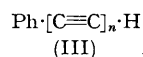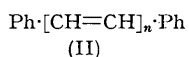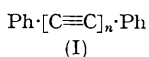Researches on Acetylenic Compounds.   Part XLI.*   The Synthesis of
Diphenylpolyacetylenes.

By J. B. Armitage, N. Entwistle, E. R. H. Jones, and M. C. Whiting.

The synthesis of a series of diphenylpoly-ynes $Ph \cdot [C \vdots C]_n \cdot Ph$ is described,
those with $n = 3, 4, 6,$ and 8 having been isolated and crystallised.   Their
ultra-violet and infra-red spectra are described and discussed, and compared
with those of the corresponding polyenes.

THE diphenylpolyenes (II) are much more stable than the purely aliphatic polyenes.
Consequently, having prepared a number of aliphatic conjugated polyacetylenes (Cook,
Jones, and Whiting, *J.*, 1952, 2883) which on the whole proved to be rather unstable,
we turned to the synthesis of the presumably more stable diphenylpoly-ynes (I).   Such a
project appeared additionally attractive since it offered the possibility of comparisons with
the well-known diphenylpolyenes, synthesised and studied by Kuhn and his collaborators
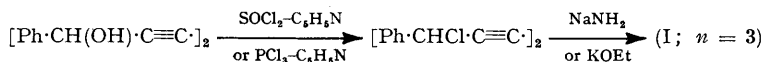(for summary see *J.*, 1938, 605).

$$Ph \cdot [C \equiv C]_n \cdot Ph \qquad Ph \cdot [CH = CH]_n \cdot Ph \qquad Ph \cdot [C \equiv C]_n \cdot H$$
$$\text{(I)} \qquad\qquad \text{(II)} \qquad\qquad \text{(III)}$$

Four new members of the series (I), where $n = 3, 4, 6,$ and 8, have been obtained, and
the general laws defining their spectrographic properties elucidated.   After the completion
of most of this work, independent syntheses of (I; $n = 3$ and 4) (Nakagawa *et al.*, *Chem.
Abs.*, 1951, **45**, 7081, 8486) and of (I; $n = 3, 4,$ and 5) (Schlubach and Franzen, *Annalen*,

* Part XL, *J.*, 1953, 3052.

1951, **572**, 116; **573**, 105), were recorded; the ultra-violet light absorption properties of the compounds were compared by the latter authors (*ibid.*, 1951, **573**, 110).

The first two hydrocarbons of series (I) have been known for many years; extension to (I; $n = 3$) was readily accomplished by employing one of the routes devised for aliphatic poly-yne synthesis (cf. Cook, Jones, and Whiting, *loc. cit.*), *viz.* :
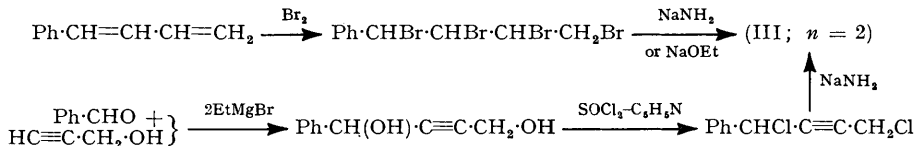
$$[\text{Ph·CH(OH)·C}\equiv\text{C·}]_2 \xrightarrow[\text{or PCl}_3-\text{C}_5\text{H}_5\text{N}]{\text{SOCl}_2-\text{C}_5\text{H}_5\text{N}} [\text{Ph·CHCl·C}\equiv\text{C·}]_2 \xrightarrow[\text{or KOEt}]{\text{NaNH}_2} (\text{I}; \ n = 3)$$

This is essentially the route used by Schlubach and Franzen (*loc. cit.*) and by Bohlmann (*Ber.*, 1951, **84**, 785). A trace of this compound was also obtained when a mixture of ethynylenedimagnesium dibromide (1 mol.) and phenylethynylmagnesium bromide (2 mols.) was treated with cupric bromide; the chief product of this reaction was (I; $n = 2$), but partial chromatographic separation gave fractions which showed a sharp absorption band at 3590 Å and therefore probably contained (I; $n = 3$).

Preliminary experiments on the synthesis of (I; $n = 4$) involved the possible method :

$$2\text{Ph·C}\equiv\text{C·MgBr} + \text{I·C}\equiv\text{C·C}\equiv\text{C·I} \longrightarrow (\text{I}; \ n = 4)$$
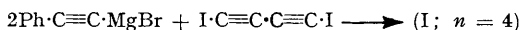
This was based on the claim by Grignard and Tcheoufaki (*Compt. rend.*, 1929, **188**, 359) to have synthesised (III; $n = 3$) by an analogous route from I·C≡C·C≡CH, a claim rendered extremely implausible by our experiments and also by recent results of Schlubach and Franzen (*Annalen*, 1951, **573**, 115). A very convenient synthesis of di-iododiacetylene from disodiodiacetylene and iodine in liquid ammonia was devised, but no trace of (I; $n = 4$) was formed in the reaction with the Grignard reagent from phenylacetylene even in the presence of a little cuprous chloride.
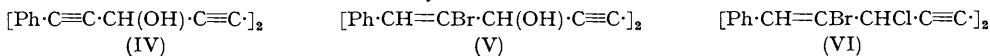
The preparation of (III; $n = 2$) was then achieved by two routes :

$$\text{Ph·CH=CH·CH=CH}_2 \xrightarrow{\text{Br}_2} \text{Ph·CHBr·CHBr·CHBr·CH}_2\text{Br} \xrightarrow[\text{or NaOEt}]{\text{NaNH}_2} (\text{III}; \ n = 2)$$

$$\left.\begin{array}{l}\text{Ph·CHO +}\\ \text{HC}\equiv\text{C·CH}_2\text{·OH}\end{array}\right\} \xrightarrow{\text{2EtMgBr}} \text{Ph·CH(OH)·C}\equiv\text{C·CH}_2\text{·OH} \xrightarrow{\text{SOCl}_2-\text{C}_5\text{H}_5\text{N}} \text{Ph·CHCl·C}\equiv\text{C·CH}_2\text{Cl} \xrightarrow{\text{NaNH}_2} $$

Now that propargyl alcohol is fairly readily available (Eglinton, Jones, and Whiting, *J.*, 1952, 2873) the second route is the more convenient. The yield was low, and in view of the instability of (III; $n = 2$), its oxidative coupling to (I; $n = 4$) was effected without previous isolation by the oxygen–cuprous chloride method (Part XXXIV, *J.*, 1952, 1998). Phenylbutadiyne was subsequently obtained pure as a low-melting solid; this was then coupled to (I; $n = 4$) by the action of cupric bromide on its Grignard derivative.

Schlubach and Franzen's method (*loc. cit.*) proceeded *via* phenylbutadiene tetrabromide and the Grignard derivative of (III; $n = 2$), coupled by means of cupric chloride.
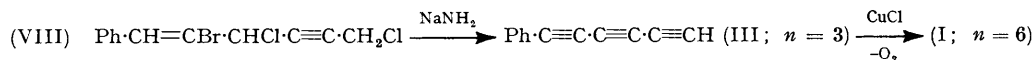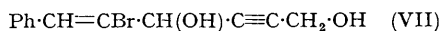
For the synthesis of (I; $n = 5$ and 6) the use of the methods employed for (I; $n = 3$ and 4) were contemplated, phenylpropargyl aldehyde being substituted for benzaldehyde. Condensation of the former with diacetylene gave a crystalline but very unstable glycol (IV), which however gave only dark tar in a preliminary experiment with phosphorus trichloride and pyridine [subsequently Schlubach and Franzen, *loc. cit.*, described the conversion of (IV), obtained in the same way, into the corresponding dichloride, and of the latter without isolation into (I; $n = 5$)]. The use of (V), derived from the much more accessible α-bromocinnamaldehyde, was then explored; the glycol was readily obtained in good yield as a stable solid and on treatment with phosphorus trichloride or thionyl chloride in pyridine gave a crystalline dichloride (VI). This however did not yield a solid product on reaction with alkaline reagents, though the light-absorption properties of the

$$\begin{array}{ccc}[\text{Ph·C}\equiv\text{C·CH(OH)·C}\equiv\text{C·}]_2 & [\text{Ph·CH=CBr·CH(OH)·C}\equiv\text{C·}]_2 & [\text{Ph·CH=CBr·CHCl·C}\equiv\text{C·}]_2 \\ (\text{IV}) & (\text{V}) & (\text{VI})\end{array}$$

gummy products leave little doubt that both (I; $n = 5$) and other polyacetylenic compounds, probably containing one or two α-bromostyryl groups, were present. This failure may well have been due rather to the unfavourable physical properties of the

sparingly soluble (VI) than to any inherent unsuitability of the methods; further work on the reaction was abandoned when Schlubach and Franzen described their quite satisfactory synthesis of the pentayne.

Condensation of phenylpropargyl aldehyde with the Grignard derivative of propargyl alcohol led to intractable products, as was hardly surprising in view of the instability of acetylenic carbonyl compounds in the presence of bases, *e.g.*, alkoxides. When α-bromo-cinnamaldehyde was employed, however, a crystalline glycol (VII) was obtained in 45% yield. When (VII) was converted into the corresponding dichloride (isolated, analytically pure, in 65% yield by chromatography) and the latter was treated with sodamide at −77°,

$$\text{Ph·CH=CBr·CH(OH)·C≡C·CH}_2\text{·OH} \quad \text{(VII)}$$

$$\text{(VIII)} \quad \text{Ph·CH=CBr·CHCl·C≡C·CH}_2\text{Cl} \xrightarrow{\text{NaNH}_2} \text{Ph·C≡C·C≡C·C≡CH} \quad \text{(III; } n = 3\text{)} \xrightarrow[-\text{O}_2]{\text{CuCl}} \text{(I; } n = 6\text{)}$$

(III; $n = 3$) was obtained. On the one occasion when this was isolated it exploded at 0° in the absence of air. Subsequently an ethereal extract of (III; $n = 3$) was evaporated at *ca.* −20° with the simultaneous addition of methanol, and oxidative coupling was effected directly in aqueous methanol after addition of cuprous and ammonium chlorides. Isolation of the product then gave (I; $n = 6$), in the surprisingly high yield of 30% from the dichloride, as beautiful orange needles. In contrast to the dimethyl analogue described previously, it proved to be stable for many months in the solid state at −5°, even without the exclusion of light. It is indeed more stable than (I; $n = 4$), which slowly becomes brown under these conditions, and satisfactory analytical and quantitative hydrogenation data were obtained.

Attention was then directed to (I; $n = 8$), the highest polyacetylene of which a synthesis seemed practicable. Condensation of α-bromocinnamaldehyde and the Grignard reagent derived from penta-2 : 4-diyn-1-ol (Part XXXIII; *J.*, 1952, 1993) gave the crystalline glycol Ph·CH=CBr·CH(OH)·C≡C·C≡C·CH$_2$·OH which was converted into the corresponding dichloride, a liquid of low stability, and thence *via* phenyloctatetrayne (III; $n = 4$), which was handled entirely in dilute solution in the cold, into (I; $n = 8$), obtained in about 0·5% overall yield from the dichloride as dark-red, photosensitive, and very unstable needles. Approximately correct analytical data were secured despite a tendency to explode on heating, and the ultra-violet light-absorption properties described below leave no doubt that the product was the essentially pure octayne. Even from the dilute ethyl acetate solution used for the spectrographic measurements black carbon-like material separated after a few hours.

The hydrocarbons (I; $n = 2$, 3, 4, and 6) in carbon tetrachloride solution displayed absorption at numerous infra-red frequencies characteristic of a phenyl group (*viz.*, 3070, 1600, 1490, 1445, 920, and 680 cm.$^{-1}$). In addition the −C≡C− stretching frequency at about 2200 cm.$^{-1}$ was observed and this increased in intensity as n increased, becoming the strongest band in the spectrum when $n = 6$, in which case it appeared as a doublet. Its variation with n is :

	(I; $n = 2$)	(I; $n = 3$)	(I; $n = 4$)	(I; $n = 6$)
Frequency (cm.$^{-1}$)	2220	2200	2205	2180, 2166

The ultra-violet absorption spectra of all the diphenylpoly-ynes prepared are given in the Table and Fig. 1. Their relation to the spectra of the aliphatic polyacetylenes, shown

Medium-intensity light-absorption maxima of diphenylpoly-ynes.

	A		B		C		D	
n	$\lambda_{max.}$ (Å)	$10^{-3}\,\varepsilon$	$\lambda_{max.}$ (Å)	$10^{-3}\,\varepsilon$	$\lambda_{max.}$ (Å)	$10^{-3}\,\varepsilon$	$\lambda_{max.}$ (Å)	$10^{-3}\,\varepsilon$
2	3270	27·8	3060	31·0	2880	22·0	—	—
3	3580	20·2	3300	30·3	3120	23·0	—	—
4	3970	21·2	3670	34·0	3415	33·8	3180	27·3
6	4600	8·75	4240	17·7	3920	17·4	3610 *	25
8 †	5090	4·45	4660	9·6	4300	12·3	3950 *	33

* Inflexion. † Ethyl acetate solution : all other spectra were determined in ethanol. The substitution of ethyl acetate for ethanol had a negligible effect (≯ 10 Å) on the positions of the absorption maxima of (I; $n = 6$).

in an earlier paper (Cook *et al.*, *loc. cit.*), is obvious.   The medium-intensity bands (*A–D* have increased in intensity from $\varepsilon = ca.$ 200 to $\varepsilon = 5000$—20,000 without losing their
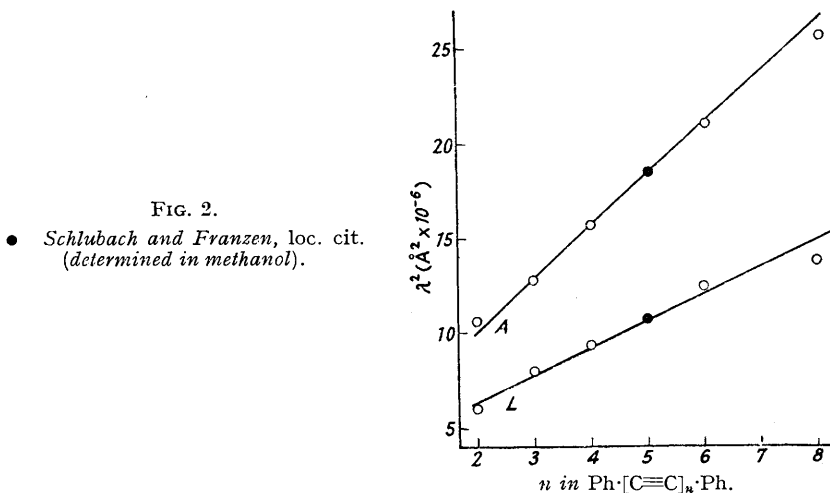
FIG. 1.   *Absorption spectra of diphenylpolyenes*, $Ph \cdot [C{\equiv}C]_n \cdot Ph.$
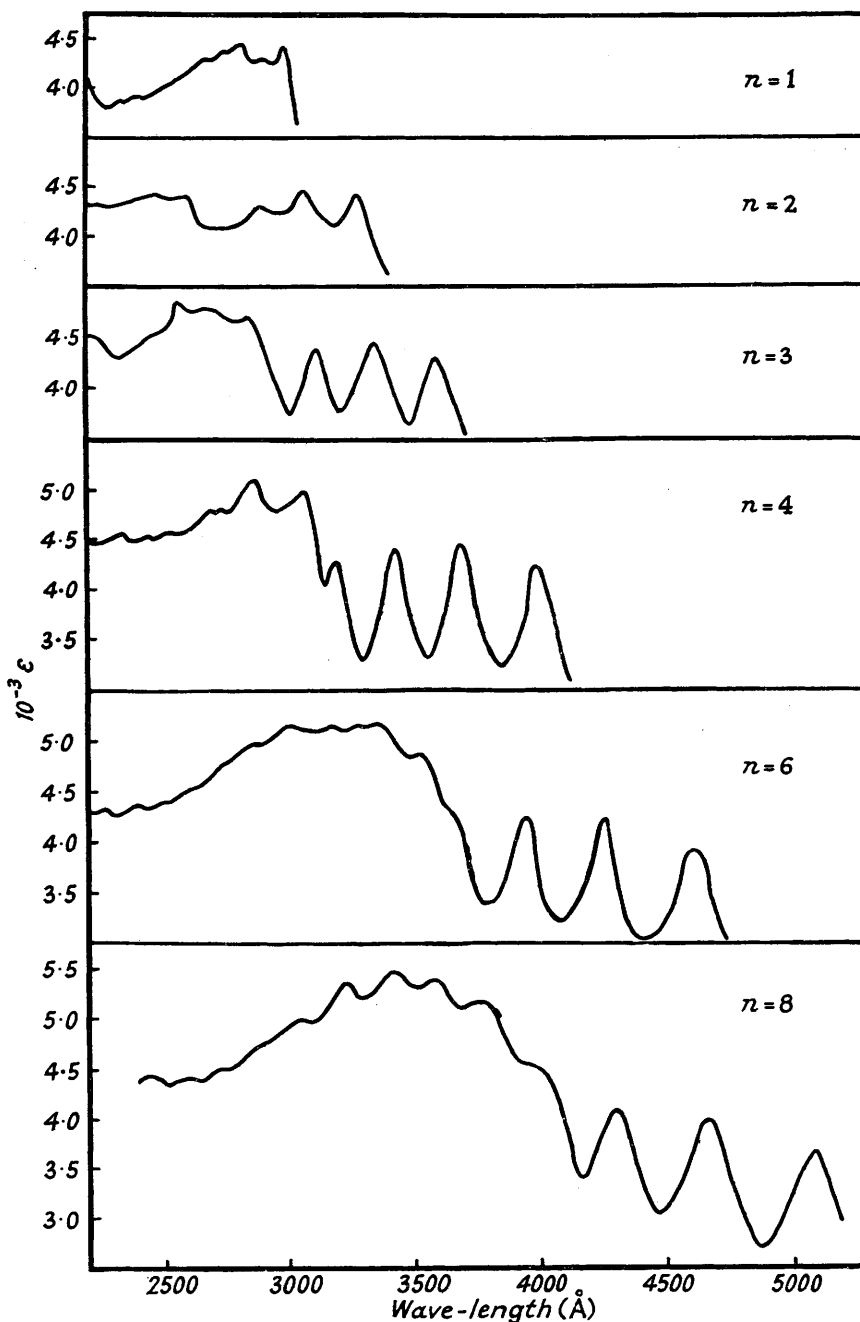
fine structure, the spacing of which falls from *ca.* 2100 cm.$^{-1}$ where $n = 2$ to *ca.* 1850 cm.$^{-1}$ where $n = 8$.   The ultra-high-intensity bands are appreciably lower in intensity than those of the aliphatic poly-ynes and they no longer exhibit the familiar spacing at *ca.*

2100 cm.$^{-1}$. As in the aliphatic series, the intense bands increase in intensity as n increases (although not as with the aliphatic compounds in proportion to n), while the medium-intensity bands become less intense. It thus seems justifiable to use the same letters to designate the medium-intensity bands in the two cases.

When the square of the wave-length of the A band is plotted against n (cf. Lewis and Calvin, *Chem. Reviews*, 1939, **26**, 237) a good approximation to a straight line is obtained for lower values of n, a slight curvature downward becoming evident where $n = 6$ and 8 (Fig. 2). This behaviour closely resembles that of the diphenyl- and other polyenes

Fig. 2.

● *Schlubach and Franzen*, loc. cit. (*determined in methanol*).

$\lambda^2 (\text{Å}^2 \times 10^{-6})$

n in Ph·[C≡C]$_n$·Ph.

(Kuhn, *loc. cit.*; Dewar, *J.*, 1952, 3544). The first band of the high-intensity region ("*L* band") is much more difficult to locate in the aromatic compounds; it appears to show a more appreciable deviation from the Lewis–Calvin equation. It is interesting to compare the slopes of the linear portions of the curves in the various cases :

    Dimethylpolyenes, 2·1 (Kuhn and Grundmann, *Ber.*, 1938, **71**, 442).
    Diphenylpolyenes, 2·0 (Hausser, Kuhn, and Smakula, *Z. phys. Chem.*, 1935, **29**, 384).
    Dimethylpoly-ynes (*A*), 3·0 (Cook, Jones, and Whiting, *loc. cit.*).
    Dimethylpoly-ynes (*L*), 1·25 (*idem, loc. cit.*).
    Diphenylpoly-ynes (*A*), 2·8.
    Diphenylpoly-ynes (*L*), *ca.* 1·5.

In each case the unit is 10^6Å^2 per multiple bond. These values obviously summarise energy relations within conjugated systems of different types, of which any successful theoretical description must give an adequate explanation.

EXPERIMENTAL

The remarks as to general technique made by Cook *et al.* (Part XXXIX, *loc. cit.*) at the beginning of the Experimental section apply to much of the work described below.

1 : 6-*Dichloro*-1 : 6-*diphenylhexa*-2 : 4-*diyne.*—1 : 6-Dichloro-2 : 4-diyne-1 : 6-diol (Armitage, Cook, Entwistle, Jones, and Whiting, *J.*, 1952, 1998) (4·0 g.) in ether (100 c.c.) and pyridine (1·2 c.c.) was treated at $-30°$ with phosphorus trichloride (1·5 c.c.) in ether (40 c.c.). Isolation of neutral fraction after treatment with an excess of water gave a semi-crystalline product which was best purified by being kept for 18 hr. in a desiccator on a porous tile, over light petroleum (b. p. 60—80°) ; the dark impurities deliquesced and were thus almost completely eliminated, giving a powder (3·1 g.), m. p. 63—66°, which appeared to be sensitive to moisture and was used without further purification (Schlubach and Franzen, *Annalen*, 1951, **572**, 116, give m. p. 92° for one stereoisomer) (Found : Cl, 23·0. Calc. for $C_{16}H_{12}Cl_2$: C, 23·8%).

Diphenylhexatriyne (I ; $n = 3$).—Powdered 1 : 6-dichloro-1 : 6-diphenylhex-2 : 4-diyne (1·22 g.) was added with stirring to sodium ethoxide (from sodium, 0·25 g.) in dry ethanol

(30 c.c.) at 0°. After 30 min. the solution was allowed to warm to room temperature, water was added, and the product isolated with ether. The dark residue was adsorbed on alumina (80 g.) from light petroleum (b. p. 40—60°), and the first 800 c.c. of eluate yielded a fraction (530 mg.), m. p. 89—91°, which was recrystallised from light petroleum (b. p. 40—60°), then ethanol, giving straw-coloured prismatic needles of diphenylhexatriyne, m. p. 96° (Found : C, 95·4; H, 4·95. Calc. for $C_{18}H_{10}$: C, 95·5; H, 4·5%). The crystals became deeper in colour after a few hours at 20° but are stable indefinitely at 0° (Nakagawa *et al.*, *loc. cit.*, gives m. p. 94—95°).

Repetition of the experiment at −20° gave a 33% yield of the pure hydrocarbon. With excess of sodamide in liquid ammonia only a 5% yield was obtained.

Phenylbutadiyne (III; *n* = 2).—1-Phenylbutadiene was prepared in 85% yield from cinnamaldehyde by the method of Braude, Jones, and Stern (*J.*, 1947, 1087). Bromination was effected in carbon tetrachloride and the product, recrystallised from light petroleum (b. p. 40—60°), formed needles, m. p. 132° (Found : C, 26·1; H, 2·6. Calc. for $C_{10}H_{10}Br_4$: C, 26·7; H, 2·25%) (Rieber, *Ber.*, 1903, **36**, 1406, gives m. p. 76° and 151° for the two forms). Recrystallisation from the same solvent gave needles, m. p. 146°.

The tetrabromide (15 g.; m. p. 132°) was added in portions and with stirring to sodamide (from sodium, 4 g.) in liquid ammonia (150 c.c.). After 2 hr. ether was added and the ammonia was allowed to evaporate. Isolation with ether and distillation gave *phenylbutadiyne* (0·8 g., 19%; b. p. 45°/0·5 mm., $n_D^{19·5}$ 1·6230, m. p. *ca.* 0° (Found : C, 94·35; H, 5·85. $C_{10}H_6$ requires C, 95·2; H, 4·8%). It discolours rapidly at room temperature but can be stored at −70°. (Nakagawa *et al.*, *loc. cit.*, gives b. p. 37—40°/0·04 mm., $n_D^{6·5}$ 1·6232).

1-Phenylbut-2-yne-1 : 4-diol.—Ethylmagnesium bromide was prepared in ethereal solution from magnesium (10·6 g.) and ethyl bromide (58 g.). Benzene was added while the ether was distilled off until the vapour temperature reached 72°. The solution was cooled to room temperature, and a solution of propargyl alcohol (11·2 g.) in benzene (50 c.c.) was run in; a vigorous reaction ensued and the mixture was allowed to boil. After cooling to 20° the mixture was stirred for 1 hr., freshly-distilled benzaldehyde (21·2 g.) in benzene was added, and the pasty mass was stirred for a further 18 hr. Sulphuric acid (15%) was added with cooling and the product was isolated with benzene, from which it crystallised on evaporation. The *diol* (13·5 g., 40%) formed small rods, m. p. 86° (Found : C, 73·9; H, 6·1. $C_{10}H_{10}O_2$ requires C, 74·05; H, 6·2%).

Diphenyloctatetrayne (I; *n* = 4).—(*a*) Phenylbutadiyne (1·25 g.) in ether (10 c.c.) was added to ethylmagnesium bromide (from Mg, 1·7 g.) in ether. After 30 min.' stirring the mixture was cooled to 0° and cupric bromide (4·1 g.) was added in portions with stirring. After a further 2 hr., water was added and the product, isolated with ether, was adsorbed on alumina from light petroleum (b. p. 40—60°). Elution with the same solvent gave a yellow solid which on crystallisation from ethanol gave yellow prisms of *diphenyloctatetrayne* (0·59 g.), m. p. 109—110° (Found : C, 95·5; H, 4·35. $C_{20}H_{10}$ requires C, 96·0; H, 4·0%). This tetra-acetylene is less stable than diphenylhextriyne; it discolours in an hour at 20° and after some months at 0°.

(*b*) 1-Phenylbut-2-yne-1 : 4-diol (6·0 g.) in ether (50 c.c.), together with pyridine (6·3 g.), was treated with thionyl chloride (9·6 g.) during 20 min. with vigorous stirring, at <30°. After overnight stirring in nitrogen, isolation with ether gave an oil (6·5 g.) which was adsorbed from benzene on to alumina (200 g.). Elution with benzene and rechromatography gave a pale yellow oil (3·5 g.), n_D^{22} 1·6240.

Sodamide was prepared from sodium (1·5 g.) in liquid ammonia (100 c.c.), and the above dichloride was added with stirring, followed after 1 hr. by ammonium chloride (5 g.). Ether was added and the ammonia allowed to evaporate. The solution was washed with water and sodium hydrogen carbonate solution and dried. After evaporation to small bulk, alcohol (50 c.c.) was added before reducing the total volume to 25 c.c.

This alcoholic solution was run into a solution of cuprous chloride (10 g.), ammonium chloride (16 g.) and concentrated hydrochloric acid (0·1 c.c.) in water (200 c.c.). A dark red mass separated. The mixture was shaken in oxygen until absorption ceased and the product was isolated with ether. Three crystallisations of the residue from aqueous ethanol gave diphenyloctatetrayne (0·5 g., 23%), m. p. 110° (slight decomp.) (Nakagawa *et al.*, *loc. cit.*, gives m. p. 115—116°; Schlubach and Franzen give m. p. 114°).

2 : 9-Dibromo-1 : 10-diphenyldeca-1 : 9-diene-4 : 6-diyne-3 : 8-diol (V).—A solution of ethyl-magnesium bromide was prepared from magnesium (5·3 g.). Diacetylene (*ca.* 5·5 g.; cf. Armitage, Jones, and Whiting, *J.*, 1951, 44) was passed in by means of a stream of nitrogen which flowed over the surface of the liquid hydrocarbon, condensed in a calibrated tube, then through the ethereal solution of the Grignard reagent. After 1 hr. the butadiynylenedi-

magnesium dibromide had separated as a pasty mass. α-Bromocinnamaldehyde (42·2 g.) in benzene (150 c.c.) was added, and the mixture was stirred for 18 hr. Addition of water and tartaric acid, followed by isolation with ether, gave a crude product which partly crystallised. After recrystallisation from benzene the *glycol* (26 g., 55%) formed prisms, m. p. 154° (Found : C, 56·45; H, 3·65. $C_{22}H_{16}O_2Br_2$ requires C, 55·9; H, 3·4%).

2 : 9-*Dibromo*-3 : 8-*dichloro*-1 : 10-*diphenyldeca*-1 : 9-*diene*-4 : 6-*diyne.*—The above glycol (10·0 g.) in ether (50 c.c.) and pyridine (5·0 g.) was treated with thionyl chloride (7·0 g.), at 25—30°. After 5 hr. ice-water was added, and the neutral fraction was isolated with ether. The resultant orange-yellow solid was dissolved in benzene and passed through alumina, to give, after evaporation, the essentially pure dichloride (6·5 g.) as a pale yellow solid. Recrystallisation from light petroleum (b. p. 80—100°) gave the *tetrahalide* as small prisms, m. p. 130—134°, possibly of a single stereoisomer (Found : C, 52·3; H, 3·2. $C_{22}H_{14}Br_2Cl_2$ requires C, 51·9; H, 2·8%). In a Carius determination, 1·25 mg. of mixed halides were formed per mg.; the formula requires 1·30 mg.).

2-*Bromo*-1-*phenylhex*-1-*en*-4-*yne*-3 : 6-*diol.*—A solution of ethylmagnesium bromide (from magnesium, 10·8 g.) in benzene was prepared as above. Propargyl alcohol (11·2 g.) in benzene (25 c.c.) was then added, the solvent being allowed to reflux. The mixture was stirred for 1 hr., a pasty solid separating. α-Bromocinnamaldehyde (42·2 g.) in benzene (400 c.c.) was added and the mixture was stirred for 18 hr. Isolation of the neutral fraction, following addition of 3N-sulphuric acid, gave a syrup which was separated by chromatography on alumina into (a) recovered aldehyde (25·0 g.), eluted with benzene and recrystallised, and (b) the required *glycol* (22·4 g.), which was eluted with ether and then formed plates, m. p. 67—69°, from benzene (Found : C, 53·6; H, 4·25; Br, 30·4. $C_{12}H_{11}O_2Br$ requires C, 53·9; H, 4·15; Br, 30·0%).

2-*Bromo*-3 : 6-*dichloro*-1-*phenylhex*-1-*en*-4-*yne.*—The above glycol (VII) (27 g.) in ether (150 c.c.) and pyridine (16 g.) was treated with thionyl chloride under nitrogen at 15—25° with mechanical stirring. After 18 hr. water was added and the *product* (25·5 g.) was isolated with ether and dissolved in benzene (100 c.c.). Adsorption on alumina and elution with benzene (*ca.* 500 c.c.) followed by evaporation below 20° gave a yellow oil (20 g., 60%), which after rechromatography had n_D^{13} 1·6225. It decomposed on attempted distillation at 10^{-5} mm. or storage, but appeared to be pure (Found : C, 47·3; H, 3·2. $C_{12}H_9BrCl_2$ requires C, 47·4; H, 3·0%).

1 : 12-*Diphenyldodecahexayne.*—The foregoing dichloride (6·1 g.) was added dropwise with stirring to a suspension of sodamide, prepared from sodium (2·0 g.) in liquid ammonia (100 c.c.) after cooling to —77°. After 1 hr., ammonium chloride (8 g.) was added and most of the ammonia was allowed to evaporate after addition of ether. After being decanted from some black polymeric material, the solution was washed with sodium hydrogen carbonate solution and evaporated to 100 c.c. under reduced pressure. Ethanol (100 c.c.) was then added and the volume again reduced to 100 c.c. under reduced pressure, yielding a dark red solution containing phenylhexatriyne. This gave a precipitate with silver nitrate and ammoniacal cuprous chloride solutions; when, on a previous occasion, such a solution (ethereal) was evaporated, the product underwent deflagration at 0° in the absence of air when most of the solvent had been removed.

The phenylhexatriyne solution was added to cuprous chloride (30 g.), ammonium chloride (48 g.), and concentrated hydrochloric acid (2 drops) in water (250 c.c.), and held at 10 mm. for a few minutes to remove the last traces of ether. The mixture was then shaken in oxygen until absorption ceased (30 min.) and extracted with ether (3 × 100 c.c.). After washing with sodium hydrogen carbonate solution and drying ($MgSO_4$), the solvent was removed under reduced pressure until the volume reached 50 c.c., and ethanol (200 c.c.) was added. After being set aside at 0° the crude *hexayne* (1·5 g.) was collected and recrystallised from ethyl acetate–ethanol (1 : 5), to give long, golden-yellow needles (0·9 g., 30% from the dichloride) whose absorption spectrum was not altered by further crystallisation (they decomposed above 100° to a carbonaceous residue without melting) (Found : C, 96·8; H, 3·5. $C_{18}H_{10}$ requires C, 96·6; H, 3·4%).

The hexayne (46 mg.) absorbed 45 c.c. of hydrogen at 23°/763 mm., when shaken with platinum in ethyl acetate, corresponding to 12·1 mols.

7-*Bromo*-8-*phenyloct*-7-*en*-2 : 4-*diyne*-1 : 6-*diol* (VIII).—To a solution of ethylmagnesium bromide, prepared from magnesium (7·8 g.) in ether, benzene was added with simultaneous evaporation of the ether until the boiling-point reached 70°. Penta-2 : 4-diyn-1-ol (Armitage, Jones, and Whiting, *J.*, 1952, 1993) (12·0 g.) in benzene (100 c.c.) was added at 0°, and the mixture was stirred for 30 min. α-Bromocinnamaldehyde (31·5 g.) was added in benzene

(100 c.c.) at 0°, and the mixture was set aside for 18 hr., slowly reaching room temperature. After decomposition of the complex with 15% sulphuric acid isolation of the neutral fraction gave a dark, uncrystallisable syrup (40 g.) which was adsorbed from benzene on deactivated alumina (300 g.). After removal of all benzene-elutable material, elution with ether–methanol gave a solution which was evaporated to a syrup which crystallised on treatment with benzene and a little light petroleum. Recrystallisation gave the *diol* as prisms (15 g., 34%), m. p. 103°, unchanged on further crystallisation from benzene (Found : C, 57·5; H, 3·6. $C_{14}H_{11}O_2Br$ requires C, 57·8; H, 3·8%).

2-Bromo-3 : 8-dichloro-1-phenyloct-1-en-4 : 6-diyne and 1 : 16-Diphenylhexadecaoctayne (I; $n = 8$).—The above glycol (5·8 g.) in ether (30 c.c.) and pyridine (3·2 g.) was treated with thionyl chloride (4·8 g.) under nitrogen with mechanical stirring, at 20—25°. After 5 hr. at room temperature ice and water were added, and the aqueous phase extracted with ether. After washing with water and potassium hydrogen carbonate solution and drying (MgSO₄), the solvent was removed under reduced pressure and the residue (4·8 g.) was at once dissolved in benzene. The solution was passed through a column of alumina, which was eluted with benzene; removal of the latter under reduced pressure gave the halide (3·8 g.) as an oil which darkened rapidly. It was dissolved in ether (25 c.c.) and added at once to a stirred suspension of sodamide, prepared from sodium (1·2 g.) in liquid ammonia (100 c.c.) in the presence of some solid ammonia. After 2 min. ammonium chloride (5 g.) was added and the ammonia was allowed to evaporate in the dark after addition of ether. The red solution thus obtained was separated from insoluble carbonaceous material, washed with N-sulphuric acid and then aqueous sodium hydrogen carbonate, and dried; the ether was removed under reduced pressure after addition of ethanol, giving finally a solution (30 c.c.) which was added directly to a mixture of cuprous chloride (20 g.), concentrated hydrochloric acid (1 drop), ammonium chloride (32 g.), and water (200 c.c.). After this had been shaken in an atmosphere of oxygen until absorption ceased, the green suspension was extracted with ethyl acetate. After washing with sodium hydrogen carbonate solution and brief drying (MgSO₄), the extract was evaporated under reduced pressure, copper-coloured needles (*ca.* 50 mg.) separating (Found : C, 95·3; H, 2·85. $C_{28}H_{10}$ requires C, 97·1; H, 2·9%). This *hydrocarbon* was extremely unstable, becoming black after a few hours at room temperature even in the dark.