

pected to be rather rigid, and a preliminary examination of its n.m.r. spectrum aroused interest, it was included in this study.

The most interesting aspect of the spectrum (Fig. 6) is the unusually low-field signal at  $-95$  c./s. which is attributed to the bridgehead protons. The direction of shift corresponds to that of the cyclohexane equatorial protons, but the magnitude of the shift (1.0 p.p.m.) is unexpected. Calculations (Table I) based upon the anisotropy of the C-C bond resulted in the chemical shifts (p.p.m.) indicated in Fig. 7. Although the calculated shift of 0.6 p.p.m. is only about half of the observed shift, the low-field position of the bridgehead protons is qualitatively explained. Because of the ring strains and non-bonded interactions of the protons below the planes of the ring, it is very likely that the shape of the five-membered rings and the bond angles are appreciably different from those assumed for the

model. Additionally, changes of bond angles and bond lengths will alter electron densities and hybridization.

It is evident that the carbon skeleton of *cis*-bicyclo[3.3.0]octane is quite rigid; otherwise there would be little resolved structure in the n.m.r. spectrum.

It is probable that only the  $\beta$ -methylene groups enter appreciably into the puckering motions of the rings.

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[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

## Unsaturated Macrocyclic Compounds. XVII.<sup>1</sup> The Prototropic Rearrangement of Linear 1,5-Enynes to Conjugated Polyenes. The Synthesis of a Series of Vinylogs of Butadiene

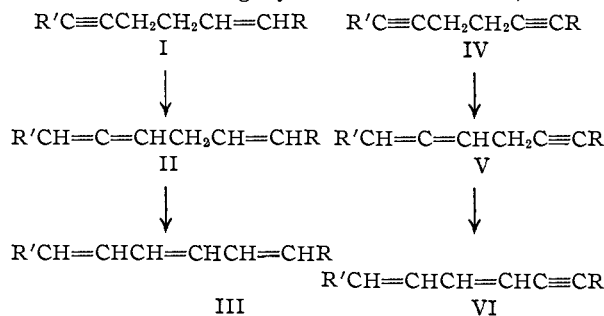
BY FRANZ SONDHEIMER, DAVID A. BEN-EFRAIM AND REUVEN WOLOVSKY

RECEIVED NOVEMBER 9, 1960

It is shown that 1,5-enynes are rearranged to conjugated polyenes by means of potassium *t*-butoxide in *t*-butyl alcohol. The method is used for the synthesis of a series of vinylogs of butadiene, containing 3, 5, 6, 8 and 10 conjugated double bonds. The ultraviolet spectra data of this simplest possible class of conjugated polyene are discussed briefly.

Large-ring compounds containing  $\alpha,\gamma$ -diacetylene units have recently become available through the oxidative coupling of aliphatic  $\alpha,\omega$ -diacetylenes.<sup>3</sup> These highly unsaturated cyclic substances promised to be suitable intermediates for the synthesis of completely conjugated cyclic polyenes, systems which are of considerable theoretical interest.

For instance if 1,5-enyne units (I) could be introduced into a ring by the above method, it was



(1) For Part XVI, see F. Sondheimer, Y. Gaoni and J. Bregman, *Tetrahedron Letters*, **26**, 25 (1960). Although the present paper and the subsequent one<sup>2</sup> are concerned only with acyclic compounds, they have been included in this series since reactions are described which served as models for analogous ones applied subsequently in the macrocyclic series.

(2) F. Sondheimer, D. A. Ben-Efraim and Y. Gaoni, *J. Am. Chem. Soc.*, **83**, 1682 (1961).

(3) F. Sondheimer, et al., *ibid.*, **78**, 4178 (1956); **79**, 4247, 5817, 6263 (1957); **81**, 4600, 6301 (1959); G. Eglinton and A. R. Galbraith, *Chemistry & Industry*, 737 (1956); *J. Chem. Soc.*, 889 (1959).

considered possible that subsequent base treatment would result in rearrangement *via* the allenes II to 1,3,5-trienes III with the consequent formation of a completely conjugated cyclic polyene. Alternatively a cyclic substance incorporating 1,5-diyne units (IV) might be isomerized *via* the allenes V to a conjugated system containing 1,3-dien-5-yne units (VI), which could then be hydrogenated to a conjugated cyclic polyene. In fact this second route to the latter class of compound has proved to be realizable, as described so far in preliminary reports.<sup>4</sup>

Before studying the rearrangement of I to III and IV to VI in the cyclic series, it was decided first to work with more accessible linear models. Related isomerizations of acids of type I and IV where R = COOH to conjugated polyene and polyenyne acids by means of potassium hydroxide had been carried out previously.<sup>5</sup> It was not known however whether removal of the conjugating influence of the carboxylic acid grouping would not cause the rearrangements to proceed differently or to require such drastic conditions as to result in polymerization of the products. Indeed the fact that a number of hydrocarbons of type I and IV had been prepared by dehydrohalogenation of halo-compounds with alcoholic potassium hydrox-

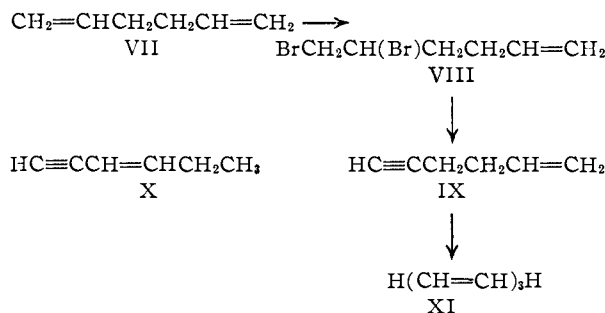
(4) F. Sondheimer and R. Wolovsky, *J. Am. Chem. Soc.*, **81**, 1771, 4755 (1959); *Tetrahedron Letters*, No. 3, 3 (1959); F. Sondheimer, R. Wolovsky and Y. Gaoni, *J. Am. Chem. Soc.*, **82**, 754, 755 (1960).

(5) E. R. H. Jones, B. L. Shaw and M. C. Whiting, *J. Chem. Soc.*, 3212 (1954); B. L. Shaw and M. C. Whiting, *ibid.*, 3217 (1954).

ide at *ca.* 100° or above<sup>6</sup> as well as the finding that the equilibration between 1-alkynes, 1,2-allenes and 2-alkynes requires heating with alcoholic potassium hydroxide in the 125–175° region<sup>7</sup> indicated the need for vigorous conditions if potassium hydroxide were employed.

It has been found that linear 1,5-enyne (I) and 1,5-diyne (IV) hydrocarbons can in fact be isomerized conveniently to the fully conjugated systems by means of potassium *t*-butoxide in *t*-butyl alcohol, the prototropic rearrangements presumably proceeding *via* the allenes as shown. In this paper we describe the synthesis of a number of conjugated polyenes (vinylogs of butadiene) from 1,5-enynes, while the corresponding synthesis of conjugated polyen-yne from 1,5-diyne is reported in the following paper.<sup>2</sup>

The first substance investigated was 1-hexen-5-yne (IX), prepared previously from allylacetone by treatment with phosphorus pentachloride and subsequent dehydrohalogenation<sup>8a</sup> as well as from allyl bromide by reaction with "propargylmagnesium bromide."<sup>8</sup> In our hands it was obtained most conveniently from biallyl (VII)<sup>9</sup> by treatment with less than one molar equivalent of bromine, followed by dehydrobromination of the resulting 1,2-dibromo-5-hexene (VIII) with sodamide in liquid ammonia. The product is assigned structure IX in view of the elemental analysis, the result



of silver nitrate titration which showed that almost exactly one acetylenic hydrogen function was present, and the infrared spectrum which indicated the existence of terminal acetylene and ethylene groupings. The ultraviolet spectral data [ $\lambda_{\text{max}}^{\text{isooctane}}$  223  $\mu$  ( $\epsilon$  1100)] however pointed to the presence of *ca.* 8% of a contaminant containing a conjugated enyne grouping, most probably 3-hexen-1-yne (X)<sup>10</sup> formed by isomerization of the double bond during the sodamide treatment. The pres-

(6) See (a) L. Henry, *Jahresbericht Fort. Chem.*, 380 (1878); *Compt. rend.*, 87, 171 (1878); (b) L. Henry, *Ber.*, 6, 956 (1873); Griner, *Ann. chim. (Paris)*, [6] 26, 347 (1892); R. Lespieau, *ibid.*, [8] 27, 152 (1912).

(7) See T. L. Jacobs, R. Akawie and R. G. Cooper, *J. Am. Chem. Soc.*, 73, 1273 (1951), and references to earlier work quoted there.

(8) L. Groizeleau-Miginiac, *Compt. rend.*, 248, 1190 (1959). This investigator showed that the reaction yields mainly the allene 1,2,5-hexatriene, from which IX was separated *via* the copper derivative. We had independently studied the condensation between allylmagnesium bromide and propargyl bromide. Although IX, and no allene, was produced in this reaction as indicated by the infrared spectrum, a bromine-free product could not be obtained despite careful fractional distillation.

(9) A. Turk and H. Chanan, "Org. Syntheses," Coll. Vol. 3, 121 (1955).

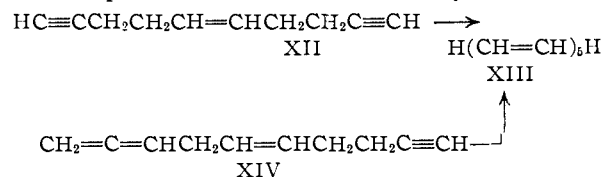
(10) J. L. H. Allan and M. C. Whiting (*J. Chem. Soc.*, 3314 (1953)) give  $\lambda_{\text{max}}$  222.5  $\mu$  ( $\epsilon$  14,000) for *trans*-3-penten-1-yne and  $\lambda_{\text{max}}$  221.5  $\mu$  ( $\epsilon$  14,500) for *cis*-3-penten-1-yne.

ence of this impurity, which was confirmed by the coupling results described below, is of no consequence for our purposes.

1-Hexen-5-yne (IX) thus produced on treatment with a concentrated solution of ethanolic potassium hydroxide at 65–70° was isomerized to 1,3,5-hexatriene (XI) as indicated by the appearance of the typical ultraviolet maxima at 248, 257 and 268  $\mu$ .<sup>11</sup> The optimum yield, arrived at after 3 hours, was, however, only *ca.* 4% (determined spectroscopically) and other bases were therefore investigated. The best results were obtained when *ca.* 40 parts of a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol at 65–70° was employed, the spectroscopic yield of XI after 3 hours (the optimum time) being *ca.* 40%. In a preparative experiment under these conditions, in which terminal acetylenes were removed as the silver derivative, 1,3,5-hexatriene of fair purity could be isolated by distillation. The ultraviolet spectrum of this material is set out in Table I and Fig. 1. The infrared spectrum exhibited the bands characteristic of *trans*- as well as of *cis*-hexatriene<sup>12</sup> and both isomers have clearly been formed, although no quantitative study of the isomer ratio was made.

In view of these results, it was decided to employ the potassium *t*-butoxide isomerization method for the synthesis of higher vinylogs of butadiene.

A suitable starting material for 1,3,5,7,9-decapentaene (XIII) appeared to be *trans*-5-decene-1,9-diyne (XII), the synthesis of which is described elsewhere.<sup>12,13</sup> Treatment with a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol at



*ca.* 75° resulted in the appearance of ultraviolet maxima at 290, 303, 317 and 334  $\mu$ , characteristic of the pentaene XIII.<sup>14</sup> The maximum yield, determined spectroscopically, was 16% and was reached after about 2 hours.<sup>13</sup> A preparative experiment was carried out under the optimum conditions and the product was purified by chromatography and crystallization. The resulting all-*trans*-decapentaene (XIII), isolated in 9% yield, showed virtually the identical melting point, infrared spectrum and ultraviolet spectrum (Table I and Fig. 1) as reported previously for this substance obtained in 5% yield from 5-chloro-1,3-pentadiene.<sup>14</sup> Attempted isomerization of XII with hot alcoholic potassium hydroxide gave no trace of the pentaene XIII.

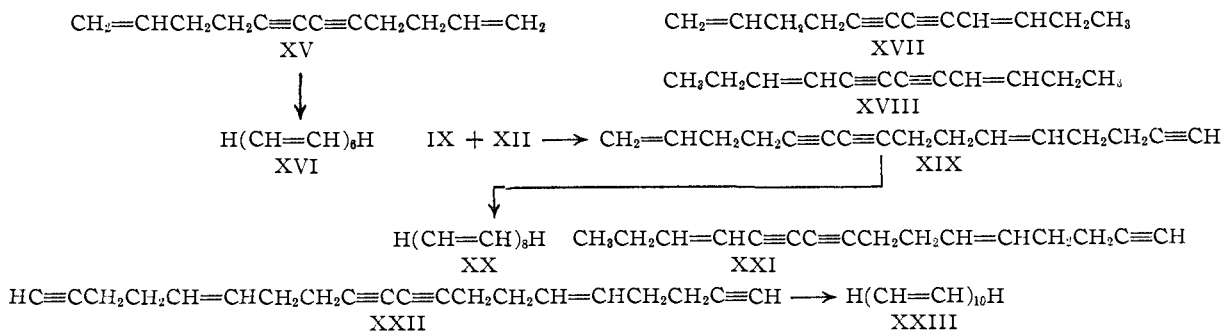
The allene 1,2,5-decatrien-9-yne (XIV)<sup>12</sup> was also subjected to rearrangement with potassium *t*-

(11) *Inter al.*, (a) G. F. Woods and L. H. Schwartzman, *J. Am. Chem. Soc.*, 70, 3394 (1948); (b) K. Alder and H. von Brachel, *Ann.*, 608, 195 (1957); (c) J. C. H. Hwa, P. L. de Benneville and H. J. Sims, *J. Am. Chem. Soc.*, 82, 2537 (1960).

(12) F. Sondheimer, R. Wolovsky and D. A. Ben-Efraim, *ibid.*, 83, 1086 (1961).

(13) For a preliminary communication, see F. Sondheimer, R. Wolovsky and Y. Gaoni, *ibid.*, 83, 755 (1960).

(14) A. D. Mebane, *ibid.*, 74, 5227 (1952).



butoxide and was found to produce the pentaene XIII in about the same yield as did XII. This result provides evidence that the rearrangement of 1,5-enynes to conjugated polyenes does indeed proceed *via* the allenes.

We next turned our attention to the synthesis of the previously unknown 1,3,5,7,9,11-dodecahexaene (XVI). To this end, the above-described 1-hexen-5-yne (IX) was coupled oxidatively by means of oxygen in the presence of ammonium chloride and cuprous chloride. The ultraviolet spectrum (see Experimental) of the resulting 1,11-dodecadiene-5,7-diyne (XV) showed it to be contaminated with *ca.* 10% of a conjugated ene-diyne and 1% of a conjugated ene-diyne-ene; these are probably 1,9-dodecadiene-5,7-diyne (XVII) and 3,9-dodecadiene-5,7-diyne (XVIII), respectively, derived from the previously mentioned 3-hexen-1-yne (X) impurity in the starting material IX.

Rearrangement of XV with potassium *t*-butoxide in *t*-butyl alcohol under the optimum conditions (1 hour at 65–70°) gave rise to *ca.* 10% of the hexaene XVI, determined spectroscopically and estimated subsequently. Analytically pure XVI was obtained as an unstable substance by direct crystallization or after chromatography. The structure follows from the ultraviolet spectrum (Table I and Fig. 1) which is of the same type as the pentaene XIII, with each of the maxima shifted by 2500 ( $\pm 30$ )  $\text{cm}^{-1}$  toward the red and the intensities increased. Moreover the relative  $\epsilon$ -values parallel those of the lower vinylog, the highest wave length band being the most intense. These facts, taken together with the infrared spectrum which closely resembles that of the pentaene XIII, also show that like the latter<sup>14</sup> the crystalline hexaene possesses the all-*trans* configuration.

The highest vinylog of butadiene known previously was 1,3,5,7,9,11,13-tetradecaheptaene, a compound which could no longer be isolated in the pure form.<sup>14</sup> The next higher member, 1,3,5,7,9,11,13,15-hexadeca-octaene (XX), has now been prepared in the following way.

Oxidative coupling as above of an equimolar mixture of 1-hexen-5-yne (IX) and *trans*-5-decene-1,9-diyne (XII), followed by chromatography, yielded 25% of the mixed product, *trans*-1,11-hexadecadiene-5,7,15-triyne (XIX). The ultraviolet spectrum of this substance (see Experimental) showed that it was contaminated with *ca.* 5% of 5,13-hexadecadiene-1,9,11-triyne (XXI), formed from X and XII. In addition the symmetrical products XV (admixed with XVII and

XVIII, as previously) as well as XXII<sup>12,13</sup> could be isolated.

Treatment of the mixed coupling product XIX with potassium *t*-butoxide in *t*-butyl alcohol at 65–70° effected the desired rearrangement, as evidenced by the appearance of ultraviolet maxima compatible with the octaene structure XX. The optimum yield, obtained after 1 hour, was *ca.* 2.5% (determined spectroscopically). Chromatographic purification and crystallization yielded the very unstable yellow-orange polyene XX, the ultraviolet spectrum of which is recorded in Table I<sup>15</sup> and Fig. 1.

The highest conjugated polyene of the butadiene type prepared was 1,3,5,7,9,11,13,15,17,19-eicosa-decaene (XXIII). The required precursor, *trans-trans*-5,15-eicosadiene-1,9,11,19-tetrayne (XXII), has been obtained by the coupling of *trans*-5-decene-1,9-diyne (XII) with oxygen in the presence of cuprous chloride and ammonium chloride, a reaction which may also lead to smaller amounts of the linear "trimer" XXIV and the corresponding "tetramer."<sup>12</sup> The rearrangement of XXII with potassium *t*-butoxide in *t*-butyl alcohol at 65–70° was carried out as previously and the product was chromatographed. The fractions with spectral properties compatible with the presence of the decaene XXIII on crystallization yielded this orange polyene<sup>13</sup> with ultraviolet data set out in Table I and Fig. 1. No intensity values were obtained in this case, in view of the extreme instability of the substance in the solid state.

TABLE I  
ULTRAVIOLET MAXIMA OF CONJUGATED POLYENES OF TYPE XXVI IN ISO-OCTANE

n	$\lambda_{\text{max}}$ in $\text{m}\mu$ ; $\epsilon$ -values $\times 10^{-3}$ in parentheses				
		A	B	C	D
3	240(19.2) <sup>a</sup>	248(30.5)	257(42.7)	268(34.6)	
4 <sup>b,c</sup>	267	278	290	304	
5	279(18.5) <sup>a</sup>	290(37.1)	303(71.2)	317(115)	334(121)
6	300(15.3) <sup>a</sup>	313(37.3)	328(73.2)	344(127)	364(138)
7 <sup>14,d</sup>	316(4.5) <sup>a</sup>	332(9.5)	350(20.0)	368(33.0)	390(36.0)
8 <sup>15</sup>	332(15.2) <sup>a</sup>	349(35.8)	367(72.8)	386(112)	410(108)
10 <sup>e</sup>	358 <sup>a</sup>	376	397	420	447

<sup>a</sup> Infection. <sup>b</sup> G. F. Woods and L. H. Schwartzman, *J. Am. Chem. Soc.*, 71, 1396 (1949). <sup>c</sup> In cyclohexane. <sup>d</sup> This substance was impure;  $\epsilon$ -values have been read from the curve. <sup>e</sup> For relative intensity values, see Table II.

Finally an attempt was made to prepare the pentadecaene XXV by potassium *t*-butoxide rearrangement of XXIV, the linear "trimer" of *trans*-5-decene-1,9-diyne (XII).<sup>12</sup> Careful chromatog-

(15) The comparatively low intensity values are probably due to some decomposition having occurred during the weighing process.

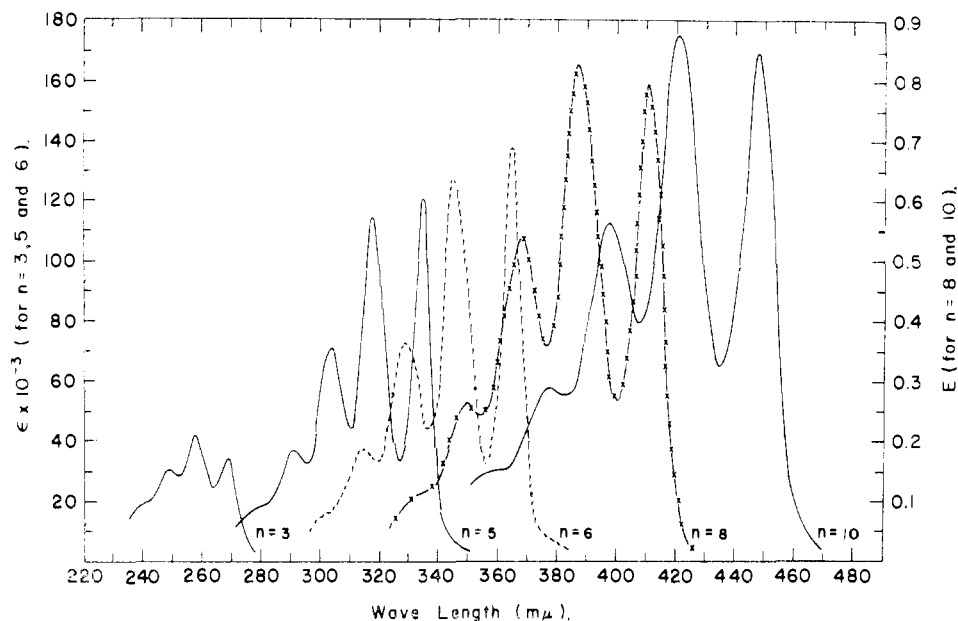


Fig. 1.—Ultraviolet absorption spectra of the conjugated polyenes of type XXVI prepared in this paper (in iso-octane).

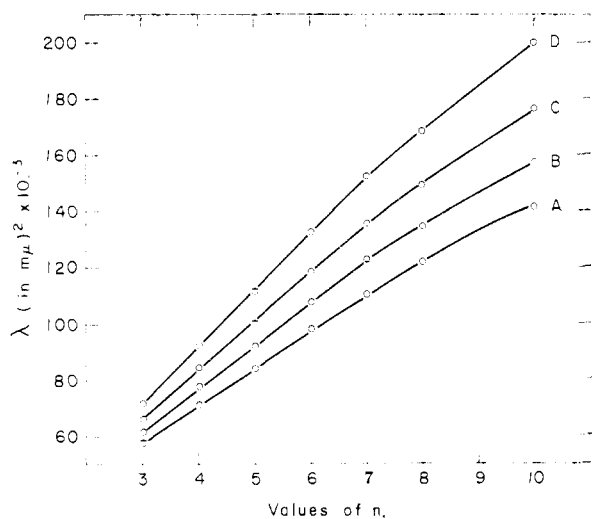
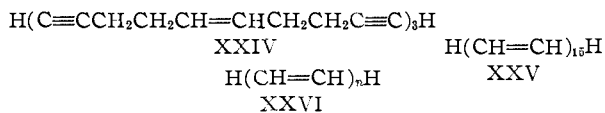


Fig. 2.—Relationship between the squares of the wave lengths and the values of  $n$  for each of the four ultraviolet maxima A-D (see Table I) of conjugated polyenes of type XXVI.

raphy of the reaction product, however, failed to yield any material with well-defined ultraviolet maxima above 400  $m\mu$ , and the limit of the method appears to have been passed.



All the polyenes of type XXVI up to  $n = 10$  are now known, with the exception of  $n = 9$ . The ultraviolet maxima of this series from  $n = 3$  are set out in Table I, and the ultraviolet curves of the members prepared in the present work ( $n = 3, 5, 6, 8$  and  $10$ ) are recorded in Fig. 1. It is of interest briefly to examine the data since these

compounds represent the simplest possible class of conjugated polyene.

All the substances show the same type of spectra with four main maxima (A-D),<sup>16</sup> of which the two highest wave length bands (C,D) are the most intense. The maxima and inflections in each compound are spaced  $1450 (\pm 150) \text{ cm.}^{-1}$  apart, as is usual for conjugated polyenes.<sup>17</sup> In Fig. 2 the  $n$ -values have been plotted against the squares of the wave length for each of the four maxima. It can be seen that straight lines are obtained as far as  $n = 7$  and small deviations then occur for  $n = 8$  and  $n = 10$ . The Lewis-Calvin equation ( $\lambda^2 = k^2n$ )<sup>18</sup> is therefore obeyed fairly well. It is apparent that the presently observed spectral properties of conjugated polyenes of type XXVI are normal and parallel those of the corresponding dimethyl- and dialkyl-polyenes which have been discussed previously.<sup>19</sup>

Finally it is of interest that during the chromatographic purification of the hexaene XVI, the octaene XX and the decaene XXIII, it was observed that in successive fractions the relative intensity of band D increased as compared with band C, while that of bands B and A decreased; moreover a small bathochromic shift of the maxima occurred as the chromatograms progressed. The same changes were effected by the crystallization process. These phenomena in the case of eicosa-decaene (XXIII) are summarized in Table II. They are most probably due to the presence of some *cis*-isomers, the all-*trans* isomers being enriched in the later chromatography fractions and by crystallization. The fact that in the purest samples of the octaene XX and the decaene XXIII

(16) In the case of  $n = 3$  there are only three maxima and an inflection takes the place of the lowest wave length maximum.

(17) See K. W. Hauser, R. Kuhn and G. Steitz, *Z. physik. Chem.* **B29**, 391 (1935).

(18) G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 273 (1939).

(19) F. Bohlmann and H. J. Mannhardt, *Ber.*, **89**, 1307 (1956) see also P. Nayler and M. C. Whiting, *J. Chem. Soc.*, 3037 (1955).

band D is slightly less intense than band C (unlike in the lower three vinylogs in which band D is the most intense) may be due to the presence still of some *cis*-isomers in these cases.

TABLE II

VARIATION IN THE RELATIVE INTENSITIES AND POSITIONS OF THE ULTRAVIOLET MAXIMA OF EICOSADECANE (XXIII) EFFECTED BY CHROMATOGRAPHY AND CRYSTALLIZATION  
 $\lambda_{\max}^{\text{icosadecane}}$  in  $\mu\mu$ ; intensity values relative to the C band in parentheses

	A	B	C	D
Fract. 155	370(1.36)	391(1.33)	413(1.00)	446(0.39)
Fract. 170	372(0.98)	393(1.13)	417(1.00)	447(.61)
Fract. 185	374(.66)	395(0.94)	418(1.00)	447(.80)
Fract. 200	374(.62)	395(.91)	419(1.00)	447(.82)
Fract. 215	374(.60)	395(.89)	419(1.00)	447(.83)
1st crystn.	375(.39)	396(.69)	419(1.00)	447(.88)
2nd crystn.	376(.33)	397(.64)	419(1.00)	447(.96)

The presently described effect of *cis-trans* isomerism on the ultraviolet spectra is similar to that found by Mebane<sup>14</sup> for decapentaene (XIII).<sup>20</sup> It is also compatible with the situation in the carotenoid and diphenylpolyene series, in which the shape of the ultraviolet curve of certain *cis* isomers compared to the all-*trans* compounds is such as would cause just the type of change observed by us when the all-*trans* isomer content in a stereoisomeric mixture is increased.<sup>21</sup>

### Experimental<sup>22</sup>

**General Remarks.**—When possible, all operations involving the conjugated polyenes were carried out at low temperature, in the presence of a trace of hydroquinone, and under purified nitrogen. These substances were generally stored in pentane or ether solution at  $-20^\circ$  in the dark. In particular the crystalline conjugated polyenes were brought into solution as soon as possible, in view of their instability in the solid state.

**1,2-Dibromo-5-hexene (VIII).**—A solution of 175 g. (2.13 moles) of biallyl (VII)<sup>9</sup> in 1 l. of ether was cooled to  $-15^\circ$  (Dry Ice-acetone) in a 3-l. three-neck flask equipped with a stirrer, a condenser cooled with Dry Ice-acetone and a dropping funnel, moisture being excluded. Bromine (172 g., 1.07 moles) was then added dropwise during 2 hr. with vigorous stirring, the internal temperature being kept at *ca.*  $-15^\circ$  by continued cooling. The ether and unchanged biallyl were distilled at atmospheric pressure into a cooled receiver and treated again with 78.5 g. of bromine (0.49 mole) during 1.5 hr. The volatile liquids were again distilled and the residues were combined. Distillation under reduced pressure then yielded 128 g. of the crude dibromide, b.p.  $53-93^\circ$  (2 mm.); the pale-brown crystalline residue (133 g.) consisted of crude 1,2,5,6-tetrabromohexane. Redistillation of the dibromide yielded the pure substance (122 g., 24%) as an almost colorless liquid (faint yellow tinge), b.p.  $54-55^\circ$  (5 mm.),  $n_D^{20}$  1.5186; infrared bands (neat) at 6.08, 10.05 and 10.94  $\mu$  (monosubstituted ethylene).<sup>23a</sup>

(20) While it was possible in that case to effect inversion of the *cis* material to the all-*trans* isomer by means of iodine, similar treatment in the eicosadecane series resulted solely in destruction of the chromophore.

(21) *Inter al.*, see L. Zechmeister, *et al.*, *J. Am. Chem. Soc.*, **65**, 1940 (1943); **69**, 1930 (1947); **76**, 2309, 4144 (1954); *Experientia*, **10**, 1 (1954); *Fortschr. Chem. org. Naturstoffe*, **18**, 223 (1960).

(22) Melting points were taken on a Fisher-Johns apparatus and are uncorrected. All chromatograms were carried out with Alcoa activated alumina, grade F-20 (Aluminum Co. of America, Pittsburgh, Pa.). Ultraviolet spectra were taken on a Unicam model S.P. 500 as well as on a Cary model 14 recording spectrophotometer. Infrared spectra were measured with a Baird double-beam recording spectrophotometer with sodium chloride optics. Analyses were carried out in our microanalytical laboratory under the direction of Mr. Erich Meier.

(23) See N. Sheppard and D. M. Simpson, *Quart. Revs. (London)*, **6**, 1 (1952); (a) Table 4; (b) Table 2; (c) Table 6.

*Anal.* Calcd. for  $C_6H_{10}Br_2$ : C, 29.78; H, 4.17; Br, 66.05. Found: C, 29.90; H, 4.03; Br, 65.77.

The above was the best of several experiments in which the relative amount of bromine was varied. When more than 0.5 molar equivalent of bromine was added at one time, the yield of tetrabromide increased considerably and the yield of dibromide decreased.

**1-Hexen-5-yne (IX).**—A suspension of sodamide in *ca.* 1.5 l. of liquid ammonia was prepared from 82 g. of sodium, the transformation being catalyzed by means of 0.5 g. of ferric nitrate hexahydrate<sup>24</sup> and the mixture being cooled to *ca.*  $-50^\circ$  by means of a Dry Ice-acetone-bath. A solution of 116 g. of the dibromide VIII in 320 cc. of dry ether was then added dropwise during 1.5 hr. with stirring and continued cooling, and the mixture was stirred and cooled for another 3 hr. The mixture was set aside overnight to allow most of the ammonia to evaporate (it was found advantageous to remove the ammonia before decomposing the sodio-derivative to prevent losses of the volatile product). Ether and then ice-water were added carefully to the residue, the aqueous layer was washed with ether and the combined organic extracts were washed with dilute sulfuric acid, sodium bicarbonate solution and water. Ether was removed from the dried extract by slow distillation through a 50-cm. vacuum-jacketed column filled with glass helices. Distillation of the residue through a small Vigreux column then furnished 24.8 g. (65%) of 1-hexen-5-yne (IX) as a colorless liquid, b.p.  $70-71^\circ$  (758 mm.),  $n_D^{20}$  1.4180; infrared bands (neat) at 3.03 and 4.72  $\mu$  (terminal acetylene)<sup>25b</sup> and 6.07, 10.05, and 10.95  $\mu$  (monosubstituted ethylene).<sup>23a</sup> no allene band at *ca.* 5.1  $\mu$ . The ultraviolet spectrum of this material showed  $\lambda_{\max}^{\text{icosadecane}}$  223  $\mu\mu$  ( $\epsilon$  1100), indicating the presence of *ca.* 8% of 3-hexen-1-yne (X)<sup>10</sup> (reported for pure IX: b.p.  $70^\circ$ ,  $n_D^{20}$  1.4318<sup>8</sup>).

*Anal.* Calcd. for  $C_6H_8$ : C, 89.94; H, 10.06; acetylenic H (1), 1.26. Found: C, 89.71; H, 10.09; acetylenic H (by titration against silver nitrate),<sup>25</sup> 1.25.

**1,3,5-Hexatriene (XI) from 1-Hexen-5-yne (IX).** (a) **Investigation of Optimum Conditions.**—In every experiment described, the product showed the hexatriene ultraviolet maxima at *ca.* 248, 257 and 268  $\mu\mu$ .<sup>11</sup> The yields are based on the intensity of the 257  $\mu\mu$  band,  $\epsilon$  43,600<sup>11b</sup> being assumed for the pure substance.

1-Hexen-5-yne (75 mg.) was heated with 10 cc. of a 24% solution of potassium hydroxide in absolute ethanol at  $65-70^\circ$  (internal temperature) under a water-cooled reflux condenser (on top of which was a Dewar condenser cooled in Dry Ice-acetone), moisture being excluded. Aliquots were withdrawn at intervals, diluted with ethanol and the ultraviolet spectra were measured against ethanol.

Time, min.	30	90	180	240
Yield, %	1.2	2.3	4.2	3.9

With a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol, the yield of hexatriene depends markedly on the amount of base, as is evident from the following experiments.

A solution containing 1 g. of 1-hexen-5-yne and 0.35 cc. of butoxide<sup>26</sup> was heated as above at  $65-70^\circ$  (internal temperature) for 45 minutes. Pentane and ether were added, and the organic layer was washed well with water and dried; yield of hexatriene, *ca.* 0.1%. In another experiment carried out in a similar way with 1 g. of the enyne and 5 cc. of butoxide<sup>26</sup> at  $65-70^\circ$  for 25 minutes, the yield of hexatriene was *ca.* 2%. In a third experiment performed similarly with 1 g. of the enyne and 40 cc. of butoxide<sup>26</sup> at  $65-70^\circ$ , the following yields were obtained:

Time, min.	15	30	45	60	90	120	180	240	300
Yield, %	5	12	16	24	27	30	41	30	24

(b) **Preparative Experiment.**—A solution containing 8 g. of 1-hexen-5-yne and 320 cc. of butoxide<sup>26</sup> was heated as

(24) T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, *J. Am. Chem. Soc.*, **56**, 2120 (1934).

(25) R. M. Evans, quoted by G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 3052 (1953).

(26) "Butoxide" refers to a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol. It was prepared by dissolving sufficient potassium in hot absolute *t*-butyl alcohol to cause precipitation of solid potassium *t*-butoxide (moisture being excluded), followed by cooling to room temperature and decantation.

before at 65–70° (internal temperature) for 3 hr. Pentane and water were added and the pentane layer was washed 30 times with water, to remove *t*-butyl alcohol. The pentane extract was then shaken with an ammoniacal silver nitrate solution (prepared by addition of 15 *N* ammonia to a solution of 21.3 g. of silver nitrate in 35 cc. of water until the precipitate which formed first redissolved). The aqueous layer in which a white precipitate was suspended was separated, freed from the solid by filtration and again shaken with the pentane layer. This procedure was repeated 15 times, a fresh precipitate being formed each time. A new ammoniacal silver nitrate solution was then prepared as before and the shaking, separation and filtration was repeated a further 10 times, by which time no more precipitation occurred. The pentane extract was washed with water, dried (spectroscopic yield of hexatriene at this stage, 38%) and the pentane was slowly distilled off through a 25-cm. vacuum-jacketed column filled with glass helices (the spectrum of the distillate showed that a considerable amount of hexatriene co-distilled). The residue was distilled rapidly to separate it from some solid which remained as residue and was then redistilled through a small Vigreux column. The resulting hexatriene (1.62 g., 20%) showed b.p. 79–83° (752 mm.); the ultraviolet data are recorded in Table I and Fig. 1. The material crystallized on being cooled to –70°, but melted again on being allowed to reach –20°. This is probably due to both the *cis* and *trans* isomer being present, a fact supported by the infrared spectrum (neat) which showed the bands at 7.00, 9.90 and 10.66  $\mu$  due to the *trans* isomer as well as at 6.89, 10.15 and 12.22  $\mu$  due to the *cis* isomer (acetylene and allene bands absent) [reported for *trans*-hexatriene: m.p. –11.7°,<sup>11a</sup> b.p. 79–80°<sup>11a</sup>;  $\lambda_{\max}$  247, 258 and 268  $m\mu$  ( $\epsilon$  34,000, 43,600 and 36,000)<sup>11b</sup>;  $\lambda_{\text{isoctane}}$  245, 255 and 265  $m\mu$  ( $\epsilon$  36,000, 53,000 and 44,000)<sup>11c</sup>; infrared bands at 7.00, 9.89 and 10.63  $\mu$ <sup>11c</sup>; for *cis*-hexatriene: b.p. 82–83°<sup>11c</sup>;  $\lambda_{\text{isoctane}}$  245, 255 and 265  $m\mu$  ( $\epsilon$  29,000, 41,000 and 30,000)<sup>11c</sup>; infrared bands at 6.89, 10.13 and 12.22  $\mu$ <sup>11c</sup>].

**1,3,5,7,9-Decapentaene (XIII) from *trans*-5-Decene-1,9-diyne (XII).**—A solution containing 1 g. of the diyne XII<sup>12,13</sup> and 30 cc. of butoxide<sup>26</sup> was heated on a water-bath at ca. 75° (internal temperature) under a reflux condenser in nitrogen, moisture being excluded. Aliquots were withdrawn at intervals, diluted with pentane, washed well with water, dried and the ultraviolet spectra were determined against pentane (all the solutions showed the maxima at ca. 290, 303, 317 and 334  $m\mu$  of decapentaene<sup>14</sup>; the yields are based on the intensity of the 334  $m\mu$  band,  $\epsilon$  121,000 being taken for the pure substance).

Time, min.	5	10	15	20	30	40
Yield, %	0.5	1.1	1.7	3.6	5.8	7.1
Time, min.	50	60	90	120	180	240
Yield, %	9.2	12.6	14.3	15.8	15.4	14.8

A preparative experiment was carried out by heating 3 g. of the diyne XII with 90 cc. of butoxide<sup>26</sup> as above at ca. 75° for 2 hr. The solution was cooled, pentane and water were added and the pentane layer was washed 20 times with water, dried and evaporated through a Vigreux column. The residue dissolved in 10 cc. of pentane was chromatographed on a column of 230 g. of alumina, which was then developed with pentane. On the basis of their ultraviolet spectra, fractions 5–20 (100 cc. each) were combined, evaporated and the residue was dissolved in warm 95% ethanol. The solution was kept at –20° for 2 hr. and the resulting crystals were collected. The decapentaene (272 mg., 9%) thus obtained formed light cream-colored needles, m.p. 146–147° (under the conditions of Mebane<sup>14</sup>), which polymerized readily on being kept at room temperature. The ultraviolet spectrum is given in Table I and Fig. 1. The infrared spectrum (KBr) showed bands, among others, at 5.55, 6.22, 7.08, 7.80, 9.90, 10.20 and 11.13  $\mu$ , and appears to be identical with that presented by Mebane<sup>14</sup> [reported<sup>14</sup> m.p. 145  $\pm$  2° (substance put on block at this temperature);  $\lambda_{\text{isoctane}}$  280 (infl.) 291, 304, 318 and 334  $m\mu$  ( $\epsilon_{\text{max}}^{34}$  118,000)].

As with 1-hexen-5-yne (IX), the rearrangement of the diyne XII proceeded more poorly when a smaller amount of butoxide was employed. Thus when 1 g. of XII was heated with 8 cc. of butoxide<sup>26</sup> at ca. 75°, the spectroscopic yield of decapentaene after 1 hr. was only 4.5%.

Treatment of 100 mg. of the diyne XII with 10 cc. of a boiling 20% solution of potassium hydroxide in absolute ethanol under reflux in nitrogen for 1 hr. gave no trace of decapentaene.

**1,3,5,7,9-Decapentaene (XIII) from 1,2,5-Decatrien-9-yne (XIV).**—A solution containing 200 mg. of the allene XIV<sup>12</sup> and 6 cc. of butoxide<sup>26</sup> was heated for 1 hr. at ca. 75° in nitrogen, as described above for the diyne XII. Isolation with pentane as before, followed by ultraviolet spectral examination, showed the maxima at 290, 303, 317 and 334  $m\mu$  of decapentaene, the estimated yield being 12%.

**1,11-Dodecadiene-5,7-diyne (XV).**—Concd. hydrochloric acid (1.5 cc.) was added to a suspension of 15 g. of cuprous chloride and 45 g. of ammonium chloride in 150 cc. of water. A solution of 4.73 g. of 1-hexen-5-yne (IX) (containing ca. 8% of 3-hexen-1-yne (X)) in 170 cc. of methanol was then added and the mixture was shaken vigorously in a standard quantitative hydrogenation apparatus which was filled with oxygen<sup>27</sup> until uptake stopped (ca. 3 hr.). Ether and water were added, the aqueous layer was extracted twice more with ether and was then clarified by addition of 7.5 *N* ammonia and again extracted with ether. The combined ether extracts were washed successively with 7.5 *N* ammonia, 2 *N* sulfuric acid, sodium bicarbonate solution and water. The dried solution was evaporated and the residue was distilled under nitrogen. The resulting 1,11-dodecadiene-5,7-diyne (XV) (2.74 g., 59%) showed b.p. 87–88° (11 mm.),  $n_D^{20}$  1.5215; infrared bands (neat) at 4.45 and 4.63  $\mu$  ( $\alpha,\gamma$ -diyne)<sup>28</sup> as well as at 6.07, 10.06 and 10.94  $\mu$  (monosubstituted ethylene),<sup>28a</sup> no band at ca. 3.0  $\mu$  (terminal acetylene absent).<sup>28b</sup>

*Anal.* Calcd. for C<sub>12</sub>H<sub>14</sub>: C, 91.08; H, 8.92. Found: C, 91.22; H, 9.19.

The ultraviolet spectrum in isoctane of this material showed maxima at 228, 240, 253, 267, 283, 294 and 313  $m\mu$  ( $\epsilon$  900, 1310, 1920, 2720, 2140, 330 and 180), whereas a normal  $\alpha,\gamma$ -diyne in isoctane shows maxima at 227, 240 and 253  $m\mu$  ( $\epsilon$  ca. 360, 350 and 200).<sup>27,29</sup> A typical conjugated ene-diyne (2-decene-4,6-diyne-1-ol) exhibits maxima in hexane at 239.5, 252, 266.5 and 282.5  $m\mu$  ( $\epsilon$  7300, 14,500, 22,000 and 19,500),<sup>30</sup> while a typical conjugated ene-diyne-ene (2,8-decadiene-4,6-diyne-1-ol) shows the two highest wave length maxima in petroleum ether at 293 and 312  $m\mu$  ( $\epsilon$  21,000 and 16,000).<sup>31</sup> The coupling product XV is therefore contaminated with ca. 10% of a conjugated ene-diyne and ca. 1% of a conjugated ene-diyne-ene, most probably 1,9-dodecadiene-5,7-diyne (XVII) and 3,9-dodecadiene-5,7-diyne (XVIII), respectively.

**1,3,5,7,9,11-Dodecahexaene (XVI).**—A solution containing 50 mg. of the diene-diyne XV and 3 cc. of butoxide<sup>26</sup> was heated at 65–70° (internal temperature), as described above for the preparation of decapentaene, and as in that case aliquots were withdrawn at intervals and worked up with pentane (all the solutions showed the ultraviolet maxima at ca. 313, 328, 344 and 364  $m\mu$  of the hexaene XVI; the yields are based on the intensity of the 364  $m\mu$  band,  $\epsilon$  138,000 being taken for the pure substance).

Time, min.	5	15	25	45	60	90	120
Yield, %	1.6	5.4	7.1	8.7	10.1	9.8	9.2

A preparative experiment was performed by heating 2.5 g. of the diene-diyne XV with 150 cc. of butoxide<sup>26</sup> at 65–70° for 1 hr. and the product was then isolated with pentane, as described above for decapentaene. Concentration of the dried pentane extract to small volume and cooling to 0° yielded pink crystals, which were collected, combined with a second crop and recrystallized from pentane. The resulting dodecahexaene (16.8 mg.) formed cream-orange colored leaflets possessing a strong odor; no m.p. could be determined, since polymerization occurred at whatever temperature the sample was placed on the block (between 100 and 300°);  $\lambda_{\text{isoctane}}$  300 (infl.), 313, 328, 344 and 364  $m\mu$  ( $\epsilon$  14,800, 35,800, 74,000, 126,000 and 134,000). The

(27) See J. B. Armitage, C. L. Cook, N. Entwistle, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 1998 (1952).

(28) See F. Sondheimer and Y. Amiel, *J. Am. Chem. Soc.*, **79**, 5817 (1957).

(29) See F. Sondheimer and Y. Gaoni, *ibid.*, **81**, 6301 (1959).

(30) T. Bruun, C. M. Haug and N. A. Sørensen, *Acta Chem. Scand.*, **4**, 850 (1950).

(31) T. Bruun, P. K. Christensen, C. M. Haug, J. Steie and N. A. Sørensen, *ibid.*, **6**, 1244 (1951).

infrared spectrum (KBr) showed bands, among others, at 5.54, 6.21, 7.06, 7.78, 9.90, 10.09 and 11.10  $\mu$ , and was very similar to that of decapentaene (dissolution of the hexaene from the pellet, after the infrared spectrum had been taken, in isoöctane and ultraviolet examination showed that it was still 92% pure).

*Anal.* Calcd. for  $C_{12}H_{14}$ : C, 91.08; H, 8.92. Found: C, 90.60; H, 9.04.

The combined mother liquors were evaporated to dryness, dissolved in 5 cc. of benzene and chromatographed on 200 g. of alumina. Fractions 42-180 eluted with pentane and 181-188 eluted with pentane-ether (9:1) (50-cc. fractions) were combined on the basis of their ultraviolet spectra, concentrated to small volume and cooled. The resulting crystals were collected to give a further 11.2 mg. of dodecahexaene (total yield 28 mg.) as light lemon-colored needles with ultraviolet data in isoöctane recorded in Table I and Fig. 1;  $\lambda_{\text{max}}^{\text{benzene}}$  321, 336, 353 and 373  $m\mu$  ( $E$  0.149, 0.299, 0.510 and 0.531). Since the ultraviolet spectra of the materials obtained by direct crystallization and by chromatography are almost identical, the difference in crystal properties is probably due to polymorphism.

The solid hexaene was found to polymerize quickly to a brown amorphous powder and the pure substance had become almost completely insoluble after being allowed to stand for 15 minutes in daylight at room temperature (the recorded  $\epsilon$ -values of the ultraviolet maxima may therefore well be too low). It is, however, comparatively stable in solution, very little change in the ultraviolet spectra being observed when dilute isoöctane solutions ( $c$   $5 \times 10^{-6}$  and  $5 \times 10^{-5}$  mole/l.) were allowed to stand for 5 days at room temperature without protection from daylight.

*trans*-1,11-Hexadecadiene-5,7,15-triyne (XIX).—Concd. hydrochloric acid (1.4 cc.) was added to a mixture of 13.7 g. of cuprous chloride and 41 g. of ammonium chloride in 140 cc. of water. A solution of 2.18 g. (0.027 mole) of 1-hexen-5-yne (IX) (containing ca. 8% of 3-hexen-1-yne (X)) and 3.60 g. (0.027 mole) of *trans*-5-decene-1,9-diyne (XII)<sup>12,13</sup> in 140 cc. of methanol was added and the mixture was shaken in oxygen in a hydrogenation apparatus<sup>27</sup> until no more gas was taken up (ca. 5 hr.). The product was isolated with ether as described above for the preparation of XV and the reaction was then repeated three times, each on the same scale. The combined products from all four experiments (22.8 g.) were dissolved in 50 cc. of pentane and chromatographed on 1.2 kg. of alumina, 100-cc. fractions being collected.

Fractions 15-29, eluted with pentane, on evaporation yielded 3.04 g. (35%) of the symmetrical coupling product XV (contaminated with XVII and XVIII) with ultraviolet and infrared properties very similar to those of the material obtained above by the coupling of IX.

Fractions 90-119, eluted with pentane-ether (39:1) gave 5.67 g. (25%) of the mixed coupling product, *trans*-1,11-hexadecadiene-5,7,15-triyne (XIX), as a colorless liquid, b.p. 130-132° (0.9 mm.),  $n_D^{25}$  1.5241; infrared bands (neat) at 3.03 and 4.72  $\mu$  (terminal acetylene),<sup>23b</sup> 4.45 and 4.63  $\mu$  ( $\alpha,\gamma$ -diyne),<sup>28</sup> 6.08, 10.07 and 10.94  $\mu$  (monosubstituted ethylene)<sup>23a</sup> and 10.33  $\mu$  (*trans*-disubstituted ethylene).<sup>23c</sup> The ultraviolet spectrum (isoöctane) showed maxima at 226, 240, 253, 267 and 283  $m\mu$  ( $\epsilon$  880, 870, 1070, 1310 and 980), indicating the presence of ca. 5% of the conjugated ene-diyne 5,13-hexadecadiene-1,9,11-triyne (XXI) (for comparison with a model system,<sup>30</sup> see above for the coupling product XV from 1-hexen-5-yne).

*Anal.* Calcd. for  $C_{16}H_{18}$ : C, 91.37; H, 8.63; acetylenic H(1), 0.48. Found: C, 91.05; H, 8.40; acetylenic H (by titration against silver nitrate),<sup>28</sup> 0.47.

Fractions 165-194, eluted with pentane-ether (9:1 to 6:1), furnished 2.46 g. (17%) of the symmetrical coupling product XXII, which on one crystallization from methanol showed m.p. 52-54°, undepressed on admixture with an authentic sample (m.p. 55-56°).<sup>12,13</sup>

1,3,5,7,9,11,13,15-Hexadecaöctaene (XX).—A solution containing 100 mg. of the mixed coupling product XIX and 3.5 cc. of butoxide<sup>26</sup> was heated at 65-70° (internal temperature) and aliquots were withdrawn and worked up with pentane, as described above for the preparation of decapentaene (all the solutions showed the ultraviolet maxima at ca. 349, 367, 386 and 410  $m\mu$  of the octaene; the yields are based on the intensity of the 410  $m\mu$  band,  $\epsilon$  160,000 being arbitrarily assumed for the pure substance).

Time, min.	5	15	25	45	60	90	120
Yield, %	0.5	1.0	1.8	2.2	2.6	2.4	2.3

A preparative experiment was carried out by heating 3.92 g. of XIX with 140 cc. of butoxide<sup>26</sup> at 65-70° for 1 hr. The product then was isolated with pentane in the usual way, dissolved in 10 cc. of benzene and chromatographed on 600 g. of alumina; the column was covered with black paper and 100-cc. fractions were collected. Ultraviolet examination of the eluates showed that fractions 75-82, eluted with pentane-ether (9:1), contained the desired polyene. These fractions were evaporated to small volume, cooled and the resulting crystals were collected. The octaene XX thus obtained (3.6 mg.) formed yellow-orange needles which polymerized on attempted m.p. determination. The ultraviolet data in isoöctane are recorded in Table I and Fig. 1<sup>15</sup>;  $\lambda_{\text{max}}^{\text{benzene}}$  358, 376, 397 and 421  $m\mu$  ( $E$  0.227, 0.444, 0.670 and 0.622). The infrared spectrum (KBr) was similar to that of the lower vinyls XIII and XVI, showing bands, among others, at 5.55, 6.22, 7.06, 9.95, 10.15 and 11.12  $\mu$ .

The solid octaene on being kept in daylight at room temperature after a few minutes became light brown and then was completely insoluble in isoöctane.

1,3,5,7,9,11,13,15,17,19-Eicosadecaene (XXIII).—A solution containing 1.2 g. of *trans*-*trans*-5,15-eicosadiene-1,9,11,19-tetraene (XXII)<sup>12,13</sup> and 175 cc. of butoxide<sup>26</sup> was heated at 65-70° (internal temperature) for 1 hr. and the product was then isolated with pentane, as described above for the preparation of decapentaene. The pentane extract was evaporated to ca. 10 cc., diluted with 10 cc. of benzene and chromatographed on 600 g. of alumina; the column was covered with black paper and 100-cc. fractions were collected. The ultraviolet spectra of fractions 155-215, eluted with pentane-ether (4:1), are recorded in Table II. On the basis of these spectra, fractions 175-215 were combined, evaporated to small volume and cooled to 0°. Collection of the resulting crystals yielded the decaene XXIII as orange needles, the ultraviolet data of which are recorded in Table II under "1st crystn." (no weighings were performed with the crystalline decaene to prevent its polymerization during the weighing process). The crystals were heated with pentane, a small amount of insoluble material was removed and the solution was concentrated. Cooling and filtration then again yielded orange crystals of the decaene, the ultraviolet data of which in isoöctane are given in Table I and Fig. 1, as well as in Table II ("2nd crystn.");  $\lambda_{\text{max}}^{\text{benzene}}$  388, 408, 433 and 462  $m\mu$  ( $E$  0.193, 0.388, 0.601 and 0.560).