373. *Researches on Acetylenic Compounds. Part XXXVII.* The Synthesis of Conjugated Tetra-acetylenic Compounds.*

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By the application of well-known methods of oxidative coupling to monosubstituted diacetylenic compounds, a number of symmetrical conjugated tetra-acetylenic hydrocarbons and glycols have been obtained. The ultra-violet light-absorption properties of these compounds, which are of an unusual nature and present many features of interest, are listed and discussed.

UNTIL recently the sole recorded example of a conjugated tetra-acetylenic compound was the highly unstable dicarboxylic acid (II; R = CO_2H), described by Baeyer and Landsberg (*Ber.*, 1885, **18**, 674, 2269). No conclusive evidence for the structure of this substance was available, apart from the analogy between the method of preparation and a well-authenticated synthesis of diacetylenedicarboxylic acid. During the preparation of the present paper Schlubach and Franzen (*Annalen*, 1951, **572**, 116) have published accounts of the synthesis of dimethyltetra-acetylene and of diphenyltetra-acetylene, both of which compounds had also been prepared in these laboratories (the diphenylpoly-ynes will be described in a forthcoming publication).

(I) $RC\equiv C\cdot C\equiv CH$ $RC\equiv C\cdot C\equiv C\cdot C\equiv C\cdot C\equiv CR$ (II)

The oxidative coupling of acetylenes has been effected by a wide variety of reagents, almost all of which require the presence of at least traces of copper or cobalt compounds. Of these, however, only a limited number are successful in the synthesis of tetra-acetylenic compounds from hydrocarbons and alcohols of type (I). Thus all experiments involving the action of potassium ferricyanide on the pre-formed copper derivative of hexa-1 : 3-diyne (I; R = Et) proved unsuccessful, apparently because of its insolubility. Treatment of a solution of the sodium derivative of penta-1 : 3-diyne with potassium permanganate in liquid ammonia (cf. Schlubach and Wolf, *Annalen*, 1950, **568**, 141) also failed to give the expected product. However, the action on penta-1 : 3-diyne (I; R = Me) of oxygen in the presence of cuprous and ammonium chlorides, or of cupric bromide or iodine on its Grignard derivative, gave good (~50%) yields of the highly crystalline deca-2 : 4 : 6 : 8-tetrayne (II; R = Me). Contrary to the experience of Schlubach and Franzen (*loc. cit.*) satisfactory analytical data were obtained. This interesting hydrocarbon decomposes below 100°, but extrapolation of the homologous series of dimethylpoly-ynes, and also its low solubility in organic solvents indicate that if stable its melting point would approach 200°. If protected from light—it is highly photosensitive (cf. p. 2003)—it is stable for some days at 20°, and it can be sublimed at $50°/10^{-5}$ mm.

Analogous methods enabled hexa-1 : 3-diyne and octa-1 : 3-diyne to be coupled, giving the corresponding tetra-ynes (II; R = Et or Bu). In the latter case, rather surprisingly,

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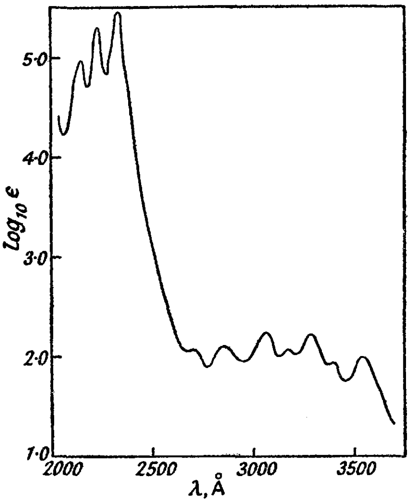
* Part XXXVI, preceding paper.

the reaction could even be effected (in lower yield and not reproducibly) with air at 65°. Dodeca-3 : 5 : 7 : 9-tetrayne (II; R = Et) melts at 26°, and is appreciably more volatile than the lower homologue at about 60°, presumably because the latter is still far below its melting point and so possesses considerable crystal-lattice energy. The dibutyl compound crystallises at *ca.* −60°. It seems reasonable to attribute the very rapid fall in melting point as the series is ascended to the abrupt decrease in symmetry from the rigidly linear molecule of deca-2 : 4 : 6 : 8-tetrayne (II; R = Me), which is very much higher-melting than its saturated analogue decane, to the Z-shaped molecule of hexadeca-5 : 7 : 9 : 11-tetrayne (II; R = Bu), which melts 70° below hexadecane. The dimethylpoly-ynes almost certainly show rotation in the solid state (Jeffrey and Rollett, personal communication), and this is no doubt partly responsible for their high melting points.

	O	*N*	*M*	*L*	*D*	*C*	*B*	*A*
Compound	$\lambda_{max.}$ (ε)	$\lambda_{max.}$ (ε)	$\lambda_{max.}$ (ε)	$\lambda_{max.}$ (ε)	$\lambda_{max.}$ (ε)	$\lambda_{max.}$ (ε)	$\lambda_{max.}$ (ε)	$\lambda_{max.}$ (ε)
II; R = Me	2050 (24,300)	2150 (91,500)	2260 (198,000)	2340 (281,000)	2860 (140)	3060 (180)	3280 (180)	3540 (105)
II; R = Et	—	—	2280 (192,000)	2380 (282,000)	2870 (160)	3080 (185)	3300 (185)	3550 (120)
II; R = Bu	—	—	2300 (176,000)	2400 (277,000)	2870 (265)	3070 (260)	3300 (215)	3560 (190)
II; R = CH_2·OH ...	2070 (23,100)	2170 (67,000)	2270 (178,500)	2380 (257,000)	2875 (480)	3065 (440)	3295 (290)	3550 (190)
II; R = CHMe·OH	2070 (38,800)	2180 (76,300)	2280 (188,000)	2390 (266,000)	2860 (205)	3080 (225)	3300 (240)	3550 (195)
II; R = CHPr·OH	2100 (28,300)	2200 (78,100)	2300 (184,000)	2410 (273,000)	2870 (180)	3090 (220)	3310 (240)	3560 (160)
II; R = CMe_2·OH...	2090 (19,250)	2190 (75,000)	2280 (197,000)	2400 (274,000)	2910 (235)	3110 (280)	3320 (245)	3600 (190)

(Wave-lengths are in Å.)



Attempts to synthesise tetra-acetylenic glycols from diacetylenic alcohols *via* their Grignard derivatives and iodine or cupric bromide proved unsuccessful. Once the improvements in the catalytic oxygenation technique described earlier (p. 1999) had been made, however, these glycols became readily available. Thus 2-methylhexa-3 : 5-diyn-2-ol gave almost a quantitative yield of (II; R = CMe_2·OH), which is thus obtainable in only three stages, with an overall yield greater than 50% from but-2-yne-1 : 4-diol, now commercially available, and acetone. This easily accessible glycol is unaffected by light, and may be kept for many months at 20° without significant decomposition.

The secondary alcohols (I; R = CHMe·OH) and (II; CHPr·OH) similarly gave tetra-acetylenic glycols, though the products were photo-labile and the yields were lower. In the former case the structure was rigidly proved by hydrogenation and oxidation of the product to the known dodecane-2 : 11-dione, which was converted into sebacic acid. Rather surprisingly the very unstable primary alcohol, penta-2 : 4-diyn-1-ol (I; R = CH_2·OH), also coupled smoothly, and the product was obtained in excellent yield.

Light-absorption Properties.—The ultra-violet absorption spectrum of deca-2 : 4 : 6 : 8-tetrayne is illustrated in the figure; in addition to a series of maxima of medium intensity in the 2800—3600 Å region, similar to those observed for the diynes and triynes, and described in the previous papers, a second series is observed which begins at 2350—2400 Å and for which maximal extinction coefficients are about 280,000. The fine structure of this series is rather more widely-spaced and less constant (average 2600 cm.$^{-1}$) than that of the medium-intensity band. Of greater interest, however, is the extraordinary intensity of absorption in this region, presumably analgous to the intense bands at ~1600 Å in the spectra of diacetylene and hexa-2 : 4-diyne, ascribed by Price and Walsh (*Trans. Faraday Soc.*, 1945, **41**, 381) to a Rydberg transition, and to the ~2100 Å band of the triacetylenes discussed in the previous paper. Typical extinction coefficients for simple aliphatic tetraenes free from steric hindrance to coplanity are 60,000—70,000 (Mowry, Brode, and Brown, *J. Biol. Chem.*, 1942, **142**, 671), and the only compound for which an $\varepsilon_{max.}$ value larger than those found for the tetraynes has been recorded is the C_{96} compound, *m*-hexadecidiphenyl (Gillam and Hey, *J.*, 1939, 1170). Here, of course, arithmetical multiplication of effectually independent chromophores is the explanation. It may be noted, however, that cyanine dyes may exhibit very intense light absorption; $Me_2N\cdot[CH{=}CH]_2\cdot CH{=}\overset{+}{N}Me_2$ has $\lambda_{max.}$ 4080 Å, $\varepsilon = 125,000$ (Simpson, *J. Chem. Phys.*, 1948, **10**, 1124).

The higher intensities recorded in the table are not merely the result of the remarkably well-defined fine structure of the tetrayne spectra; Mr. C. L. Cook has calculated the oscillator strength ("*f*-value") for the dimethyl compound by graphical integration of the ε–ν curve, and obtained a result exceeding 3·0.

[Added, March, 1952]: Dorough, Miller, and Huennekens have recently (*J. Amer. Chem. Soc.*, 1951, **73**, 4315) described the absorption spectra of some metallic derivatives of $\alpha\beta\gamma\delta$-tetraphenylporphine in which extinction coefficients of up to 610,000 were reported. Despite the great extent of the resonating systems involved, however, oscillator strengths were smaller than that calculated for (II; R = Me). Bohlmann (*Chem. Ber.*, 1951, **84**, 785) has also determined and discussed the light absorption properties of polyacetylenic compounds.

EXPERIMENTAL

Absorption spectra were obtained with a Beckman DU or Unicam spectrophotometer, ethanolic solutions being used.

Deca-2 : 4 : 6 : 8-*tetrayne* (II; R = Me).—The reaction was carried out in a three-necked flask fitted with stirrer, reflux condenser, and nitrogen inlet. To ethylmagnesium bromide, prepared from magnesium (0·67 g.) in dry ether (30 c.c.), penta-1 : 3-diyne (1·5 g.) in ether (20 c.c.) was added, and the solution was refluxed for 1 hour with stirring. Iodine (3·1 g.) in dry ether (25 c.c.) was added and the mixture refluxed for 1½ hours. After cooling, ice and dilute acetic acid (20 c.c.; 2N) were added. The product was extracted with ether (4 × 50 c.c.), and the combined ether extracts were washed with sodium hydrogen carbonate solution and dried. Removal of the ether under reduced pressure gave the crude hydrocarbon (1·2 g., 80%) as a brown solid. Deca-2 : 4 : 6 : 8-tetrayne (1·0 g., 66%) crystallised from light petroleum (b. p. 80—100°) as long needles, decomposing above 80°, which become pink after 2 minutes in air. Alternatively the tetrayne was isolated by sublimation at 50° (bath temp.)/10^{-5} mm. (Found: C, 95·4; H, 4·7. Calc. for $C_{10}H_6$: C, 95·2; H, 4·8%).

Hydrogenation. The hydrocarbon (36 mg.) in ethyl acetate (50 c.c.) was shaken in hydrogen in the presence of a platinic oxide (Adams's) catalyst (5 mg.) until absorption was complete; 55 c.c. were taken up at 18°/758 mm., corresponding to an uptake of 8·0 moles of hydrogen per mole of decatetrayne.

Dodeca-3 : 5 : 7 : 9-*tetrayne* (II; R = Et).—To ethylmagnesium bromide, prepared from magnesium (1·34 g.) in dry ether (50 c.c.), hexa-1 : 3-diyne (3·9 g.) in ether (10 c.c.) was added and the solution refluxed for 2 hours with stirring. Cupric bromide (11·2 g.; anhydrous) was added in ten portions and the mixture refluxed for 30 minutes. After cooling, ice was added, the product was extracted with ether (4 × 50 c.c.), and the combined ether extracts dried. Removal of the solvent under reduced pressure gave the crude hydrocarbon (2·6 g.) which was distilled to give *dodeca*-3 : 5 : 7 : 9-*tetrayne* (1·8 g., 47%) as a pale yellow oil, b. p. 60° (bath temp.)/10^{-5} mm. When kept it solidified and was crystallised from light petroleum (b. p. 40—60°), forming needles, m. p. 26°, which became blue after 2 minutes in air (Found: C, 93·5: H, 6·8. $C_{12}H_{10}$ requires C, 93·5; H, 6·5%).

Hydrogenation. The hydrocarbon (55 mg.) in ethyl acetate (30 c.c.) was shaken in hydrogen in the presence of a platinic oxide (Adams's) catalyst (10 mg.) until absorption was complete; 65 c.c. were taken up at 18°/774 mm., corresponding to an uptake of 8·0 moles of hydrogen per mole of dodecatetrayne.

Hexadeca-5 : 7 : 9 : 11-*tetrayne* (II; R = Bu).—(*a*) To ethylmagnesium bromide, prepared from magnesium (0·67 g.) in dry ether (50 c.c.), octa-1 : 3-diyne (2·7 g.) in ether (10 c.c.) was added and the solution refluxed for 2 hours with stirring. Cupric bromide (5·6 g.; anhydrous), in five portions, was added and the mixture refluxed for 30 minutes. After cooling, ice was added, the product was extracted with ether, and the combined ether extracts dried. Removal of the solvent under reduced pressure and distillation gave *hexadeca*-5 : 7 : 9 : 11-*tetrayne* (1·3 g., 50%) as a pale yellow oil, b. p. 80° (bath temp.)/10^{-5} mm., n_D^{15} 1·6200 (Found : C, 91·2; H, 8·6. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%).

(*b*) Octa-1 : 3-diyne (2·2 g.) in ethanol (2 c.c.) was added to a mixture of ammonium chloride (16 g.), cuprous chloride (10 g.), concentrated hydrochloric acid (0·1 c.c.), and water (46 c.c.). The mixture was stirred at 65° for 15 minutes and then air was bubbled through for 3 hours. After cooling, excess of dilute hydrochloric acid was added and the product was extracted with pentane. Removal of the solvent gave a black oil which was distilled from a small retort to give hexadeca-5 : 7 : 9 : 11-tetrayne (0·5 g., 23%) as a pale yellow oil, b. p. 70° (bath temp.)/10^{-5} mm., with light-absorption properties identical with those of a sample prepared by method (*a*).

Deca-2 : 4 : 6 : 8-*tetrayne*-1 : 10-*diol* (II; R = CH_2•OH).—Penta-2 : 4-diyn-1-ol (1·2 g.) in methanol (10 c.c.) was added to a mixture of ammonium chloride (8 g.), cuprous chloride (5 g.), and water (50 c.c.) at 15°. The mixture was shaken in oxygen until absorption was complete; 400 c.c. were taken up in 2½ hours. The product was extracted with ether, washed with water, and dried. Removal of ether gave a yellow solid (1·0 g.), turning dark blue on exposure to light. Recrystallisation from ethyl acetate–light petroleum (b. p. 80—100°) gave *deca*-2 : 4 : 6 : 8-*tetrayne*-1 : 10-*diol* (0·8 g., 74%) as pale yellow plates. No satisfactory analytical data could be obtained (Found : C, 74·4; H, 4·0. $C_{10}H_6O_2$ requires C, 75·8; H, 3·8%).

Hydrogenation. The glycol (430 mg.) was shaken in an atmosphere of hydrogen in ethyl acetate solution, a platinic oxide catalyst being used. The uptake was equivalent to 7·5 moles; the product solidified and then had m. p. 68—70° (Chuit, *Helv. Chim. Acta*, 1926, **9**, 265, gives m. p. 72—74° for decane-1 : 8-diol). Oxidation with chromic and sulphuric acid gave sebacic acid, m. p. and mixed m. p. 131—133°.

Dodeca-3 : 5 : 7 : 9-*tetrayne*-2 : 11-*diol* (II; R = CHMe•OH).—Hexa-3 : 5-diyn-2-ol (3·2 g.) in ethanol (5 c.c.) was added to a mixture of ammonium chloride (16 g.), cuprous chloride (10 g.), concentrated hydrochloric acid (0·2 c.c.), and water (50 c.c.). The mixture was shaken in oxygen until absorption was complete; 600 c.c. were taken up in 4 hours. The product was extracted with ether, washed with sodium hydrogen carbonate solution and water, and dried. Removal of the ether gave a pasty red mass (3·0 g.). Repeated crystallisations from benzene–light petroleum (b. p. 60—80°) (1 : 3) gave *dodeca*-3 : 5 : 7 : 9-*tetrayne*-2 : 11-*diol* (2·5 g., 78%) as pale cream rods. The solid became brown, even in the absence of light, at room temperature (Found : C, 77·9; H, 5·5. $C_{12}H_{10}O_2$ requires C, 77·4; H, 5·4%).

Hydrogenation. A solution of the glycol (500 mg.) in ethyl acetate (30 c.c.) was shaken in hydrogen in the presence of a platinum oxide (Adams's) catalyst (5 mg.) until absorption was complete; 520 c.c. were taken up at 18°/750 mm., corresponding to an uptake of 8·0 moles. Crystallisation of the product from light petroleum (b. p. 40—60°) gave dodecane-2 : 11-diol (450 mg.) as plates, m. p. 54—55° (Bowden, Heilbron, Jones, and Sargent, *J.*, 1947, 1579, give m. p. 54—55°). Oxidation with chromic acid in aqueous sulphuric acid gave dodecane-2 : 11-dione as leaflets, m. p. 67°, from light petroleum (b. p. 40—60°) (Cason and Prout, *J. Amer. Chem. Soc.*, 1944, **66**, 48, give m. p. 67·4—67·8°).

Hexadeca-5 : 7 : 9 : 11-*tetrayne*-4 : 13-*diol* (II; R = CHPr•OH).—Octa-5 : 7-diyn-4-ol (2·8 g.) in ethanol (5 c.c.) was added to a mixture of ammonium chloride (16 g.), cuprous chloride (10 g.), concentrated hydrochloric acid (0·2 c.c.), and water (50 c.c.). The mixture was shaken in oxygen until absorption was complete; 400 c.c. were taken up during 3 hours. The product was extracted with ether, washed with sodium hydrogen carbonate solution and water, and dried. Removal of the ether gave a dark red viscous oil (2·8 g.) which later solidified. Repeated crystallisation from benzene–light petroleum (b. p. 60—80°) (1 : 3) gave *hexadeca*-5 : 7 : 9 : 11-*tetrayne*-4 : 13-*diol* (1·4 g., 50%) as matted needles, m. p. 98° (decomp.). The pale cream glycol became blue when kept at room temperature in light (Found : C, 79·5; H, 7·7. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·5%).

2 : 11-*Dimethyldodeca*-3 : 5 : 7 : 9-*tetrayne*-2 : 11-*diol* (II; R = CMe_2•OH).—2-Methylhexa-3 : 5-diyn-2-ol (2·5 g.) in ethanol (5 c.c.) was added to a mixture of ammonium chloride (16 g.), cuprous chloride (10 g.), concentrated hydrochloric acid (0·2 c.c.), and water (50 c.c.). The mixture was shaken in oxygen until absorption was complete; 600 c.c. were taken up during 1 hour. The product was extracted with ether, washed with sodium hydrogen carbonate

solution and water, and dried. Removal of the ether gave a pale brown solid (2·5 g.), m. p. 150—152° (decomp.). Recrystallisation from benzene gave 2 : 11-*dimethyldodeca*-3 : 5 : 7 : 9-*tetrayne*-2 : 11-*diol* (2·2 g., 89%) as large plates. Alternatively the glycol was isolated by sublimation at 100° (bath temp.)/10^{-5} mm. (Found : C, 78·4; H, 6·6. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%).

Hydrogenation. The diol (420 mg.) in ethyl acetate (30 c.c.) was shaken in hydrogen in the presence of a platinic oxide (Adams's) catalyst (10 mg.) until absorption was complete; 370 c.c. were taken up at 20°/764 mm., corresponding to an uptake of 7·8 moles. Crystallisation of the product from light petroleum (b. p. 40—60°) gave 2 : 11-dimethyldodecane-2 : 11-diol (400 mg.) as fine matted needles, m. p. 58° (Kisslowskaja, *Chem. Zentr.*, 1914, I, 1641, gives m. p. 57·5—58°).

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