546. *Researches on Acetylenic Compounds. Part XXXIX.* General Routes to Aliphatic Polyacetylenic Hydrocarbons and Glycols.*

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The reactions described in earlier parts of this series for the synthesis of various aliphatic di-, tri-, and tetra-acetylenic compounds have been extended and generalised to give routes formally applicable to the synthesis of aliphatic polyacetylenes with more than four triple bonds. Several compounds containing five or six conjugated acetylenic linkages are described, and their light-absorption properties are discussed.

Recent communications (Part XXVIII, Armitage, Jones, and Whiting, *J.*, 1951, 44; Parts XXXIII—XXXVII, Armitage, Cook, Entwistle, Jones, and Whiting, *J.*, 1952, 1993—2014) have described syntheses of di- and tri-acetylene (III; $n = 2$ and 3) and of numerous di-, tri-, and tetra-acetylenic compounds. For the investigation of polyacetylenic systems in general, however, it was desirable to prepare a more extensive range, including compounds with more than four conjugated acetylenic linkages. To this end, attempts have now been made to develop routes of general applicability, and some progress has been made.

Conversion of but-2-yne-1 : 4-diol (I; $n = 1$) *via* the corresponding dichloro-compound and disodiodiacetylene into hexa-2 : 4-diyne-1 : 6-diol (I; $n = 2$) (Part XXVIII, *loc. cit.*), and of the latter *via* analogous intermediates into octa-2 : 4 : 6-triyne-1 : 8-diol (I; $n = 3$) (Part XXXVI, *loc. cit.*) indicates a possible general route to the higher poly-ynes. This sequence of reactions has the advantage that the parent compounds (III) would be formed, although the extreme instability of triacetylene suggests that their isolation would probably not be possible.

The glycol (I; $n = 3$) was converted into the corresponding dichloride (II; $n = 3$) in excellent (80%) yield when suitable modifications were made in the reaction conditions used for the lower homologues. It was obtained as a low-melting solid of reasonable stability. Treatment with sodamide in liquid ammonia at −77° (cf. Part XXXVI, *loc. cit.*) followed by neutralisation and extraction with pentane gave a solution which was examined spectroscopically. Bands were observed at 2070, 2170, and 2270 Å (relative intensities 1, 2·0, 2·7), analogous to similar intense bands in the spectrum of (IV; $n = 4$) (Part XXXVII, *loc. cit.*), but shifted by *ca.* 60 Å to shorter wave-lengths. It therefore seems that octa-1 : 3 : 5 : 7-tetrayne (III; $n = 4$) had indeed been obtained in solution; when ε was assumed to be 280,000 for the 2270-Å band the yield was estimated as about 12%. In an attempt to concentrate the solution at 0° brown polymeric material separated.

$\mathrm{HO{\cdot}CH_2{\cdot}[C{\equiv}C]_n{\cdot}CH_2{\cdot}OH}$ (I) $\mathrm{CH_2Cl{\cdot}[C{\equiv}C]_n{\cdot}CH_2Cl}$ (II) $\mathrm{H{\cdot}[C{\equiv}C]_n{\cdot}H}$ (III) $\mathrm{CH_3{\cdot}[C{\equiv}C]_n{\cdot}CH_3}$ (IV)

When acetone was added to the solution of the disodium derivative of (III; $n = 4$) the glycol (V; $n = 4$) was obtained in small yield; its properties agreed with those of a specimen obtained by the oxidative coupling of the corresponding diacetylenic alcohol. This route to symmetrical tetra-acetylenic compounds is not, however, of preparative importance, since these are more easily obtained by oxidative coupling of the corresponding monosubstituted diynes. The glycol (I; $n = 4$), required for the further extension of the general method, has already been prepared in this way; it was converted in 80% yield by thionyl chloride and pyridine into (II; $n = 4$), m. p. 73°, extraordinarily sensitive to light. Treatment of the latter with sodamide at −77° and extraction with hexane after neutralisation gave a solution which showed light-absorption maxima at 2270, 2400, and 2540 Å (relative intensities 1, 1·6, 1·8) in the positions expected for deca-1 : 3 : 5 : 7 : 9-pentayne (III; $n = 5$); their intensity leads to an estimate of the yield as 1%. When the

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* Part XXXVIII, preceding paper.

disodium derivative was condensed with methyl iodide or acetone, rather better yields of penta-acetylenic products were obtained; in the latter case the glycol (V; $n = 5$) was isolated in a nearly pure state. The reaction with methyl iodide gave a 3% yield of (IV; $n = 5$), identified and estimated spectroscopically. Thus as n increases the yields in the process (II) $\longrightarrow$ [III] $\longrightarrow$ (IV) or (V) fall rapidly, from nearly quantitative where n (in IV) $= 2$, through about 50% where $n = 3$ and about 12% for $n = 4$, to only *ca.* 3% for $n = 5$. It thus appears that the general method discussed cannot usefully be extended further without modifications in the reaction conditions.

$$\mathrm{OH{\cdot}CMe_2{\cdot}[C{\equiv}C]_{\mathit{n}}{\cdot}CMe_2{\cdot}OH} \quad \text{(V)}$$

An approach to the synthesis of polyacetylenic hydrocarbons complementary to the route involving diprimary poly-yne glycols as intermediates is that illustrated below, involving disecondary glycols.

$$\underset{\text{(VI)}}{\mathrm{CH_3{\cdot}CH(OH){\cdot}[C{\equiv}C]_{\mathit{n}-1}{\cdot}CH(OH){\cdot}CH_3}} \xrightarrow[\mathrm{C_5H_5N}]{\mathrm{SOCl_2}} \underset{\text{(VII)}}{\mathrm{CH_3{\cdot}CHCl{\cdot}[C{\equiv}C]_{\mathit{n}-1}{\cdot}CHCl{\cdot}CH_3}} \xrightarrow{\mathrm{NaNH_2}} \underset{\text{(IV)}}{\mathrm{CH_3{\cdot}[C{\equiv}C]_{\mathit{n}}{\cdot}CH_3}}$$

Investigation of the simplest case ($n = 2$) showed that the conversion of (VI) into (VII) could be accomplished in good yield with thionyl chloride and pyridine only under more drastic conditions than were necessary for the primary compounds (I $\longrightarrow$ II). Dehydrohalogenation then proceeded smoothly. In this case the product is more accessible by other routes, but the synthesis of (IV; $n = 3$) by this method in 56% overall yield from the glycol (VI; $n = 3$) is probably a more convenient route to this hydrocarbon than that previously described (Part XXXVI, *loc. cit.*). Attempts to carry out these reactions in the case where $n = 4$ were frustrated by the failure to obtain a crystalline triacetylenic glycol with acetaldehyde, but in the more interesting case, where $n = 5$, the requisite glycol had already been prepared (Part XXXVII, *loc. cit.*). The above reaction sequence in this case yielded a dichloride (VII; $n = 4$) and dimethylpenta-acetylene (IV; $n = 5$). As was expected, the latter proved to be very easily decomposed both by light and by moderate temperatures. Repeated crystallisation in weak artificial light gave cream-coloured needles with $\varepsilon_{\text{max.}} = 352{,}000$ at 2605 Å, not raised by further purification.

For the synthesis of hexa-acetylenic compounds the use of the above methods would involve many stages and an attempt was therefore made to realise a shorter route involving monosubstituted triacetylenes, a combination of the methods previously employed.

$$\mathrm{CH_2Cl{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH_2Cl} \xrightarrow[\mathrm{MeI}]{\mathrm{NaNH_2};} \mathrm{CH_3{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}C{\equiv}CH} \xrightarrow[\mathrm{O_2}]{\mathrm{CuCl};} (\text{IV};\ n = 6).$$

Considerable difficulty was encountered, since monosubstituted triacetylenes proved to be extremely unstable, and the crude products were contaminated with the even more unstable triacetylene (III; $n = 3$) and the corresponding disubstituted triacetylene. It was necessary to purify the heptatriyne by extraction of the liquid ammonia solution with butane, followed by sublimation at 20°/0·01 mm.; a solid, m. p. *ca.* $-10°$, then separated on a "finger" cooled with liquid air. Since the hydrocarbon when isolated decomposed explosively, even at 0° in the absence of air, it was rapidly transferred in an atmosphere of nitrogen into the cuprous chloride solution; oxidative coupling then proceeded smoothly, but isolation of the dimethylhexa-acetylene (IV; $n = 6$) proved difficult. Crystallisation in subdued light finally gave pale yellow prismatic needles which, like (IV; $n = 5$), gave only approximately correct analytical values, but which showed maximal light absorption at 2840 Å with $\varepsilon = 445{,}000$ and therefore were probably essentially pure. Unlike the lower polyacetylenes, solutions of this hydrocarbon showed some tendency to decompose on exposure to light.

By similar reactions the corresponding diethylhexa-acetylene was prepared but it failed to crystallise, and a 15% concentrate, obtained by chromatography, could not be purified further (see also below). Condensation of monosodiotriacetylene with acetone gave a mixture of the alcohol (VIII) and the corresponding glycol (V; $n = 3$), (cf. Part XXXVI, *loc. cit.*) which was resolved (not quite completely) by chromatography. The alcohol proved to be very unstable, and on one occasion decomposed explosively at 0° *in vacuo*; it was subjected to the oxidative coupling reaction, but its red copper derivative was precipitated even at pH 2, and the reaction was slow. Chromatographic purification of the product gave a 10% concentrate, and the positions of the ultra-high-intensity absorption maxima could therefore be determined, but much of the product consisted, apparently, of dehydration products showing intense absorption beyond 3000 Å.

$$OH\cdot CMe_2\cdot C{\equiv}C\cdot C{\equiv}C\cdot C{\equiv}CH \quad \text{(VIII)}$$

Of considerable potential value is the alternative method of obtaining monosubstituted polyacetylenic hydrocarbons by the application of the chlorination–dehydrochlorination procedure to primary-secondary glycols :

$$CH_3\cdot CH(OH)\cdot[C{\equiv}C]_{n-1}\cdot CH_2\cdot OH \longrightarrow Me\cdot CHCl\cdot[C{\equiv}C]_{n-1}\cdot CH_2Cl \xrightarrow{NaNH_2} Me\cdot[C{\equiv}C]_n\cdot H.$$

In the simplest case (where $n = 2$) this method was found to proceed smoothly, though the isolation of penta-1 : 3-diyne again proved difficult (cf. Part XXXIII, *loc. cit.*). The unsymmetrical glycol was prepared in moderate yield by condensation of acetaldehyde with the Grignard derivative of propargyl alcohol; attempts to condense formaldehyde with the Grignard derivative of but-1-yn-3-ol were unsuccessful. The reactions between the disodium derivatives of propargyl alcohol and but-1-yn-3-ol, and acetaldehyde and formaldehyde respectively, gave heterogeneous products. A somewhat impure glycol was obtained from condensation of the disodium derivative of hepta-4 : 6-diyn-3-ol and formaldehyde. A Grignard reaction would undoubtedly have been preferable in this case; however, chlorination, dehydrochlorination, and oxidative coupling gave a rather better concentrate (estimated at 20%) of the diethylhexa-acetylene than the alternative method.

Light absorption properties.

The ultra-high-intensity light absorption exhibited by tri- and tetra-acetylenic compounds (Parts XXXVI and XXXVII, *locc. cit.*), was observed at progressively longer wave-lengths in the higher members of the series now examined (Fig. 1 and Tables). Unfortunately only two of the penta- and one of the hexa-acetylenic compounds could be obtained in a state of approximate purity. In the other cases, however, measurements with partially purified concentrates sufficed to give the positions of the maxima. Fortunately the sharpness and extreme intensity of these bands makes this possible, even in the presence of much general absorption due to the impurities constituting 80—90% of the material in some of these cases.

TABLE 1. *Light-absorption maxima of pentaynes,* $R\cdot[C{\equiv}C]_5\cdot R$.

(a) *Ultra-high intensity bands.*

Substance	$\lambda_{max.}$ (Å) (ε) *P*	$\lambda_{max.}$ (Å) (ε) *O*	$\lambda_{max.}$ (Å) (ε) *N*	$\lambda_{max.}$ (Å) (ε) *M*	$\lambda_{max.}$ (Å) (ε) *L*
(III) *	—	—	2290 (1) †	2400 (1·65) †	2540 (1·83) †
(IV)	2150 (10,000)	2240 (29,000)	2335 (95,000)	2470 (243,000)	2605 (352,000)
(V)	2180 (15,000)	2280 (44,000)	2390 (116,000)	2520 (240,000)	2650 (355,000)

(b) *Medium-intensity bands.*

Substance	$\lambda_{max.}$ (Å) (ε) *D*	$\lambda_{max.}$ (Å) (ε) *C*	$\lambda_{max.}$ (Å) (ε) *B*	$\lambda_{max.}$ (Å) (ε) *A*
(IV)	3245 (230)	3475 (210)	3735 (150)	3940 (120)
(V)	3140 (785)	3375 (670)	3635 (640)	3930 (525)

* In hexane. † Relative intensity; scale arbitrary.

The medium-intensity long-wave-length absorption shown by the lower polyacetylenes was also observed in the three cases where the products were isolated. In this region, however, even traces of light-absorbing impurities profoundly affect the shape of the curves. The results for dimethylpenta-acetylene (IV; $n = 5$), which are illustrated, are probably fairly accurate, but the intensities recorded for the *A*, *B*, *C*, etc., bands of the glycol (V; $n = 5$) are much higher than would be expected, and only the first band (*A*) lies close to the expected position, the others being displaced to shorter wave-lengths by the superposition of rising absorption. The intensities for (IV; $n = 6$) are also much too high. The 4250-Å maximum, however, lies at the position expected by extrapolation for the *A* band, and indications of the *B*, *C*, and *D* bands are observed at about the positions expected, on the assumption that the usual 2300-cm.$^{-1}$ spacing is observed in this case.

It is now profitable to discuss the general laws connecting the position of the maxima with the extent of the polyacetylenic chain, using the series (IV; $n = 1$—6) as an example; the elucidation of these correlations and their comparison with the corresponding laws for polyene spectra were one of the major objectives of these investigations.

In the first place, it can be discerned that the frequency spacing of the *A*—*E* bands, and of the *L*—*Q* bands does not vary appreciably with the value of *n*. It is about 2300 cm.$^{-1}$ in the first case and about 2100 cm.$^{-1}$ in the second, compared with the typical polyene fine-structure spacing of 1600 cm.$^{-1}$. These values presumably represent the spacing of the principal vibrational levels in the first and second excited states, respectively, and it is interesting to note that the first agrees closely with the —C≡C— bond-stretching levels in the ground state, as determined by the infra-red measurements discussed below.

FIG. 1. *Light absorption of dimethylpenta- and dimethylhexa-acetylenes (in alcohol).*

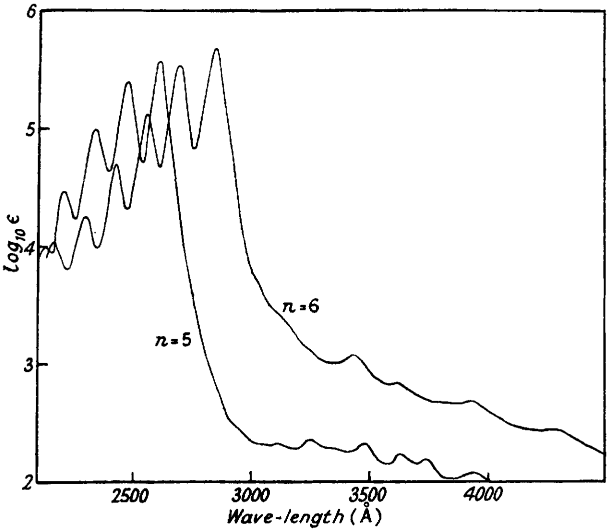
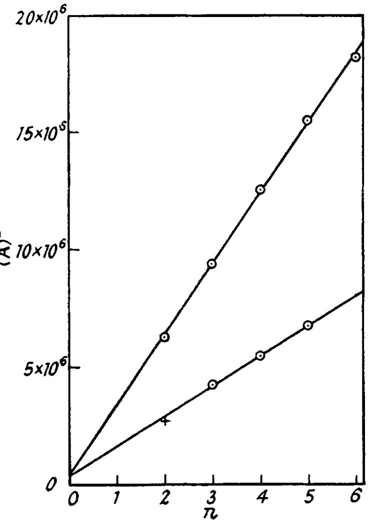


FIG. 2.



If attention is confined to the bands (*A* and *L*), involving transitions to the lowest vibrational levels of the two electronic states observed, the variation of wave-length

TABLE 2. *Ultra-high intensity maxima of hexaynes,* R·[C≡C]$_6$·R

R.	$\lambda_{max.}$ (Å) (ε)	$\lambda_{max.}$ (Å) (ε)	$\lambda_{max.}$ (Å) (ε)
	Q	*P*	*O*
Me	2210 (11,000)	2310 (17,500)	2420 (47,000)
Et †	2220 (9,000)	2295 (14,000)	2450 (14,000)
Et * †	—	2315 (15,000)	2435 (22,000)
CMe$_2$·OH †	—	2350 (28,000)	2450 (30,000)
	N	*M*	*L*
Me	2550 (128,000)	2685 (317,000)	2840 (445,000)
Et †	2580 (26,000)	2710 (55,000)	2860 (75,000)
Et * †	2560 (50,000)	2700 (74,000)	2850 (90,000)
CMe$_2$·OH †	2580 (34,000)	2720 (40,000)	2890 (48,000)

* In hexane. † Determined on non-crystalline concentrates.

with n is illustrated in Fig. 2 [Price and Walsh's result (+) for hexa-2 : 4-diyne in the vapour phase (*Trans. Faraday Soc.*, 1945, **41**, 384) is included]. For both transitions an accurate proportionality between λ^2 and n is observed, as has been found also for the principal bands of polyenes, especially the diphenylpolyenes (Hausser, R. Kuhn, and Smakula, *Z. physikal. Chem.*, 1935, *B*, **29**, 384). In the latter case the theoretical implications of this relationship have been discussed (Lewis and Calvin, *Chem. Reviews*, 1939, **25**, 273; H. Kuhn, *Helv. Chim. Acta*, 1949, **32**, 2247).

Now that the main bands of the spectra of the hydrocarbons (III; $n = 4$ and 5) have been recorded, it is evident that the bathochromic effects of alkyl substitution are small when the intense short-wave-length bands are considered; the two terminal methyl groups displace these maxima by about 60 Å ($n = 4$) and 55 Å ($n = 5$) to longer wave-lengths. These may be compared with the similarly small increment (+20 Å) observed for the *A* band, following the introduction of the second alkyl group into diacetylenes (Part XXXIV, *loc. cit.*), and with the rather larger increments (+50 Å per alkyl group) observed for alkyl substitution in polyenes (Fieser, *J. Org. Chem.*, 1950, **15**, 930).

The profound effects of hyperconjugative auxochromes on the light-absorption properties of diacetylenes (Armitage and Whiting, Part XXXV, *loc. cit.*) are again observed in the higher poly-ynes.

The small displacements attributable to α-hydroxyl groups are evident from Tables 1, and 2, and Table 3 shows the greater influence of two chlorine atoms in the propargylic positions on the light-absorption maxima of (II and IV; $n = 3$ and 4); the displacements of the *A* and the *L* bands are summarised for these substances, and for the corresponding di-ynes in Table 4 from which it can be seen that the effect of a chlorine substituent decreases as n increases, and, if frequency shifts are considered, is greater for the *L* band than for the *A* band.

TABLE 3. *Effects of chlorine atoms on light-absorption properties.*

	(IV; $n = 4$ *)		(II; $n = 4$)		(IV; $n = 3$ *)		(II; $n = 3$)	
Band	$\lambda_{max.}$ (Å)	(ε)	$\lambda_{max.}$ (Å)	(ε)	$\lambda_{max.}$ (Å)	(ε)	$\lambda_{max.}$ (Å)	(ε)
A	3540	(105)	3650	(700)	3060	(120)	3180	(990)
B	3280	(180)	3390	(1,210)	2860	(200)	2990	(1,650)
C	3060	(180)	3150	(1,710)	2680	(200)	2800	(1,230)
D	2860	(140)	2970	(1,600)	2530	(130)	2650	(840)
E	2680	(125)	2790	(1,260)	2390	(105)	2510	(520)
L	2345	(281,000)	2450	(202,000)	<2070	(>140,000)	2190	(>140,000)
M	2235	(198,000)	2335	(150,000)				
N	2145	(91,500)	2220	(71,000)				
O	2040	(24,000)	2080	(26,000)				

* Parts XXXVI and XXXVII, *locc. cit.*

TABLE 4. *Variation in bathochromic effect of chlorine substituents with* n.

	A Band	*L* Band
$n = 2$ *	+170 Å. (−250 cm.$^{-1}$)	—
$n = 3$	+120 Å. (−147 cm.$^{-1}$)	+>120 Å. (−>270 cm.$^{-1}$)
$n = 4$	+110 Å. (−86 cm.$^{-1}$)	+ 105 Å. (−187 cm.$^{-1}$)

* Parts XXXIV and XXXV.

Various extrapolation procedures permit deductions, probably of considerable reliability, as to the spectra of higher and lower polyacetylenes, and simple acetylenes. These need not be discussed in detail.

The infra-red absorption spectra of the dimethylpoly-ynes (IV; $n = 2$—6) were determined in carbon tetrachloride, with a Perkin-Elmer Double Beam Spectrometer, Model 21. Apart from one band, the spectra were very similar. The C≡C stretching band, however, varied in intensity and to some slight extent in position. In (IV; $n = 6$) it was the only band clearly observed, as the substance is unstable and only very sparingly soluble. The slight variation in frequency with n is shown below:

n	2	3	4	5	6
Frequency (cm.$^{-1}$)	2210	2220	2236	2220	2206

EXPERIMENTAL

In work recorded below in which sensitive compounds were being handled [*i.e.*, all polyacetylenic compounds apart from type [(V); $n = 4, 5,$ or 6; (I) and (II); $n = 3$], all operations were carried out below 50°, and whenever possible below 20°. Monosubstituted triacetylenes were handled below 0° and in a nitrogen atmosphere. Whenever possible substances were stored in dilute ethereal solution; otherwise they were kept at $-70°$. Analyses were usually performed within an hour of final purification, but, despite all precautions, satisfactory data could not always be obtained, even though spectrographic measurements indicated a high degree of purity. Photosensitive substances were finally recrystallised in weak artificial light in a cold room at $-5°$. The polyacetylenic compounds which decomposed before melting were recrystallised until the ultra-high-intensity light absorption maxima in the ultra-violet reached constant intensity; in all cases ethanol was used as solvent, except where otherwise specified.

Light petroleum refers to the fraction, b. p. 60—80°, unless otherwise stated; m. p.s were determined on a Kofler block, and " alumina " and " deactivated alumina " refer to material from P. Spence, of Grade O, which in the latter case was washed with methanol and dried at 100° for 3 hours before use, with reduction of the Brockmann grade from II to III. Where the source of a starting material is not stated, it is described or referred to in Parts XXVIII or XXXIII—XXXVII (*locc. cit.*).

Most experiments with liquid ammonia as solvent were carried out in small vacuum-flasks, the contents of which could be cooled to $-77°$ by direct addition of liquid nitrogen.

1 : 6-*Dichlorohexa*-2 : 4-*diyne* (II; $n = 2$).—To a solution of hexa-2 : 4-diyne-1 : 6-diol (165 g.) in pyridine (210 c.c.), thionyl chloride (270 c.c.) was added with mechanical stirring during 3 hours, the temperature being kept at 30° by external cooling. After a further 18 hours at 20° the product was isolated with ether; the extract was washed with water, sodium carbonate solution, and dilute sulphuric acid. Distillation gave 1 : 6-dichlorohexa-2 : 4-diyne (175 g., 80%), b. p. 61°/0·5 mm., n_D^{16} 1·5770 (Hunsmann, *Ber.*, 1950, **83**, 213, gives b. p. 65°/0·1 mm., n_D^{20} 1·5740).

1 : 8-*Dichloro-octa*-2 : 4 : 6-*triyne* (II; $n = 3$).—Thionyl chloride (2·0 c.c.) was added to a solution of octa-2 : 4 : 6-triyne-1 : 8-diol (1·4 g.) in ether (10 c.c.) and pyridine (2 c.c.) at 30—35°, with stirring. After 18 hours at 20° water was added and the neutral fraction was isolated. Chromatographic purification on alumina with light petroleum as eluent gave 1 : 8-*dichloro-octa*-2 : 4 : 6-*triyne* (1·4 g., 80%) as flat needles, m. p. 30°, not raised by crystallisation from light petroleum (Found : C, 55·95; H, 2·7. $C_8H_4Cl_2$ requires C, 56·2; H, 2·35%). This compound possesses strong vesicant properties, and slowly becomes brown on exposure to light.

Octa-1 : 3 : 5 : 7-*tetrayne* (III; $n = 4$).—The above dichloride (0·2 g.) in ether (10 c.c.) was added to a suspension of sodamide, prepared from sodium (0·2 g.) in liquid ammonia (30 c.c.) at $-77°$. Extraction with hexane gave a solution which was made up to 100 c.c., washed, and dried. After 200-fold dilution it showed absorption maxima at 2270, 2170, and 2070 Å, $E_{2\,\text{mm.}} = 0{\cdot}425$, 0·305, and 0·155. On the assumption that $E^{1\%}_{1\,\text{cm.}} = 28{,}000$ at 2270 Å, this corresponds to a 12% yield of (III; $n = 3$).

2 : 11-*Dimethyldodeca*-3 : 5 : 7 : 9-*tetrayne*-2 : 11-*diol* (V; $n = 4$).—To a suspension of sodamide, prepared from sodium (0·5 g.) and liquid ammonia (50 c.c.), 1 : 8-dichloro-octa-2 : 4 : 6-triyne (1·0 g.) was added in ether (10 c.c.) at $-77°$. After 5 minutes, acetone (0·6 g.) and, after a further 15 minutes, ammonium nitrate (1·0 g.) were added and the ammonia was allowed to evaporate with the addition of ether. Extraction of the resultant mixture of inorganic salts and polymeric material with more ether gave on evaporation a semi-crystalline residue (0·3 g.) which had $E^{1\%}_{1\,\text{cm.}} = 3000$, 2000, and 1250 at 2400, 2260, and 2130 Å, respectively, and therefore contained about 65 mg. of (V; $n = 4$). This compound was isolated, with $E^{1\%}_{1\,\text{cm.}}$ values in agreement with those previously recorded (Part XXXVII, *loc. cit.*), by crystallisation from benzene–light petroleum.

1 : 10-*Dichlorodeca*-2 : 4 : 6 : 8-*tetrayne* (II; $n = 4$).—Thionyl chloride (9 c.c.) was added at 25—30° with stirring to a solution of the corresponding glycol (I; $n = 4$) (5·3 g.) in ether (20 c.c.) and pyridine (8 c.c.). The mixture was then warmed to 40° for 30 minutes, stirred for a further 1½ hours at 20°, and treated with ice-water. Isolation of the neutral fraction gave a solid which was purified by chromatography on alumina from light petroleum followed by crystallisation from carbon disulphide, giving 1 : 10-*dichlorodeca*-2 : 4 : 6 : 8-*tetrayne* as needles, m. p. 73°, which rapidly became blue-green on exposure to light (Found : C, 61·9; H, 2·0. $C_{10}H_4Cl_2$ requires C, 61·6; H, 2·05%).

Deca-1 : 3 : 5 : 7 : 9-*pentayne* (III; $n = 5$).—A suspension of sodamide, prepared from sodium (0·1 g.) and liquid ammonia (50 c.c.), was cooled to −77° and treated with a solution of the above dichloride (0·2 g.) in ether (5 c.c.). After 10 minutes ammonium nitrate (0·5 g.) was added and hexane extraction gave a solution which was washed with water, dried ($MgSO_4$), and made up to 200 c.c. After ten-fold dilution this had light-absorption maxima at 2540, 2400, and 2270 Å, $E_{2\,\text{mm.}} = 0{\cdot}320, 0{\cdot}288$, and $0{\cdot}175$. If the pure hydrocarbon has $E^{1\%}_{1\,\text{cm.}} = 29{,}000$ at 2540 Å, this corresponds to a yield of about 1%.

Dodeca-2 : 4 : 6 : 8 : 10-*pentayne* (IV; $n = 5$).—A suspension of sodamide prepared from sodium (0·2 g.) in liquid ammonia (50 c.c.) was cooled to −77°; a solution of (II; $n = 4$) (0·3 g.) in ether (10 c.c.) was added. After 1 minute methyl iodide (0·4 g.) was added, then after 20 minutes ammonium nitrate (0·5 g.). Extraction of the ammonia phase with hexane gave a solution which was washed, dried, and made up to 100 c.c. After 100-fold dilution, this had light-absorption maxima with $E_{2\,\text{mm.}} = 0{\cdot}320, 0{\cdot}206$, and $0{\cdot}102$ at 2590, 2460, and 2320 Å, respectively. If $E^{1\%}_{1\,\text{cm.}} = 23{,}000$ at 2590 Å, this corresponds to a yield of the pure hydrocarbon of 3% (see below for alternative method of preparation).

2 : 13-*Dimethyltetradeca*-3 : 5 : 7 : 9 : 11-*pentayne*-2 : 13-*diol* (V; $n = 5$).—A suspension of sodamide, prepared from sodium (2·3 g.) and liquid ammonia (100 c.c.), was treated with (II; $n = 4$) (4·8 g.) in ether (20 c.c.) at −77°. After one minute's stirring acetone (3·0 g.) was added, and after a further 20 minutes the sodium derivative was decomposed with ammonium chloride (10 g.). After the ammonia had been allowed to evaporate freely with occasional addition of ether the neutral product was isolated as a brownish semi-crystalline mass (0·8 g., 14%) which by spectrographic assay was shown to be about 30% pure. Repeated crystallisation from benzene–light petroleum gave the glycol (*ca.* 20 mg.) as pale-yellow plates which became orange on exposure to light (Found : C, 77·85; H, 6·5. $C_{10}H_{14}O_2$ requires C, 80·6; H, 5·9%). Despite the poor analytical figures, its light-absorption properties (Table 1) suggest that the final specimen was essentially pure.

2 : 5-*Dichlorohex*-3-*yne* (VII; $n = 2$) (with T. Y. SHEN).—A mixture of hex-3-yne-2 : 5-diol (Dupont, *Ann. Chim.*, 1913, **30**, 485) (11·4 g.) and pyridine (24 g.) was stirred while thionyl chloride (30 g.) was added dropwise, the temperature being kept at *ca.* 30° by external cooling. The temperature was then raised to 50° for 1 hour. After cooling, ice was added, and the neutral fraction was distilled, giving 2 : 5-dichlorohex-3-yne (11·5 g., 76%), b. p. 55°/10 mm., n_D^{20} 1·4802 (Found : C, 47·95; H, 5·25. $C_6H_8Cl_2$ requires C, 47·7; H, 5·35%).

Hexa-2 : 4-*diyne*.—A suspension of sodamide, prepared from sodium (2·9 g.) in liquid ammonia (100 c.c.), was treated with 2 : 5-dichlorohex-3-yne (9·6 g.). Isolation of the crude product with butane gave after evaporation a crystalline residue, which from pentane at −40° gave hexa-2 : 4-diyne (3·4 g., 70%) as rhombohedra, m. p. 64°, undepressed on admixture with an authentic sample.

2 : 7-*Dichloro-octa*-3 : 5-*diyne* (VII; $n = 3$).—Thionyl chloride (30 g.) was added to a solution of octa-3 : 5-diyne-2 : 7-diol (13·8 g.) in pyridine (24 g.), the temperature being kept at about 35°. After 18 hours' stirring at 20° ice was added and the product was isolated with ether; distillation gave 2 : 7-*dichloro-octa*-3 : 5-*diyne* (11·9 g., 68%), b.p. 58—60°/10^{-2} mm., n_D^{19} 1·5375 (Found : C, 55·1; H, 4·8. $C_8H_8Cl_2$ requires C, 54·9; H, 4·65%).

Octa-2 : 4 : 6-*triyne* (IV; $n = 3$).—A suspension of sodamide prepared from sodium (2·0 g.) in liquid ammonia (100 c.c.) was treated with 2 : 7-dichloro-octa-3 : 5-diyne (7·2 g.) at −77°. After addition of ammonium chloride and the evaporation of the ammonia the product was isolated with ether and sublimed (h-tube, Part XXVIII, *loc. cit.*) at 80° (bath-temp.)/10^{-2} mm., to give octa-2 : 4 : 6-triyne (3·1 g., 75%) as rhombohedra, m. p. 128°, undepressed on admixture with a specimen prepared according to Part XXXVI (*loc. cit.*).

2 : 11-*Dichlorododeca*-3 : 5 : 7 : 9-*tetrayne* (VII; $n = 4$).—A solution of the corresponding glycol (VI; $n = 4$) (10·3 g.) in ether (20 c.c.) and pyridine (9 c.c.) was treated with thionyl chloride (10 c.c.) with stirring, the reaction mixture being kept at 30—35° during the addition and for a further 2 hours. Ice-water was then added, and the neutral fraction was isolated and chromatographed on alumina from light petroleum. The non-polar fraction (4·5 g., 37%) did not give good analytical figures for the expected dichloride, but it showed ultra-violet light absorption maxima at 2460, 2340, and 2230 Å with $\varepsilon = 160{,}000, 120{,}000$, and $60{,}200$ respectively and was therefore probably about 80% pure.

Dodeca-2 : 4 : 6 : 8 : 10-*pentayne* (IV; $n = 5$) (Second Method).—The above dichloride (4·5 g). was added to a suspension of sodamide, prepared from sodium (0·9 g.) in liquid ammonia (100 c.c.) at −77°. After 15 minutes ammonium chloride (2 g.) was added, the contents of the vacuum-flask were poured out, and most of the ammonia was evaporated rapidly by warming after light petroleum (200 c.c.) and benzene (10 c.c.) had been added. Filtration from the mineral salts and black polymeric matter and evaporation *in vacuo* gave a yellowish solid (0·25 g.). Crystallisation from light petroleum at 40° gave the *hydrocarbon* as cream-coloured prismatic needes (0·1 g., 3%), which became brown in air in the dark at −5° in a few minutes (Found : C, 94·8, H, 5·05. $C_{12}H_6$ requires C, 95·95; H, 4·05%). Despite the analytical data, the ultra-violet light-absorption properties (Fig. 1 and Table 1) indicate that the final specimen was probably almost pure; it rapidly became blue on exposure to light.

Hepta-1 : 3 : 5-*triyne*.—To a suspension of sodamide, prepared from sodium (6·9 g.) in liquid ammonia (150 c.c.) and cooled to −77°, 1 : 6-dichlorohexa-2 : 4-diyne (14·7 g.) was added. After 1 minute methyl iodide (14·2 g.) was added, and the mixture was set aside for 20 minutes. Addition of ammonium chloride (10·g.) and repeated extraction of the ammonia phase with butane, followed by evaporation of most of the latter, gave a yellow liquid which was transferred to the one limb of a simple modification of the h-tube illustrated in Part XXVIII (*loc. cit.*), in which a tap had been introduced into the bottom of the limb below the "finger." The tube was then evacuated, the remainder of the butane evaporating and reducing the temperature to about −20°. When the pressure reached 0·2 mm., liquid nitrogen was added to the "finger," and the temperature of the limb containing the product was allowed to rise; hepta-1 : 3 : 5-triyne distilled and condensed on the finger. On removal of the refrigerant the product (*ca.* 1·5 g.) melted at about −10° and ran into the left-hand limb; after admission of nitrogen (or carbon dioxide) the product could be transferred to another apparatus *via* the lower tap. The non-volatile residue contained most of the octa-2 : 4 : 6-triyne, which sublimes only very slowly at *ca.* 10°, while the hexa-1 : 3 : 5-triyne was largely eliminated with the butane; much polymeric material is formed in the reaction, and this residue exploded on one occasion after the distillation when air was finally admitted. Heptatriyne also explodes very easily above 0°.

Tetradeca-2 : 4 : 6 : 8 : 10 : 12-*hexayne* (IV; $n = 6$).—The above heptatriyne was carefully transferred to a solution of cuprous chloride (10 g.) and ammonium chloride (16 g.) in water (150 c.c.) and methanol (10 c.c.). An orange precipitate formed immediately. The flask was evacuated and filled with oxygen and shaken, whilst cooling to 0°, until absorption ceased. The crude product was isolated with ether, the solution was dried and evaporation and crystallisation of the residue from light petroleum at −40° gave the *tetradeca*-2 : 4 : 6 : 8 : 10 : 12-*hexayne* (400 mg., 5%) as small yellow crystals. These rapidly became brown in diffused light even at −5°. Although the compound was too unstable to furnish satisfactory analytical data (Found : C, 94·3; H, 4·8. $C_{14}H_6$ requires C, 96·5; H, 3·5%) spectrographic data (see Fig. 1 and Table 2) indicate a high degree of purity.

2 : 15-*Dimethylhexadeca*-3 : 5 : 7 : 9 : 11 : 13-*hexayne*-2 : 15-*diol* (V; $n = 6$).—Triacetylene was prepared from 1 : 6-dichlorohexa-2 : 4-diyne (14·7 g.) in liquid ammonia (150 c.c.) at −77° with sodamide from sodium (6·9 g.). The mixture was stirred while acetone (5·8 g.) was added and this was followed immediately by ammonium nitrate (8 g.). The ammonia was allowed to evaporate while ether was added from time to time. (Attempts to isolate the alcohol were unsuccessful since the crude material invariably deflagrated at room temperature and once while being dried at 0°/10^{-2} mm.) In this instance the product was purified to some extent by chromatography from ethereal solution on deactivated alumina. The ether was evaporated and replaced by aqueous methanol (1 : 1), and the solution was added to a solution of cuprous chloride (20 g.) and ammonium chloride (30 g.) in water (100 c.c.), an immediate orange precipitate being formed. After the whole had been shaken with oxygen until absorption ceased the product was isolated with ether and purified to some extent by chromatography on deactivated alumina from ethereal solution. As judged by its light absorption (Table 2) a 10% concentrate of the glycol was obtained, but the presence of much high-intensity absorption above 3000 Å indicated the probable presence of dehydration products.

Pent-2-*yne*-1 : 4-*diol*.—To a solution of ethylmagnesium bromide, prepared in ether (150 c.c.) from magnesium (5·0 g.), benzene (150 c.c.) was added steadily while the ether was distilled off. Propargyl alcohol (5·6 g.) in benzene (7 c.c.) was then added with external cooling to 0°, and the mixture was stirred at 20° for 1 hour. Cooling was resumed while acetaldehyde (4·4 g.) was added; after 16 hours at 20° the neutral product, isolated by continuous extraction, was distilled, giving pent-2-yne-1 : 4-diol (5·5 g., 37%), b. p. 86—88°/0·5 mm., n_D^{19} 1·4762 (I.G. Farbenind., U.S.P. 2,238,471, gives b. p. 110—112°/7 mm.). The *bis*-3 : 5-*dinitrobenzoate*, crystallised from benzene, had m. p. 139° (Found : C, 47·0; H, 2·8. $C_{19}H_{12}O_{12}N_4$ requires C, 46·75; H, 2·5%).

1 : 4-*Dichloropent*-2-*yne*.—The above glycol (6·4 g.) and pyridine (10 g.) were stirred while thionyl chloride (20 g.) was added, the temperature being kept at about 30° by external cooling. The reaction mixture was warmed to 40° for 1 hour, then cooled and treated with ice. Isolation

of the neutral fraction with ether and distillation gave 1 : 4-*dichloropent*-2-*yne* (6·6 g., 76%), b. p. 58—60°/12 mm., n_D^{18} 1·4880 (Found : C, 44·0; H, 4·45. $C_5H_6Cl_2$ requires C, 43·8; H, 4·4%).

Penta-1 : 3-*diyne*.—1 : 4-Dichloropent-2-yne (9·5 g.) was added to a suspension of sodamide, prepared from sodium (3·4 g.) and liquid ammonia (100 c.c.). After 15 minutes ammonium chloride (5 g.) was added, followed by butane (4 × 50 c.c.), the mixture being stirred and the greater part of the butane layer being poured off each time. Evaporation through a 15-cm. Widmer column under partial reflux (carbon-dioxide–acetone) and distillation gave penta-1 : 3-diyne (2·2 g., 50%), b. p. 76°, n_D^{18} 1·4750 (Schlubach and Wolf, *Annalen*, 1950, **568**, 141, give b. p. 76—77°, n_D^{20} 1·4717; Armitage, Jones, and Whiting, *J.*, 1952, 1993, give b. p. 76·5°, n_D^{15} 1·4790).

Hepta-4 : 6-*diyn*-3-*ol*.—To a suspension of sodamide, prepared from sodium (19·2 g.) in liquid ammonia (200 c.c.), 1 : 4-dichlorobut-2-yne (24·6 g.) was added. After 1 minute the mixture was treated with freshly distilled propaldehyde (11·6 g.) in ether (50 c.c.) and set aside for 16 hours. Ammonium chloride (15 g.) was added and the ammonia was allowed to evaporate with the addition of ether. Distillation gave *hepta*-4 : 6-*diyn*-3-*ol* (5·7 g., 26%), b. p. 57°/0·05 mm., n_D^{18} 1·5005 (Found : C, 76·4; H, 7·35. C_7H_8O requires C, 77·8; H, 7·45%).

Octa-2 : 4-*diyne*-1 : 6-*diol*.—To a suspension of sodamide, prepared from sodium (1·5 g.) in liquid ammonia (150 c.c.), hepta-4 : 6-diyn-3-ol (3·0 g.) was added. After 20 minutes the mixture was treated with paraformaldehyde (1·0 g., dried over phosphoric oxide) and set aside for 16 hours. Ammonium chloride (3 g.) was added and the ammonia allowed to evaporate with the addition of ether. Distillation gave *octa*-2 : 4-*diyne*-1 : 6-*diol* (2 g., 52%), b. p. 120°/0·01 mm., $n_D^{21\cdot5}$ 1·5335 (Found : C, 68·3; H, 7·45. $C_8H_{10}O_2$ requires C, 69·5; H, 7·3%).

Hexadeca-3 : 5 : 7 : 9 : 11 : 13-*hexayne*.—(*a*) To a solution of octa-2 : 4-diyne-1 : 6-diol (5·8 g.) in pyridine (6 c.c.), kept at 30°, thionyl chloride (8 c.c.) was added. After 3 hours' stirring at 30° the product was isolated with ether. Distillation of the residue gave slightly impure 1 : 6-dichloro-octa-2 : 4-diyne (3·1 g., 42%) as an oil, b. p. 67°/0·01 mm., n_D^{23} 1·5540 (Found : C, 56·6; H, 4·8. $C_8H_8Cl_2$ requires C, 54·9; H, 4·65%).

A suspension of sodamide, prepared from sodium (0·4 g.) in liquid ammonia (50 c.c.), was treated with the above 1 : 6-dichloro-octa-2 : 4-diyne (2·4 g.) at −77°. The crude octa-1 : 3 : 5-triyne (1·1 g.), n_D^{21} 1·5282 (see also below), isolated with butane showed ultra-violet light absorption maxima at 3040, 2800, 2645, 2500 Å, $E_{\text{rel.}}$ 11, 22, 20, 14. Its instability precluded further purification and therefore it was used immediately in the coupling reaction.

The crude triyne (1·1 g.) was added to a solution of cuprous chloride (5 g.) and ammonium chloride (8 g.) in water (75 c.c.) and methanol (5 c.c.), and the mixture was shaken in oxygen until absorption ceased. After extraction with ether, a residue (0·9 g.) was obtained which showed light absorption (see Table 2), indicating that it contained about 20% of hexadeca-3 : 5 : 7 : 9 : 11 : 13-hexayne.

(*b*) To a suspension of sodamide from sodium (3·45 g.) in liquid ammonia (200 c.c.) at −77° to which had been added 1 : 6-dichlorohexa-2 : 4-diyne (7·35 g.), ethyl iodide (7·8 g.) was introduced. After 20 minutes the product was isolated with butane and sublimation at 20° (bath-temp.)/10^{-2} mm. gave octa-1 : 3 : 5-triyne with absorption maxima at 3050, 2800, 2650, and 2510 Å, $\varepsilon_{\text{max.}}$ = 90, 190, 265, and 260, respectively.

The triyne was coupled as described above. Removal of the solvent gave a yellow liquid which by chromatography on activated alumina from hexane solution gave a concentrate, estimated by its light absorption (Table 2) to contain 15% of the hexa-acetylene.

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