Researches on Polyenes. Part III. The Synthesis and Light Absorption of Dimethylpolyenes.*

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[Reprint Order No. 6288.]

A general synthesis of dimethylpolyenes (I) is described [namely, reduction of the diols (II) with lithium aluminium hydride]; the ultraviolet absorption spectra observed are compared with predictions made by means of molecular-orbital calculations.

THE synthesis of the dimethylpolyenes (I), a series of especial interest in view of present theoretical attempts to correlate electronic absorption spectra with constitution, was attempted by R. Kuhn and Grundmann (*Ber.*, 1938, **71**, 442). They obtained the members where $n = 3$ and 4, and a concentrate of the compound (I; $n = 6$) for which the spectroscopic-intensity data (R. Kuhn, *Angew. Chem.*, 1937, **50**, 703) now suggest a purity of about 35%. Blout and Fields later (*J. Amer. Chem. Soc.*, 1948, **70**, 189) reported more accurate spectroscopic data for the two members (I; $n = 4$ and 6), prepared by Kuhn's method, and Bohlmann (*Chem. Ber.*, 1952, **85**, 386) reported a synthesis of the dodecapentaene (I; $n = 5$) and the preparation of material believed to contain the higher member (I; $n = 9$). [Data attributed by Barany, Braude, and Pianka (*J.*, 1949, 1898) to the compound where $n = 8$ apparently refer to dihydro-β-carotene.]

Bates, Jones, Nayler, and Whiting (unpublished work) found that 1 : 4-diphenylbut-2-yne-1 : 4-diol gave a moderate yield of 1 : 4-diphenylbuta-1 : 3-diene when treated with lithium aluminium hydride. The application of this method to glycols of type (II), which are easily accessible by one- or two-step condensation of acetylene with the well-known

(I) $CH_3\cdot[CH{=}CH]_n\cdot CH_3$ $CH_3\cdot[CH{=}CH]_a\cdot CH(OH)\cdot C{\equiv}C\cdot CH(OH)\cdot[CH{=}CH]_b\cdot CH_3$ (II)

polyene aldehydes, $CH_3\cdot[CH{=}CH]_a\cdot CHO$ (Heilbron, Jones, and Raphael, *J.*, 1944, 136; Cymerman, Heilbron, Johnson, and Jones, *J.*, 1944, 141), should give the dimethylpolyenes (I) more conveniently than earlier methods. Even the simplest glycol (II; $a = b = 0$) gave hexa-2 : 4-diene (*ca.* 11% yield, spectroscopically estimated and isolated as its maleic anhydride adduct and tetrabromide), together with other products. The next glycol (II; $a = 1, b = 0$) gave the triene in 32% yield, together with octa-4 : 6-diene-2 : 3-diol, presumably formed by anionotropic rearrangement of octa-3 : 6-diene-2 : 5-diol (Ahmad, Sondheimer, Weedon, and Woods, *J.*, 1952, 4089). In corresponding reactions, giving the tetraene and pentaene from the glycols (II; $a = b = 1$, and $a = 2, b = 1$, respectively) in yields of 25% and 15%, the more polar by-products were not investigated; the hydrocarbons were recrystallised to constant intensity of ultraviolet absorption maxima, the positions agreeing well with the results of Blout and Fields and of Bohlmann, respectively (*locc. cit.*). Approximate analytical data, and infrared absorption spectra (see below) consistent with structure (I), were also obtained. For the hexaene (I; $n = 6$) prepared from the diol (II; $a = b = 2$) in markedly reduced yield, it was not possible to reach constant $\varepsilon_{max.}$ values, although the very high intensities observed (see below) for the purest specimen implied that it was essentially pure.

The higher dimethylpolyenes, where $n = 5$ and 6, polymerise rapidly, even in nitrogen, and are sparingly soluble in organic solvents; it was clear that in attempts to extend the series beyond $n = 6$ the experimental difficulties of manipulation would increase rapidly, and it would be necessary to handle these compounds almost entirely as dilute solutions, relying on the characteristic ultraviolet absorption spectra for identification and estimation. A further handicap was the sharp diminution in the yield of dimethylpolyene obtained in the reduction, as n increased above 5. Condensation of the bisbromomagnesium derivative of octa-4 : 6-dien-1-yn-3-ol with octatrienal gave the glycol (II; $a = 3, b = 2$), which on reduction at 0° or 15° and chromatographic isolation of the non-polar fraction yielded a product, the absorption spectrum of which (see Fig. 1) indicated the presence of the

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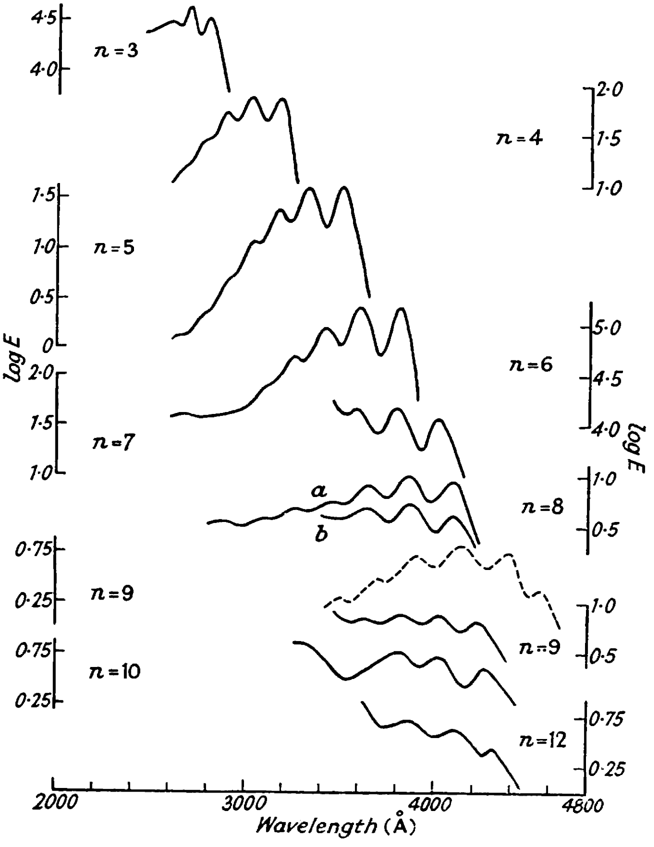
* Part II, *J.*, 1954, 4006.

heptaene (I; $n = 7$) as the component mainly responsible for the long-wavelength absorption. The more accessible symmetrical glycol (II; $a = b = 3$) gave, on isolation of the non-polar fraction, a solution from which an apparently crystalline solid was isolated. Its spectrum (Fig. 1) indicates that the octaene (I; $n = 8$) must have been almost the only soluble light-absorbing substance present, although the intensity implies that the content of this was probably only *ca.* 20% (a roughly linear extrapolation from the lower polyenes being assumed). Alternatively the specimen may have been nearly pure, but so sparingly soluble that much remained undissolved. At this point the belief that the non-polar substances responsible for the long-wavelength absorption were indeed the dimethylpolyenes was checked by condensing hex-2-en-5-yn-4-ol with dodeca-2 : 4 : 6 : 8 : 10-pentaenal: the glycol (II; $a = 5, b = 1$) was isolated chromatographically as a *ca.* 40% concentrate. On reduction it gave a non-polar fraction, the absorption bands of which agreed accurately with those observed for the reduction product of the diol (II; $a = b = 3$). The yield was much lower than from the symmetrical glycol.

FIG. 1. *Absorption spectra of dimethylpolyenes* (I) *in chloroform.*



- - - - From Bohlmann, *Chem. Ber.*, 1952, **85**, 386 (in benzene). (*a*) Prepd. from (II; $a = b = 3$). (*b*) Prepd. from (II; $a = 5, b = 1$).

(*N.B.* Except for $n = 3$ and $n = 6$, log E values are instrument readings, obtained with solutions of unknown concentration.)

For the preparation of the nonaene (I; $n = 9$), the glycol (II, $a = 5, b = 2$) was required. The Grignard reaction with dodeca-2 : 4 : 6 : 8 : 10-pentaenal was effected in tetrahydrofuran, and the desired product was obtained crystalline and essentially pure, although analytical data were, as usual with such polyenes, somewhat inaccurate. On reduction and isolation of the non-polar fraction a chloroform solution was obtained which showed sharp absorption bands at 3810, 4010, and 4195 Å, together with more intense absorption at shorter wavelengths. A more polar fraction, eluted from deactivated alumina only by ether, showed bands at 3780, 4080, and 4360 Å; these fractions darkened considerably when shaken with aqueous 2 : 4-dinitrophenylhydrazine hydrochloride solution, indicating the presence of conjugated carbonyl compounds. The curve published by Bohlmann (*loc. cit.*) for a product, obtained by treating docosa-2 : 4 : 6 : 8 : 12 : 14 : 16 : 18-octaene-10 : 11-diol (30 mg.) with phosphorus di-iodide, filtration through alumina, and recrystallisation from benzene–methanol, showed several maxima in benzene at up to 4360 and 4500 Å (see Fig. 1). This procedure might well give carbonyl compounds by pinacol-type dehydration, which would probably not be separated by the isolation procedure used; it is therefore not necessary to ascribe the longer-wavelength bands observed to the nonaene (I; $n = 9$). Our belief that the non-polar fractions obtained in the reduction of the diol (II; $a = 5$, $b = 2$) contained the nonaene (I; $n = 9$) depends upon analogy with the behaviour of lower members of the series of glycols (II), and upon the position of the absorption maxima in relation to those of the lower members of series (I), where constitution is securely established. The discrepancy with Bohlmann's results cannot, however, be explained by solvent effects, as benzene and chloroform give similar $\lambda_{\text{max.}}$ values in series (I) ($\Delta\lambda \not> 10$ Å).

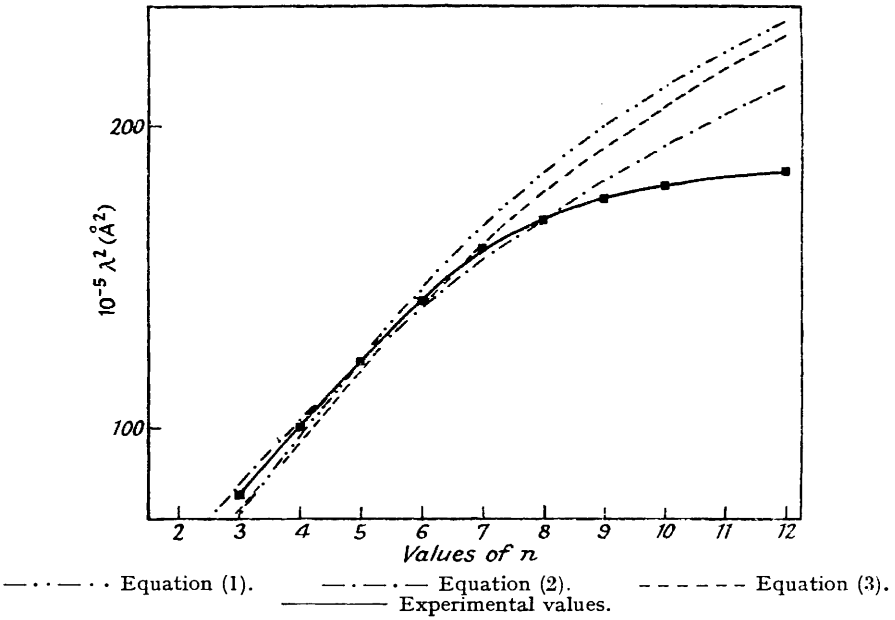
Condensation of dodeca-2 : 4 : 6 : 8 : 10-pentaenal with the bisbromomagnesium derivative of deca-4 : 6 : 8-trien-1-yn-3-ol gave the glycol (II; $a = 5$, $b = 3$) as a chromatographic concentrate of about 30% purity, easily recognised and assayed by the numerous absorption maxima corresponding to the chromophores present. Low-temperature reduction with lithium aluminium hydride and isolation of the non-polar portion of the benzene-soluble fraction (now a very small proportion of the total product, which was mainly polymeric) gave a solution with the spectrum shown (Fig. 1), which can fairly be attributed to the decaene (I; $n = 10$).

Preparation of the dodecaene (I; $n = 12$) would require the symmetrical glycol (II; $a = b = 5$). Attempts to obtain this from acetylenedi(magnesium bromide) failed; but an ethynylcarbinol was obtained from dodecapentaenal in low yield by using lithium acetylide. Treatment of its bisbromomagnesium derivative with dodecapentaenal gave a very sparingly soluble substance which from its infrared and ultraviolet absorption was the required glycol, plus some polymer. When it was reduced at —20°, and the non-polar fraction isolated, a solution was obtained which—in two experiments—showed a sharp absorption band at 4310 Å, as well as broader and more intense bands at about 4100 and 3870 Å (see Fig. 1). The first can be ascribed to the dodecaene (I; $n = 12$) in view of its position relative to the corresponding bands of the octaene and decaene. Vibrational sub-maxima of shorter wavelength should be of an intensity similar to, or smaller than, that of the longest-wavelength band [cf. results for the compounds (I; $n = 6$ or 8) or typical carotenoids], so the 4100 and 3870 Å bands must be due almost entirely to contaminants with a shorter polyene chromophore. For the same reason, the lower-wavelength bands of the other members of the series are, of course, distorted and increased in relative intensity where complete purification was impracticable.

Infrared results for the hydrocarbons (I; $n = 3$, 4, and 5) revealed in each case bands at 2900 cm.$^{-1}$, etc., and at 1380 and 1450 cm.$^{-1}$, attributable to the terminal methyl groups, and at 3000 cm.$^{-1}$ (olefinic C–H stretching). In the C=C stretching region, the strongest band was almost constant in position at 1640 cm.$^{-1}$, with weaker satellites at 1855, 1788, 1755, and 1672 cm.$^{-1}$ ($n = 3$), and 1875, 1817, 1722, and 1679 cm.$^{-1}$ ($n = 4$); the pentaene (I; $n = 5$) was insufficiently soluble for detection of such weak bands. The three polyenes differed somewhat in the olefinic C–H bending region, where the triene showed a sharp, intense band at 992 cm.$^{-1}$ and weaker bands at 958 and 916 cm.$^{-1}$; the tetraene showed a broad and strong band at 985 cm.$^{-1}$, another of comparable but lower intensity at 925 cm.$^{-1}$, and a sharp weak band at 940 cm.$^{-1}$; and the pentaene showed a strong, broad, complex band at 996 cm.$^{-1}$ with a relatively weak band at 926 cm.$^{-1}$. None absorbed at 660—750 cm.$^{-1}$, where *cis*-ethylenes have strong or medium absorption bands. The overall similarity of the spectra was unmistakable, and hydroxylic and carbonyl-containing contaminants were clearly absent.

Discussion.—The ultraviolet absorption spectra of the hydrocarbons (I), the main object of this work, are illustrated in Fig. 1. The octaene (I; $n = 8$) is important as bridging the gap between the well-defined and relatively tractable members of the series where $n = 2$—6, and the higher polyenes which were handled entirely in solution. The spectra for the members (I; $n = 7$, 9, and 10) are sufficiently complete and similar to that of the octaene for reasonable confidence to be placed in their authenticity; but that of the dodecaene (I; $n = 12$) is not, and relies for the acceptance of its 4310-Å maximum entirely on the smooth curve relating n and $\lambda_{\text{max.}}$ for the longest-wavelength band (Fig. 2). This shows clearly the breakdown of the Lewis–Calvin equation $\lambda^2 = kn$ (*Chem. Rev.*, 1939, **25**, 237) for polyenes (I) where $n > 6$. Series (I) converges much more sharply than the isoprenoid series $[CH{=}CMe{\cdot}CH{=}CH]_{\frac{1}{2}n}$ illustrated by the results of Karrer *et al.* (see Karrer and Eugster, *Helv. Chim. Acta*, 1951, **34**, 1805); one might estimate limiting wavelengths of 4500 and 6300 Å respectively in $CHCl_3$, or perhaps 4400 and 5900 Å in light petroleum.

FIG. 2. *Lewis-Calvin plot for longest-wavelength bands.*



Three equations have recently been deduced theoretically for differences in energy levels of conjugated polyenes, and hence electronic absorption spectra, as a function of the chain length. They are (n = number of double bonds):

$$\lambda = a\{1 - b\cos[\pi/(n-1)]\}^{-0\cdot5} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(W. Kuhn, *Helv. Chim. Acta*, 1948, **31**, 1780) where a and b are parameters, calculated to be $1{\cdot}57 \times 10^3$ and $0{\cdot}922$ respectively;

$$\lambda = 1{\cdot}23 \times 10^{-4}/[18{\cdot}8(2n+1)^{-1} + V_0(1 - \tfrac{1}{2}n^{-1})] \quad . \quad . \quad . \quad . \quad (2)$$

(H. Kuhn, *J. Chem. Phys.*, 1949, **17**, 1198), where V_0 is the only parameter, taken as 2·0; and

$$\lambda = D(1 - a^{2n-2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(Dewar, *J.*, 1952, 3544), where D and a are treated as parameters, and assigned values of 6352 and $2^{\frac{1}{2}}$ respectively.

Each author has claimed good agreement with " experimental values." It is difficult to discuss the (very impressive) agreement between equation (1) and 18 polyenes chosen to represent the latter, since these are not specified; four different empirical corrections were made to *n*, to allow for the effects of various end groups. Both H. Kuhn and Dewar (*locc. cit.*) assumed that the position of the absoprtion maximum was determined by the length of the polyene chain, and they neglected other environmental factors, *e.g.*, the numbers of alkyl substituents on the chromophore and of exocyclic double bonds (Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 72), and the presence of non-coplanar trimethyl*cyclo*hexenyl groupings (Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890; Oroshnik, Karmas, and Mebane, *J. Amer. Chem. Soc.*, 1952, **74**, 295) or of imperfectly insulated non-conjugated ethylenic linkages (Braude, *J.*, 1949, 1902). These factors, however, are not negligible; indeed, beyond a certain chain-length the positions of the absorption maxima of a polyene depend more upon the degree of substitution than upon the number of conjugated linkages. This approximation has resulted in a systematic error, in that both authors have chosen simple examples among the lower polyenes, but (of necessity) complex, highly alkylated examples of higher polyenes. Variations in the spectra of polyenes which differ in the respects indicated allow a considerable amount of freedom in the selection of experimental values to suit a given theoretical expression. In one case the arithmetical latitude has been increased through an error in the literature; Dewar (*loc. cit.*) used a number of wavelengths from a table by Karrer and Eugster (*loc. cit.*), but rejected that (4100 Å) given for dihydro-β-carotene in favour of another for the same substance (4200 Å; Braude, *Ann. Rep.*, 1945, **42**, 105) in better agreement with the calculated value of 4220 Å. Braude's value is, however, a mis-reading of the curve published by Karrer and Rüeger (*Helv. Chim. Acta*, 1940, **23**, 955), and later quoted correctly by Karrer and Eugster (*loc. cit.*).

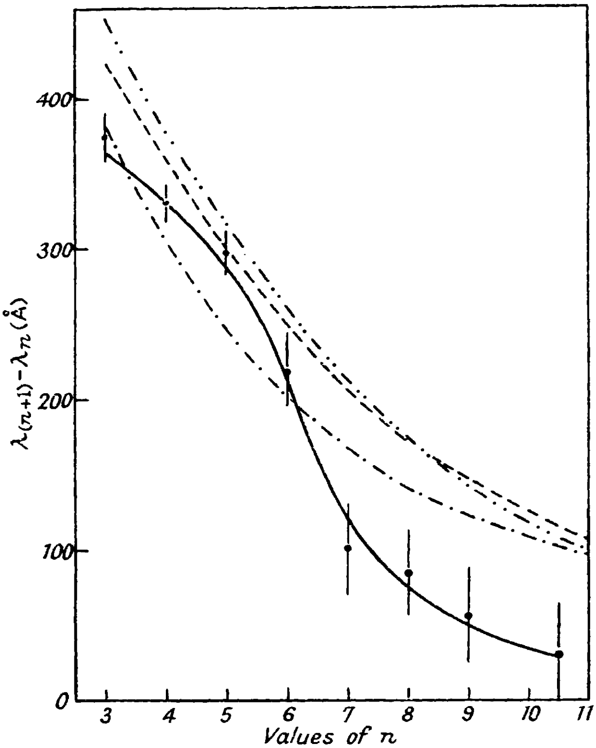


FIG. 3.

— • • — • • Equation (1).
— • — • — Equation (2).
- - - - - - Equation (3).
———— Experimental values.

An adequate experimental test of these theoretical equations clearly requires the examination of comparable substances under similar conditions; we believe that series (I) is the best yet available for this purpose. We have chosen, in Fig. 1, to plot the longest-wavelength band. This has the practical advantage of being the sharpest and most easily distinguished, and the theoretical advantage that it must represent the zero–zero transition as regards the main vibrational processes in the newly excited molecule and therefore measures directly the energy difference in question. The other bands are spaced at a constant value of about 1450 cm.$^{-1}$, which does not vary significantly between the triene (I; $n = 3$) and the octaene (I; $n = 8$); this spacing, characteristic for polyenes, is in fact complex, being the result of two superimposed intervals of 1570 and 1230 cm.$^{-1}$ according to Hausser, R. Kuhn, and Seitz (*Z. phys. Chem.*, 1935, *B*, **29**, 391). H. Kuhn and Dewar (*locc. cit.*) have considered the second vibrational band, which is usually (but see Mebane, *J. Amer. Chem. Soc.*, 1952, **74**, 5227) the most intense.

It is possible to plot λ or λ^2 against n directly; then all three theoretical curves resemble qualitatively that of the experimental results. A more searching test is given by the differential curve, in which $(\lambda_{n+1} - \lambda_n)$ is plotted against n (Fig. 3); an average value only is known for $(\lambda_{11} - \lambda_{10})$ and $(\lambda_{12} - \lambda_{11})$, and this is therefore shown. Even when allowance is made for possible experimental errors in the exact locations of absorption maxima, indicated by vertical lines, it is clear that the experimental results require a point of inflexion at about $n = 7$, not present in any of the theoretical curves. This qualitative difference suggests that attempts to recalculate parameters would not give values consistent over the entire range with any of the equations; in the case of equation (3) this can be demonstrated. Differentiating three times and equating with zero gives:

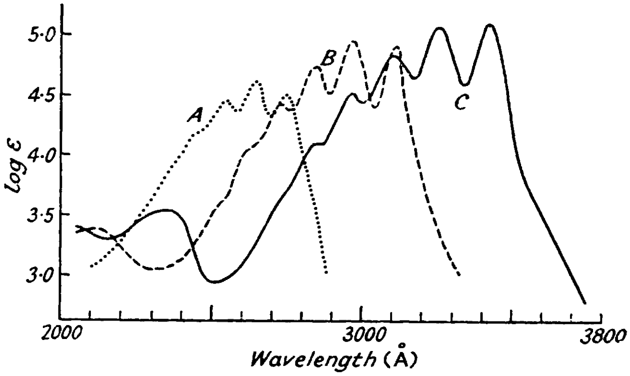


FIG. 4. *Absorption spectra of dimethylpolyenes (I) in hexane.*

A, $n = 3$; *B*, $n = 4$; *C*, $n = 5$.

$$d^3\lambda/dn^3 = 8D(\log_e a)^3 a^{-2n-2} = 0$$

a condition which is met only when $D = 0$, or $a = 1$, which substitutions lead to absurd results for finite values of n. It follows that no values of a and D can be found that permit a point of inflexion in the curve for $d\lambda/dn$ *versus* n.

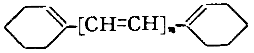
TABLE 1. *Absorption maxima of polyene series.*

n	(III) (hexane, etc.[a])		(I) (hexane)		(I) ($CHCl_3$)		(IV)	
	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε
3	2675	56 [b]	2745	30·2	2790	33·4 [g]	2810	35 [e]
4	3040	? [c]	3100	76·5	3165	? [h]		
5	3343	118 [d]	3410	122	3495	? [i]		
6	—	—	—	—	3800	146·5		
7	3900	? [d]	—	—	4010	—		
8	—	—	—	—	4110	—	4260	132 [f]

[a] In hexane, heptane, or *iso*octane. [b] Woods and Schwartzman, *J. Amer. Chem. Soc.*, 1948, **70**, 3394. [c] *Idem, ibid.*, 1949, **71**, 1396. [d] Mebane, *loc. cit.* [e] In EtOH. Burkhardt and Hindley, *J.*, 1938, 987. [f] In ether. Bohlmann, *Chem. Ber.*, 1951, **84**, 545. [g] $\lambda_{max.}$ 2745 Å, ε 30,200 in hexane. [h] $\lambda_{max.}$ 3100, ε 76,500 in hexane. [i] $\lambda_{max.}$ 3420, ε 122,000 in hexane.

Our values for series (I) (longest-wavelength band only) are tabulated (Table 1) for comparison with data recorded for series (III) and (IV), and accurate curves for the members (I; $n = 3$—5) in hexane are shown in Fig. 4. The tabulated results show a close similarity between series (I) and (III), but series (IV) must converge to a somewhat longer limiting wavelength. It should be noted that the value for the heptaene (III; $n = 7$) refers to a mixture of geometrical isomers and is thus not exactly comparable with other data for series (I) and (III).

(III) $H{\cdot}[CH{=}CH]_n{\cdot}H$


(IV)

The availability of accurate intensity data for the hydrocarbons (I; $n = 3$—6) has permitted the calculation of oscillator strength values, using the equation

$$f = 4{\cdot}31 \times 10^{-9}\int \varepsilon d\bar{\nu}$$

(Maccoll, *Quart. Rev.*, 1947, **1**, 46). In Table 2 these are given alongside the corresponding experimental values for the di-*tert.*-butylpoly-ynes and Bayliss's theoretical predictions (*ibid.*, 1952, **6**, 319). Bayliss quoted the consequence of the free-electron approximation for polyenes as

$$f = 0{\cdot}134(n + 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where n is the number of double bonds. It is clear that, although the order of magnitude is correctly predicted, the true relation between f and n is qualitatively different from that implied by equation (4). Attempts to use carotenoids for comparison with theoretical relations are particularly misleading for absorption *intensities*, since non-coplanarity of terminal 2 : 2 : 6-trimethyl*cyclo*hexenyl groupings introduces large negative errors, evident when the values for vitamin A (1·05) and the pentaene (I; $n = 5$) (1·66) are compared.

In contrast, the experimental results now reported support the very simple chromophore-area theory proposed by Braude (*J.*, 1950, 379), which requires essentially that f should show a linear increase with n, neglecting end-of-chain anomalies which would be most prominent with the lower polyenes. Even the proportionality constant is near to that derived from these geometrical considerations, approaching a value given by $\varepsilon_{\text{max.}} = 25{,}000n$ for the two longest-wavelength bands; this may be compared with the constant value of $72{,}000n$ approached by the dimethylpoly-ynes (Cook, Jones, and Whiting, *J.*, 1952, 2883) or *ca.* $85{,}000n$ for the di-*tert.*-butylpoly-ynes (Bohlmann, 1953, **86**, 63). In agreement with this theory also is the consistent ratio for the polyene and the poly-yne series, the downward trend presumably representing the diminution of end-effects. The limiting value would be of considerable interest, if it could be accurately determined; H. Kuhn's theoretical value of 2·66 (*loc. cit.*) seems definitely too high.

TABLE 2. *Oscillator strengths.*

	Dimethylpolyenes		Di-*tert.*-butyl-	
n	calc.	exp.	poly-ynes	Ratio
3	0·94	0·74	2·08	2·81
4	1·21	1·11	2·99	2·69
5	1·47	1·66	4·10	2·48
6	1·74	2·17	5·15	2·37

EXPERIMENTAL

Ultraviolet absorption spectra were obtained with a Unicam SP 500 or Beckman DU spectrophotometer, with 95% EtOH as solvent unless otherwise stated. Infrared absorption spectra were measured with a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. M. p.s were determined on a Kofler block and are corrected. Light petroleum refers to the fraction of b. p. 40—60°, alumina to " Grade H " (Peter Spence, Ltd.), and deactivation implies treatment with 5% (by wt.) of 10% acetic acid. Reactions involving the use of lithium aluminium hydride or Grignard reagents were carried out in purified dry nitrogen, and whenever compounds with more than four conjugated linkages were handled solvents were redistilled in nitrogen before use and air was excluded as far as possible in evaporation, chromatography, and crystallisation; ether, benzene, etc., were usually evaporated at or below room temperature.

Sorbaldehyde and octa-2 : 4 : 6-trienal were prepared by the method of R. Kuhn *et al.* (*Ber.*, 1930, **63**, 2164; 1936, **69**, 98), whose yields were approximately reproduced. The latter aldehyde was also made by Kuhn and Grundmann's technique (*Ber.*, 1937, **70**, 1318), but then considerable quantities of dihydro-*o*-tolualdehyde, not mentioned in this paper, were formed, and the yield of the trienal was much lower than claimed. The use of very pure piperidine (Davies and McGee, *J.*, 1950, 678) gave rather higher yields, and when the quantity of piperidine acetate was trebled the yield reached two-fifths of that reported. Schmitt and Overmeit's method (*Annalen*, 1941, **547**, 285) for preparing dodeca-2 : 4 : 6 : 8 : 10-pentaenal failed completely in our hands, violent reaction supervening. Blout and Fields (*loc. cit.*) described similar experiences with these self-condensation reactions, which are possibly very sensitive to impurities, present in piperidine and capable of inhibition or promotion of the catalyst (cf. R. Kuhn, *loc. cit.*).

Octa-4 : 6-dien-1-yn-3-ol.—A rapid stream of purified acetylene was passed into a stirred solution of lithamide (from 3·72 g. of lithium) in liquid ammonia (500 c.c.), contained in a vacuum-flask, until the formation of lithium acetylide was complete. A solution of sorbaldehyde (30 g.) in ether (100 c.c.) was added during 45 min. with slow passage of acetylene. The acetylene was replaced by nitrogen, and stirring continued for 1 hr. After decomposition with ammonium chloride (30 g.) and stirring for 30 min. the mixture was transferred to a beaker with the aid of ether (300 c.c.), covered with Cellophane, and protected from light. When all the ammonia had evaporated the residue was extracted with ether and the extracts were dried at 0° in the presence of quinol. Evaporation and distillation gave the *alcohol* (29·9 g., 79%), b. p. 50°/0·1 mm., n_D^{15} 1·5180 (Heilbron, Jones, and McCombie, *J.*, 1944, 134, give b. p. 71—4°/0·5 mm., n_D^{20} 1·5126).

Deca-4 : 6 : 8-trien-1-yn-3-ol.—This was prepared as above, from lithium (0·5 g.) in liquid ammonia (75 c.c.) and octa-2 : 4 : 6-trienal (4·0 g.) in ether (50 c.c.). Evaporation of the extract and crystallisation from light petroleum (b. p. 60—80°) gave the alcohol (3·5 g., 73%), m. p. 73° (Heilbron *et al.*, *loc. cit.*, give m. p. 73—74°).

Tetradeca-4 : 6 : 8 : 10 : 12-pentaen-1-yn-3-ol.—This was prepared as above from lithium (0·3 g.) in liquid ammonia (150 c.c.) and dodeca-2 : 4 : 6 : 8 : 10-pentaenal (1·0 g.) in tetrahydrofuran (75 c.c.). Crystallisation of the crude product from benzene–light petroleum gave the alcohol (0·8 g.). Light-absorption measurements indicated *ca.* 60% purity. A portion (0·12 g.) was chromatographed on alumina (50 g.). Elution with ether and crystallisation from light petroleum (b. p. 80—100°) gave fine yellow needles contaminated with amorphous polymer (50 mg.), decomp. above 100°. Light absorption : max., 3140, 3290, 3460 Å (ε 50,000, 71,500, 73,000) ; hence purity *ca.* 70%.

Dodeca-2 : 4 : 10-trien-7-yne-6 : 9-diol.—To a stirred solution of ethylmagnesium bromide (from 3·3 g. of magnesium) in benzene (250 c.c.) at 0° a solution of hex-4-en-1-yn-3-ol (Heilbron, Jones, and Weedon, *J.*, 1945, 81) (6·2 g.) in benzene (6 c.c.) was added and the mixture was stirred at 20° for 4 hr. After cooling to 0° a solution of sorbaldehyde (6 g. ; freshly distilled) in benzene (6 c.c.) was added dropwise and the yellow solution was stirred at 20° for 14 hr. The Grignard complex was decomposed with saturated ammonium chloride solution. Isolation with ether and removal of the solvents under nitrogen gave a crude product which was chromatographed on alumina (120 g. ; deactivated). Evaporation of the ether eluate gave an oil (3·1 g.) which on treatment with ether (2 c.c.) at 0° slowly crystallised, to give the *glycol* (2·5 g., 20%), obtained as needles, m. p. 80°, from benzene (Found : C, 74·6; H, 8·4. $C_{12}H_{18}O_2$ requires C, 74·9; H, 8·4%). Light absorption : max., 2300 Å (ε 28,000).

Hexadeca-2 : 4 : 6 : 12 : 14-pentaen-9-yne-8 : 11-diol.—To a stirred solution of ethylmagnesium bromide (from 3·0 g. of magnesium) in tetrahydrofuran (60 c.c.) at 0° a solution of octa-4 : 6-dien-1-yn-3-ol (7·1 g.) in tetrahydrofuran was added and the mixture was stirred at 20° for 2 hr. After cooling to 0° a solution of octa-2 : 4 : 6-trienal (7·1 g.) in tetrahydrofuran (40 c.c.) was added dropwise and the resulting red solution was stirred at 20° for 2 hr. After cooling to 0° the Grignard complex was decomposed with saturated ammonium chloride solution, and isolation with ether gave a red gum (13 g.) which was chromatographed in alumina (200 g. ; deactivated). Evaporation of the ether eluate and crystallisation from di*iso*propyl ether–pentane gave the *glycol* (3·7 g., 26%) as needles, m. p. 114—116° (Found : C, 77·7; H, 8·15. $C_{16}H_{20}O_2$ requires C, 78·65; H, 8·25%). Light absorption : max., 2305, 2690, 2790 Å (ε 33,800, 56,000, 45,000) ; infl. 2605 Å (ε 42,000).

Hydrogenation. The glycol (0·11 g.) in 95% ethanol (23 c.c.) was shaken in hydrogen in the presence of platinic oxide until absorption was complete : 70 c.c. were taken up at 26°/760 mm., corresponding to 7·0 mols.

Octadeca-2 : 4 : 6 : 8 : 10 : 16-hexaen-13-yne-12 : 15-diol.—To a solution of ethylmagnesium bromide (from 0·5 g. of magnesium) in tetrahydrofuran (25 c.c.) at 0° a solution of hex-4-en-1-yn-3-ol (0·9 g.) in tetrahydrofuran was added and the mixture was stirred at 20° for 5 hr. After cooling to 0° a solution of dodeca-2 : 4 : 6 : 8 : 10-pentaenal (1·7 g.) in tetrahydrofuran (75 c.c.) was added and stirring at 20° was continued for 14 hr. Decomposition as above and isolation with ether gave a yellow solid, which was chromatographed on alumina (100 g. ; deactivated).

Elution with benzene removed unchanged dodecapentaenal (0·3 g.), and elution with ether then gave a glycol fraction (0·4 g.), about 40% pure [max., 3020, 3140, 3300, 3460 Å (ε 16,800, 27,200 38,000, 37,000)].

Docosa-2 : 4 : 6 : 8 : 10 : 16 : 18-*heptaen*-13-*yne*-12 : 15-*diol, etc.*—The C_{20} diol was prepared as above, by using ethylmagnesium bromide (from 1·4 g. of magnesium), octa-4 : 6-dien-1-yn-3-ol (3·6 g.), and dodeca-2 : 4 : 6 : 8 : 10-pentaenal (5·0 g.). Isolation of the crude product with ether and repeated crystallisation from benzene gave the glycol (1·3 g.) as a pale yellow solid, decomp. >120° (Found : C, 77·7; H, 7·95. Calc. for $C_{20}H_{24}O_2$: C, 81·05; H, 8·15%), evidently about 80% pure [max., 2300, 3030, 3150, 3300, 3470 Å (ε 23,400, 25,200, 49,300, 76,000, 73,500)].

Dodocosa-2 : 4 : 6 : 8 : 10 : 16 : 18 : 20-octaen-13-yne-12 : 15-diol was prepared as above, by using ethylmagnesium bromide (from 0·4 g. of magnesium), deca-4 : 6 : 8-trien-1-yn-3-ol (1·3 g.), and dodeca-2 : 4 : 6 : 8 : 10-pentaenal (1·0 g.). Isolation of the crude product with ether gave a dark brown solid, which was chromatographed on alumina (50 g.; deactivated). Elution of the glycol fraction with ether gave a gum (0·3 g.) for which light-absorption data indicate *ca.* 30% purity, the rest of the material being mainly polymeric [max. 2580, 2660, 2770, 3020, 3160, 3280, 3460 Å (ε 15,500, 18,500, 17,200, 21,200, 26,700, 32,000, 32,000)].

Hexadocosa-2 : 4 : 6 : 8 : 10 : 16 : 18 : 20 : 22 : 24-decaen-13-yne-12 : 15-diol was prepared as above, from ethylmagnesium bromide (from 0·16 g. of magnesium), tetradeca-4 : 6 : 8 : 10 : 12-pentaen-1-yn-3-ol (0·6 g., *ca.* 60% pure), and dodeca-2 : 4 : 6 : 8 : 10-pentaenal (0·6 g.) with a reaction period of 2 hr. at room temperature. Isolation with ether gave an orange solid which on extraction with hot benzene gave unchanged dodecapentaenal, m. p. 160—163°, $\lambda_{max.}$ 3780 Å (ε 50,000). The residue on repeated crystallisation from ethyl acetate–light petroleum gave the glycol (200 mg.) for which light-absorption data indicate *ca.* 60% purity [max. 3070, 3200, 3360, 3520 Å (ε 39,400, 70,500, 104,000, 112,000)].

Hexa-2 : 4-*diene.*—Hex-3-yne-2 : 5-diol (7·0 g.) (Iositch, *Bull. Soc. chim. France*, 1904, **32**, 553) in ether (*ca.* 30 c.c.) was added to lithium aluminium hydride (7·0 g.) in ether (200 c.c.), and the mixture was heated under reflux for 6 hr. Cautious addition of water and dilute sulphuric acid gave an ether layer which was dried and concentrated through a short Fenske column to about 2 c.c. *cyclo*Hexane (4 c.c.) was added, and the liquid was distilled at atmospheric pressure to a bath-temperature of 100°. Hexa-2 : 4-diene was estimated spectroscopically in the distillate (cf. Booker, Evans, and Gillam, *J.*, 1940, 1453); the yield was 11%. Separate portions were treated with bromine, giving 2 : 3 : 4 : 5-tetrabromohexane, m. p. 180° (Reif, *Ber.*, 1908, **41**, 2744, gives m. p. 180°), and with maleic anhydride, giving 3 : 6-dimethyl-1 : 2 : 3 : 6-tetrahydrophthalic anhydride, m. p. 95—96° (Diels and Alder, *Annalen*, 1929, **470**, 102, give m. p. 96°).

Octa-2 : 4 : 6-*triene.*—Oct-6-en-3-yne-2 : 5-diol (4·0 g.), lithium aluminium hydride (3·2 g.), and ether (150 c.c.) were heated under reflux for 5 hr. Addition of aqueous tartaric acid and evaporation of the dried ether layer gave a residue which was extracted with light petroleum (b. p. 30—40°), which was then evaporated. Crystallisation of the residue twice from methanol gave octa-2 : 4 : 6-triene (1·0 g., 32%) as plates, m. p. 50° (slight decomp.) (Kuhn and Grundmann, *loc. cit.*, give m. p. 52°). Isolation of the more polar fraction from the aqueous phase and the petrol-insoluble residue, and distillation, gave *octa*-4 : 6-*diene*-2 : 3-*diol* (1·3 g., 32%), b. p. 100—105°/10^{-3} mm., n_D^{17} 1·5150 (Found : C, 67·65; H, 9·9. Calc. for $C_8H_{14}O_2$: C, 67·6, H, 9·95%). Light absorption : max. 2290 Å (ε 24,400) [Ahmad, Sondheimer, Weedon, and Woods, *loc. cit.*, give b. p. 80° (bath-temp.)/10^{-4} mm., n_D^{20} 1·5100, $\lambda_{max.}$ 2290 Å (ε = 25,500)]. Quantitative periodate oxidation by Jackson's method ("Organic Reactions," Vol. II, Wiley, New York, 1944, p. 341) indicated a vicinal glycol content of 95%; on a larger scale (0·2 g.), periodate oxidation, steam-distillation, conversion into 2 : 4-dinitrophenylhydrazones, separation by chromatography, and fractional crystallisation gave the derivatives of acetaldehyde (0·1 g., 35%), m. p. and mixed m. p. 167°, and sorbaldehyde (0·15 g., 40%), m. p. and mixed m. p. 192°.

Deca-2 : 4 : 6 : 8-*tetraene.*—Deca-2 : 8-dien-5-yne-4 : 7-diol (Heilbron, Jones, and Raphael, *J.*, 1943, 268) (4·7 g.), lithium aluminium hydride (4·5 g.), and ether (200 c.c.) were heated under reflux for 18 hr. and the product was isolated with ether and extracted with light petroleum. Evaporation, sublimation at 60—70° (bath-temp.)/10^{-1} mm., and crystallisation from ethanol gave the hydrocarbon (0·95 g., 25%), as needles, m. p. 115° (decomp.) [Kuhn and Grundmann, *loc. cit.*, give m. p. 125° (sealed tube)].

Dodeca-2 : 4 : 6 : 8 : 10-*pentaene.*—The preparation was carried out as above from dodeca-2 : 4 : 10-trien-7-yne-6 : 9-diol (1·25 g.) and lithium aluminium hydride (1·0 g.) with a reaction period of 24 hr. Evaporation of the light petroleum (b. p. 60—80°) extracts gave a solid (0·4 g.). Sublimation of a portion (0·1 g.) at 60—70° (bath-temp.)/10^{-3} mm. and repeated crystallisation from ethanol gave the hydrocarbon (0·05 g., 15%) as minute cream leaflets, m. p. 150° (decomp.), which rapidly polymerised (Bohlmann, *loc. cit.*, gives m. p. 155°) (Found: C, 88·6; H, 10·0. Calc. for $C_{12}H_{16}$: C, 89·95; H, 10·05%).

Tetradeca-2 : 4 : 6 : 8 : 10 : 12-*hexaene*.—This was prepared as above from tetradeca-2 : 4 : 10 : 12-tetraen-7-yne-6 : 9-diol (Heilbron, Jones, and Raphael, *loc. cit.*, 1944) (2·5 g.) in tetrahydrofuran (50 c.c.), and lithium aluminium hydride (2·5 g.) in ether (200 c.c.), with a reaction period of 4 hr. at 20°. The residue after evaporation of the ethereal extracts was extracted with benzene and the extracts were filtered through alumina. Evaporation of the benzene gave a solid (1 g.). Sublimation of a portion (0·4 g.) at 120° (bath-temp.)/10^{-5} mm. and crystallisation from ethanol gave the hydrocarbon (0·025 g.) as pale yellow plates, m. p. *ca.* 200° (decomp.) [Kuhn and Grundmann, *loc. cit.*, give m. p. 205° (evacuated tube)].

Hexadeca-2 : 4 : 6 : 8 : 10 : 12 : 14-*heptaene*.—The preparation was carried out as above, from hexadeca-2 : 4 : 10 : 12 : 14-pentaen-7-yne-6 : 9-diol (2·0 g.) in tetrahydrofuran (100 c.c.), and lithium aluminium hydride (2·0 g.), with a reaction period of 4 hr. at 0°, the solution becoming deep green. The residue after evaporation of the ethereal extracts was extracted with benzene, and the extract chromatographed on alumina. The benzene eluate was evaporated and the residue taken up in chloroform, to give a concentrate of the hydrocarbon ($\lambda_{max.}$ 3605, 3800, 4010 Å in $CHCl_3$). A second experiment gave a concentrate with max. at 3610, 3820, and 4020 Å.

Octadeca-2 : 4 : 6 : 8 : 10 : 12 : 14 : 16-*octaene*.—(*a*) The preparation was carried out as above, from octadeca-2 : 4 : 6 : 12 : 14 : 16-hexaen-9-yne-8 : 10-diol (Heilbron, Jones, and Raphael, *loc. cit.*, 1944) (0·4 g.) in tetrahydrofuran (25 c.c.), and lithium aluminium hydride (0·4 g.) in ether (60 c.c.), with a reaction period of 4 hr. at 20°. Evaporation of the ethereal extracts gave a residue which was warmed with ether, and the solution was passed through alumina (30 g.). Evaporation of the pale yellow filtrate and extraction with cold benzene (20 c.c.) gave a solution which was concentrated by blowing nitrogen over the surface; the hydrocarbon was precipitated as an apparently crystalline solid (3·7 mg.). Light-absorption data indicate that it was at least 20% pure [max. 3470, 3660, 3870, 4110 Å (ε 22,000, 31,000. 40,000, 35,200 in $CHCl_3$)].

(*b*) The preparation was carried out as above, from octadeca-2 : 4 : 6 : 8 : 10 : 16-hexaen-13-yne-12 : 15-diol (0·4 g., 40% pure) in tetrahydrofuran (50 c.c.), and lithium aluminium hydride (0·4 g.) in ether (50 c.c.), with a reaction period of 5 hr. Working up gave a hydrocarbon concentrate showing $\lambda_{max.}$ 3650, 3870, 4120 Å in $CHCl_3$.

Docosa-2 : 4 : 6 : 8 : 10 : 12 : 14 : 16 : 18-*nonaene*.—The preparation was carried out as above, using docosa-2 : 4 : 6 : 8 : 10 : 16 : 18-heptaen-13-yne-12 : 15-diol (1 g.; 80% pure) in tetrahydrofuran (50 c.c.), and lithium aluminium hydride (0·7 g.) in tetrahydrofuran (100 c.c.), with a reaction period of 1 hr. at −20°. The ethereal extracts were concentrated to small volume, benzene (80 c.c.) was added, and the solution was washed with water three times to remove tetrahydrofuran. The dried benzene solution was chromatographed on alumina (30 g.; deactivated). The benzene eluate was concentrated to half its volume and methanol (30 c.c.) was added. After concentration to 4 c.c., a further quantity of methanol (30 c.c.) was added and the solution was again concentrated to 4 c.c. Water (15 c.c.) was then added and the solution was extracted with hexane (10 c.c.). The hexane solution was evaporated nearly to dryness and the residue was taken up in chloroform. The solution showed light absorption with maxima at 3630, 3810, 4010 and 4195 Å. Elution of the more polar fractions with ether and evaporation nearly to dryness gave a yellow residue, $\lambda_{max.}$ 3780, 4080, 4300 Å in $CHCl_3$, which darkened when shaken in benzene with aqueous 2 : 4-dinitrophenylhydrazine hydrochloride.

Dodocosa-2 : 4 : 6 : 8 : 10 : 12 : 14 : 16 : 18 : 20-*decaene*.—The preparation was carried out as above, from dodocosa-2 : 4 : 6 : 8 : 10 : 16 : 18 : 20-octaen-13-yne-12 : 15-diol (0·3 g., 30% pure) in tetrahydrofuran (20 c.c.), and lithium aluminium hydride (0·5 g.) in ether (60 c.c.), with a reaction period of 4 hr. at 20°. Evaporation of the ethereal extract, extraction of the residue with benzene, and chromatography on alumina (20 g.) gave a hydrocarbon fraction which on concentration and extraction with chloroform gave a solution showing light absorption with maxima at 3840, 4040, and 4250 Å.

Hexadocosa-2 : 4 : 6 : 8 : 10 : 12 : 14 : 16 : 18 : 20 : 22 : 24-*dodecaene*.—The preparation was carried out as above, from hexadocosa-2 : 4 : 6 : 8 : 10 : 16 : 18 : 20 : 22 : 24-decaen-13-yne-12 : 15-diol (0·2 g., 50% pure) in tetrahydrofuran (20 c.c.), and lithium aluminium hydride (0·2 g.) in tetrahydrofuran (25 c.c.), with a reaction period of 1 hr. at −20°. Evaporation of the tetrahydrofuran and ethereal extracts and extraction with ether, followed by chromatography on alumina (20 g.), gave a hydrocarbon fraction which on concentration and extraction with chloroform showed maxima at 3870, 4100, and 4310 Å. A second experiment gave a concentrate with maxima at 3850, 4120, and 4310 Å.

The authors thank Professor E. R. H. Jones, F.R.S., for his interest and advice. They are indebted to the Department of Scientific and Industrial Research for a Maintenance Grant to one of them (P. N.), to Messrs. E. S. Morton and H. Swift for microanalyses, and to Miss W. Peadon and Mrs. J. Hopkins for infrared absorption spectra.

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[*Received, April* 1*st*, 1955.]