699. *Researches on Acetylenic Compounds. Part LXIV.* The Preparation of Conjugated Octa- and Deca-acetylenic Compounds.*

By E. R. H. JONES, H. H. LEE, and M. C. WHITING.

Polyacetylenic hydrocarbons with t-butyl end-groups and having eight and ten conjugated acetylenic linkages have been prepared. Their physical properties are discussed.

PARTS XXXIX and XLI [1] described the preparation of polyacetylenic compounds with methyl and phenyl end-groups. For the former, the longest chain obtainable had six acetylenic linkages; and for the latter, eight. In each case the last obtainable member of the series was extremely difficult to handle because of low solubility and instability. Independently, Bohlmann [2] prepared a similar series of polyacetylenes having t-butyl groups at both ends. These hydrocarbons were obtained up to $n = 7$, and even this member of the series appeared, from the published description, to be soluble in most solvents and reasonably stable. These differences were plausibly explained [2] as due to the ability of the bulky and cylindrically-symmetrical end-groups to keep the rod-like polyacetylenic chains well outside bonding distance. (At the same time, the possibility of attack, *e.g.*, by free radicals, on any hydrogen atoms on a carbon atom at the end of the chain would obviously be eliminated.) The same principle was later applied, with outstandingly successful results, to the preparation of stable aliphatic cumulenes.[3]

When electronic absorption spectra became accurately known for longer [4] (8—10) as well as shorter [5] (3—7) polyenes with simple end-groups, it became desirable to extend similarly the range of known aliphatic polyacetylenes; the use of t-butyl end-groups was obviously necessary. It seemed that progress might be made in this direction by the use of penta-1,4-diyn-3-ol, which became readily accessible only recently.[6] In principle, it was necessary merely to modify a reaction scheme already used by Bohlmann: [2]

$$\mathrm{Bu^t{\cdot}C{\equiv}C{\cdot}CHO + BrMg{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}O{\cdot}MgBr \longrightarrow Bu^t{\cdot}C{\equiv}C{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}CH_2{\cdot}OH}$$

$$\mathrm{\longrightarrow Bu^t{\cdot}C{\equiv}C{\cdot}CHCl{\cdot}C{\equiv}C{\cdot}CH_2Cl \longrightarrow Bu^t{\cdot}[C{\equiv}C]_3{\cdot}H \longrightarrow Bu^t{\cdot}[C{\equiv}C]_6{\cdot}Bu^t}$$

(*a*) by substituting penta-1,4-diyn-3-ol for propargyl alcohol, to obtain the octayne (IV), and (*b*) by using the homologous aldehyde (VI), to prepare the decayne. The latter aldehyde was prepared by Bohlmann [2] who has not, however, reported its condensation with propargyl alcohol to obtain, by the same route, the octayne. In practice the addition of further acetylenic linkages rendered many of the methods hitherto used ineffective, and alternatives had to be devised.

Penta-1,4-diyn-3-ol was stated [6] to be a remarkably stable solid; and this is true of the pure alcohol. However, a very violent explosion took place when the crude product was distilled, and we wish to draw attention to the modified technique for the isolation described in the Experimental section. When a solution of the alcohol in tetrahydrofuran was treated with ethylmagnesium bromide (2 mol.), a soluble bisbromomagnesium derivative (II) was obtained which with 4,4-dimethylpent-2-ynal [2] (I) gave a good yield of a chromatographically isolated glycol fraction with the expected ultraviolet transparency and infrared spectrum. Attempts to oxidise it to the hexa-acetylenic tetraol were unsuccessful, the glycol being recovered in good yield. Treatment with thionyl chloride alone [2] gave unsatisfactory results but, after treatment with thionyl chloride in pyridine,[1] spectroscopic results suggested that a very unstable dichloride (III) had been obtained;

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* Part LXIII (incorrectly numbered LXII), *J.*, 1960, 341.

[1] Cook, Jones, and Whiting, *J.*, 1952, 2883; Armitage, Entwistle, Jones, and Whiting, *J.*, 1954, 147.

[2] Bohlmann, *Chem. Ber.*, 1953, **86**, 63, 657.

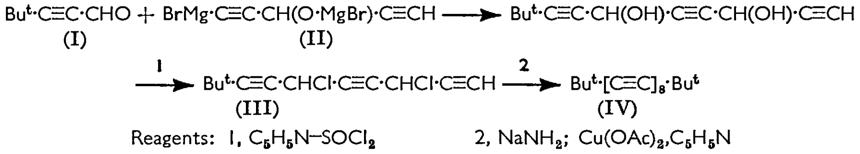
[3] Bohlmann and Kieslich, *Chem. Ber.*, 1954, **87**, 1363.

[4] Bohlmann and Mannhardt, *Chem. Ber.*, 1956, **89**, 1307.

[5] Nayler and Whiting, *J.*, 1955, 3037.

[6] Jones, Skattebøl, and Whiting, *J.*, 1956, 4765.

no attempt was made to purify this compound. A number of mild bases [cold potassium ethoxide, triethylamine, and alkaline alumina (see below)] failed to convert it into any product having the characteristic intense bands of the tetrayne system at 2350 Å, etc.



$$\underset{\text{(I)}}{\mathrm{Bu^t{\cdot}C{\equiv}C{\cdot}CHO}} + \underset{\text{(II)}}{\mathrm{BrMg{\cdot}C{\equiv}C{\cdot}CH(O{\cdot}MgBr){\cdot}C{\equiv}CH}} \longrightarrow \mathrm{Bu^t{\cdot}C{\equiv}C{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}CH(OH){\cdot}C{\equiv}CH}$$

$$\xrightarrow{1} \underset{\text{(III)}}{\mathrm{Bu^t{\cdot}C{\equiv}C{\cdot}CHCl{\cdot}C{\equiv}C{\cdot}CHCl{\cdot}C{\equiv}CH}} \xrightarrow{2} \underset{\text{(IV)}}{\mathrm{Bu^t{\cdot}[C{\equiv}C]_8{\cdot}Bu^t}}$$

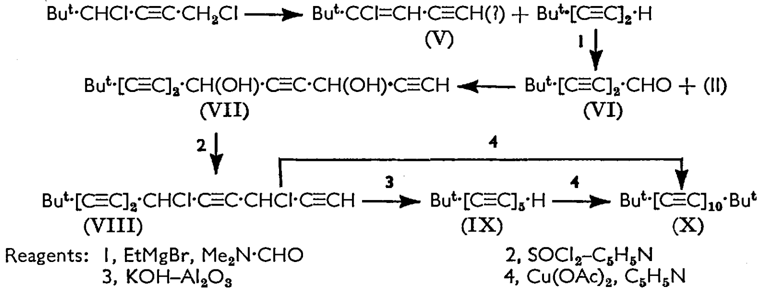
Reagents: 1, $C_5H_5N–SOCl_2$ 2, $NaNH_2$; $Cu(OAc)_2,C_5H_5N$

Sodamide in liquid ammonia at −33° did so, and after chromatographic purification a concentrate of the desired tetrayne was obtained in about 6% overall yield (spectrographically estimated) from the crude glycol.

Early attempts to couple this hydrocarbon oxidatively failed, apparently because of the extreme insolubility of its cuprous derivative (conjugated terminal di- and especially tri-acetylenes often give such unreactive derivatives). The elegant method of Eglinton and Galbraith [7] was therefore used, and readily gave the desired octayne (IV) which proved to be highly crystalline and almost as stable as its lower homologues.

For the decayne it was necessary to use 6,6-dimethylhepta-2,4-diynal (VI); and we found that, as prepared by the method of Bohlmann,[2] the intermediate 5,5-dimethylhexa-1,3-diyne was contaminated with about 10% of a dimethylchlorohexenyne (V), which was separated by fractional distillation. As the methods earlier described for converting this hydrocarbon into the aldehyde (VI) were unsatisfactory, we employed the Bouveault synthesis,[8] and obtained a 30% yield, although the instability of the product prevented analysis. The condensation with penta-1,4-diyn-3-ol proceeded as for the lower homologue; but because the product again resisted crystallisation, and a further sequence of unstable non-crystallisable intermediates lay ahead, it was subjected to counter-current distribution between benzene–light petroleum and aqueous ethylene glycol. The glycol (VII) was thereby obtained as a syrup showing well-defined low-intensity bands of the $[C{\equiv}C]_2$ system with the expected intensity, a sensitive test of purity.

The conversion of this glycol (VII) into the dichloride (VIII) gave difficulty, which was traced to a reaction, probably initially prototropic,[9] with pyridine itself. A modified technique was evolved which minimised this although the resultant solution showed unwanted maxima at long wavelengths attributable to rearranged products. It was again possible to use the extremely intense polyacetylene bands (of the $[C{\equiv}C]_5$ system) to assay the products of dehydrohalogenation experiments. Again, potassium hydroxide, potassium carbonate, and triethylamine were unsuccessful, and this time sodamide also gave unsatisfactory results; but alkaline alumina [10] now proved effective, and a *ca.* 17% yield



$$\mathrm{Bu^t{\cdot}CHCl{\cdot}C{\equiv}C{\cdot}CH_2Cl} \longrightarrow \underset{\text{(V)}}{\mathrm{Bu^t{\cdot}CCl{=}CH{\cdot}C{\equiv}CH(?)}} + \mathrm{Bu^t{\cdot}[C{\equiv}C]_2{\cdot}H} \xrightarrow{1}$$

$$\underset{\text{(VII)}}{\mathrm{Bu^t{\cdot}[C{\equiv}C]_2{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}CH(OH){\cdot}C{\equiv}CH}} \longleftarrow \underset{\text{(VI)}}{\mathrm{Bu^t{\cdot}[C{\equiv}C]_2{\cdot}CHO}} + \text{(II)}$$

$$\xrightarrow{2} \underset{\text{(VIII)}}{\mathrm{Bu^t{\cdot}[C{\equiv}C]_2{\cdot}CHCl{\cdot}C{\equiv}C{\cdot}CHCl{\cdot}C{\equiv}CH}} \xrightarrow{3} \underset{\text{(IX)}}{\mathrm{Bu^t{\cdot}[C{\equiv}C]_5{\cdot}H}} \xrightarrow{4} \underset{\text{(X)}}{\mathrm{Bu^t{\cdot}[C{\equiv}C]_{10}{\cdot}Bu^t}}$$

$$\text{(VIII)} \xrightarrow{4} \text{(X)}$$

Reagents: 1, EtMgBr, $Me_2N{\cdot}CHO$ 2, $SOCl_2–C_5H_5N$
3, $KOH–Al_2O_3$ 4, $Cu(OAc)_2$, C_5H_5N

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[7] Eglinton and Galbraith, *J.*, 1959, 889.

[8] Bouveault, *Bull. Soc. chim. France*, 1904, **31**, 1322; cf. Jones, Skattebøl, and Whiting, *J.*, 1958, 1054.

[9] Nineham and Raphael, *J.*, 1949, 118.

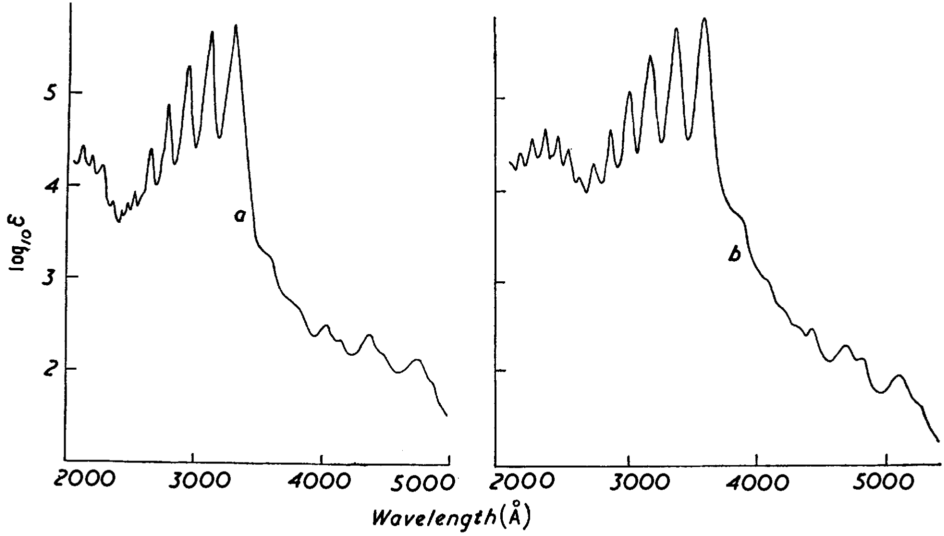
[10] Castells and Fletcher, *J.*, 1956, 3245.

of pentayne (IX) (from diol) was obtained. Eglinton–Galbraith coupling [7] gave the decayne (X) without difficulty. Alternatively, and remarkably, the Eglinton–Galbraith reagent, cupric acetate in aqueous-methanolic pyridine, converted the dichloride directly into the decayne, giving a 24% yield from the glycol (VII).

The decayne (X) forms salmon-coloured needles, stable for periods of days in air and light at room temperature. It is fairly soluble in organic solvents, and is altogether easier to handle than the dimethyl analogue with only four triple bonds. Admittedly it decomposed, without melting, at about 100°, and when touched with a hot glass rod it or its lower homologue (IV) deflagrated mildly, with the formation of much carbonaceous matter.

The absorption spectra of the two hydrocarbons (IV) and (X) are illustrated in Fig. 1 and tabulated below. The medium-intensity bands at long wavelengths—well into the visible—are comparable in intensity with those of lower homologues. These results confirm the impression that the intensity of absorption in this region is independent of the chain-length of a poly-yne, though the overlapping absorption from the next very intense transition prevents evaluation of the oscillator strength. The ultra-high-intensity bands are, as expected, more intense on a molar extinction basis than those of any other substances yet described; the highest value in the literature hitherto is, we believe, 610,000 for the dilithium derivative of *meso*-tetraphenylporphin.[11]

FIG. 1. *The ultraviolet absorption spectra of* (*a*) *the octayne* (IV) *and* (*b*) *the decayne* (X).



As has been observed for the dimethylpoly-ynes,[1] the simple di-t-butylpoly-ynes show more complex fine-structure in the long-wavelength medium-intensity transition than do polyacetylenic compounds having one or more ethylenic or similar end-groups. Although it is possible to discern some periodicity of rather less than the usual 2000 cm.$^{-1}$ interval in the absorption in this region, detailed treatment would not be justified. In the ultra-high-intensity bands, however, the vibrational spacing is well resolved and proves to be about 1900 and 1800 cm.$^{-1}$ for (IV) and (X), respectively. In Fig. 2 the spacing-frequency of these bands is plotted against chain-length, and (despite some understandable experimental scatter) is seen to diminish steadily. Analogous data for the dimethylpolyenes [4,5] show no comparable trend.

In addition to the two sets of bands known from earlier work on lower poly-ynes, the spectra illustrated (Fig. 1) reveal one or more additional electronic transitions at short

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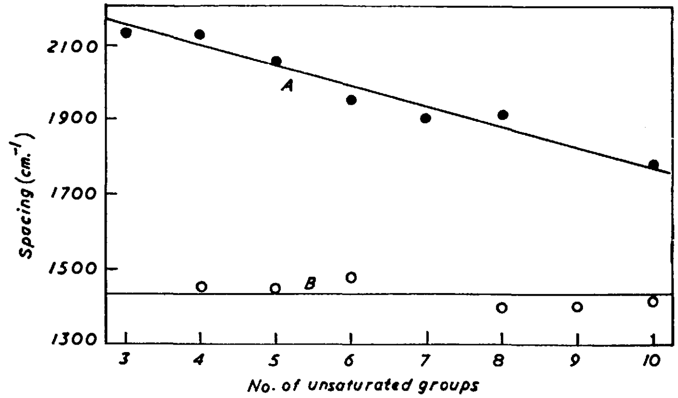
[11] Dorough, Miller, and Huennekens, *J. Amer. Chem. Soc.*, 1951, **73**, 4315.

wavelengths with intensities of the order of 10^4. These also show well-defined vibrational fine-structure which is not, however, spaced at about 2000 cm.$^{-1}$ as for the two more familiar transitions at longer wavelengths. They are not sharply separated from the ultra-high-intensity transition, and they no doubt make a considerable contribution to the observed oscillator strength values for the polyacetylenes (IV) and (X). These were calculated from the equation,[12] $f = 4{\cdot}31 \times 10^{-4} \int \varepsilon \, d\nu$, with integration from 2000 Å upwards. It is therefore hardly surprising that the values, 12·0 and 14·3, obtained lie far from those indicated by extrapolation of Bohlmann's results with the lower di-t-butylpoly-ynes.

FIG. 2. *Vibrational spacing vales for (A) poly-ynes and (B) polyenes.*



Absorption maxima in hexane.

Octayne (IV) (Fig. 1*a*)				Decayne (X) (Fig. 1*b*)			
λ (Å)	ε	λ (Å)	ε	λ (Å)	ε	λ (Å)	ε
2110	31,900	3100	580,000	2180	30,000	3395	695,000
2150 *	19,800	3295	705,000	2270	44,000	3625	850,000
2195	24,000	3565 *	2,000	2370	54,000	3880 *	6,100
2270	18,400	3595 *	1,800	2420 *	26,500	4095 *	1,200
2355	7,700	4045	340	2470	44,500	4215 *	550
2420	5,800	4145	230	2555	32,000	4330 *	350
2475	7,100	4370	270	2635	15,500	4445	330
2525	9,700	4515 *	140	2750	22,000	4710	220
2585 *	9,000	4755	150	2885	53,000	4840	150
2645	29,000	4880 *	80	3030	140,000	5130	100
2775	94,000			3200	345,000	5275 *	50
2930	245,000						

* Denotes a shoulder.

EXPERIMENTAL

" Light petroleum " refers to the fraction of b. p. 30—40°, unless otherwise stated, and " alumina " to Peter Spence's Grade 0; " deactivation " involved treatment with 10% of 10% acetic acid.

Penta-1,4-*diyn*-3-*ol* (improved method; the technique for isolation given earlier is now known to be hazardous).—Ethynylmagnesium bromide was prepared from magnesium (48 g.) in tetrahydrofuran (2 l.), and a solution of ethyl formate (50 g.) in tetrahydrofuran (100 c.c.) was added at 0°. The mixture was stirred for 18 hr. at 20°, then ammonium chloride (500 g.) was added as a saturated aqueous solution. The lower layer was extracted with ether (3 × 250 c.c.), and the organic layers were dried (Na_2SO_4) and evaporated through a short Dufton column to 500 c.c., then at 200 mm. until no more solvent distilled. The dark syrup was extracted

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[12] Armitage, Cook, Entwistle, Jones, and Whiting, *J.*, 1952, 1998.

continuously with light petroleum (b. p. 40—60°), and the insoluble residue, presumably containing higher polymers of the type $X{\cdot}[CH(OH){\cdot}C{\equiv}C]{\cdot}Y$, was discarded. The light petroleum was evaporated and the light-brown residue was distilled at *ca.* 15 mm., and bath-temp. 70—90°. Crystallisation of the distillate from benzene–light petroleum gave the alcohol (23 g., 43%).

9,9-*Dimethyldeca*-1,4,7-*triyne*-3,6-*diol*.—Ethylmagnesium bromide was prepared under nitrogen from magnesium (1·6 g.) in dry tetrahydrofuran (50 c.c.). While still warm, the Grignard reagent was transferred under nitrogen to a dropping funnel, and added dropwise at 20—25° to a stirred solution of penta-1,4-diyn-3-ol[6] (2·4 g.) in dry tetrahydrofuran (25 c.c.). After being stirred for an additional 30 min. the resulting yellow solution was cooled to 0° and treated with 4,4-dimethylpent-2-ynal[2] (3·1 g.) in dry tetrahydrofuran (10 c.c.). The mixture was stirred under nitrogen for a further 4 hr. at 20°, then decomposed with saturated ammonium chloride solution. Isolation with ether gave a brown gum which was chromatographed on deactivated alumina. From the benzene–ether (1 : 1) and ether eluates the expected diol (4·1 g., 75%) was obtained as a light-brown syrup which resisted attempts at crystallisation and showed virtually no ultraviolet absorption. It had $\nu_{max.}$ (in CCl_4) 3600, 3300, 2250, 2130, and 1365 cm.$^{-1}$ (shoulder at 1375 cm.$^{-1}$). Attempts to couple the diol in the presence of cuprous chloride and aqueous ammonium chloride (adjusted to pH 2 with concentrated hydrochloric acid) under oxygen[12] were not successful. Very little coupling took place as determined by ultraviolet absorption, and, in each case, the starting material (identified by its infrared spectrum) was recovered in good yield with slight decomposition.

2,2,19,19-*Tetramethyleicosa*-3,5,7,9,11,13,15,17-*octayne* (IV).—Thionyl chloride (2·0 g.) was added dropwise with stirring to a solution of the above diol (1·2 g.) in dry ether (25 c.c.) and pyridine (1·3 g.) at 20—25°. The tarry mixture was stirred for a further 1 hr. at 20°, then heated under reflux for 2 hr. Decomposition with ice and isolation with ether gave a dark solution which was washed with sodium hydrogen carbonate solution, dried ($MgSO_4$), concentrated to ~15 c.c. under reduced pressure, and added dropwise with stirring to a suspension of sodamide [prepared from sodium (1·0 g.) in liquid ammonia (50 c.c.)] at −33°. After 15 min., ammonium chloride (4 g.) was added, followed by light petroleum (75 c.c.) whilst the ammonia was allowed to evaporate. The organic solution was decanted from the solid residue which was further extracted with light petroleum (50 c.c.). The combined light petroleum extracts were washed with N-sulphuric acid, then saturated sodium hydrogen carbonate solution, dried, and passed through deactivated alumina (40 g.) in the dark. The eluate (150 c.c.) had $\lambda_{max.}$ 2130, 2220, and 2350 Å. If we assume $\varepsilon = 300,000$ at 2350 Å,[1,2] the yield of 9,9-dimethyldeca-1,3,5,7-tetrayne was approximately 6%.

The eluate was concentrated to ~50 c.c. in the dark at 0° in nitrogen and under reduced pressure. Methanol (100 c.c.) was added and the solution was again concentrated, to ~30 c.c. Finally, the methanolic solution was added to a solution of cupric acetate (15 g.) in pyridine (45 c.c.) and water (40 c.c.) and set aside in the dark at 15—17° for 72 hr. After dilution with water, the product was isolated with ether; the ether solution was washed with N-sulphuric acid and aqueous sodium hydrogen carbonate and dried ($MgSO_4$). Removal of ether under reduced pressure left a brown solid which was purified by chromatography on deactivated alumina in the dark. The light petroleum (b. p. 30—40°) eluate, on evaporation, gave the expected *hydrocarbon* (IV) (40 mg., 4% based on the diol) which crystallised from light petroleum–methanol as yellow-brown needles, decomp. >130° (Found: C, 93·6; H, 6·35. $C_{24}H_{18}$ requires C, 94·05; H, 5·95%).

Attempts to obtain the tetrayne by dehydrohalogenation of the dichloride with milder reagents, *e.g.*, alkaline alumina,[10] triethylamine, or potassium ethoxide, were unsuccessful. In no case did the ether extract show detectable absorption characteristic of the tetrayne chromophore.

5,5-*Dimethylhexa*-1,3-*diyne*.—1,4-Dichloro-5,5-dimethylhex-2-yne (50 g.) was prepared and dehydrohalogenated with sodamide (from 21 g. of sodium in 400 c.c. of liquid ammonia) according to Bohlmann's procedure.[2] The product (20·5 g.) had b. p. 42—44°/50 mm. and $\lambda_{max.}$ 2265 (ε 1585) and 2355 Å (ε 1440). This was combined with the product from a similar preparation (26 g.; from 67 g. of the dichloride) and fractionated through a Dixon column (1 × 24 cm.), giving partial separation of two products, b. p. 34—35°/30 mm. (34·5 g.), n_D^{22} 1·4590—1·4610, $\lambda_{max.}$ 2365 Å (ε 1020—1810), and b. p. 50—58°/30 mm. (10 g.), n_D^{22} 1·4635—1·4648, $\lambda_{max.}$ 2365 Å (ε 7000). Repeated fractionation of the lower-boiling material gave the almost pure hydrocarbon (28·8 g.), becoming brown rapidly when kept, b. p. 34—35°/30 mm.,

n_D^{21} 1·4590—1·4600, $\lambda_{max.}$ 2150 (ε 330—380), 2250 (ε 430—450), 2365 (ε 400—450), and 2500 Å (ε 200—270), which was used for subsequent work. The higher-boiling material on refractionation afforded a sample, b. p. 52—53°/20 mm., n_D^{20} 1·4690, which had light-absorption maxima at 2265 (ε 11,000) and 2355 Å (ε 9300) characteristic of a vinylacetylene, and $\nu_{max.}$ (in CCl_4 and CS_2) (among others) 3300, 2100, 1600, 900, and 750 cm.$^{-1}$. On the above evidence and analytical data (Found: C, 67·1; H, 7·6; Cl, 25·6. $C_8H_{11}Cl$ requires C, 67·35; H, 7·75; Cl, 24·85%) the *compound* was believed to be 3- or 4-chloro-5,5-dimethylhex-3-en-1-yne (V).

6,6-*Dimethylhepta*-2,4-*diynal* (VI).—5,5-Dimethylhexa-1,3-diyne (5·6 g.) in dry ether (15 c.c.) was added at 15—17°, dropwise with stirring and under nitrogen, to a solution of ethylmagnesium bromide prepared from magnesium (1·6 g.) and a slight excess of ethyl bromide in ether (50 c.c.). The solution was heated under reflux for 1 hr., cooled, transferred under nitrogen to a dropping funnel, and added dropwise to a rapidly stirred solution of dimethylformamide (20 g.) in ether (40 c.c.) at −10°. The resulting complex was stirred and allowed to warm to 15—17° in 0·5 hr., and then poured into a stirred solution of 5% sulphuric acid (500 c.c.). The ethereal layer was separated, washed, and dried ($MgSO_4$). The aqueous layer was further covered with ether (100 c.c.) and set aside at 15—17° in the dark for 48 hr., giving a yellow ether layer which was separated, washed, dried, and combined with the ether solution above. After removal of the solvent under reduced pressure, distillation gave the expected[2] unstable aldehyde (VI), b. p. 40—43°/0·2 mm. (1·95 g., 30%), which darkened rapidly at 20°, $\lambda_{max.}$ 2300, 2450, 2580, 2715, and 2890 Å in EtOH.

11,11-*Dimethyldodeca*-1,4,7,9-*tetrayne*-3,6-*diol* (VII).—Ethylmagnesium bromide was prepared under nitrogen from magnesium (0·9 g.) and a slight excess of ethyl bromide in dry tetrahydrofuran (40 c.c.). While still warm, the Grignard solution was transferred under nitrogen to a dropping funnel and added dropwise at 20—25° to a stirred solution of penta-1,4-diyn-3-ol (1·4 g.) in dry tetrahydrofuran (30 c.c.). After an additional 2 hours' stirring, the brown solution was cooled in an ice-bath and treated with a solution of 6,6-dimethylhepta-2,4-diynal (2·0 g.) in tetrahydrofuran (10 c.c.). The mixture was stirred under nitrogen for a further 4 hr. at 15—17°, then cooled and decomposed with saturated ammonium chloride solution. The product was isolated with ether and purified by chromatography over deactivated alumina. From the ether eluate was obtained a light brown syrup (1·85 g., 58%) whose $\nu_{max.}$ (in CS_2 and CCl_4) indicated it to be essentially the expected diol. Ultraviolet absorption data, however ($\lambda_{max.}$ 2180, 2305, 2425, 2565, 2730, 2900, and 3075 Å), indicated the presence of contaminants; this material was therefore further purified by counter-current distribution between 30% aqueous ethylene glycol and 7 : 3 benzene–light petroleum (b. p. 40—60°). The pure glycol (VII), a light yellow syrup, showed $\lambda_{max.}$ (in MeOH) 2190 (ε 480), 2310 (ε 517), 2430 (ε 510), and 2565 Å (ε 312) and no absorption at longer wavelengths. It still resisted crystallisation.

2,2,23,23-*Tetramethyltetracosa*-3,5,7,9,11,13,15,17,19,21-*decayne* (X).—A mixture of thionyl chloride (2·5 g.) and pyridine (1·5 g.) in dry ether (10 c.c.) was added at 15—17° to a stirred solution of the diol (VII) (850 mg.) in dry ether (50 c.c.). After being stirred at 15—17° for 3 hr., the mixture was heated under reflux for 0·5 hr., cooled, and poured into ice and ether (200 c.c.). The ethereal solution was separated, washed with aqueous sodium hydrogen carbonate, and dried ($MgSO_4$).

Part of the ether solution (220 c.c. from a total of 280 c.c.) was passed through a column of alumina (200 g., Peter Spence's " Grade H ") in the dark. The ether eluate (400 c.c.) had $\lambda_{max.}$ 2595, 2465, 2340, and 2220 Å. On the basis of $\varepsilon = 400{,}000$ at 2595 Å, the yield of pentayne (IX) was ~17%. The ether eluate was concentrated in the dark under reduced pressure to ~150 c.c., ethanol (100 c.c.) was added, and the solution was again concentrated (to 100 c.c.). The ethanolic solution was finally added to a solution of cupric acetate in aqueous pyridine (400 c.c.; prepared from 92 g. of cupric acetate, 240 c.c. of pyridine, and 270 c.c. of water) and set aside in the dark at 15—17° for 72 hr. After dilution with excess of water, the product was extracted with ether (3 × 200 c.c.); the ethereal solution was washed to neutrality and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure gave a residue which was chromatographed in light petroleum on deactivated alumina. From the light petroleum eluate was obtained the *decayne* (X) [216 mg., 39% based on the diol (VII)] which crystallised from the same solvent as orange needles, decomp. *ca.* 100° (Found: C, 94·75; H, 5·05. $C_{28}H_{18}$ requires C, 94·9; H, 5·1%).

As the yield of decayne was greater than that of its nominal precursor, the pentayne, it was clear that the former was also being formed by the action of the Eglinton–Galbraith reagent on some other substance, most probably some unchanged dichloride. The remaining ether solution (60 c.c.) from the chlorination of the diol (VII) was therefore added to ethanol (100 c.c.), and the solution concentrated under reduced pressure in the dark (~50 c.c.). The ethanolic solution was added to a solution (125 c.c.) of cupric acetate in aqueous pyridine, as above, and set aside at 15—17° for 72 hr. Isolation and purification afforded the orange-coloured decayne [35 mg., 24% based on the diol (VII)].

Attempts to dehydrohalogenate the dichloride (VIII) [from the diol (VII)] with 0·05N-potassium hydroxide or aqueous potassium carbonate in ethanol were not successful. In the former case, the product after 30 min. had $\lambda_{\text{max.}}$ 3840, 3560, 3320, 3120, 2850, 2720, 2410, and 2280 Å. In the latter case, the product showed the same maxima and also additional bands, attributed to the pentayne chromophore, at 2595 and 2470 Å. When triethylamine was used as the dehydrohalogenating agent, light-absorption characteristics after 10 min. were suggestive of the presence of the ene-tetrayne chromophore.

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THE DYSON PERRINS LABORATORY, UNIVERSITY OF OXFORD. [*Received, February 9th,* 1960.]