# 372. *Researches on Acetylenic Compounds. Part XXXVI.* The Synthesis of Symmetrical Conjugated Triacetylenic Compounds.*

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Dehydrohalogenation of 1 : 6-dichlorohexa-2 : 4-diyne with sodamide in liquid ammonia gives triacetylene or its mono- or di-sodium derivatives. The isolation of the unstable parent hydrocarbon and the reactions of the disodium derivative with alkyl halides and carbonyl compounds are described. An account is given of the ultra-violet light-absorption properties of some triacetylenic compounds.

This work and that described in the following paper was summarised in a Tilden Lecture given in October, 1949 (cf. *J.*, 1950, 754).

Although numerous conjugated diacetylenes have been described since Glaser's synthesis of diphenyldiacetylene in 1869, substances containing more than two conjugated acetylenic linkages have been almost unknown until recently. Grignard and Tcheoufaki (*Compt. rend.*, 1929, **188**, 359) claimed, without giving full experimental details, that they had prepared 1-iodo- and 1-phenyl-hexa-1 : 3 : 5-triyne (V; R = I and Ph, respectively). After the completion of most of the present work, however, Hunsmann (*Ber.*, 1950, **83**, 213) described the isolation of triacetylene, as its condensation product (IV; R = Me) with acetone, from the high-boiling residue obtained in the Hüls arc process for the synthesis of acetylene. He also described a rational synthesis of triacetylene from the dichloro-compound (I). During the preparation of this paper Schlubach and Franzen (*Annalen*,

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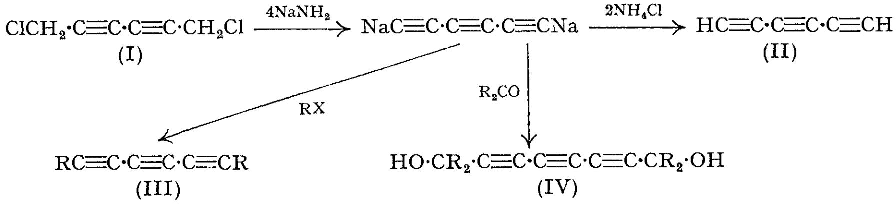
* Part XXXV, preceding paper.

1951, **572**, 116) announced the synthesis of diphenyltriacetylene, which, along with some higher members of the series, has also been prepared (cf. Jones, Whiting, Armitage, Cook, and Entwistle, *Nature*, 1951, **168**, 900); Kuhn and Zahn (*Ber.*, 1951, **84**, 566) described the glycol (IV; R = Ph) and the corresponding fluorenone derivative; and Bohlmann (*Angew. Chem.*, 1951, **63**, 218) described briefly the preparation and ultra-violet light-absorption properties of diphenyltriacetylene, the glycols (IV; R = Ph) and (IV; $R_2 = [CH_2]_5$), and di*cyclo*hexenyltriacetylene.

An apparent analogy exists between 1 : 4-dichlorobut-2-yne, on the one hand, and vicinal dihalides on the other, in that both undergo dehydrohalogenation on treatment with sodamide in liquid ammonia (Armitage, Jones, and Whiting, *J.*, 1951, 44). An extension of this analogy led to the conclusion that 1 : 6-dichlorohexa-2 : 4-diyne (I) should undergo a similar reaction, involving double 1 : 6-dehydrochlorination and giving the interesting hydrocarbon, hexa-1 : 3 : 5-triyne or triacetylene (II).



$RC{\equiv}C{\cdot}C{\equiv}C{\cdot}C{\equiv}CH$ (V)

Moreover, the use of four molecular proportions of sodamide should give a sodium derivative of triacetylene convertible into disubstituted triacetylenic hydrocarbons (III), and triacetylenic glycols (IV), by reactions *in situ* with alkyl halides and carbonyl compounds, respectively. All these reactions have now been realised.

In preliminary experiments it became obvious that in the dehydrochlorination of 1 : 6-dichlorohexa-2 : 4-diyne at −33° insoluble carbonaceous matter was the principal product. At *ca.* −70°, or better at −77°, in the presence of some solid ammonia, the reaction was still rapid, and then gave a much higher yield of triacetylene, as estimated by further condensation reactions (see below). For the preparation of the parent hydrocarbon, however, the problem of isolating (II) was more serious than that of preparing it; isolation was finally achieved by a technique involving the extraction of the triacetylene from the liquid-ammonia solution with butane. Extensive polymerisation occurred even though the temperature was kept as far as possible below −50°, but the hydrocarbon was obtained in a fairly pure condition from two experiments. It forms fairly well-defined needle-shaped crystals, is apparently stable at liquid-air temperatures, but slowly becomes red at *ca.* −50°. It melts below 0°; on one occasion it was characterised by conversion into a crystalline octabromide (cf. the formation of a hexabromide from diacetylene, Noyes and Tucker, *Amer. Chem. J.*, 1897, **19**, 123; Strauss and Kolleck, *Ber.*, 1926, **59**, 1664), while on another the liquid darkened instantly on exposure to air and a few minutes later exploded violently without provocation.

When four molecuar proportions of sodamide were employed in the dehydrohalogenation reaction, the disodium derivative was formed, and addition of methyl iodide then gave octa-2 : 4 : 6-triyne (III; R = Me), a beautifully crystalline substance, m. p. 128°, in 28% yield. Accurate *X*-ray diffraction measurements have been made on this compound by Jeffrey and Rollett, and a preliminary account of the results obtained has already appeared (*Nature*, 1950, **166**, 479).

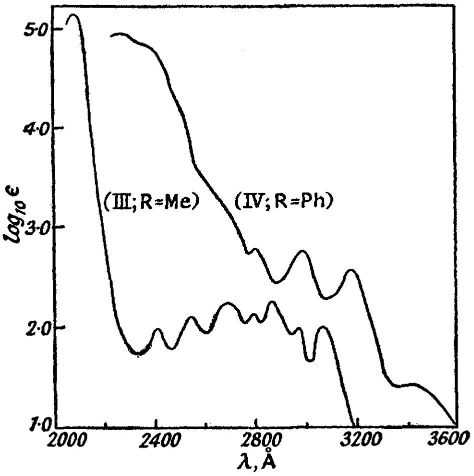
Substitution of ethyl bromide for methyl iodide gave the corresponding triacetylenic hydrocarbon (III; R = Et) as a liquid of moderate stability.

When the solution of disodiotriacetylene was treated with acetone the expected triacetylenic glycol (IV; R = Me) was obtained in good yield. Benzophenone gave the analogous tetraphenyl compound; both ditertiary glycols were crystalline solids stable for months at room temperature. When formaldehyde was employed the diprimary glycol (III; R = H) was obtained in fair yield.

*Light-absorption Properties.*—The ultra-violet absorption spectra of octatriyne and 1 : 1 : 8 : 8-tetraphenylocta-2 : 4 : 6-triyne-1 : 8-diol are shown in the diagram, and the data determined for other triynes are tabulated below (wave-lengths are in Å). Ethanolic solutions were employed.

| Compound | $\lambda_{max.}$ ($\epsilon$) *L* | $\lambda_{max.}$ ($\epsilon$) *E* | $\lambda_{max.}$ ($\epsilon$) *D* | $\lambda_{max.}$ ($\epsilon$) *C* | $\lambda_{max.}$ ($\epsilon$) *B* | $\lambda_{max.}$ ($\epsilon$) *A* |
|---|---|---|---|---|---|---|
| III; R = Me | <2070 (>135,000) | 2390 (105) | 2530 (130) | 2680 (200) | 2860 (200) | 3060 (120) |
| III; R = Et | <2110 (165,000) | 2400 (105) | 2550 (155) | 2690 (220) | 2865 (220) | 3070 (130) |
| IV; R = H | 2125 (>140,000) | 2470 (190) | 2610 (245) | 2750 (320) | 2930 (320) | 3120 (190) |
| IV; R = Me | 2135 (190,000) | 2450 (70) | 2570 (130) | 2740 (200) | 2920 (230) | 3120 (145) |
| IV; R = Ph | 2270 (98,000) | — | — | 2790 (670) | 2955 (680) | 3180 (540) |

In addition to a region of medium-intensity absorption showing vibrational fine-structure (bands *A*—*E*) similar to that shown by diacetylenes (*J.*, 1952, 2003) but at somewhat longer wave-lengths, triacetylenes show light absorption of extremely high intensity at short wave-lengths (band *L*). The $\varepsilon_{max.}$ values in this region are about five times as large as those of typical trienes. There can be little doubt that whereas the 2390—3200-Å region corresponds to the <2050—2650-Å region for diacetylenes, the new ultra-high-intensity region corresponds to the very intense bands below 1630 Å observed by Walsh (*Trans. Faraday Soc.*, 1945, **41**, 381) in the vapour-phase spectra of diacetylene and hexa-2 : 4-diyne. This latter region is discussed in greater detail in the following paper in the case of tetra-acetylenic compounds. Here it may be noted that the vibrational fine-structure in the medium-intensity region shows a spacing essentially similar (average 2300 cm.$^{-1}$) to that observed in the diacetylenes discussed earlier, provided that the very small maxima in the spectrum of octatriyne, the consequence of the resolution of more than merely the most prominent vibrational lines in this case, are disregarded.



When the results for the aliphatic triacetylenic glycols, and (since the diprimary glycol was too unstable to purify completely) in particular for 2 : 9-dimethyldeca-3 : 5 : 7-triyne-2 : 9-diol (IV; R = Me), are compared with those observed for the hydrocarbons, it is at once evident that the introduction of two α-hydroxy-groups shifts the medium-intensity maxima to longer wave-lengths, as was notably the case with the diacetylenic compounds discussed earlier (p. 2001). An even more pronounced effect is evident in the ultra-high-intensity band. Similarly the conspicuous effects of the four phenyl groups upon the triyne chromophore are analogous to the phenomena observed with the corresponding diacetylenic compounds (p. 2003) and are similarly explicable.

## EXPERIMENTAL

Absorption spectra were obtained in ethanolic solution with a Beckman Model DU. or a Unicam Spectrophotometer. M. p.s were determined on the Kofler block.

*Hexa*-1 : 3 : 5-*triyne* (II).—A suspension of sodamide was prepared under nitrogen from sodium (4·6 g.) and liquid ammonia (150 c.c.) and cooled externally to −70°. 1 : 6-Dichlorohexa-2 : 4-diyne (7·4 g.; prepared as described in the previous paper) was added dropwise, with stirring, during 10 minutes; after a further 5 minutes ammonium chloride (8 g.) was added, and the solution was allowed to warm to −33° in a nitrogen atmosphere and concentrated to about 60 c.c. Butane (4 × 50 c.c.) was then added in portions, with agitation, the bulk of the extract being poured off carefully each time. The resultant extract was evaporated under reduced pressure, giving a yellow, largely polymeric semi-solid residue which was quickly warmed to 0°. The liquid portion was transferred to an H-tube (illustrated in *J.*, 1951, 46) and surrounded by a bath at about −5°; when the pressure was reduced to ~0·1 mm. rapid sublimation on to a tube cooled with liquid air gave hexa-1 : 3 : 5-triyne (~300 mg.) as a white microcrystalline solid, stable in light *in vacuo* for several minutes. When the liquid air was replaced by ice-water, the solid melted to a pale yellow liquid, which instantly turned black when air was admitted, though it remained fluid. A few minutes later most of this material, in several separate portions, detonated with remarkable violence (a ~30-mg. specimen lying on a cotton-wool pad in a sawn-off Carius tube shattered the latter). One specimen was stored at −70°, and this crystallised, but it too exploded later when allowed to attain room temperature.

In a similar experiment the crude hexatriyne was sublimed at 25°(bath temp.)/10 mm. and condensed at about −50°, giving prismatic crystals 3 mm. long; at this temperature it quickly became pink in diffused light. On this occasion it did not darken after melting and admission of air; the liquid was at once treated with an excess of bromine in carbon tetrachloride. Evaporation and recrystallisation gave the *octabromide* (1 : 1 : 2 : 3 : 4 : 5 : 6 : 6-*octabromohexa*-2 : 4-*diene*?) as colourless needles, m. p. 157° (Found : C, 10·4; H, 0·5. $C_6H_2Br_8$ requires C, 10·1; H, 0·3%). Light absorption in alcohol; maximum, 2510 Å, $\varepsilon = 4700$.

*Octa*-2 : 4 : 6-*triyne* (III; R = Me).—To a suspension of sodamide, prepared from sodium (4·6 g.) and liquid ammonia (150 c.c.) under nitrogen, 1 : 6-dichlorohexa-2 : 4-diyne (7·4 g.) was added dropwise during 10 minutes with stirring and cooling to −70°. Methyl iodide (14·2 g.) was then added and the mixture was stirred for 3 hours. The ammonia was allowed to evaporate in a stream of nitrogen with the occasional addition of pentane. The black solid residue was extracted with pentane (4 × 50 c.c.); removal of the solvent under nitrogen at 20° gave the crude product (2·6 g., 50%) which sublimed at 80°(bath temp.)/0·01 mm. to give *octa*-2 : 4 : 6-*triyne* (1·5 g., 28%) as rhombohedra, m. p. 128° (Found : C, 94·0; H, 5·8. $C_8H_6$ requires C, 94·1; H, 5·9%).

The hydrocarbon (14 mg.) in ethyl acetate (30 c.c.) was shaken in hydrogen in the presence of platinic oxide (Adams's) (5 mg.) until absorption was complete; 20 c.c. (5·9 mol.) were taken up at 18°/746 mm.

*Deca*-3 : 5 : 7-*triyne* (III; R = Et).—A suspension of sodamide, obtained from sodium (9·6 g.) and liquid ammonia (100 c.c.), was stirred and cooled to −77° by direct addition of liquid nitrogen. Dichlorohexadiyne (14·7 g.) was added, and after 2 minutes, ethyl iodide (15·6 g.). After a further 45 minutes the liquid contents of the vacuum flask were extracted with butane, which on evaporation left a yellow liquid. Distillation gave *deca*-3 : 5 : 7-*triyne* (2·0 g., 40%), b. p. 65°(bath temp.)/$10^{-2}$ mm., $n_D^{17}$ 1·5858 (Found : C, 92·2; H, 7·65. $C_{10}H_{10}$ requires C, 92·3; H, 7·7%).

*Octa*-2 : 4 : 6-*triyne*-1 : 8-*diol* (IV; R = H).—To a suspension of sodamide, prepared from sodium (9·2 g.) in liquid ammonia (20 c.c.) at −77°, 1 : 6-dichlorohexa-2 : 4-diyne (14·7 g.) was added dropwise with stirring and cooling. Paraformaldehyde (6·0 g.; dried over phosphoric oxide) was added as a suspension in ether (100 c.c.); after the solution had been stirred for 2 hours ammonium chloride (10 g.) was added, and the ammonia was allowed to evaporate while more ether was added. Extraction of the residue with ether (4 × 50 c.c.) and removal of the solvent under reduced pressure gave a solid, crystallisation of which from ethyl acetate–light petroleum (b. p. 60—80°) gave the *glycol* (2·2 g., 17%) as plates, m. p. 138—140°, which on exposure to light became reddish-purple (Found : C, 72·0; H, 4·8. $C_8H_6O_2$ requires C, 71·7; H, 4·5%). On hydrogenation (uptake 5·83 mol.) with a platinic oxide catalyst in ethyl acetate, octane-1 : 8-diol, m. p. 57—60°, was obtained (Hill and Hibbert, *J. Amer. Chem. Soc.*, 1923, **45**, 3131, give m. p. 63°); oxidation with chromic acid in aqueous sulphuric acid gave suberic acid, m. p. and mixed m. p. 138—140°.

2 : 9-*Dimethyldeca*-3 : 5 : 7-*triyne*-2 : 9-*diol* (IV; R = Me).—To a suspension of sodamide, prepared from sodium (4·6 g.) and liquid ammonia (150 c.c.) under nitrogen, 1 : 6-dichlorohexa-2 : 4-diyne (7·4 g.) was added dropwise during 10 minutes with stirring and cooling to −70°. Acetone (5·8 g.) was added and the mixture was stirred at −60° for 3 hours. Ammonium chloride (10 g.) was added and the ammonia allowed to evaporate whilst ether was added. The black solid residue was extracted with ether (4 × 50 c.c.); removal of the solvent at 20° gave the crude glycol (9 g., 94%), m. p. 134—138°. 2 : 9-Dimethyldeca-3 : 5 : 7-triyne-2 : 9-diol (4·5 g., 47%) was obtained after repeated crystallisation from benzene as needles, m. p. 154—155°. Alternatively the glycol could be isolated by sublimation at 90°(bath temp.)/$10^{-4}$ mm. (Found : C, 76·0; H, 7·5. Calc. for $C_{12}H_{14}O_2$ : C, 75·8; H, 7·4%) (Hunsmann, *loc. cit.*, gives m. p. 154°).

1 : 1 : 8 : 8-*Tetraphenylocta*-2 : 4 : 6-*triyne*-1 : 8-*diol* (IV; R = Ph).—A solution of disodiotriacetylene, prepared at −77° from sodium (4·6 g.), liquid ammonia (100 c.c.), and dichlorohexadiyne (7·4 g.), was treated with a solution of benzophenone (18·2 g.) in ether (100 c.c.). After 2 hours the product was isolated; recrystallisation from benzene–light petroleum (b. p. 60—80°) gave the glycol (7·2 g.) as needles, m. p. 158—160°. Kuhn and Zahn (*loc. cit.*) give m. p. 156—158°.

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