon has been the subject of much investigation; previous work is reviewed by Schlubach and Wolf (*loc. cit.*). Its preparation on a scale of about 20 g. by the present procedure involved no difficulties other than those inherent in its physical properties; it has m. p. 67° and b. p. 129° and is so volatile that purification by recrystallisation was deemed impracticable. On the other hand, distillation at 760 mm. or 100 mm., on a fairly large scale, resulted in explosive decomposition; but sublimation, with the apparatus illustrated, proved convenient.

The preparation of octa-3 : 5-diyne (I; R = Et) and of dodeca-5 : 7-diyne (I; R = Bu) by the action of ethyl iodide and butyl bromide, respectively, on disodiodiacetylene in about 50% yield, indicates that this reaction is general for primary aliphatic halides. On the other hand, the use of benzyl chloride and of 2 : 4-dinitrochlorobenzene gave only intractable tars. When allyl bromide was used, there was obtained a 25% yield of an approximately homogeneous liquid which certainly was not the expected deca-1 : 9-diene-4 : 6-diyne (I; R = $CH_2{=}CH{\cdot}CH_2$) since it showed light-absorption maxima at 2300 and 2800 A., $E^{1\%}_{1\,\text{cm.}}$ = 830 and 55, and formed an insoluble silver derivative. In view of the instability of the compound, and of the known complexity of the reactions between allyl halides and sodium acetylide (Lespieau and Journaud, *Bull. Soc. chim.*, 1931, **49**, 423; see also Eglinton and Whiting, *J.*, 1950, 3650) further investigations were not attempted.

When the solution of disodiodiacetylene was treated with carbonyl compounds, diacetylenic glycols of type (II) were obtained. In the case of aliphatic ketones (including pinacone) the yields are excellent (86—93%); methyl nonyl ketone alone gave less satisfactory results (yield 36%). Aliphatic aldehydes (formaldehyde, acetaldehyde, and butyraldehyde) also gave good yields (60—90%), but a longer reaction period was needed and the results were more adversely affected by the presence of water in the liquid ammonia (*cf.* Clapperton and McGregor, *J. Amer. Chem. Soc.*, 1949, **71**, 3234). Aromatic ketones also gave good (~50%) yields after a long reaction period when the reaction was carried out in a 1 : 3 mixture of ether and liquid ammonia; but benzaldehyde gave only a 7% yield of the corresponding glycol, which was not improved by working at −70°, substituting lithium or calcium for sodium, or wide variations in reaction time and in the ratio of the reactants. In most of these cases the glycols were known substances and had melting points in agreement with literature values. The present method is complementary to that involving oxidative coupling of ethynylcarbinols, and is in general preferable for small-scale experiments and in cases where the latter are difficultly accessible, *e.g.*, for the glycols derived from formaldehyde and acetophenone.

Attempts to extend this reaction to αβ-unsaturated aldehydes (acraldehyde and crotonaldehyde) were uniformly unsuccessful, only polymeric materials being obtained despite wide variations in reaction conditions. Three αβ-unsaturated ketones were investigated; mesityl oxide gave only the ammonia-adduct, diacetoneamine, β-ionone was recovered unchanged in 84% yield after a 24-hour reaction-period, and benzylideneacetone gave a 50% yield of a syrup which is believed, from physical properties and analytical and spectrographic data, to have consisted essentially of the expected glycol (II; R_1 = $Ph{\cdot}CH{=}CH$, R_2 = Me). Kuhn and Wallenfells (*loc. cit.*) described this as a crystalline solid, but here, as with all glycols from unsymmetrical carbonyl compounds, the formation of a mixture of *meso*- and racemic forms is to be expected.

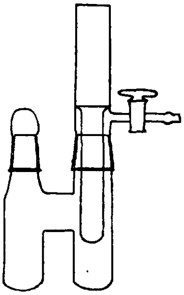
Attempts to induce disodiodiacetylene to react with ethylene oxide, propylene oxide, and epichlorohydrin proved unsuccessful. It is clear that there is no close parallel between the reactions of sodium acetylide and the derivative of diacetylene; the most conspicuous difference is observed in the reactions with acetophenone, when the latter gives a much higher yield (60%, as against 20%) in a shorter time, and with benzaldehyde, where the yields are 7% and *ca.* 80%, respectively. The explanation may lie in the greater acid strength of diacetylene, which on the one hand implies reduced reactivity of its anion as a nucleophilic reagent toward somewhat inert carbonyl compounds, *e.g.*, β-ionone, and on the other diminishes its tendency to react with readily enolisable, and therefore acidic, ketones, (*e.g.*, acetophenone) merely by proton transfer. The light-absorption properties of the diacetylenic compounds prepared will be discussed in a later publication. Dehydrohalogenation reactions of the type exemplified by the conversion of 1 : 4-dichlorobut-2-yne into diacetylene have been found to occur with great ease, and have made possible the synthesis of a wide range of conjugated di-, tri- and tetra-acetylenic compounds, the preparation and some of the properties of which will be described in the near future. A brief account of this work was given recently in a Tilden Lecture (Jones, *J.*, 1950, 754).

EXPERIMENTAL.

Diacetylene.—A mixture of 1 : 4-dichlorobut-2-yne (6·1 g.), potassium hydroxide (6 g.), water (60 c.c.), and dioxan (6 c.c.) was stirred vigorously and heated under reflux. The gas evolved, after passing up the reflux condenser, was led over calcium chloride and into a graduated trap at −25°. Diacetylene collected as a liquid (1·5 g.; 60%) which readily crystallised as well-formed plates on cooling to −70°. It was transferred slowly by means of a stream of nitrogen into a solution of ethylmagnesium bromide, prepared from magnesium (1·6 g.), in dry ether (60 c.c.). The solution thus obtained was stirred for 30 minutes, acetone (3·48 g.) was slowly added with cooling, and the solution was refluxed for one hour. Isolation of the product gave a pale-yellow solid (3·4 g.) which was crystallised from water to give 2 : 7-dimethylocta-3 : 5-diyne-2 : 7-diol (3·1 g.; 62%) as needles, m. p. 129° (Strauss, Kollek, and Hauptmann, *Ber.*, 1930, **63**, 1886, give m. p. 129—130°).

Disubstituted Diacetylenes.—General method. To a suspension of sodamide prepared without mechanical stirring in a small vacuum flask from liquid ammonia (100 c.c.), sodium (4·6 g.), and ferric nitrate (0·05 g.) by the procedure described by Vaughn, Vogt, and Nieuwland (*J. Amer. Chem. Soc.*, 1934, **56**, 2120), 1 : 4-dichlorobut-2-yne (6·1 g.) was added slowly with shaking. After one minute the second reactant was added, and the mixture was set aside for some time. Ammonium chloride (12 g.) was added and the contents of the flask were transferred to a beaker; after the ammonia had largely evaporated the residue was repeatedly extracted with ether, and the product was isolated by crystallisation or distillation.

Hexa-2 : 4-*diyne*. This hydrocarbon was prepared essentially by the general method but on a much larger scale in a 3-l. vacuum flask from sodium (37 g.), 1 : 4-dichlorobut-2-yne (49 g.), and methyl iodide (114 g.); the reaction period was three hours. The crude product was isolated with ether, and the ether removed through a 50-cm. Fenske column. The pale-brown residual solid was sublimed in four portions, the apparatus shown being used, at 30° (bath temp.)/9 mm., to give the pure hydrocarbon (20 g.; 65%) as prisms, m. p. 67° (Prévost, *Ann. Chim.*, 1928, **10**, 372, gives m. p. 64·5°, b. p. 129°; Schlubach and Wolf, *Annalen*, 1950, **568**, 141, give m. p. 68·5°).



Octa-3 : 5-*diyne*. The reaction was carried out by the general method by using ethyl iodide (15·6 g.) with a reaction period of three hours. The crude product was distilled to give octa-3 : 5-diyne (2·3 g.; 43%), b. p. 69°/17 mm., n_D^{22} 1·4928 (Dupont, *Compt. rend.*, 1909, **148**, 1522, gives b. p. 163—164°, n_D 1·4968).

Dodeca-5 : 7-*diyne*. The reaction was carried out by the general method by using butyl bromide (13·7 g.) with a reaction period of 19 hours. The crude product was distilled to give dodeca-5 : 7-diyne (4·0 g.; 50%), b. p. 83°/0·5 mm., n_D^{16} 1·4920. The use of butyl iodide gave a similar yield of product (Grignard and Tcheoufaki, *Compt. rend.*, 1929, **188**, 358, give b. p. 103°/8 mm.)

Reaction of Allyl Bromide with Disodiodiacetylene.—The reaction was carried out essentially by the general method in a 1·5-l. vacuum vessel by using sodium (18·4 g.), 1 : 4-dichlorobut-2-yne (24·6 g.), and allyl bromide (48·4 g.); the reaction period was three hours. The crude product was distilled to give a liquid (5·2 g.), b. p. 38°/0·02 mm., n_D^{20} 1·5176 (Found: C, 91·5; H, 8·5. $C_{10}H_{10}$ requires C, 92·3; H, 7·7%). *Active hydrogen* (Zerewitinoff). The product (5·54 mg.) evolved 0·49 c.c. of methane at 20°/766·4 mm., corresponding to 0·5 active hydrogen atom per $C_{10}H_{10}$ unit.

Hydrogenation. The product (0·707 g.) in ethyl alcohol (50 c.c.) was shaken in hydrogen in the presence of platinic oxide (Adams) catalyst (10 mg.) until absorption was complete (uptake 648 c.c. at 23°/765 mm.; 5 moles of hydrogen per mole of $C_{10}H_{10}$).

Hexa-2 : 4-*diyne*-1 : 6-*diol.*—The reaction was carried out essentially by the general method but on a 1-molar scale, in a 3 l.-vacuum vessel by using sodium (92 g.), ferric nitrate (1 g.), 1 : 4-dichlorobut-2-yne (123 g.), and paraformaldehyde (60 g.; dried over concentrated sulphuric acid) with a reaction period of 24 hours. The crude product, isolated as a pale-yellow solid (102 g.; 93%), had m. p. 110—112° and was therefore already fairly pure; a portion (5·1 g.) was recrystallised from ethyl acetate–light petroleum (b. p. 80—100°) to give the pure glycol (4·85 g., equivalent to 88% yield) as plates, m. p. 112°. Alternatively, sublimation at 80° (bath temp.)/10^{-4} mm. gave the glycol, m. p. 112° (Lespieau, *Ann. Chim.*, 1897, **11**, 232, gives m. p. 111—112°).

Octa-3 : 5-*diyne*-2 : 7-*diol.*—The reaction was carried out by the general method by using acetaldehyde (4·4 g.) in dry ether (50 c.c.) with a reaction period of 24 hours. Isolation of the product gave a solid (6·2 g.; 89%), m. p. 83—85°, which was recrystallised from benzene to give the almost colourless pure glycol (4·9 g.; 71%), m. p. 65—66°. Alternatively, sublimation at 80° (bath temp.)/10^{-5} mm. gave the glycol as long rectangular plates, m. p. 65—66°. (Zalkind and Gverdsiteli, *J. Gen. Chem. Russia*, 1939, **9**, 971, give m. p. 108—109° for one of the stereoisomeric forms. The other has m. p. 67·5—68°

according to Lespieau, *Ann. chim.*, 1912, **27**, 137.) When the reaction period was reduced to two hours the yield of glycol after crystallisation from benzene, was 0·7 g. (10%).

Dodeca-5 : 7-*diyne*-4 : 8-*diol*.—The reaction was carried out by the general method by using butyraldehyde (7·2 g.) in dry ether (50 c.c.) with a reaction time of 24 hours. Distillation of the crude product gave the glycol (6·5 g.) as a viscous liquid, b. p. 147°/0·5 mm., n_D^{20} 1·5170 (Bowden, Heilbron, Jones, and Sargent, *J.*, 1947, 1581, give b. p. 138°/10^{-3} mm., $n_D^{19\cdot5}$ 1·5175).

1 : 6-*Diphenylhexa*-2 : 4-*diyne*-1 : 6-*diol*.—The reaction was carried out by the general method by using benzaldehyde (10·6 g.) with a reaction time of one hour. The crude product was a deep-red, very viscous liquid which partially crystallised. Trituration with benzene gave a light-brown solid (0·9 g.), m. p. 127—130°, which after crystallisation from benzene formed needles, m. p. 131—133° (Kuhn and Wallenfells, *loc. cit.*, give m. p.s 81—85° and 131—132·5° for the two stereoisomeric forms). Chromatography of the residue failed to give more crystalline material, and the use of reaction periods of five minutes and of 24 hours, and of 1½ hours at −70° led to the formation of uncrystallisable dark syrups. When lithium (1·4 g.) was used in place of sodium with a reaction period of 15 minutes the yield of glycol, m. p. 133° (recrystallised), was 0·8 g.

2 : 7-*Dimethylocta*-3 : 5-*diyne*-2 : 7-*diol*.—The reaction was carried out by the general method by using acetone (5·8 g.) with a reaction period of 60 minutes. Isolation of the crude product gave a solid (8·2 g.; 97%), m. p. 126—128°, which was sublimed at 90° (bath temp.)/10^{-4} mm. to give the pure glycol (7·5 g.; 87%) as long needles, m. p. 129°. Recrystallisation from water, the small amount of tarry impurity being removed by filtration, was an equally satisfactory method of purification (Strauss, Kolleck, and Hauptmann, *loc. cit.*, give m. p. 129—130^{c}). When the reaction period was reduced to five minutes the yield of crude glycol was 83%.

3 : 8-*Dimethyldeca*-4 : 6-*diyne*-3 : 8-*diol*.—The reaction was carried out by the general method by using methyl ethyl ketone (7·2 g.) with a reaction period of three hours. Isolation of the crude product gave a solid (9 g.; 93%), m. p. 83—88°, which after crystallisation from ethyl acetate–light petroleum (b. p. 80—100°) gave the pure glycol (8·5 g.) as small prisms, m. p. 89°. The crude glycol could also be purified by sublimation at 100° (bath temp.)/10^{-4} mm. (I.G. Farben., G.P. 765,469, give m. p. 89°).

10 : 15-*Dimethyltetracosa*-11 : 13-*diyne*-10 : 15-*diol*.—The reaction was carried out by the general method by using methyl nonyl ketone (17 g.) with a reaction period of 24 hours. Isolation of the crude product gave a dark-red viscous liquid (10 g.) which was distilled to give the pure glycol (7 g.; 36%), b. p. 150° (bath temp.)/10^{-4} mm., m. p. 45—46° (Bowden, Heilbron, Jones, and Sargent, *loc. cit.*, give b. p. 210°/10^{-2} mm., m. p. 40—43°).

2 : 2 : 3 : 8 : 9 : 9-*Hexamethyldeca*-4 : 6-*diyne*-3 : 8-*diol*.—The reaction was carried out by the general method by using pinacone (10 g.) with a reaction period of three hours. Isolation of the crude glycol gave a pale-yellow solid (12·5 g.), m. p. 248—252°, which was recrystallised from aqueous methanol to give the *monohydrate* (12 g.; 90%) as needles (Found, in a sample dried at 20° in a desiccator : C, 71·45; H, 10·85. $C_{16}H_{26}O_2,H_2O$ requires C, 71·6; H, 10·5%). On being heated above 100° or dried at 50°/10^{-4} mm. the monohydrate was decomposed giving the anhydrous *glycol*, m. p. 248—251°, which when cool rapidly absorbed moisture from the air (Found : C, 76·8; H, 10·7. $C_{16}H_{26}O_2$ requires C, 76·8; H, 10·5%).

Di-(1-*hydroxy*cyclo*hexyl*)*butadiyne*.—The reaction was carried out by the general method by using *cyclo*hexanone (9·8 g.) with a reaction time of one hour. The product was isolated as a brown solid (11·5 g.; 93%), m. p. 170—174°, which was recrystallised from benzene to give the glycol (10·2 g.; 83%) as needles, m. p. 174° (Zalkind and Aizikovitch, *J. Gen. Chem. Russia*, 1937, **7**, 227, give m. p. 173—174°; Kuhn and Wallenfells, *loc. cit.*, give m. p. 170°).

2 : 7-*Diphenylocta*-3 : 5-*diyne*-2 : 7-*diol*.—The reaction was carried out by the general method by using acetophenone (12 g.) with a reaction period of 24 hours. Isolation of the crude product gave a solid (8·8 g.; 61%), m. p. 193—195°, which was recrystallised from benzene to give the pure glycol (8·6 g.) as needles, m. p. 195° (Strauss, Kollek, and Hauptmann, *loc. cit.*, give m. p. 195° and 142—143° for the two stereoisomeric forms).

1 : 1 : 6 : 6-*Tetraphenylhexa*-2 : 4-*diyne*-1 : 6-*diol*.—The reaction was carried out by the general method by using benzophenone (18·2 g.) in dry ether (50 c.c.) with a reaction period of 24 hours. The crude product was a deep-red, very viscous liquid. After several days a benzene solution deposited brown crystals (10·5 g.), m. p. 138—140°, which after recrystallisation from benzene gave the glycol (10·0 g., 48%) as needles, m. p. 140—141° (Kuhn and Wallenfells, *loc. cit.*, give m. p. 140—141°).

3 : 8-*Dimethyl*-1 : 10-*diphenyldeca*-1 : 9-*diene*-4 : 6-*diyne*-3 : 8-*diol*.—The reaction was carried out by the general method by using benzylideneacetone (14·6 g.) in dry ether (50 c.c.) with a reaction period of 24 hours. Isolation of the crude product gave a dark-red syrup which was dissolved in dry benzene (100 c.c.) and extracted with ethylene glycol (3 × 100 c.c.). Dilution of the glycol solution with water and isolation with ether gave a light-brown syrup (9 g.; 52%) which could not be induced to crystallise. No satisfactory analytical data could be obtained (Found : C, 82·0; H, 6·5. $C_{24}H_{22}O_2$ requires C, 84·2; H, 6·5%) but the light absorption of the product (Maximum, 2510—2550 A., $\varepsilon = 27{,}000$) is in accordance with the expected value (styrene has maximum, 2440 A.; $\varepsilon = 12{,}000$: Hirshberg, *J. Amer. Chem. Soc.*, 1949, **71**, 3241).

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THE UNIVERSITY, MANCHESTER, 13.

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