Unsaturated Macrocyclic Compounds. XVIII.[1] The Prototropic Rearrangement of Linear 1,5-Diynes to Conjugated Polyen-ynes

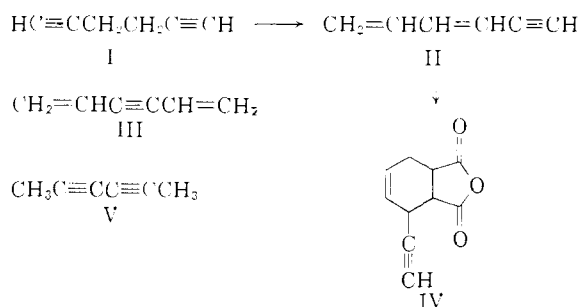BY FRANZ SONDHEIMER, DAVID A. BEN-EFRAIM AND YEHIEL GAONI

It is shown that 1,5-diynes are rearranged to conjugated polyen-ynes by means of potassium t-butoxide in t-butyl alcohol. In this way 1,5-hexadiyne (I) smoothly gives 1,3-hexadien-5-yne (II) (consisting of 65% of the cis and 35% of the trans isomer), in contrast to the previously reported isomerization of I with alcoholic potassium hydroxide to 2,4-hexadiyne (V). 1,5,9-Decatriyne (VI) with potassium t-butoxide produces the "internal" tetraenyne VII and/or VIII as well as the "terminal" tetraen-yne IX. 1,5,7,11-Dodecatetrayne (X) under similar conditions is isomerized to a mixture of conjugated tetraene-diynes, from which 1,3,9,11-dodecatetraene-5,7-diyne (XI) (also obtained by the oxidative coupling of II) can be separated.

The prototropic rearrangement of linear 1,5-enynes to conjugated polyenes with potassium t-butoxide in t-butyl alcohol was reported in the preceding paper.[1] We now describe the extension of this type of reaction to 1,5-diynes, which have been found to undergo an analogous rearrangement to conjugated polyen-ynes.

The first compound studied was 1,5-hexadiyne (dipropargyl) (I)[2] which was observed to react exothermically on being heated to 70° with a saturated solution of potassium t-butoxide in t-butyl alcohol (0.35 cc. per gram of I). Isolation with pentane after ca. 15 minutes reaction time followed by fractional distillation resulted in 33% of an unstable liquid (b.p. 82–83°), which was identified as 1,3-hexadien-5-yne (ethinylbutadiene) (II) for the reasons given.

The ultraviolet spectrum in isoöctane showed a single maximum at 252 mμ (ε 25,500). This

$$HC\equiv CCH_2CH_2C\equiv CH \longrightarrow CH_2=CHCH=CHC\equiv CH$$

$$I \qquad\qquad II$$

$$CH_2=CHC\equiv CCH=CH_2$$
$$III$$

$$CH_3C\equiv CC\equiv CCH_3$$
$$V$$

is in excellent agreement with the reported maximum for the dien-yne II at 252 mμ (ε 23,700–26,300),[3] but differs from the spectrum of 1,5-hexadien-3-yne (III), the other possible dien-yne, which exhibits maxima at 241, 253 and 266 mμ (the ε-value of the 253 mμ band being 14,500–16,700).[3] The infrared spectrum, which indicated the presence of a terminal acetylene and the absence of an allene grouping, was similar to that reported for II and differed from that of III.[3] Titration against silver nitrate[4] revealed the presence of almost exactly one acetylenic hydrogen function. Finally, reaction with maleic anhydride yielded the adduct IV (m.p. 84–85°), the infrared spectrum of which still showed the presence of a terminal acetylene grouping.[5]

The spectroscopic yield of II before fractionation was 65%, the lower yield of material actually isolated doubtless being a result of the instability and volatility of II.[6] The present method consequently is a useful one for the laboratory synthesis of 1,3-hexadien-5-yne, especially in solution. This substance has been obtained previously from propargylaldehyde and allyl bromide by the Wittig reaction,[7] by pyrolysis of esters of 3-hexen-5-yn-2-ol,[8] as well as a by-product in the polymerization of acetylene.[3,9]

Analysis of II by gas–liquid partition chromatography (g.l.p.c.) resulted in the appearance of two separate peaks with areas in the ratio 65:35, the first peak being the larger; in addition, a shoulder due to the presence still of ca. 3% of starting material was apparent. Essentially identical results were obtained when the total volatile material from the rearrangement of I, in pentane solution, was subjected to g.l.p.c. analysis. This non-homogeneity must be due to the presence of both the cis and the trans isomer of II.[10]

Preparative g.l.p.c. yielded a first fraction which gave only the first peak on g.l.p.c. analysis and a second fraction which gave both peaks with about equal areas. Infrared examination of these fractions revealed that the 10.60 μ band, present in the original material and which may be ascribed to the CH out-of-plane deformation of a conjugated trans-double bond,[11] was absent from the

(1) For Part XVII, see F. Sondheimer, D. A. Ben-Efraim and R. Wolovsky, J. Am. Chem. Soc., 83, 1675 (1961); see also footnote 1 in that paper.

(2) See R. A. Raphael and F. Sondheimer, J. Chem. Soc., 120 (1950), and references cited therein.

(3) K. K. Georgieff, W. T. Cave and K. G. Blaikie, J. Am. Chem. Soc., 76, 5494 (1954).

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

(5) The diacid corresponding to the anhydride IV has been reported in the patent literature [A. S. Carter, U. S. Patent 2,173,272 (Sept. 19, 1939) (C. A., 34, 453 (1940)); U. S. Patent 2,263,378 (Nov. 18, 1941) (C.A., 36, 1337 (1942))].

(6) An attempt to improve the yield of isolated II by distilling off the pentane solvent through a spinning-band column during 15 hours resulted in an explosion when the residue was distilled.

(7) F. Bohlmann and E. Inhoffen, Ber., 89, 21 (1956).

(8) R. Farnsworth, Chemistry Part II Thesis, Oxford University, 1957; R. Farnsworth, E. R. H. Jones and M. C. Whiting, J. Chem. Soc., in press.

(9) For leading references, see Beilstein's "Handbuch der Organischen Chemie," Springer Verlag, Berlin, 4th Edition, 3rd Supplement, Vol. I (Part 1), 1958, p. 1058.

(10) The only publication regarding the stereochemistry of 1,3-hexadien-5-yne (II) we were aware of when this work was performed was one indicating that the substance from propargylaldehyde and allyl bromide consisted of the trans isomer.[7] Subsequently Prof. E. R. H. Jones and Dr. M. C. Whiting (Oxford University) kindly informed us that both the cis and trans isomer of II had been prepared in their laboratory.[8]

(11) Inter al., J. L. H. Allan, G. D. Meakins and M. C. Whiting, J. Chem. Soc., 1874 (1955).

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TABLE I

ULTRAVIOLET SPECTRA OF CONJUGATED POLYEN-YNES IN ISOÖCTANE

λ_{max} in mμ; ϵ-values $\times$ 10^{-3} in parentheses

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VII and/or VIII (liq.)	225(25.6)	231(26.6)	293(34.5)	307(40.0)	....	327(40.5)
VII or VIII (solid)	223(15.3)	229(15.3)	294(27.6)	308(41.3)	313(37.5)[a]	328(48.0)
IX	....	232(6.7)	289(19.1)[a]	300(37.4)	313(59.5)	329(59.7)
1,3,5,7,9-Decapentaene[1]	....	279(18.5)[a]	290(37.1)	303(71.2)	317(115)	334(121)
XI (from X)	231(31.0)	244(34.6)	251(37.4)	262(36.8)	272(37.8)	288(35.2)
				307(30.0)	328(41.2)	352(36.7)
XI (from II)	232(28.4)	244(31.7)	251(33.1)	264(32.5)	273(35.0)	286(31.6)
				307(30.4)	328(42.3)	352(38.2)

[a] Inflection

first but enhanced in the second. It follows that the first and second g.l.p.c. peaks are due to the *cis* and *trans* isomer, respectively, and consequently that the rearrangement of I leads to about twice as much of *cis*-II as of *trans*-II. The correctness of the configurational assignment was confirmed by the observation that a reduction in the area of the second g.l.p.c. peak compared with the first was effected by treatment of II with maleic anhydride in boiling ether–pentane, conditions under which only the *trans* form would be expected to undergo appreciable reaction.[12] Undoubtedly it is for the same reason that the above-mentioned maleic anhydride adduct IV was formed only in poor yield.

It is of interest to note that the presently described rearrangement of I to II proceeds faster and results in a higher yield of conjugated product than does the analogous rearrangement of 1-hexen-5-yne to 1,3,5-hexatriene.[1] Moreover the isomerization of 1,5-hexadiyne (I) requires much less base than that of 1-hexen-5-yne, as evidenced by the fact[1] that the latter substance had yielded no more than 0.1% of 1,3,5-hexatriene when treated at 65–70° for 45 minutes with the same relative amount of saturated potassium *t*-butoxide solution as resulted in the 65% yield of II from I. The finding that the rearrangement of 1,5-diynes to polyen-ynes is a considerably more facile process than the rearrangement of 1,5-enynes to polyenes was also noted in the other examples described below and became of importance when these reactions were applied subsequently in the cyclic series.

The results obtained with potassium *t*-butoxide are to be compared with the classical rearrangement of 1,5-hexadiyne (I) to 2,4-hexadiyne (dimethyldiacetylene) (V) with alcoholic potassium hydroxide.[13] We are investigating at present the factors responsible for the apparently different course of the reaction.[14]
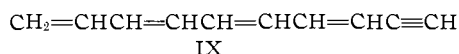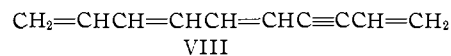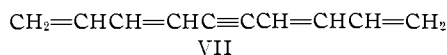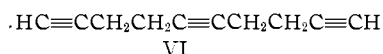
(12) *Inter al.*, R. L. Frank, R. D. Emmick and R. S. Johnson, *J. Am. Chem. Soc*, **69**, 2313 (1947); D. Craig, *ibid.*, **72**, 1678 (1950); K. Alder, *Ann.*, **571**, 157 (1951); J. C. H. Hwa, P. L. de Benneville and H. J. Sims, *J. Am. Chem. Soc.*, **82**, 2537 (1960).

(13) A. Faworsky, *J. prakt. Chem.*, [2] **44**, 232 (1891). R. Lespieau (*Ann. chim. (Paris)*, [9] **2**, 289 (1914)) also has shown that treatment of 1,2,5,6-tetrabromohexane with alcoholic potassium hydroxide yields 2,4-hexadiyne besides 1,5-hexadiyne, the conjugated diyne presumably having been formed by rearrangement of the initially formed unconjugated one.

(14) Also relevant to our work is the recent communication of G. Eglinton, R. A. Raphael and R. G. Willis (*Proc. Chem. Soc.*, 247 (1960)) describing the conversion of various diynes to substituted benzenes by means of potassium *t*-butoxide in boiling 2,2'-dimethoxydiethyl ether (b.p. 160°). Under these conditions 1,5-hexadiyne, the only 1,5-diyne studied, was reported to yield a vinyl ether but no benzene.

The next 1,5-diyne studied was 1,5,9-decatriyne (VI), the preparation of which is described elsewhere.[15] Rearrangement was effected with potassium *t*-butoxide in boiling *t*-butyl alcohol–benzene and the product was chromatographed on alumina.

Spectral analysis of the various fractions revealed that the reaction had proceeded in more than one direction.

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.HC≡CCH₂CH₂C≡CCH₂CH₂C≡CH

VI

CH₂=CHCH=CHC≡CCH=CHCH=CH₂

VII

CH₂=CHCH=CHCH=CHC≡CCH=CH₂

VIII

CH₂=CHCH=CHCH=CHCH=CHC≡CH

IX

</div>

The less polar material, isolated as a liquid in 27% yield, consisted of 1,3,7,9-decatetraen-5-yne (VII) and/or 1,3,5,9-decatetraen-7-yne (VIII) since the ultraviolet spectrum (Table I) indicated the existence of a conjugated tetraen-yne system (*cf.* the spectrum of 1,3,5,7,9-decapentaene also given in Table I) and the infrared spectrum showed that an internal acetylene was present (band at 4.58 μ but not at *ca.* 3.03 μ). A small amount of a solid substance (m.p. 46–47°) with similar ultraviolet (Table I) as well as infrared properties could be crystallized, which is either the pure 5-yne VII or the 7-yne VIII. That only a small amount of material crystallized may be due to both the isomers VII and VIII being present and/or the existence of *cis–trans* isomerism.

The more polar material from the rearrangement of VI, obtained in 20% yield, proved to be 1,3,5,7-decatetraen-9-yne (IX). This formulation follows from the ultraviolet absorption properties (Table I)[16] which like the previously discussed isomer(s) resembled those of 1,3,5,7,9-decapentaene, and the infrared spectrum which showed the presence of a terminal acetylene grouping (strong band at 3.03 μ, weak band at 4.76 μ).

The decatetraen-ynes described proved to be very unstable compounds which decomposed rapidly unless kept in solution. Although not
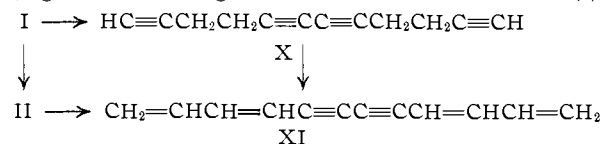
(15) F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **83**, 1259 (1961); for a preliminary communication, see F. Sondheimer, R. Wolovsky and Y. Gaoni, *ibid.*, **82**, 754 (1960).

(16) As in other cases,[2,17] the highest wave length maximum of the "terminal" acetylenic polyen-yne IX is more intense than that of the "internal" polyen-yne VII or VIII but less intense than that of 1,3,5,-7,9-decapentaene in which the acetylene has been replaced by a double bond.

(17) *Inter al.*, I. M. Heilbron, E. R. H. Jones and R. A. Raphael, *J. Chem. Soc.*, 268 (1943); I. M. Heilbron, E. R. H. Jones and J. T. McCombie, *ibid.*, 134 (1944).

reported previously, they are probably formed together with their lower vinylogs by the polymerization of acetylene,[3,9] their instability having prevented their isolation.

The most complex 1,5-diyne investigated was 1,5,7,11-dodecatetrayne (X), a product of the oxidative coupling of 1,5-hexadiyne (I).[18] Rearrangement with potassium t-butoxide in t-butyl alcohol at 65–70° for 15 minutes (the optimum time) produced material containing conjugated dodecatetraene-diynes, since the ultraviolet spectrum (highest wave length maxima at 327 and 352 mμ)

I $\longrightarrow$ HC≡CCH$_2$CH$_2$C≡CC≡CCH$_2$CH$_2$C≡CH

$\quad\quad\quad\quad\quad\quad\quad$ X

II $\longrightarrow$ CH$_2$=CHCH=CHC≡CC≡CCH=CHCH=CH$_2$
$\quad\quad\quad\quad\quad\quad\quad$ XI

resembled that of the known 1,3,9,11-dodecatetraene-5,7-diyne (XI) (highest wave length maxima at 328 and 352 mμ).[7] Since no intensity values for the latter substance had been reported,[7] it was prepared by us (presumably as a mixture of cis and $trans$ isomers) by the oxidative coupling of the above-described 1,3-hexadien-5-yne (II) with oxygen in the presence of cuprous chloride and ammonium chloride. On the basis of the ultraviolet spectrum of the resulting XI (Table I), the yield of tetraene-diynes obtained by the rearrangement of X is estimated to be of the order of 40%.

Chromatography of the rearrangement product from X on alumina and spectral examination of the fractions showed that a complex mixture of conjugated tetraene-diynes had been produced. About 10% of a substance could, however, be obtained from the less polar fractions, which is almost certainly the α,γ-diyne XI as evidenced by the close resemblance of the ultraviolet spectrum (Table I) as well as of the infrared spectrum to that of the authentic material.

It can be seen that the prototropic rearrangement of higher linear 1,5-diynes to polyen-ynes, though proceeding readily, is complicated by the fact that the acetylenic bond or bonds in the products can take up one of several positions, a situation which of course does not arise in the rearrangement of 1,5-enynes to polyenes.[1]

The application of the type of isomerization carried out in this paper to cyclic 1,5-diynes will be reported subsequently.

Experimental[19]

1,3-Hexadien-5-yne (Ethinylbutadiene) (II) from 1,5-Hexadiyne (I).—A solution containing 32 g. of 1,5-hexadiyne[2] and 11.2 cc. of a saturated solution of potassium t-butoxide in t-butyl alcohol was heated during 6 minutes to 70°, under a reflux condenser in nitrogen, moisture being excluded. Although the bath was then removed, the internal temperature rose to 80–85° (boiling) indicating that an exothermic reaction was taking place. The temperature remained in this range for another 12 minutes (without external heating) and then began to drop. The brown solution was cooled in ice, diluted with 300 cc. of pentane and washed 15 times with water. The dried and filtered

(18) F. Sondheimer, Y. Amiel and R. Wolovsky, *Proc. Chem. Soc.*, 22 (1957); *J. Am. Chem. Soc.*, **79**, 4247, 6263 (1957).

(19) For general experimental details, see footnote 22 in the preceding paper.[1] The same precautions have been taken in handling the conjugated polyen-ynes as had been taken with the conjugated polyenes (see "General Remarks" in that paper).

pentane solution was then distilled rapidly from a simple distillation flask until the boiling point reached 95°, in order to remove high-boiling and polymeric material. Ultraviolet examination of the colorless distillate ($\lambda_{max}^{pentane}$ 252 mμ) showed that it contained 65% of the dien-yne II ($\epsilon_{max}^{252\,m\mu}$ 26,300[3] being taken for the pure substance).

The pentane was then distilled off through a 60-cm. Dufton column during 3 hr. (the ultraviolet spectrum of the distillate showed that some dien-yne had co-distilled).[6] Distillation of the residue through a Vigreux column gave 10.5 g. (33%) of 1,3-hexadien-5-yne, b.p. 82–83° (756 mm.), n^{24}D 1.5053; $\lambda_{max}^{isooctane}$ 252 mμ (ϵ 25,500; c 2.2 × 10^{-5} mole/l.); infrared bands (neat) at 3.03(s) and 4.75(m) μ (terminal acetylene); 9.98(s) and 10.93(s) μ (monosubstituted ethylene); 10.60(m) μ (conjugated $trans$-ethylene); as well as at 3.23(m), 3.29(m), 5.47(m), 5.78(w), 6.17(w), 6.31(m), 6.40(m), 6.98(m), 7.77(m), 8.01(m), 8.25(s), 11.82(w) and 12.76(m) μ^{20} [reported for II from acetylene: b.p. 83.4° (760 mm.),[9] n^{20}D 1.5095[9]: $\lambda_{max}^{isooctane}$ 252 mμ (ϵ 26,300 ± 500; c 2.6 × 10^{-5} moles/l.)[3]; infrared bands (vapor) at 2.99(s), 3.20(m), 3.26(m), 4.78(w), 5.49(m), 5.76(w), 6.21(w), 6.35(w), 6.97(w), 7.78(w), 8.03(m), 8.26(s), 10.00(s), 10.62(m), 10.95(s), 11.01(s), 11.83(w) and 12.80(m) μ^3].

Anal. Calcd. for C$_6$H$_6$: C, 92.26; H, 7.74; acetylenic H(1), 1.29. Found: C, 91.98; H, 7.66; acetylenic H,[4] 1.26.

A lower yield of II was obtained when the reaction of I with potassium t-butoxide was allowed to proceed for a longer time. Attempted distillation of the dien-yne II after it had been stored for 3 months at −10° resulted in a violent explosion.

The **maleic anhydride adduct IV** was prepared by boiling under reflux for 4 hr. a solution containing 1.50 g. (0.0192 mole) of the dien-yne II and 1.84 g. (0.0188 mole) of freshly distilled maleic anhydride in 5 cc. of dry benzene, moisture being excluded. The resulting brown mixture was evaporated to dryness. Distillation of the residue under reduced pressure gave at first unchanged maleic anhydride and then 0.33 g. (10%) of the adduct IV as a viscous oil, b.p. 160–180° (bath temp.) (0.8 mm.), which gradually solidified. Crystallization from ether–pentane followed by re-distillation at 90–100° (bath temp., 0.1 mm.) gave an analytical sample, m.p. 84–85°; infrared bands (KBr) at 3.03(s) and 4.76(w) μ (terminal acetylene) and 5.40(s) and 5.63(s) μ (five-membered cyclic anhydride).

Anal. Calcd. for C$_{10}$H$_8$O$_3$: C, 68.18; H, 4.58. Found: C, 68.42; H, 4.73.

Gas–Liquid Partition Chromatography (g.l.p.c.) of 1,3-Hexadien-5-yne (II).—A sample of the dien-yne II was submitted to g.l.p.c. on a Perkin–Elmer Model 154A Fractometer using a column (4 mm. × 2 m.) filled with a 2:1 mixture of diatomaceous earth fire brick (Johns–Manville C-22; 60–80 mesh) and tri-o-tolyl phosphate at 25° and a helium flow-rate of 36 cc./minute. Two peaks appeared with retention times of 49 and 54 minutes, respectively, having areas in the ratio 65:35; in addition a shoulder (retention time ca. 45 minutes) was observed. Essentially identical results were obtained when the total volatile material from the rearrangement of I, in pentane solution, was subjected to g.l.p.c., except of course for the appearance of the additional pentane peaks.

The above-mentioned shoulder was shown to be due to unchanged I by comparison with the retention time of an authentic sample, and to amount to ca. 3% by a separate chromatogram using Octoil as stationary phase whereby its peak appeared clearly before cis- or $trans$-II.

For identification of the major peaks, 70 mg. of II was chromatographed at 25° on a preparative column (20 mm. × 2 m.) with tri-o-tolyl phosphate as stationary phase as before, the helium flow-rate being 600 cc./minute. The gas flow was slowed to 150 cc./minute when the first peak began to appear. Two fractions were then collected in traps cooled in liquid air, the traps being changed immediately after the maximum of the first peak had appeared (this procedure was followed in view of considerable overlap of the peaks). The first fraction by g.l.p.c. analysis gave only the first peak together with the shoulder due to unchanged I, while the second gave both peaks with about equal areas. The two fractions showed similar infrared

(20) s = strong, m = medium, w = weak.

spectra (neat), except that the 10.60 and 11.82 μ peaks, present in II before chromatography, had disappeared in the first but appeared strengthened in the second; the ultraviolet spectra of both fractions, determined qualitatively in pentane, showed maxima at 252 mμ.

A solution of 150 mg. of II and 190 mg. of maleic anhydride in 5 cc. of ether and 5 cc. of pentane was boiled under reflux for 3 hr. and then subjected directly to g.l.p.c. analysis, as before. The relative areas of the two peaks due to II were found to be 85:15, the first peak being the larger.

1,3,5,7-Decatetraen-9-yne (IX) and the Isomer VII and/or VIII from 1,5,9-Decatriyne (VI).—A solution containing 1.3 g. of 1,5,9-decatriyne,[16] 300 cc. of a saturated solution of potassium t-butoxide in t-butyl alcohol and 300 cc. of benzene was boiled gently under reflux for 1.5 hr. (a small-scale experiment, in which the ultraviolet spectra of aliquots were determined, had shown this to be the optimum time). The solution was poured into water, ether was added and the organic extract was washed repeatedly with water, dried and evaporated. The residue then was dissolved in 20 cc. of pentane and chromatographed on a column of 400 g. of alumina, which was developed with pentane (100-cc. fractions).

Fractions 9–28 contained the conjugated tetraen-yne with internal acetylene, as evidenced by the spectra of representative members (longest ultraviolet maxima at $ca.$ 307 and 327 mμ; infrared bands at 4.58 but not at $ca.$ 3.03 μ). These fractions on evaporation yielded 0.35 g. (27%) of the tetraen-yne VII and/or VIII as a colorless liquid with ultraviolet properties in isoöctane recorded in Table I; $\lambda_{max}^{benzene}$ 298, 312 and 332 mμ. A small sample was distilled at 100–120° (bath temp., 0.5 mm.) and yielded a liquid with almost unchanged ultraviolet spectral properties; infrared bands (chloroform) at 4.58(w) μ (disubstituted acetylene), 9.99(s) and 10.94(s) μ (monosubstituted ethylene) and 10.62(m) μ (conjugated $trans$-ethylene), no terminal acetylene or allene bands at $ca.$ 3.03 or 5.10 μ.

Anal. Calcd. for $C_1 H_{10}$: C, 92.26; H, 7.74. Found: C, 91.85; H, 7.70.

The substance polymerized rapidly on being allowed to stand in light and air. Even a pentane solution started to form an insoluble polymer after several days in the dark at −10°. It was not found possible to prepare a crystalline maleic anhydride adduct.

Re-chromatography of the undistilled material (0.25 g.) on 50 g. of alumina and elution with pentane yielded some fractions, more polar than the rest, which partially solidified. Slow crystallization from pentane gave $ca.$ 20 mg. of the crystalline tetraen-yne VII or VIII as colorless prisms, m.p. 46–47°; ultraviolet properties in isoöctane recorded in Table I; $\lambda_{max}^{benzene}$ 300(infl.), 313, 318(infl.) and 334 mμ; infrared bands (chloroform) at 4.57(w) μ (disubstituted acetylene), 10.00(s) and 10.95(s) μ (monosubstituted ethylene) and 10.63(s) μ ($trans$-ethylene), no bands at $ca.$ 3.03 or 5.10 μ.

Anal. Calcd. for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.42; H, 7.88.

The crystalline substance after 24 hr. in light and air had become completely insoluble. A pentane solution was unchanged after being kept for 8 days at −10° in the dark.

Fractions 42–80 from the original chromatogram contained the conjugated tetraen-yne IX with terminal acetylene (longest ultraviolet maxima at $ca.$ 313 and 329 mμ; infrared bands at 3.03(s) and 4.76(w) μ). These fractions on evaporation gave 0.26 g. (20%) of IX as a colorless oil with ultraviolet data in isoöctane recorded in Table I; $\lambda_{max}^{benzene}$ 295(infl.), 307, 321 and 338 mμ; infrared bands (chloroform) at 3.03(s) and 4.76(w) μ (terminal acetylene); 9.92(s), 10.13(s) and 10.97(s) μ (monosubstituted ethylene); and 10.52(m) μ ($trans$-ethylene). A part was distilled at 100–110° (bath temp., 0.4 mm.) and yielded a specimen with essentially identical ultraviolet and infrared spectral properties. The substance was very unstable and had become completely insoluble after being allowed to stand for 2 hr. in air and light.

Anal. Calcd. for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 91.20; H, 7.70.

1,3,9,11-Dodecatetraene-5,7-diyne (XI) from 1,3-Hexadien-5-yne (II).—Concentrated hydrochloric acid (1.7 cc.) was added to a solution of 17 g. of cuprous chloride and 51 g. of ammonium chloride in 160 cc. of water. A solution of 5.2 g. of the dien-yne II (from I) in 150 cc. of methanol was added and the mixture was shaken vigorously in oxygen until uptake stopped ($ca.$ 10 hr.).[21] Ether and water were added, the aqueous layer was extracted twice more with ether and was then diluted with 7.5 N ammonia and again extracted with ether. The combined ether extracts were washed with dilute ammonia, sulfuric acid, sodium bicarbonate solution and water. The dried solution was evaporated and the residue, dissolved in 20 cc. of pentane, was chromatographed on a column of 1.2 kg. of alumina (covered with black paper), which was developed with pentane. Fractions 31–63 (100 cc. each) on evaporation gave 3.25 g. of the liquid coupling product XI, which by ultraviolet examination was $ca.$ 80% pure (yield 50%). Distillation of a sample at 70–80° (bath temp., 0.003 mm.) gave pure XI as a light yellow viscous liquid, n^{26}D 1.6745; ultraviolet properties in isoöctane recorded in Table I; $\lambda_{max}^{benzene}$ 290, 312, 334 and 359 mμ; infrared bands (chloroform) at 4.56(w) and 4.70(w) μ (α,γ-diyne), 10.02(s) and 10.93(s) μ (monosubstituted ethylene) and 10.63(m) μ ($trans$-ethylene) (reported[7]: λ_{max} 231, 251, 265, 273, 285, 307, 328 and 352 mμ).

Anal. Calcd. for $C_{12}H_{10}$: C, 93.46; H, 6.54. Found: C, 93.03; H, 6.28.

1,3,9,11-Dodecatetraene-5,7-diyne (XI) and Isomers from 1,5,7,11-Dodecatetrayne (X).—A solution containing 50 mg. of the tetrayne X[18] and 17 cc. of a saturated solution of potassium t-butoxide in t-butyl alcohol was heated at 65–70° (internal temperature) under a reflux condenser in nitrogen. Aliquots were removed at intervals, diluted with pentane, washed well with water, dried and the ultraviolet spectra were determined against pentane. All the solutions showed the multiple maxima with the two highest wave length bands at $ca.$ 328 and 352 mμ of a conjugated tetraen-yne (after 25 minutes an additional band at 335 mμ and other changes were observed, indicative of secondary reactions). The yields are based on the 352 mμ band (ϵ 38,200) of pure XI.

Time, min.	5	10	15	20	25	30	45	60
Yield, %	25	32	42	39	34	31	24	24

A preparative experiment was carried out by heating 550 mg. of the tetrayne X with 185 cc. of butoxide for 15 minutes at 65–70°, followed by isolation with pentane as previously. The total product showed a weak infrared band (chloroform) at 3.04 μ, indicative of the presence of some terminal acetylene. It was dissolved in 20 cc. of pentane and chromatographed on a column of 600 g. of alumina (covered with black paper), which was developed with pentane. Representatives of fractions 25–35 (100 cc. each) showed ultraviolet spectra very similar to that of the coupling product XI. Combination and evaporation of these yielded 57 mg. (10%) of a pale yellow viscous liquid with ultraviolet data recorded in Table I. The infrared spectrum (chloroform) showed bands at 4.55(w) and 4.69(w) μ (α,γ-diyne), 10.02(s) and 10.94(s) μ (monosubstituted ethylene) and 10.64(m) μ ($trans$-ethylene), and was virtually identical with that of XI from II.

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