Unsaturated Macrocyclic Compounds. LVIII.[1] The Reaction of *trans*-1,4-Dibromo-2-butene and *trans*-1,4-Dichloro-2-butene with Ethynylmagnesium Bromide. The Synthesis of Precursors of Fully Conjugated 14-, 16-, 20-, and 26-Membered Ring Cyclic Compounds

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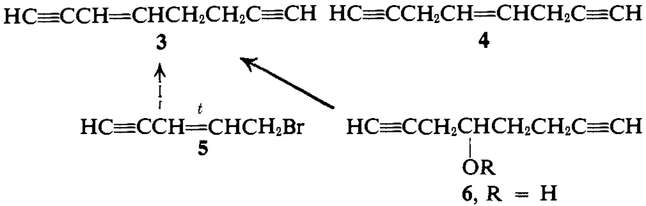
Abstract: Condensation between *trans*-1,4-dibromo-2-butene (**8**) and an excess of ethynylmagnesium bromide (**10**) gave *trans*-4-octene-1,7-diyne (**14**), as well as smaller amounts of *trans,trans*-4,10-tetradecadiene-1,7,13-triyne (**15**) and *all-trans*-4,10,16-eicosatriene-1,7,13,19-tetrayne (**16**). Similarly, condensation between *trans*-1,4-dichloro-2-butene (**9**) and an excess of **10** led to **14** and **15**. *trans*-1-Bromo-2-hexen-5-yne (**11**) and *trans*-1-chloro-2-hexen-5-yne (**12**) are presumably intermediates in these reactions, and these substances were shown to be formed from **8** and **9**, respectively, by condensation with no more than 1 molar equiv of **10**. Neither **11** nor **12** could be obtained pure, but the corresponding iodide **13** was isolated in the pure state by treatment of crude **12** with sodium iodide. Reaction of the iodide **13** with the bis-Grignard derivative of **15** led to *all-trans*-4,10,16,22-hexacosatetraene-1,7,13,19,25-pentayne (**17**). Rearrangement of **14** with potassium *t*-butoxide readily gave 1,3,5-octatrien-7-yne (**18**) and a small amount of *trans*-4-octene-2,6-diyne (**20**), while similar rearrangement of **15** yielded tetradecahexaenyne(s) (type **22**). Substances **14**, **15**, **16**, and **17** are members of a series of linear 1,4-enynes containing terminal acetylenes, which were expected to give dehydroannulenes by oxidative coupling and subsequent rearrangement. In practice, **14**, **15**, and **16** have been converted by this method to dehydro[16]-, dehydro[14]-, and dehydro[20]annulenes, respectively, as reported elsewhere (the oxidative coupling of **16** to the cyclic monomer **24** is described in the present paper). Although **17** did not give a dehydro[26]annulene by this method, it has been possible to convert the iodide **13** to a tridehydro[26]annulene by a different route.

It has been shown by our group that fully conjugated 12-,[3] 18-,[4,5] 24-,[4] and 30-membered[4] ring cyclic polyenynes (dehydroannulenes) can be obtained from 1,5-hexadiyne (**1**) by oxidative coupling to the cyclic dimer, trimer, tetramer, and pentamer, respectively, followed by prototropic rearrangement. Similar coupling of 1,5,9-decatriyne (**2**), and rearrangement of the resulting cyclic dimer and trimer, led to dehydro[20]- and dehydro[30]annulenes.[6] The presently described work was initiated in 1959 in order to obtain fully conjugated macrocyclic compounds belonging to the 16-membered ring series by a similar reaction sequence. For this purpose, it appeared appropriate to synthesize either 3-octene-1,7-diyne (**3**) or 4-octene-1,7-diyne (**4**) (the *trans* or *cis* isomers), which on oxidative coupling to the cyclic dimers and subsequent rearrangement were expected to give a bisdehydro[16]annulene.

$$\underset{\mathbf{1}}{HC{\equiv}CCH_2CH_2C{\equiv}CH} \qquad \underset{\mathbf{2}}{HC{\equiv}CCH_2CH_2C{\equiv}CCH_2CH_2C{\equiv}CH}$$



$$\underset{\mathbf{3}}{HC{\equiv}CCH{=}CHCH_2CH_2C{\equiv}CH} \qquad \underset{\mathbf{4}}{HC{\equiv}CCH_2CH{=}CHCH_2C{\equiv}CH}$$

$$\underset{\mathbf{5}}{HC{\equiv}CCH\overset{t}{=}CHCH_2Br} \qquad HC{\equiv}CCH_2\underset{OR}{CH}CH_2CH_2C{\equiv}CH$$

6, R = H
7, R = Ts

Preliminary experiments were carried out in order to synthesize the conjugated isomer **3**. This substance could not be obtained by the reaction of *trans*-1-bromo-2-penten-4-yne (**5**)[7] with the magnesium or the aluminum derivative of propargyl bromide.[8] An alternative synthesis of **3** was investigated, which used 4-pentyn-1-ol[9] as starting material. Oxidation by the Schinz modification of the Oppenauer method[10] led to 4-pentyn-1-al, which was condensed with the magnesium derivative of propargyl bromide.[8] Conversion of the resulting 1,7-octadiyn-4-ol (**6**) to the *p*-toluenesulfonate (**7**) and subsequent treatment with potassium hydroxide[11] then gave crude **3** (presumably a mixture of *trans* and *cis* isomers)[11] in very poor overall yield.

In view of these unpromising results, we concentrated our efforts on the synthesis of the unconjugated isomer **4**. In the present paper we describe a convenient syn-

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[1] For Part LVII, see K. Grohmann and F. Sondheimer, *J. Amer Chem. Soc.*, **89**, 7119 (1967).

[2] To whom inquiries should be addressed at the Chemistry Department, University College London, London W. C. 1, England.

[3] R. Wolovsky and F. Sondheimer, *J. Amer. Chem. Soc.*, **87**, 5720 (1965); F. Sondheimer, R. Wolovsky, P. J. Garratt, and I. C. Calder, *ibid.*, **88**, 2610 (1966).

[4] F. Sondheimer and R. Wolovsky, *ibid.*, **84**, 260 (1962).

[5] R. Wolovsky, *ibid.*, **87**, 3638 (1965).

[6] F. Sondheimer and Y. Gaoni, *ibid.*, **84**, 3520 (1962).

[7] H. B. Henbest, E. R. H. Jones, and I. M. S. Walls, *J. Chem. Soc.*, 3646 (1950); F. Bohlmann and H. G. Viehe, *Chem. Ber.*, **87**, 712 (1954).

[8] See C. Prévost, M. Gaudemar, and J. Honigberg, *C. R. Acad. Sci., Paris*, **230**, 1186 (1950); L. Crombie, *J. Chem. Soc.*, 4338 (1952); M. Gaudemar, *Ann. Chim.* (Paris), [13] **1**, 190 (1956); L. Groizeleau-Miginiac, *C. R. Acad. Sci., Paris*, **248**, 1190 (1959); C. Prévost, M. Gaudemar, L. Miginiac, F. Bardone-Gaudemar, and M. Andrac, *Bull. Soc. Chim. Fr.*, 679 (1959); F. Sondheimer, R. Wolovsky, and D. A. Ben-Efraim, *J. Amer. Chem. Soc.*, **83**, 1686 (1961); F. Sondheimer, Y. Amiel, and Y. Gaoni, *ibid.*, **84**, 270 (1962).

[9] *Inter alia*, E. R. H. Jones, G. Eglinton, and M. C. Whiting, *Org. Syn.*, **33**, 68 (1953).

[10] A. Lauchenauer and H. Schinz, *Helv. Chim. Acta*, **32**, 1265 (1949).

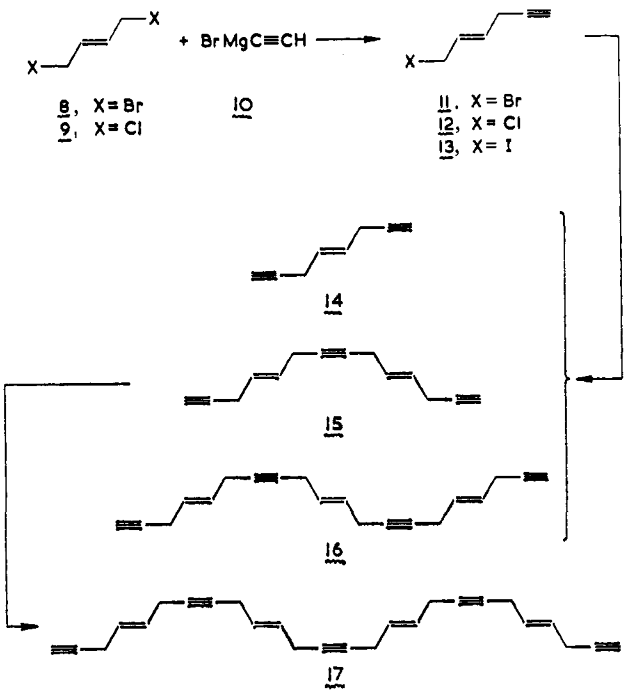
[11] For analogous eliminations, see (a) G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 3650 (1950); (b) J. L. H. Allan and M. C. Whiting, *ibid.*, 3314 (1953); (c) W. H. Okamura and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 5991 (1967).

thesis of the *trans* stereoisomer (**14**) and of several related 1,4-enynes, as well as certain transformations of these substances.[12–17] The conversion of **14** to four dehydro[16]annulenes and [16]annulene is reported in the following paper.[18]

It has been shown that allyl bromide can be condensed with the Grignard derivatives of monosubstituted acetylenes to give 1,4-enynes when the reaction is catalyzed with cuprous chloride.[19] Although ethynylmagnesium bromide (**10**)[20] does not appear to have been used successfully in this type of reaction,[21] the possibility existed that the condensation between a *trans*-1,4-dihalogeno-2-butene (**8**, **9**) and 2 molar equiv of this reagent in the presence of cuprous chloride would lead to the required *trans*-4-octene-1,7-diyne (**14**).[22] In the event, treatment of *trans*-1,4-dibromo-2-butene (**8**) with ethynylmagnesium bromide (**10**)[20] (prepared from *ca.* 3 molar equiv of magnesium) and cuprous chloride gave **14** (mp 15°) in 25% yield (Chart I). The corresponding reaction with *trans*-1,4-dichloro-2-butene (**9**) led to **14** in approximately the same yield. Although the yields are not high, these syntheses of **14** are satisfactory in view of their simplicity and the ready availability of the starting materials.

The structure of **14** is based mainly on the spectral data, given in the Experimental Section. Although the freshly prepared compound is comparatively stable, it appears to form peroxides on standing and care must be taken when aged material is distilled. In one instance, the residue remaining after distillation of *ca.* 2-year-old material exploded violently, and injured the operator (Dr. P. J. Garratt).

Chart I



Although **14** was the major product from the reaction of **8** with an excess of **10**, less volatile hydrocarbons were also formed. Two additional substances were isolated, which proved to be *trans,trans*-4,10-tetradecadiene-1,7,13-triyne (**15**, 10% yield, mp 71–72°) and *all-trans*-4,10,16-eicosatriene-1,7,13,19-tetrayne (**16**, 2% yield, mp 99–100°). Substance **15** was also obtained (in 6% yield) as a by-product from the reaction of **9** with excess **10**. The structures of **15** and **16** are again based mainly on the spectral data, as well as on the facts that catalytic hydrogenation gave *n*-tetradecane and *n*-eicosane, respectively.

The reaction of **8** or **9** with excess **10** presumably first gives *trans*-1-bromo-2-hexen-5-yne (**11**) or the corresponding chloride **12**, either of which then condenses with a second molecule of **10** to furnish the C$_8$ compound **14**. The C$_{14}$ compound **15** may well be derived by reaction between the mono-Grignard derivative of **14** (formed by interchange with **10**) and **11** or **12**. Similarly, the C$_{20}$ compound **16** may be derived by reaction between the mono-Grignard derivative of **15** and **11**.

The next higher homolog in this series of linear 1,4-enynes containing terminal acetylenes is *all-trans*-4,10,16,22-hexacosatetraene-1,7,13,19,25-pentayne (**17**). Although this C$_{26}$ compound was not isolated from the reaction of **8** or **9** with **10**, it could be obtained (22% yield, mp 114–115°) by the cuprous chloride catalyzed condensation between the bis-Grignard derivative of the C$_{14}$ compound **15** and an excess of *trans*-1-iodo-2-hexen-5-yne (**13**) (see below). The spectral data of **17** were similar to those of the lower homologs **14**, **15**, and **16**, and the structure was confirmed by a mass spectral molecular weight determination.

The above-postulated *trans*-1-bromo-2-hexen-5-yne (**11**) and *trans*-1-chloro-2-hexen-5-yne (**12**) were obtained from **8** and **9**, respectively, by the cuprous chloride catalyzed reaction with no more than 1 molar equiv of ethynylmagnesium bromide (**10**). Unfortunately, neither **11** nor **12** could be isolated in pure form, since fractional distillation did not effectively separate these substances from unchanged starting material or from **14** which had also been formed. The best method for obtaining a halide of type **11** or **12** was to condense the dichloride **9** with 0.5 molar equiv of ethynylmagnesium bromide (**10**) and then to treat the product with sodium iodide in acetone. The unchanged **9** was thereby apparently converted to butadiene and iodine,[23]

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[12] This work has been reported in part in preliminary communications.[13–16] The synthesis of *cis*-4-octene-1,7-diyne (*cis*-4) has also been reported in preliminary form.[17]

[13] C$_8$ compound (**14**): F. Sondheimer and Y. Gaoni, *J. Amer. Chem. Soc.*, **83**, 4863 (1961).

[14] C$_{14}$ compound (**15**): F. Sondheimer and Y. Gaoni, *ibid.*, **82**, 5765 (1960).

[15] C$_{20}$ compound (**16**): F. Sondheimer and Y. Gaoni, *ibid.*, **83**, 1259 (1961).

[16] C$_6$ iodide (**13**): C. C. Leznoff and F. Sondheimer, *ibid.*, **89**, 4247 (1967).

[17] D. A. Ben-Efraim and F. Sondheimer, *Tetrahedron Lett.*, 313 (1963).

[18] I. C. Calder, Y. Gaoni, and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 4946 (1968).

[19] J. P. Danehy, D. B. Killian, and J. A. Nieuwland, *ibid.*, **58**, 611 (1936).

[20] (a) E. R. H. Jones, L. Skatteböl, and M. C. Whiting, *J. Chem. Soc.*, 4765 (1956); (b) *Org. Syn.*, **39**, 56 (1959).

[21] Jones, *et al.*,[20a] reported that the attempted condensation between benzyl bromide and ethynylmagnesium bromide in the presence of cobaltous chloride led to no low-boiling products. The claim by V. Grignard, L. Lapayre, and T. Faki [*C. R. Acad. Sci., Paris*, **187**, 517 (1928)] to have condensed allyl bromide with ethynylmagnesium bromide to give 1-penten-4-yne has been shown to be incorrect (R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. Fr.*, 417 (1953); E. R. H. Jones and M. C. Whiting, *Chem. Ber.*, **93**, 761 (1960)).

[22] For the corresponding reaction between *trans*-1,4-dibromo-2-butene (**8**) and phenylacetylenemagnesium bromide (catalyzed with cuprous chloride) to give *trans*-1,8-diphenyl-4-octene-1,7-diyne, see M. Akhtar, T. A. Richards, and B. C. L. Weedon, *J. Chem. Soc.*, 933 (1959).

[23] It has been shown that 1,4-diiodo-2-butene, the presumed primary product, eliminates iodine on standing in solution at room tem-

while **12** gave *trans*-1-iodo-2-hexen-5-yne (**13**). The last-mentioned compound could then be isolated in pure form in *ca.* 40% yield (based on **10**) by simple distillation.

We have shown previously that linear 1,5-enynes can be rearranged to conjugated polyenes by heating with potassium *t*-butoxide in *t*-butyl alcohol.[24] Similarly, linear 1,5-diynes can be rearranged to conjugated polyenynes,[25] and this type of reaction was utilized in the above-mentioned syntheses of dehydroannulenes from the 1,5-diynes **1** and **2**. The synthesis of several linear 1,4-enynes containing terminal acetylenes (**14**, **15**, **16**, **17**) has been described in the present paper, and the possibility existed that these substances could be converted to dehydroannulenes by oxidative coupling to cyclic monomers, dimers, etc., followed by prototropic rearrangement. As a model, it was of interest to investigate the rearrangement of the linear 1,4-enynes themselves. Substances **14** and **15** were studied, and it was found that both were isomerized to conjugated polyenynes with potassium *t*-butoxide in *t*-butyl alcohol merely by treatment at room temperature for several minutes. As expected, the rearrangement of 1,4-enynes therefore takes place under considerably milder conditions than those used for 1,5-enynes[24] or 1,5-diynes.[25]

Treatment of **14** with a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol for 5 min led mainly to 1,3,5-octatrien-7-yne (**18**), the spectroscopic yield being *ca.* 40%.[26] The product from a preparative experiment (carried out by brief warming of **14** in benzene with the base) on chromatography on alumina gave *ca.* 25% of the liquid **18**. The ultraviolet maxima [$\lambda_{max}^{isooctane}$ 272 mμ (ε 30,100), 283 (42,800), and 297 (38,400)] agreed well with those reported for this substance, obtained by the polymerization of acetylene [$\lambda_{max}^{isooctane}$ 271, 282, and 298.5 mμ, no ε values given].[27] The ultraviolet spectrum of the isomeric 1,3,7-octatrien-5-yne (**19**) is similar,[27] but structure **18** was confirmed by the presence of terminal acetylene bands at 3.02 (s) and 4.77 μ (w) in the infrared spectrum. The infrared spectrum also exhibited a conjugated *trans*-ethylene band at 10.67 μ (s), but the exact steric configuration or steric homogeneity of **18** was not established.

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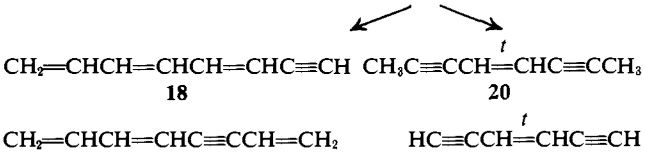

$$CH_2{=}CHCH{=}CHCH{=}CHC{\equiv}CH \qquad CH_3C{\equiv}CCH\overset{t}{=}CHC{\equiv}CCH_3$$

18 **20**

$$CH_2{=}CHCH{=}CHC{\equiv}CCH{=}CH_2 \qquad HC{\equiv}CCH\overset{t}{=}CHC{\equiv}CH$$

19 **21**

Chromatography of rearranged **14** also gave in poor yield (*ca.* 1%) a crystalline solid (mp 77–78°), assigned the *trans*-4-octene-2,6-diyne structure **20** on the basis of the spectral data. The ultraviolet spectrum [$\lambda_{max}^{isooctane}$ 257 mμ (ε 25,000), 261 (23,900), and 271 (24,900)] showed a bathochromic shift of *ca.* 8 mμ compared with *trans*-hex-3-ene-1,5-diyne (**21**) [λ_{max}^{MeOH} 251 mμ (ε 20,400) and 263 (18,100)],[11c] compatible with the presence in **20** of two additional methyl substituents.[28] The infrared spectrum exhibited an internal acetylene band at 4.47 μ (m) and a conjugated *trans*-ethylene band at 10.65 μ (s), but no bands due to terminal acetylene or terminal ethylene. Substance **20** (which contains the rare 3-ene-1,5-diyne chromophore)[11c] is derived from **14** by the shift of the two terminal acetylenes to internal positions, a reaction which has ample precedent.[29]

The C_{14} compound **15** in benzene was also treated with a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol at room temperature for 5 min. Isolation with ether then gave a solution, the ultraviolet spectrum of which indicated that tetradecahexaenyne(s) (type **22**) had been formed. Chromatography on alumina of the product from a preparative experiment (carried out by brief warming of **15** in benzene with the base) showed that the resulting polyenyne was inhomogeneous. The ultraviolet spectra of the more strongly absorbed fractions [λ_{max}^{ether} (>300 mμ) 312 mμ sh (relative optical density 0.16), 327 (0.32), 344 (0.61), 362 (0.99), and 385 (1.00)] were very similar to that of 1,3,5,7,9,11,13-tetradecaheptaene (**23**) [$\lambda_{max}^{isooctane}$ (>300 mμ) 316 mμ sh (relative optical density 0.13), 332 (0.26), 350 (0.56), 368 (0.92), and 390 (1.00)],[24,30] but a hypsochromic shift of *ca.* 5 mμ of each maximum was apparent. Such a shift is to be expected when a double bond in a conjugated polyene is replaced by an acetylene (*inter alia*, see ref 25), and supports the tetradecahexaenyne structure (type **22**). The material was very unstable, and we could not determine the sequence of the double bonds and the acetylene. It is possible that compounds of type **22** are formed as heptamers (together with the lower vinylogs) in the polymerization of acetylene with cuprous chloride and ammonium chloride,[27,31] but have not been detected due to their instability.

$$\mathbf{15} \longrightarrow \underset{\mathbf{22}}{H{-}(CH{=}CH)_6{-}C{\equiv}CH} \qquad \underset{\mathbf{23}}{H{-}(CH{=}CH)_7{-}H}$$

Chromatography of rearranged **15** also led to a very unstable yellow crystalline substance (mp 91–93°) in poor yield (*ca.* 3%). The ultraviolet spectrum indicated an extended chromophore, but its structure was not determined.

Application of the above-described type of rearrangement to cyclic coupling products of the linear 1,4-enynes **14**, **15**, **16**, and **17** was expected to lead to dehydroannulenes. The C_8 compound **14** in fact has been converted to dehydro[16]annulenes by this reaction sequence, as described in the following paper.[18] Similarly, the C_{14} compound **15** has been transformed to a number of dehydro[14]annulenes,[14,32,33] as will be reported in detail in a subsequent paper in this series.

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perature [A. A. Petrov, *Dokl. Akad. Nauk SSSR*, 72, 515 (1950); *Chem. Abstr.*, 45, 539*b* (1951)].

[24] F. Sondheimer, D. A. Ben-Efraim, and R. Wolovsky, *J. Amer. Chem. Soc.*, **83**, 1675 (1961).

[25] F. Sondheimer, D. A. Ben-Efraim, and Y. Gaoni, *ibid.*, **83**, 1682 (1961).

[26] The corresponding rearrangement of the 1,8-diphenyl derivative of **14** to the 1,8-diphenyl derivative of **18** with potassium hydroxide in boiling methanol has been described by Akhtar, *et al.*[22]

[27] K. K. Georgieff, W. T. Cave, and K. G. Blaikie, *J. Amer. Chem. Soc.*, **76**, 5494 (1954).

[28] See R. B. Woodward, *ibid.*, **64**, 72 (1942).

[29] See T. L. Jacobs, R. Akawie, and R. G. Cooper, *ibid.*, **73**, 1273 (1951), and references cited there.

[30] A. D. Mebane, *ibid.*, **74**, 5227 (1952).

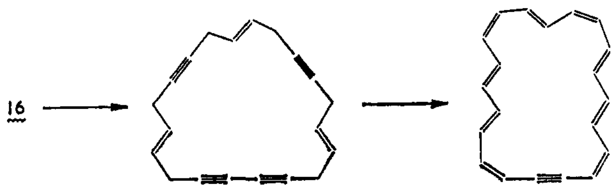
[31] J. A. Nieuwland, W. S. Calcott, F. B. Downing, and A. S. Carter, *ibid.*, **53**, 4197 (1931).

[32] F. Sondheimer, Y. Gaoni, L. M. Jackman, N. A. Bailey, and R. Mason, *J. Amer. Chem. Soc.*, **84**, 4595 (1962).

[33] For reviews, see F. Sondheimer, *Pure Appl. Chem.*, 7, 363 (1963); F. Sondheimer, *Proc. Roy. Soc.* (London), **A297**, 173 (1967); F. Sondheimer, *et al.*, Special Publication No. 21, The Chemical Society, London, 1967, p 75.

The C_{20} compound **16** has given rise to two monodehydro[20]annulenes (*e.g.*, **25**) by oxidative coupling to the cyclic monomer **24** and subsequent rearrangement, as described in a preliminary communication.[15,34] The details of the oxidation of **16** to **24** (Chart II), which was carried out in 19% yield with cupric acetate in pyridine and ether (Eglinton conditions)[35] at 70° under comparatively high dilution conditions, are given in the Experimental Section. The cyclic monomer **24** (mp 116–117°) showed infrared and ultraviolet spectra compatible with the assigned structure and gave cycloeicosane on catalytic hydrogenation. The rearrangement of **24** to the monodehydro[20]annulenes (*e.g.*, **25**) was complex and was carried out (in 1960) without the benefits of thin layer chromatography, nmr spectroscopy, or mass spectroscopy. We intend to reinvestigate this rearrangement and apply these techniques to the separation and structure identification of the products.

Chart II



24 **25**

The C_{26} compound **17** could not be oxidized to the corresponding cyclic monomer (which was expected to give a monodehydro[26]annulene on rearrangement), neither with cupric acetate in pyridine (experiments carried out by Dr. W. H. Okamura) nor with oxygen, cuprous chloride, and ammonium chloride.[33,35] However, it has now been possible to convert the above-described *trans*-1-iodo-2-hexen-5-yne (**13**) to a tridehydro[26]annulene by a different route, as described in a recent communication.[16]

Experimental Section

General Procedures. Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were measured with a Perkin-Elmer Infracord 137 or a Unicam SP 200 spectrophotometer (s = strong, m = medium, w = weak), ultraviolet spectra with a Cary 14 spectrophotometer, and nmr spectra with a Varian HA-100 spectrometer (tetramethylsilane used as internal reference). Mass spectra were determined with an AEI MS-9 mass spectrometer (direct inlet system). Glpc analyses were carried out with a F & M 720 instrument.

3-Octene-1,7-diyne (3). The oxidation of 4-pentyn-1-ol[9] to 4-pentyn-1-al was investigated under various conditions (Jones reagent, chromium trioxide in acetic acid or pyridine, sodium dichromate in sulfuric acid, Oppenauer conditions, etc.), but in no case was the aldehyde obtained in satisfactory yield. The best oxidation conditions, involving the Schinz modification of the Oppenauer method,[10] are described.

4-Pentyn-1-ol (20 g, 0.238 mol)[9] and aluminum isopropoxide (16.2 g, 0.079 mol) were placed in a three-necked flask, equipped as described by Lauchenauer and Schinz (for the oxidation of aliphatic alcohols).[10] A vacuum of 60–70 mm was applied, and the mixture was warmed to 70° and then gradually to 105° during 1 hr. The temperature was maintained at 105° for a further 30 min and was then raised rapidly to 130°. Cinnamaldehyde (54 g, 0.409 mol) was now added slowly during 30 min, while the vacuum was adjusted to 25 mm and the temperature gradually increased to 150°. The liquid which distilled was added to the distillate from another identical experiment, and the combined products (*ca.* 25 g) were redistilled through a Vigreux column. This procedure led to a mixture (10.1 g) of 4-pentyn-1-ol and 4-pentyn-1-al: bp 64–69° (26 mm); infrared bands ($CHCl_3$) at 2.90 μ (s) (hydroxyl), 3.00 (s), 4.70 μ (m) (terminal acetylene), and 3.65 (w), 5.80 μ (s) (aldehyde). The mixture readily gave a 2,4-dinitrophenylhydrazone as yellow needles, mp 133–134° (lit.[36] mp for 4-pentyn-1-al 2,4-dinitrophenylhydrazone, 130°).

Anal. Calcd for $C_{11}H_{10}N_4O_4$: C, 50.38; H, 3.84; N, 21.37. Found: C, 50.80; H, 3.91; N, 21.63.

The mixture (10.1 g) of 4-pentyn-1-ol and 4-pentyn-1-al was added during 30 min to the magnesium derivative of propargyl bromide [prepared from magnesium (3.3 g, 0.135 g-atom), propargyl bromide (16.0 g, 0.135 mol), and mercuric chloride (*ca.* 0.1 g)][8] in ether (70 ml) at −5°. The mixture was then stirred at 10° for 1 hr and poured into ice and ammonium chloride solution. The aqueous layer was extracted with ether, and the combined ether layers were washed with water and saturated sodium chloride solution. The dried extract was evaporated, and the residue distilled through a short Vigreux column. The resulting crude 1,7-octadiyn-4-ol (**6**, 0.61 g) showed bp 63–65° (2 mm); $n^{20}\text{D}$ 1.4711; infrared bands ($CHCl_3$) at 2.78 (m), 2.89 μ (m) (hydroxyl) and 3.01 (s), 4.71 μ (m) (terminal acetylene); no allene band at *ca.* 5.1 μ.

A solution of the alcohol **6** (0.5 g, 4.1 mmol) and *p*-toluenesulfonyl chloride (0.86 g, 4.5 mmol) in pyridine (2 ml) was allowed to stand at room temperature for 16 hr. Isolation with ether and crystallization from pentane–ether gave the *p*-toluenesulfonate **7** (0.68 g): mp 77–78°; infrared bands ($CHCl_3$) at 3.00 (s), 4.71 μ (w) (terminal acetylene) and 7.36 (s), 8.55 μ (s) (sulfonate).

Anal. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.84. Found: C, 65.12; H, 5.83.

A solution of potassium hydroxide (0.13 g, 2.3 mmol) in water (1.8 ml) was added to the *p*-toluenesulfonate **7** (0.55 g, 2.0 mmol) in ethanol (6 ml), and the solution was boiled under reflux for 1 hr. Isolation with ether and evaporation of the solvent then gave crude 3-octene-1,7-diyne (**3**, presumably a mixture of *trans* and *cis* isomers) (0.17 g) as a liquid; infrared bands ($CHCl_3$) at 3.01 (s), 4.70 μ (w) (terminal acetylene) and 10.46 μ (m) (conjugated *trans* double bond?); $\lambda_{\max}^{\text{isooctane}}$ 223 mμ (ϵ 9700) and 230 sh (7400). The ultraviolet spectrum indicated a purity of *ca.* 70%, compared with $\lambda_{\max}$ 222.5 mμ (ϵ 14,000) and 230 sh (10,800) reported for *trans* 3-penten-1-yne,[11b] and $\lambda_{\max}$ 221.5 mμ (ϵ 14,500) and 228.5 sh (10,700) reported for *cis*-3-penten-1-yne[11b] (values read from curves).

***trans*-4-Octene-1,7-diyne (14), *trans,trans*-4,10-Tetradecadiene-1,7,13-triyne (15), and *all-trans*-4,10,16-Eicosatriene-1,7,13,19-tetrayne (16) from *trans*-1,4-Dibromo-2-butene (8).** A solution of ethynylmagnesium bromide (**10**) in tetrahydrofuran (2 l.) was prepared from magnesium (48.6 g, 2 g-atoms), ethyl bromide (240 g, 2.2 mol), and acetylene, as described by Jones, *et al.*[20b] Cuprous chloride (2 g) was added, and a solution of *trans*-1,4-dibromo-2-butene (**8**, 140 g, 0.65 mol; mp 52–53°)[37] in tetrahydrofuran (250 ml) was then dropped in during 15 min with stirring (no appreciable exothermic reaction occurred). The mixture was stirred for a further 30 min, and more cuprous chloride (1 g) was then added. The stirred mixture was heated slowly during 1 hr in a water bath to an internal temperature of 55–60°, when an exothermic reaction occurred and external heating was stopped. The internal temperature began to fall after *ca.* 30 min. The mixture was then heated at 55–60° for a further 1.5 hr and stirred overnight at room temperature. Ether and ice–water were added, and the aqueous layer was reextracted with ether. The combined organic extracts were washed with water and saturated sodium chloride solution and were then dried and evaporated under reduced pressure. Distillation of the residue through a short column gave the fractions listed in Table I.

The combined fractions **2** and **3** on low-temperature crystallization from an equal volume of pentane yielded *trans*-4-octene-1,7-diyne (**14**, 17.0 g, 25%) as large plates: mp 15°; bp 59–60° (25 mm); $n^{19}\text{D}$ 1.4718; infrared bands ($CHCl_3$) at 3.00 (s), 4.70 μ (m) (terminal acetylene) and 10.27 μ (s) (*trans* double bond); no high-intensity absorption in the ultraviolet (isooctane); nmr spectrum (CCl_4), 2 H multiplet at τ 4.28 (olefinic protons), 4 H multiplet at

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[34] Syntheses of 1,11-bisdehydro[20]annulene and [20]annulene, which were also reported in this communication,[15] have subsequently been described in detail.[6]

[35] See G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959); G. Eglinton and W. McCrae, *Advan. Org. Chem.*, 4, 225 (1963).

[36] M. H. Durand and L. Piaux, *C. R. Acad. Sci., Paris*, 248, 2763 (1959). These investigators obtained the derivative from 1,1-diethoxy-4-pentyne (4-pentyn-1-al diethyl acetal).

[37] Substance **8** was prepared from 1,3-butadiene and bromine, according to E. M. Shantz, *J. Amer. Chem. Soc.*, 68, 2553 (1946).

Table I

Fraction	Bp (mm), °C	Weight, g
1	30–56 (22)	4.1
2	56–61 (22)	10.8
3	61–63 (22)	8.7
4	90–115 (1.5)	1.3
5	115–120 (1.5)	2.5
6	120–131 (1.5)	10.1
7	Residue[a]	15.9

[a] Occasionally a vigorous decomposition of the residue occurred.

τ 7.08 (methylene protons), and 2 H multiplet at τ 8.01 (acetylenic protons).

Anal. Calcd for C_8H_8: C, 92.26; H, 7.74; acetylenic H (2), 1.93. Found: C, 92.28; H, 7.80; acetylenic H, 2.01.[38]

The combined solid fractions **5** and **6** on crystallization from pentane–ether gave *trans,trans*-4,10-tetradecadiene-1,7,13-triyne (**15**, 5.95 g, 10%) as brilliant plates: mp 71–72°; infrared bands ($CHCl_3$) at 3.00 (s), 4.73 μ (w) (terminal acetylene) and 10.32 μ (s) (*trans* double bond); no high-intensity absorption in the ultraviolet (isooctane); nmr spectrum (CCl_4), 4 H multiplet at τ 4.36 (olefinic protons), 8 H broad singlet at τ 7.10 (methylene protons), and 2 H multiplet at τ 8.05 (acetylenic protons); mass spectrum, molecular ion peak at *m/e* 182.

Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74; acetylenic H (2), 1.11. Found: C, 92.15; H, 8.00; acetylenic H, 1.06.[38]

Full hydrogenation of **15** (platinum, ethyl acetate) led to *n*-tetradecane, mp 5–6°, undepressed on admixture with an authentic sample (mp 5–6°).[39]

The partially crystalline residue from the distillation was dissolved in benzene (*ca.* 75 ml) and chromatographed on alumina (500 g, Alcoa F-20). The fractions eluted with pentane–ether (9:1 to 4:1) which showed mp >90° were combined, evaporated, and triturated with pentane. The resulting solid on crystallization from pentane–ether gave *all-trans*-4,10,16-eicosatriene-1,7,13,19-tetrayne (**16**, 1.15 g, 2.0%) as brilliant plates, mp 99–100°; infrared bands (KBr) at 3.03 (s), 4.70 μ (w) (terminal acetylene) and 10.25 μ (s) (*trans* double bond); no high-intensity absorption in the ultraviolet (ether).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74; acetylenic H (2), 0.77. Found: C, 91.89; H, 7.69; acetylenic H, 0.74.[38]

Full hydrogenation of **16** (platinum, ethyl acetate, product crystallized from ethanol) produced *n*-eicosane, mp 35–36°, undepressed on admixture with an authentic sample (mp 36–37°).

***trans*-4-Octene-1,7-diyne (14) and *trans,trans*-4,10-Tetradecadiene-1,7,13-triyne (15) from *trans*-1,4-Dichloro-2-butene (9).** A solution of ethynylmagnesium bromide (**10**) in tetrahydrofuran (3 l.) was prepared from magnesium (73 g, 3 g-atoms), ethyl bromide (360 g, 3.3 mol), and acetylene.[20b] Cuprous chloride (7 g) was added to the stirred solution, followed by *trans*-1,4-dichloro-2-butene (**9**, 125 g, 1 mol; Eastman Kodak) in tetrahydrofuran (150 ml, addition time, 1 hr). The mixture was then heated at 55–60° for 2 hr, stirred overnight at room temperature, and finally heated at 55–60° for a further 1 hr. The products were isolated by successive ether extraction, distillation, and crystallization, as described above. This procedure yielded *trans*-4-octene-1,7-diyne (**14**, 28 g, 27%), mp 14–15°, and *trans,trans*-4,10-tetradecadiene-1,7,13-triyne (**15**, 5.1 g, 5.6%), mp 70–71°. Identity with the corresponding compounds obtained from *trans*-1,4-dibromo-2-butene (**8**) was established by mixture melting point determination and infrared spectral comparison. No attempt was made to isolate **16** in this experiment.

***trans*-1-Chloro-2-hexen-5-yne (12), *trans*-1-Iodo-2-hexen-5-yne (13), and *trans*-1-Bromo-2-hexen-5-yne (11).** A solution of ethynylmagnesium bromide (**10**) in tetrahydrofuran (1 l.), prepared from magnesium (24.3 g, 1 g-atom), ethyl bromide (120 g, 1.1 mol), and acetylene,[20b] was added during 1 hr to a stirred mixture of *trans*-1,4-dichloro-2-butene (**9**, 250 g, 2 mol) and cuprous chloride (6 g) in tetrahydrofuran (800 ml), under nitrogen. The mixture was heated at 60° for 1.5 hr, and then stirred overnight at room temperature. Water was added, followed by dilute hydrochloric acid (10%, *ca.* 1 l.), and the products were extracted with ether. The organic layer was washed successively with dilute hydrochloric acid, saturated sodium chloride solution, and water. Evaporation of the dried extract and distillation of the residue gave a liquid (181 g), bp *ca.* 40–90° (9 mm). Analysis by glpc (Apiezon L, 60–80 Chromosorb W, programmed from 65 to 200°) showed the presence of three compounds, two of which were identified as unchanged **9** and *trans*-4-octene-1,7-diyne (**14**) by comparison of the retention times with authentic samples. The peak with the highest retention time is *trans*-1-chloro-2-hexen-5-yne (**12**), since the mass spectrum of the mixture showed peaks due to **12** at *m/e* 116, 114 (M^+) and a base peak at *m/e* 79 (M − Cl). Careful distillation of the mixture through a Vigreux column did not effectively separate the components. Separation by preparative glpc was not possible, since all the fractions were contaminated with **9**.

The mixture of **9**, **12**, and **14** (181 g) was added to a solution of sodium iodide (750 g) in acetone. The solution was stirred for 16 hr at room temperature, when a large amount of iodine had been liberated. Water and ether were added, and the organic layer was washed with sodium thiosulfate solution until free of iodine. The dried extract was evaporated, and the residue was distilled through a short Vigreux column. A forerun of **14** [19.5 g, bp 46–56° (6–9 mm)] was obtained, followed by *trans*-1-iodo-2-hexen-5-yne (**13**) [80.4 g, 39% based on **10**; bp 56–57° (3.5 mm)]. Analysis by glpc showed this material to be contaminated with *ca.* 4% of **14**, which could be removed by redistillation. Substance **13** was a lachrymatory liquid: infrared bands (neat) at 3.03 (s), 4.72 μ (w) (terminal acetylene) and 10.37 μ (s) (*trans* double bond); no high-intensity absorption in the ultraviolet (ether); nmr spectrum (CCl_4), 2 H multiplet at τ 3.78–4.50 (olefinic protons), 2 H doublet (J = 7 cps) at τ 6.16 ($-CH_2I$), 2 H multiplet at τ 7.06 ($-CH_2C{\equiv}C-$), and 1 H multiplet at τ 7.94 (acetylenic proton); mass spectrum, molecular ion peak at *m/e* 205.958 (calcd for $^{12}C_6{}^1H_7{}^{127}I$, 205.959).

Anal. Calcd for C_6H_7I: C, 34.98; H, 3.43; I, 61.59. Found: C, 35.30; H, 3.30; I, 61.60.

An analogous experiment using *trans*-1,4-dibromo-2-butene (**8**) instead of **9** gave a mixture of **8**, **14**, and *trans*-1-bromo-2-hexen-5-yne (**11**). This was indicated by glpc and the mass spectrum of the mixture, which showed peaks due to **11** at *m/e* 160, 158 (M^+) and a base peak at *m/e* 79 (M − Br). Careful distillation or preparative glpc again effected no satisfactory separation.

***all-trans*-4,10,16,22-Hexacosatetraene-1,7,13,19,25-pentayne (17).** A solution of **15** (4.5 g, 25 mmol) in tetrahydrofuran (150 ml) was added during 15 min to a stirred solution of ethylmagnesium bromide in tetrahydrofuran (100 ml), prepared from magnesium (1.82 g, 75 mg-atoms) and ethyl bromide (8.7 g, 80 mmol). Cuprous chloride (1 g) was then added, followed by the iodide **13** (15.5 g, 75 mmol). The mixture was stirred at 60° for 1 hr and then at room temperature for 16 hr. Water and ethyl acetate were added, and the organic layer was washed successively with dilute hydrochloric acid, saturated sodium chloride solution, and water. The dried extract was concentrated to *ca.* 150 ml and cooled. The resulting solid on recrystallization from benzene gave *all-trans*-4,10,16,22-hexacosatetraene-1,7,13,19,25-pentayne (**17**, 1.81 g, 22%) as shiny plates: mp 114–115°; infrared bands (KBr) at 3.03 (s), 4.69 μ (w) (terminal acetylene) and 10.26 μ (s) (*trans* double bond); no high-intensity absorption in the ultraviolet; nmr spectrum ($CDCl_3$), 8 H multiplet at τ 4.29 (olefinic protons), 16 H broad singlet at τ 7.04 (methylene protons), and 2 H multiplet at τ 7.90 (acetylenic protons); mass spectrum, molecular ion peak at *m/e* 338 (very weak).

Anal. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.30; H, 8.05.

Rearrangement of *trans*-4-Octene-1,7-diyne (14) with Potassium *t*-Butoxide (with G. W. Brown). A saturated solution of potassium *t*-butoxide in *t*-butyl alcohol (10 ml) was added to substance **14** (100 mg), and the solution was allowed to stand at room temperature for 5 min. It was then poured into water, and the product was extracted with ether. The dried ether extract showed λ_{max} 272 mμ (ϵ 17,800), 284 (17,800), and 297 (15,300), due to **18**; the estimated yield was *ca.* 40%, based on ϵ_{297} 38,400 of the pure substance (see below).

A preparative experiment was carried out by adding a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol (100 ml) to **14** (1.5 g) dissolved in benzene (100 ml) and heating the solution under reflux on a steam bath for 5 min. Addition of water and isolation with ether gave material (1.1 g), which was chromatographed on alumina (400 g, Alcoa F-20). Combination of the earlier fractions eluted with pentane (all containing a terminal acetylene, as determined by the infrared spectra) and evaporation yielded 1,3,5-octatrien-7-yne (**18**) (345 mg, 23%) as an almost colorless liquid

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(38) Determined by titration against silver nitrate, according to R. M. Evans [quoted by G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 3052 (1953)].

(39) *Inter alia*, F. Sondheimer, Y. Amiel, and R. Wolovsky, *J. Amer. Chem. Soc.*, **79**, 6263 (1957).

which rapidly became yellow on standing. The analytical sample, obtained by distillation at 80° (bath temperature) (16 mm), showed $n^{24}\text{D}$ 1.5940; infrared bands ($CHCl_3$) at 3.02 (s), 4.77 μ (w) (terminal acetylene), 9.94 (s), 10.99 μ (s) (monosubstituted double bond), and 10.67 μ (s) (conjugated *trans* double bond), no internal acetylene band at 4.47 μ (see below); ultraviolet spectrum, see Discussion.

Anal. Calcd for C_8H_8: C, 92.26; H, 7.74. Found: C, 90.34;[40] H, 7.82.

The infrared spectra of the later fractions eluted with pentane showed terminal acetylene bands at 3.02 (m) and 4.77 μ (w) due to **18**, as well as an internal acetylene band at 4.47 μ (w) due to **20**. The combined fractions were evaporated, and the semisolid residue (343 mg) was crystallized from pentane. This procedure led to *trans*-4-octene-2,6-diyne (**20**, 15 mg, 1%) as prisms: mp 77–78°; infrared bands ($CHCl_3$) at 4.47 μ (m) (internal acetylene) and 10.65 μ (s) (conjugated *trans* double bond), no terminal acetylene band at *ca.* 3.00 μ or monosubstituted double bond band at *ca.* 10.0 or 11.0 μ; ultraviolet spectrum, see Discussion. The substance was very unstable in the solid state and rapidly decomposed on standing.

Anal. Calcd for C_8H_8: C, 92.26; H, 7.74. Found: C, 90.83;[40] H, 7.52.

Rearrangement of *trans,trans*-4,10-Tetradecadiene-1,7,13-triyne (15) with Potassium *t*-Butoxide (with G. W. Brown). A saturated solution of potassium *t*-butoxide in *t*-butyl alcohol (10 ml) was added to substance **15** (10 mg) dissolved in benzene (5 ml), and the solution was allowed to stand at room temperature for 5 min. It was then poured into water, and the product was extracted with ether. The dried ether extract showed $\lambda_{\max}^{\text{ether}}$ (>300 mμ) 344 mμ (ε 25,700), 361 (28,800), and 378 (22,600).

A preparative experiment was carried out by adding a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol (17.5 ml) to **15** (700 mg) dissolved in benzene (35 ml) and heating the solution under reflux on a steam bath for 3 min. Addition of water and isolation with ether gave material, which was chromatographed on alumina (300 g, Alcoa F-20). The column was eluted with pentane, and then with pentane–ether (9:1, 8:2, and 7:3). Earlier fractions showed $\lambda_{\max}^{\text{ether}}$ (>300 mμ) 337 mμ (relative optical density 0.89), 357 (1.00), and 377 (0.90). A bathochromic shift was observed in later fractions, the last fractions showing $\lambda_{\max}^{\text{ether}}$ (>300 mμ) 312 mμ sh (relative optical density 0.16), 327 (0.32), 344 (0.61), 362 (0.99), and 385 (1.00). In addition, earlier fractions exhibited a pronounced maximum at 273 mμ (more intense than the maxima >300 mμ), which steadily decreased in intensity in later fractions.

The earlier fractions on evaporation gave a yellow oil (160 mg), which partially crystallized. Pentane was added and the insoluble polymer which had formed was removed by filtration. Concentration of the filtrate and cooling gave yellow plates (22 mg, 3.1%): mp 91–93°; infrared bands (KBr) at 9.94 (s), 11.01 μ (s) (monosubstituted double bond) and 10.64 μ (m) (conjugated *trans* double bond?), no terminal acetylene band at *ca.* 3.00 μ; $\lambda_{\max}^{\text{isooctane}}$ 230 mμ (ε 15,200), 264 (36,000), 273 (46,200), *ca.* 335 sh (24,000), *ca.* 350 sh (27,200), 356 (29,600), and 376 (26,400). The substance was unstable and had completely decomposed after being allowed to stand for 24 hr in the dark.

Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.05; H, 7.79.

***all-trans*-1,7,13-Cycloeicosatriene-4,10,16,18-tetrayne (24).** The coupling of **16** to **24** was carried out under several different conditions, but only the experiment giving the best yield is described. A solution of **16** (1.9 g) in pyridine (100 ml) and ether (100 ml) was added dropwise during 4 hr to a stirred solution of cupric acetate monohydrate (10 g) in pyridine (900 ml) kept at 70°, additional 5-g portions of cupric acetate being added after the first and the second hour. The mixture was then stirred for a further 1 hr at 70°, cooled, diluted with benzene (500 ml) and ether (500 ml), and poured into 5% hydrochloric acid (3 l.). Most of the aqueous layer was removed, and the copper salts were removed by filtration. The organic layer was washed with dilute hydrochloric acid and water. The dried extract was evaporated under reduced pressure, and the residue (1.1 g, yellow solid) in benzene (*ca.* 10 ml) was chromatographed on alumina (400 g, Alcoa F-20). The fractions eluted with pentane–ether (4:1) on evaporation and crystallization from pentane–ether gave *all-trans*-1,7,13-cycloeicosatriene-4,10,16,18-tetrayne (**24**, 365 mg, 19%) as heavy prisms, mp 114–116°; recrystallization yielded the analytical sample, mp 116–117°; infrared bands (KBr) at 4.39 (w), 4.59 μ (w) (1,3-diyne) and 10.38 μ (s) (*trans* double bond), no terminal acetylene band at *ca.* 3.0 μ; $\lambda_{\max}^{\text{ether}}$ 229 mμ (ε 480), 238 (470), and 254 (240).

Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.60; H, 6.75.

Full hydrogenation of **24** (platinum, ethyl acetate, product crystallized from methanol and ethyl acetate) led to cycloeicosane, mp 60–61°, undepressed on admixture with an authentic sample (mp 61–62°).[41]

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(40) The low carbon value is presumably due to the ready oxidation of the polyenyne.

(41) F. Sondheimer, Y. Amiel, and R. Wolovsky, *ibid.*, **81**, 4600 (1959).