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THE SYNTHESIS AND SOME REACTIONS OF A SERIES OF "SKIPPED" POLYACETYLENES CONTAINING TERMINAL ACETYLENE GROUPS*

D. A. BEN-EFRAIM and F. SONDHEIMER†
Chemistry Department, Weizmann Institute of Science, Rehovoth, Israel

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Abstract—The synthesis and some reactions of a series of linear 1,4-polyynes containing terminal acetylene groups (Ia–e) are described. Reaction of propargyl bromide (II) with ethynylmagnesium bromide (III) in the presence of CuCl gave 1,4-pentadiyne (Ia). Rearrangement of Ia with $KOBu^t$ led to 1,3-pentadiyne (IV), while treatment with Br_2 furnished 1,2,4,5-tetrabromo-1,4-pentadiene (V). Oxidation of Ia with O_2, CuCl and NH_4Cl yielded the linear dimer (VIa) [rearranged to 2,4,6,8-decatetrayne (VIII) with KOH] and linear trimer (VIb). Hydrogenation of the crude oxidation product gave saturated hydrocarbons derived from VIa, VIb, the linear tetramer (VIc) and the cyclic tetramer (VII), but none derived from the cyclic dimer or cyclic trimer of Ia. Similarly, oxidation of Ia with $Cu(OAc)_2$ in pyridine and subsequent hydrogenation led to saturated hydrocarbons derived from VIa and VIb, but none derived from the cyclic dimer or cyclic trimer. In order to prepare cyclodecane as a comparison compound, the cycloethylenedithioketal (X) derived from cyclodecanone was treated with Raney Ni in boiling EtOH, but the reaction led mainly to *cis*-cyclodecene. Treatment of 1,4-dibromo-2-butyne (XIII) with an excess of III in the presence of CuCl yielded 1,4,7-octatriyne (Ib), 1,4,7,10,13-tetradecapentayne (Id) and 1,4,7,10,13,16,19-eicosaheptayne (Ie). Rearrangement of Ib with alkaline Al_2O_3 or $KOBu^t$ at room temp gave 2,4,6-octatriyne (XVII), while treatment with boiling ethanolic KOH or $KOBu^t$ in hot Bu^tOH led to 2-ethoxy-2-octene-4,6-diyne (XVIIIa) or 2-*t*-butoxy-2-octene-4,6-diyne (XVIIIc), respectively. 1,4,7,10-Undecatetrayne (Ic) was prepared from crude Ia by conversion to the bis-Grignard derivative, followed by reaction with propargyl bromide (II) in the presence of CuCl.

THE synthesis and some reactions of compounds Ia–e are described in this paper. These are members of a series of linear polyacetylenes containing terminal acetylene

$$HC{\equiv}C{-}(CH_2{-}C{\equiv}C)_n{-}H$$

Ia, $n = 1$ (m.p. −21 to −19°)
b, $n = 2$ (m.p. 21–21·5°)
c, $n = 3$ (m.p. 44–45°)
d, $n = 4$ (m.p. 73–74°)
e, $n = 6$ (m.p. 112–113·5°)

groups, in which all the acetylenes are in a 1,4-relationship. As suggested by Gensler *et al.*,[1] these substances are referred to as "skipped" polyacetylenes.‡ We have shown previously that certain related linear 1,4-enynes[3,4] and 1,5-diynes[5] containing

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* Unsaturated Macrocyclic Compounds. LXV. (for Part LXIV, see G. W. Brown and F. Sondheimer, *J. Am. Chem. Soc.* **91**, 760 (1969). Although the present paper and the following one are concerned mainly with acyclic compounds, they have been included in this series since substances and reactions are described which were designed to lead to unsaturated macrocyclic compounds.

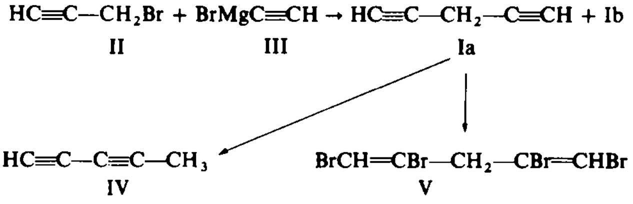
† Author to whom inquiries may be addressed: Chemistry Department, University College London, Gower Street, London, W.C.1., England.

‡ For the synthesis and reactions of other "skipped" polyacetylenes, see Ref. 2.

terminal acetylenes can be converted to fully conjugated cyclic polyenynes (dehydroannulenes) through oxidative coupling and subsequent rearrangement. The 1,4-polyynes Ia–e were prepared, since the possibility existed that by application of this reaction sequence they might be convertible to dehydroannulenes more highly unsaturated than those prepared previously. Of particular interest were the two substances Ia and Ic, since they are potential precursors of conjugated macrocyclic systems containing an odd number of carbon atoms in the ring.[6]

Rather surprisingly, even the simplest member of the series, 1,4-pentadiyne (Ia), was unknown when this work was carried out (in 1960–1963). Previous attempts to prepare this compound, by the reaction of sodium acetylide with propargyl bromide (II) or with methylene chloride in liquid ammonia, had led to the rearrangement product, 1,3-pentadiyne (IV).[7] It is known that the cuprous chloride catalyzed reaction between the Grignard derivatives of monosubstituted acetylenes and propargylic bromides gives rise to 1,4-diynes,[1,2] and that ethynylmagnesium bromide (III)[8] in a related reaction with an allylic bromide yields a 1,4-enyne.[3] It was therefore anticipated that the cuprous chloride catalyzed reaction between ethynylmagnesium bromide (III) and propargyl bromide (II) would lead to 1,4-pentadiyne (Ia), and this proved to be the case.

Propargyl bromide (II) was treated with excess III[8] and cuprous chloride in tetrahydrofuran, whereby an exothermic reaction occurred. Addition of aqueous sodium chloride solution and flash distillation of the dried organic layer gave a solution of Ia and ethyl bromide[*] (ca. 1:1) in tetrahydrofuran, as determined by GLC. The assignment of the 1,4-pentadiyne structure Ia to the new compound at this stage was based mainly on the facts that its GLC retention time differed from that of an authentic sample of 1,3-pentadiyne (IV),[7,9] and catalytic hydrogenation over platinum converted the new substance to n-pentane (GLC analysis). The yield of Ia was ca. 70%, as determined by titration against silver nitrate.[10] It was convenient to utilize this solution of Ia for most preparative purposes. Chromatography of the distillation residue (on acid-washed alumina) gave 1,4,7-octatriyne (Ib) in low yield. This substance, which was obtained in much better yield by the method described below, is probably formed by reaction between the mono-Grignard derivative of Ia (formed by interchange with III) and II.



$$\underset{\text{II}}{HC{\equiv}C{-}CH_2Br} + \underset{\text{III}}{BrMgC{\equiv}CH} \rightarrow \underset{\text{Ia}}{HC{\equiv}C{-}CH_2{-}C{\equiv}CH} + \text{Ib}$$

$$\underset{\text{IV}}{HC{\equiv}C{-}C{\equiv}C{-}CH_3} \qquad \underset{\text{V}}{BrCH{=}CBr{-}CH_2{-}CBr{=}CHBr}$$

The isolation of Ia in the pure state proved to be difficult, in view of its relative instability, its volatility, and the similarity of the boiling point and GLC retention time to those of tetrahydrofuran. After some experimentation, it was found possible to obtain a sample of pure Ia (m.p. −21 to −19°, b.p. 63–64°) by replacing the tetrahydrofuran with pentane, followed by preparative GLC. The structure of Ia

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[*] The presence of ethyl bromide is due to the fact that an excess of this reagent had been employed in the preparation of the ethylmagnesium bromide used for making III.

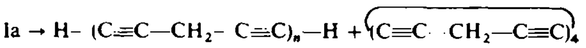
follows from the IR and NMR spectra (Experimental), the elemental analysis, and the determination of acetylenic hydrogen by titration against silver nitrate.[10] The properties of Ia were distinctly different from those of the two known isomers, 1,3-pentadiyne (IV)[7,9] and 1,2-pentadien-4-yne.[11] The diyne Ia is a colourless liquid, which turned yellow within a few minutes on being allowed to stand at room temperature. A concentrated solution in tetrahydrofuran was also found to be rather unstable, but a dilute solution in this solvent could be kept at 0° for several weeks with only little decomposition. **Warning:** a violent explosion occurred during an attempt to isolate Ia via the silver salt (Experimental).

After completion of this work, Serratosa[12a] and Casnati *et al.*[12b] reported the synthesis of Ia from II and III, but the substance was not isolated in pure form.

Rearrangement of 1,4-pentadiyne (Ia) in tetrahydrofuran with potassium t-butoxide in t-butanol at room temperature for 20 hr led to 1,3-pentadiyne (IV) in ca. 25% yield (determined spectroscopically), identified by the UV spectrum and GLC comparison with an authentic sample[7,9] (for related rearrangements of 1,4-diynes to 1,3-diynes, Ref 2). Addition of an excess of bromine to Ia in tetrahydrofuran, followed by crystallization of the product, led to one stereoisomer of 1,2,4,5-tetrabromo-1,4-pentadiene (V) (m.p. 64–65·5°). The structure V is based on the IR, UV and NMR spectra, as well as on the elemental analysis. The stereochemical configuration was not determined.

The oxidative coupling of Ia was investigated, both with oxygen, cuprous chloride and ammonium chloride (Glaser conditions),[13] as well as with cupric acetate in pyridine (Eglinton conditions).[13] Related α,ω-diethynyl-n-alkanes (homologues of Ia) has previously been shown to give a variety of linear and cyclic oligomers on oxidation under these conditions (Glaser,[5d,14] Eglinton[5a,15]).

The Glaser oxidation of Ia in tetrahydrofuran was carried out most conveniently by shaking with oxygen in a hydrogenation apparatus,[16] rather than passing oxygen through the mixture,[14] in view of the volatility of the diyne. This experiment led to a complex mixture of substances, as shown by TLC examination and catalytic hydrogenation of the crude material in ethyl acetate over a platinum catalyst. Analysis of the hydrogenation product by GLC showed that at least fourteen substances were present, four of which could be identified as n-decane, n-pentadecane, n-eicosane and cycloeicosane, by comparison of the retention times with those of the respective authentic samples. These four hydrocarbons were presumably derived from the linear dimer



$$\text{Ia} \rightarrow \text{H}-(\text{C}\equiv\text{C}-\text{CH}_2-\text{C}\equiv\text{C})_n-\text{H} + \overbrace{(\text{C}\equiv\text{C}-\text{CH}_2-\text{C}\equiv\text{C})_4}$$

VIa: $n = 2$ VII

b: $n = 3$

c: $n = 4$

(VIa), linear trimer (VIb), linear tetramer (VIc) and cyclic tetramer (VII), respectively. Cyclodecane and cyclopentadecane were found to be absent, indicating that the cyclic dimer and cyclic trimer of Ia had not been formed in the coupling reaction.

Chromatography on silica gel of the Glaser oxidation product from Ia led to the pure linear dimer (1,4,6,9-decatetrayne, VIa, m.p. 65–66°) and linear trimer (1,4,6,9,11,-14-pentadecahexayne, VIb, m.p. 103–104°) in poor yields, but the tetramers VIc and

VII could not be isolated. The structures of the rather unstable VIa and VIb are based on the spectral data, and the facts that catalytic hydrogenation as before gave n-decane and n-pentadecane, respectively, as sole products.

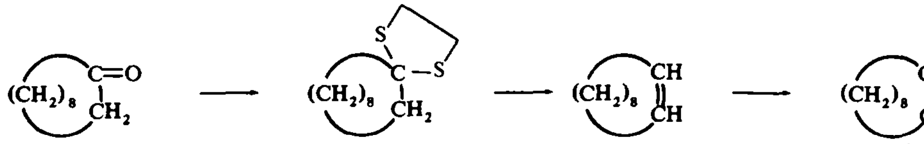
Treatment of 1,4,6,9-decatetrayne (VIa) with potassium hydroxide in methanol for ca. 1 hr at room temperature caused smooth rearrangement to the known 2,4,6,8-decatetrayne (VIII)[17] in over 80% yield (determined spectroscopically). The conjugated tetrayne VIII was obtained most conveniently (in ca. 5% yield, based on Ia)

$$\underset{\text{VIa}}{HC{\equiv}C{-}CH_2{-}C{\equiv}C{-}C{\equiv}C{-}CH_2{-}C{\equiv}CH} \rightarrow \underset{\text{VIII}}{CH_3{-}(C{\equiv}C)_4{-}CH_3}$$

by rearrangement of the total crude Glaser oxidation product from Ia with potassium hydroxide in methanol, followed by chromatography on alumina.

Eglinton oxidation of the tetrahydrofuran solution of Ia with cupric acetate in pyridine and ether at 30–35° for 2·5 hr gave a mixture of products, from which no pure compound could be isolated. Some rearrangement appeared to have taken place under the reaction conditions, as indicated by presence of VIII and allenic material in the product (UV and IR spectral analysis). Catalytic hydrogenation of the mixture in ether over platinum led to n-decane and n-pentadecane (in addition to other, unidentified, substances), presumably derived from the linear dimer VIa and the linear trimer VIb (or their rearrangement products), respectively. Cyclodecane and cyclopentadecane were again shown to be absent, indicating that the cyclic dimer and cyclic trimer of Ia had not been formed.

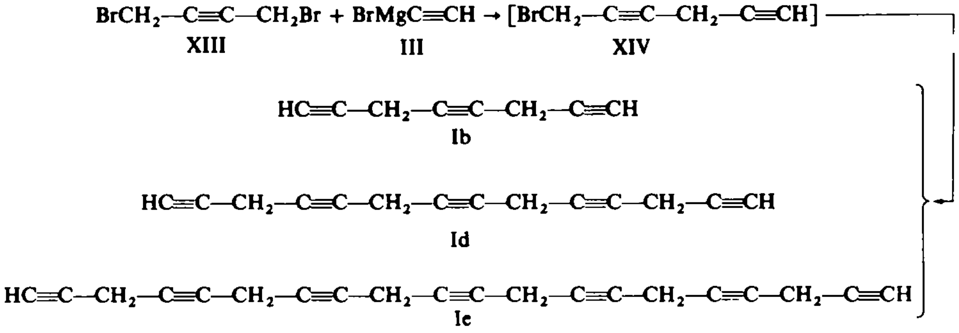
In connection with the above-described work, cyclodecane (XII) was prepared as a comparison compound from cyclodecanone (IX). Treatment of IX with 1,2-ethanedithiol and boron trifluoride etherate led to the thioketal X,[18] which was



IX X XI XII

desulfurized with Raney nickel (W 2) in boiling ethanol for 30 hr. The resulting hydrocarbon proved to be mainly *cis*-cyclodecene (XI),[19] admixed with only a small amount of cyclodecane (XII) (GLC analysis). Catalytic hydrogenation in ether over platinum then yielded pure XII. Since this work was carried out, similar conversions of dithioketals to olefins in the cyclopentane, cyclohexane and acyclic series have been described to occur under certain conditions (boiling in acetone or methyl ethyl ketone with W 2 Raney nickel;[20] boiling in ethanol with deactivated W 7 Raney nickel[21]).

Higher homologues of Ia were obtained by the reaction of 1,4-dibromo-2-butyne (XIII)[22] with ethynylmagnesium bromide (III) (prepared from ca. 4 equivalents of magnesium)[8] in tetrahydrofuran in the presence of cuprous chloride. Chromatography of the resulting mixture on acid-washed alumina gave 18% of 1,4,7-octatriyne (Ib) (m.p. 21–21·5°), 4·3% of 1,4,7,10,13-tetradecapentayne (Id) (m.p. 73–74°) and 1·4% of 1,4,7,10,13,16,19-eicosaheptayne (Ie) (m.p. 112–113·5°). The yield of the unstable triyne Ib was raised to 29% when the relative amount of III was doubled and the



$$\underset{\text{XIII}}{\mathrm{BrCH_2{-}C{\equiv}C{-}CH_2Br}} + \underset{\text{III}}{\mathrm{BrMgC{\equiv}CH}} \rightarrow \underset{\text{XIV}}{[\mathrm{BrCH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}CH}]}$$

$$\underset{\text{Ib}}{\mathrm{HC{\equiv}C{-}CH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}CH}}$$

$$\underset{\text{Id}}{\mathrm{HC{\equiv}C{-}CH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}CH}}$$

$$\underset{\text{Ie}}{\mathrm{HC{\equiv}C{-}CH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}CH}}$$

product was isolated mainly by direct distillation, but no Id or Ie was obtained in this case since the residue decomposed explosively. The structures of Ib, Id and Ie are based on the spectral data, elemental analyses, acetylenic hydrogen determination[10] (Ib, Id) and catalytic hydrogenation to the corresponding saturated n-alkanes (Id, Ie).

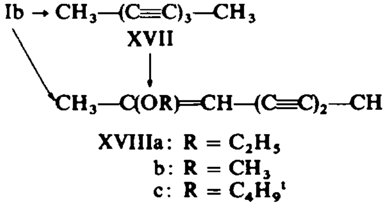
The conversion of 1,4-dibromo-2-butyne (XIII) to Ib, Id and Ie is analogous to the previously described conversion of *trans*-1,4-dibromo-2-butene (XV) to XVIa, XVIb and XVIc by treatment with an excess of ethynylmagnesium bromide (III).[3]

$$\underset{\text{XV}}{\mathrm{BrCH_2{-}CH\overset{t}{=}CH{-}CH_2Br}} + \underset{\text{III}}{\mathrm{BrMgC{\equiv}CH}} \rightarrow \mathrm{HC{\equiv}C{-}(CH_2{-}CH\overset{t}{=}CH{-}CH_2{-}C{\equiv}C)_n{-}H}$$

XVIa, $n = 1$
b, $n = 2$
c, $n = 3$

Reaction of XIII with III presumably first leads to 1-bromo-2,5-hexadiyne (XIV), which then condenses with a second molecule of III to give the C_8-compound Ib. The C_{14}-compound Id is probably derived by reaction between the mono-Grignard derivative of Ib (formed by interchange with III) and XIV. Similarly, the C_{20}-compound Ie is probably derived by reaction between the mono-Grignard derivative of Id and XIV.

The mixture obtained from the reaction of XIII with III underwent rearrangement on attempted separation by chromatography on alkaline alumina. The only pure product obtained from this experiment (in 4·9% yield) proved to be the known 2,4,6-octatriyne (XVII),[9b, 17c, 23] presumably formed from 1,4,7-octatriyne (Ib) by the action of the alkaline alumina. In addition, material containing terminal allene grouping(s) was formed, as evidenced by the IR spectrum. In a separate experiment, treatment of the unconjugated triyne Ib with alkaline alumina was indeed found to give rise to the conjugated triyne XVII, as well as allene-containing material.



$$\mathrm{Ib} \rightarrow \underset{\text{XVII}}{\mathrm{CH_3{-}(C{\equiv}C)_3{-}CH_3}}$$

$$\mathrm{CH_3{-}C(OR){=}CH{-}(C{\equiv}C)_2{-}CH_3}$$

XVIIIa: $R = C_2H_5$
b: $R = CH_3$
c: $R = C_4H_9{}^t$

The rearrangement of Ib was also studied under different conditions. The conjugated triyne XVII was obtained again (25% yield) when an ethereal solution of Ib was treated with potassium t-butoxide in t-butanol at room temperature for 1 hr. Reaction of Ib with boiling ethanolic potassium hydroxide for 45 min led to 2-ethoxy-2-octene-4,6-diyne (XVIIIa) (m.p. 42·5–43°) in 13% yield. Substance XVIIIa presumably arose from Ib by rearrangement to XVII followed by addition of ethanol. Treatment of XVII with boiling ethanolic potassium hydroxide in fact led to the ethoxy-compound XVIIIa. The analogous addition of methanol to XVII (with sodium methoxide in methanol at 100°) to give 2-methoxy-2-octene-4,6-diyne (XVIIIb) has been described previously.[24] The structure of XVIIIa was confirmed by the IR, UV and NMR spectra, as well as by the elemental composition. The NMR spectrum indicated that the crystalline XVIIIa consists of one stereoisomer, the olefinic proton signal appearing at τ 5·43. By comparison, the olefinic proton signal in the NMR spectrum of the closely related 2-methoxy-2-hexen-4-yne appears at τ 5·40 for the "*cis*" isomer and at τ 5·49 for the "*trans*" isomer.[25] Unfortunately, these values are too similar to allow a stereochemical assignment to be made to XVIIIa in the absence of the other isomer. The corresponding t-butoxy ether XVIIIc (m.p. 22–33°) was formed when the reaction of Ib with potassium t-butoxide in t-butanol was carried out with heating. The melting point range shown by XVIIIc may be due to the presence of both possible stereoisomers, but this was not investigated further.

1,4,7,10-Undecatetrayne (Ic) was prepared from the crude reaction mixture obtained from the treatment of propargyl bromide (II) with ethynylmagnesium bromide (III), containing 1,4-pentadiyne (Ia) as well as a small amount of 1,4,7-octatriyne (Ib) (see above). The mixture was treated with an excess of ethylmagnesium bromide in order to form the bis-Grignard derivatives XIX and XX, followed by cuprous chloride and an excess of propargyl bromide (II). Chromatography of the complex mixture of products on acid-washed alumina and then on silica gel led to the unstable C_{11}-compound Ic (m.p. 44–45°) in low yield. The structure of Ic was based on the spectral data and acetylenic hydrogen determination,[10] and was confirmed by catalytic hydrogenation in ether over platinum to n-undecane. Similar hydrogenation of the mixture before chromatography gave n-undecane and n-tetradecane as major components (GLC analysis). The n-tetradecane was presumably derived from the C_{14}-compound Id, although this substance was not isolated in this case. The C_{11}-compound Ic may have been formed from XIX by reaction with 2 molecules of II, or from XX by reaction with 1 molecule of II. Similarly the C_{14}-compound Id may have been formed from XX by reaction with 2 molecules of II, or from a Grignard complex of Ic (obtained by an interchange reaction) with 1 molecule of II.

$$\begin{array}{c}
\text{Ia, b} \\
\Big\downarrow \ \mathrm{EtMgBr} \\
\underbrace{\mathrm{BrMgC{\equiv}C{-}CH_2{-}C{\equiv}CMgBr}}_{\text{XIX}} + \underbrace{\mathrm{BrMgC{\equiv}C{-}CH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}CMgBr}}_{\text{XX}} \\
\Big\downarrow \ \mathrm{HC{\equiv}C{-}CH_2Br\ (II)} \\
\underbrace{\mathrm{HC{\equiv}C{-}CH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}CH}}_{\text{Ic}} + \text{Id}
\end{array}$$

EXPERIMENTAL

General procedures. M.ps (Fisher–Johns apparatus) and b.ps are uncorrected. IR spectra: on a Perkin–Elmer "Infracord" spectrophotometer (only significant bands are given: s = strong, m = medium, w = weak). UV spectra: on a Cary Model 14 spectrophotometer. NMR spectra: on a Varian Model A-60 or V-4300-B instrument, both operating at 60 Mc/s (TMS used as internal standard; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Column chromatography: on Alcoa activated Al_2O_3 grade F-20 (Aluminium Co. of America), Merck acid-washed Al_2O_3, or SiO_2 (Mallinckrodt, 100 mesh). Analytical TLC: on Kieselgel G (Merck AG, Darmstadt) using pentane and spraying with $KMnO_4$–$Cu(OAc)_2$ reagent; preparative TLC: on 20 × 20 cm plates, 1 mm thickness of absorbent. Analytical GLC: on a Pye Argon instrument using "column A" [1:2 tri-*o*-tolylphosphate on diatomaceous fire brick (60–80 mesh) or on Chromsorb W (30–60 mesh); 4 ft × 0·2 in] or "column S" [5% SE 30 silicon rubber on Chromsorb W (30–60 mesh); 4 ft × 0·2 in]; also on an Aerograph "Autoprep" Model A-700 instrument, using "column Y" [1:2 tri-*o*-tolylphosphate on Chromsorb W (30–60 mesh); 5 ft × 0·375 in.] or "column S2" [10% SE 30 silicon rubber on Chromsorb W (30–60 mesh); 4 ft × 0·2 in]. Preparative GLC: on last-mentioned instrument. Analyses were carried out in our microanalytical department under the direction of Mr. R. Heller.

1,4-*Pentadiyne* (Ia) *and* 1,4,7-*octatriyne* (Ib) *from propargyl bromide* (II) *and ethynylmagnesium bromide* (III)

A soln of III in THF (1·65 l.) was prepared from Mg (36·5 g, 1·5 g atoms), EtBr (150 ml, ca. 2·0 moles) and acetylene, essentially as described by Jones *et al.*[8] CuCl (2 g) was added, and a soln of II (59·5 g, 0·5 mole) in dry THF (60 ml) was then dropped in during 40 min with stirring (exothermic reaction). More CuCl (2 g) was added, the mixture was stirred for a further 2 hr and was then allowed to stand for 16 hr. The dark brown mixture was cooled to −20° and cold satd NaCl aq (ca. 1 l.) was added dropwise. The organic layer was washed 10 times with satd NaCl aq, dried over Na_2SO_4 and filtered. Flash distillation on a hot water bath into a cooled receiver gave a colourless distillate (800 ml, b.p. 50–67°) containing Ia, which was again dried over Na_2SO_4. Chromatography of the brown residue (14·2 g) on Al_2O_3 (Merck, 500 g), elution with pentane, evaporation to a small volume and cooling yielded Ib (0·16 g, 0·5%), m.p. 18–20°, identified by comparison (mixture m.p., IR) with the compound described below.

GLC analysis of the distillate (column A, 20°) showed peaks due to Ia and EtBr (ca. 1:1) in addition to the THF peak; IV was absent, as shown by GLC comparison with an authentic sample.[7,9] The yield of Ia was ca. 22·4 g (28 mg/ml, 70%), determined by titration against $AgNO_3$.[10] This soln of Ia (which was generally stored at −15°) was used for most preparative purposes. Catalytic hydrogenation of a sample over Pt led to a soln containing *n*-pentane and EtBr (ca. 1:1) in THF, as determined by GLC (column A, 20°).

Washing the distillate (100 ml) repeatedly with cold satd NaCl aq gave an organic layer (1·3 ml) containing 330 mg Ia/ml (15% recovery), as determined by titration against $AgNO_3$.[10] Although concentration of Ia could therefore be achieved in this way, considerable losses occurred.

A sample of pure Ia was obtained as follows. The distillate (200 ml) was washed repeatedly with cold satd NaCl aq until the organic layer was reduced to 20 ml. Pentane (9 ml) was added, and the soln was washed again several times with cold satd NaCl aq. The dried and filtered organic layer (5·5 ml) on analytical GLC examination (column A, 20°) showed the presence of Ia, EtBr and pentane, and only traces of THF. The soln contained 161 mg Ia/ml (16% recovery), as determined by titration against $AgNO_3$.[10] Separate samples (ca. 1 ml each) of the soln were submitted to preparative GLC (column Y, 20°, He flow rate 200 ml/min), Ia being collected in receivers cooled in liq air. The purity of Ia was checked by analytical GLC, and the appropriate physical property was determined as rapidly as possible in view of the instability of the substance. Ia is a colourless liquid, homogeneous by GLC (column A, 20°), m.p. ca. −21° to −19°, b.p. 63–64° (determined by the micro-method of Garcia[26]), n_D^{24} 1·4280; IR λ_{max} ($CHCl_3$) μ: 3·02(s), 4·68(w) (HC≡C); UV (EtOH): end absorption only: NMR (A-60, CCl_4)τ: 2H t (J = 3 c/s) at 6·88 (—C$\underline{H}_2$—) (see Ref. 2) and 2H t (J = 3 c/s) at 8·05 ($\underline{H}$C≡). (Found: C, 93·71; H, 6·42; acetylenic H, 3·02.[10] C_5H_4 requires: C, 93·71; H, 6·29; acetylenic H (2), 3·14%).

The colourless Ia on standing at room temp without protection from air or day light became pale yellow after 5 min, and dark yellow after 16 hr at −15° in the dark. A 16% soln in THF had become dark brown and precipitated a brown polymer after 2 days at −15° in the dark, but a 3% soln in THF had become only pale yellow after 4 weeks at 0° in the dark.

An attempt was made to isolate Ia via the Ag salt. The soln of Ia in THF (100 ml, 28 mg/ml) was diluted with EtOH (100 ml), and then shaken with 70% $AgNO_3$aq (50 ml). The resulting ppt was washed by decantation successively with ether, EtOH and H_2O. The ppt was then heated with 43% NaCN aq (50 ml) in order to regenerate Ia. When the bath temp reached 80°, a very violent explosion occurred, which shattered the apparatus and injured the operator.

Rearrangement of 1,4-*pentadiyne* (Ia) *to* 1,3-*pentadiyne* (IV)

The THF soln of Ia (40 ml, 28 mg/ml) was added dropwise with stirring to a satd soln of $KOBu^t$ in Bu^tOH during 15 min, moisture being excluded. The mixture was stirred at room temp for 20 hr (after 30 min, an aliquot on isolation with ether gave a soln which showed only end absorption in the UV), and poured into ice-H_2O. The product was extracted with ether, the ether soln was washed with satd NaCl aq and was then dried over Na_2SO_4. The UV spectrum [λ_{max} (EtOH) mμ (rel opt dens): 225 (0·96), 236 (0·85), 248 (0·50)] indicated the presence of IV [reported:[16] λ_{max} (EtOH) mμ (ε): 227 (370), 236·5 (390), 249 (210)]. The spectroscopic yield was ca. 280 mg (25%), based on the intensity of the 249 mμ maximum. GLC analysis (column A, 20°) showed the presence of IV and the absence of Ia, by comparison of the retention times with those of authentic samples.[7,9]

Bromination of 1,4-*pentadiyne* (Ia) *to* 1,2,4,5-*tetrabromo*-1,4-*pentadiene* (V)

Br_2 was added dropwise to the THF soln of Ia (40 ml, 28 mg/ml), with stirring, until decolourization ceased. The residue obtained by evaporation crystallized in part on cooling. The liquid was decanted off and the solid was dissolved in pentane. The soln was washed with H_2O, dried over Na_2SO_4 and evaporated. Repeated crystallization from pentane and then from EtOH gave V as long colourless needles, m.p. 64–65°; IR (CCl_4 or KBr): no acetylene bands at ca. 4·3–4·8 μ; UV λ_{max} (EtOH) mμ (ε): 216 (18, 700), 221 (18,100); NMR (A-60, $CDCl_3$) τ: 2H s at 3·15 ($C\underline{H}Br{=}$) and 2H s at 5·91 ($—C\underline{H}_2—$). (Found: C, 15·99; H, 1·00; Br, 82·94. $C_5H_4Br_4$ requires: C, 15·65; H, 1·05; Br, 83·31%).

Glaser oxidation of 1,4-*pentadiyne* (Ia) *to* 1,4,6,9-*decatetrayne* (*linear dimer*, VIa) *and* 1,4,6,9,11,14-*pentadecahexayne* (*linear trimer*, VIb)

A mixture of Ia in THF (100 ml, 28 mg/ml), CuCl (10 g), NH_4Cl (16 g) and H_2O (160 ml) was shaken at room temp with O_2 in an atmospheric hydrogenation apparatus in a flask wrapped with Al foil until absorption stopped (6·5 hr). The mixture was extracted with ether, and the extract was washed with H_2O. Evaporation of the dried (Na_2SO_4) soln gave a brown residue, which consisted of at least 6 components (TLC analysis). Of these, 3 appeared to possess the *n*-decane carbon skeleton, since rearrangement of each (isolated by preparative TLC) with KOH (see below) led to 2,4,6,8-decatetrayne (VIII), identified by the typical UV spectrum.

A portion (5%) of the oxidation product in EtOAc (25 ml) was shaken in H_2 over pre-reduced PtO_2 (ca. 50 mg) until absorption stopped, the mixture was filtered, and the filtrate was evaporated. Analytical GLC (column S, 50–150°) indicated the presence of n-decane, n-pentadecane, n-eicosane and cycloeicosane, and the absence of cyclodecane and cyclopentadecane (comparison of retention times with those of authentic samples). In addition, 10 unidentified compounds were found to present, with retention times intermediate between those of n-decane and n-eicosane.

Another portion (75%) of the oxidation product in benzene (5 ml) was chromatographed on SiO_2 (300 g). Elution with pentane–ether (99:1 to 98:2) and crystallization from pentane gave VIa (27 mg, 1·3%) as colourless needles, homogeneous by TLC: m.p. 65–66° (placed on block at 62°); IR λ_{max} ($CHCl_3$) μ: 3·01(s), 4·66(w) (HC≡C), 4·36(w) (C≡C): UV λ_{max} (isoöctane) mμ (ε): 225 (490), 237 (480), 251 (240). (Found: C, 95·16; H, 4·96; acetylenic H, 1·58.[10] $C_{10}H_6$ requires: C, 95·21; H, 4·79; acetylenic H (2), 1·60%). Catalytic hydrogenation of VIa in ether over Pt gave n-decane as sole product (GLC comparison with authetic sample: column S, 50). VIa was unstable, and was converted to a brown insoluble polymer after standing for 3 days at room temp without protection from air or day light.

Further elution with pentane–ether (98:2) and crystallization from pentane yielded VIb (12 mg, 0·6%) as cream-coloured crystals, homogeneous by TLC; m.p. 103–104° (placed on block at 101°); IR λ_{max} ($CHCl_3$) μ: 3·01(s), 4·68(w) (HC≡C), 4·38 (w) (C≡C); UV λ_{max} (isoöctane) mμ (ε): 227 (760), 238 (720), 252 (460). (Found: C, 96·00; H, 4·31. $C_{15}H_8$ requires: C, 95·72; H, 4·28%). Catalytic hydrogenation of VIb in ether over Pt gave n-pentadecane as sole product (GLC comparison with authentic sample; column S, 100°). VIb was partly converted to a brown insoluble polymer after being kept for 1 week at −15° in the dark.

No other crystalline compound could be isolated from the chromatogram.

2,4,6,8-*Decatetrayne* (VIII)

(a) *From Glaser oxidation product from* Ia. The remaining portion (20%) of the above described crude Glaser oxidation product from Ia was dissolved in MeOH (85 ml), and a soln of KOH (0·85 g) in MeOH (17 ml) and H_2O (2 drops) was added. The soln, which immediately turned black, was allowed to stand for 1 hr, and ether was then added. Repeated washing with H_2O, drying (Na_2SO_4) and evaporation gave material showing a UV spectrum essentially identical to that of VIII (spectroscopic yield, 64 mg, 12%, based on Ia). TLC analysis indicated the presence of at least 10 substances. The material was chromatographed on Al_2O_3 (F-20, 400 g), and the fractions showing the typical UV spectrum of VIII (eluted with pentane) were combined. Evaporation to small volume and cooling gave VIII (29 mg, 5·3% based on Ia) as colourless crystals, which rapidly turned pink and then red, and decomposed above 80° on attempted m.p. determination; homogeneous by TLC; IR λ_{max} ($CHCl_3$) μ: 4·46(s), 4·90(w) (C≡C); UV λ_{max} (EtOH) mμ (ε): 213 (87,000), 223, (207,000), 234 (285,000, 280 (87), 284 (126), 297 (104), 303 (149), 306 (160), 316 (115), 327 (171), 339 (74), 352 (99). The properties and spectra agree well with those reported for VIII.[17]

(b) *From* VIa. A soln of KOH (10 mg) in MeOH (0·2 ml) was added to a soln of VIa (5·35 mg) in MeOH (0·5 ml), and the mixture was allowed to stand for 50 min. Isolation with ether gave a soln showing the typical UV spectrum of VIII,[17b] the spectroscopic yield being 4·38 mg (82%).

Eglinton oxidation of 1,4-*pentadiyne* (Ia)

The THF soln of Ia (50 ml, 28 mg/ml) was diluted with ether (100 ml) and added to $Cu(OAc)_2 . H_2O$ (20 g) and pyridine (140 ml). The black mixture was stirred at 30° for 30 min and then at 35° for 2 hr. The mixture was filtered, the ppt was washed with hot C_6H_6, and the combined filtrates were washed with cold 10% HClaq and H_2O. Evaporation of the dried (Na_2SO_4) extract gave a brown residue; IR λ_{max} ($CHCl_3$) μ; 3·02(w) (HC≡C), 4·53(m) (C≡C), 5·09(m) (allene); UV λ_{max} (C_6H_6) mμ (rel opt dens): 283 (0·59), 299 (0·61), 310 sh (0·54), 319 (0·64), 341 (0·43), 363 (0·42), 390 (0·36), 423 (0·18). TLC analysis showed the material to be a mixture. No pure substance could be obtained by preparative TLC, but fractions were obtained showing the typical UV spectrum of VIII.

A part (ca. 20%) of the crude material in ether (50 ml) was shaken in H_2 over pre-reduced PtO_2 (ca. 50 mg) until absorption stopped. Analytical GLC (column S, 50–150°) indicated the presence of n-decane and n-pentadecane, and the absence of cyclodecane and cyclopentadecane (comparison of retention times with those of authentic samples). In addition, 4 unidentified compounds were found to be present, with retention times intermediate between those of n-decane and n-pentadecane.

cis-*Cyclodecene* (XI) *and cyclodecane* (XII) *from cyclodecanone* (IX)

A mixture of IX (1 g), 1,2-ethanedithiol (1 ml) and BF_3 etherate (1 ml) was allowed to stand at 0° for 50 min and then at 20° for 50 min. The resulting crystals of X[18] (m.p. 48–50°) were collected, washed with cold MeOH and dried; the yield was 1·05 g (70%). X (0·9 g) was then boiled for 30 hr with Raney Ni (W2, 15 g) in EtOH (110 ml). The metal was removed, the solvent was evaporated through a Vigreux column, and the residue in pentane was filtered through a column of Al_2O_3 (F-20, 20 g). Evaporation gave a colourless liquid (0·42 g, 78%) consisting mainly of XI, giving a positive test with $C(NO_2)_4$. (Found: C, 86·50: H, 13·30. Calc. for $C_{10}H_{18}$: C, 86·88, H, 13·12%). The IR spectrum (neat) closely resembled that reported for XI,[19] and differed from that of *trans*-cyclodecene[19] or of authentic XII. Analytical GLC (column S, 50°) showed a main peak due to XI, with a shoulder due to XII.

The crude XI (100 mg) in ether (20 ml) was shaken in H_2 over pre-reduced PtO_2 (ca. 50 mg) until absorption stopped. Filtration and evaporation gave XII as a colourless liquid. This gave a negative test with $C(NO_2)_4$, and on analytical GLC (column S, 50°) showed only one peak due to XII (comparison of retention time with that of authentic sample).

1,4,7-*Octatriyne* (Ib), 1,4,7,10,13-*tetradecapentayne* (Id) *and* 1,4,7,10,13,16,19-*eicosaheptayne* (Ie) *from* 1,4-*dibromo*-2-*butyne* (XIII) *and ethynylmagnesium bromide* (III)

A soln of III in THF (800 ml) was prepared from Mg (19 g, 0·78 g atoms), EtBr (65 ml, ca. 0·86 mole) and acetylene, as described by Jones *et al.*[8] CuCl (1 g) was added, the mixture was stirred at 45–50° for 15 min, and a soln of XIII[22] (42·4 g, 0·2 mole) in dry THF (100 ml) was then added during 7 min at this temp. The mixture was stirred at 60° for 45 min, and was then boiled under reflux for 3 hr. After standing at room temp for 16 hr, the mixture was diluted with ice-H_2O and extracted repeatedly with ether. The ether extract was washed with H_2O, dried (Na_2SO_4) and evaporated. The IR spectrum ($CHCl_3$) of the resulting brown oil showed acetylene bands at ca. 3·0(s), 4·3(w) and 4·7(w)μ, but no allene band at ca. 5·1 μ. Shaking a small sample in pentane with Al_2O_3 (F-20) for 16 hr resulted in the appearance of a strong IR band at ca. 5·1 μ (see also below), but Al_2O_3 (Merck) caused no appreciable change under these conditions. The oil was therefore chromatographed on Al_2O_3 (Merck, 2·45 kg), 100 ml fractions being collected.

Fractions 86–140, eluted with pentane, all deposited an insoluble brown polymer after standing for 2 days. These fractions were then combined, filtered, concentrated to small volume under reduced pressure, and cooled. Filtration through a cooled Buchner funnel yielded Ib (3·71 g, 18%) as colourless crystals. For analysis, a sample was distilled at 60–70° (bath temp) (0·6 mm), and then subjected to successive low temp crystallization from ether-pentane and pentane. The resulting Ib formed colourless glistening leaflets, homogeneous by GLC (column S, 20°), m.p. 21–21·5° (brown melt); n_D^{22} 1·4833, n_D^{30} 1·4804; IR λ_{max} ($CHCl_3$) μ: 3·02(s), 4·69(w) (HC$\equiv$C), 4·30(w) (C$\equiv$C); UV (isoöctane): end absorption only. [Found (analysis carried out immediately after prep of sample): C, 93·92; H, 5·82; acetylenic H, 1·90.[10] C_8H_6 requires: C, 94·08; H, 5·92; acetylenic H (2), 1·97%]. On standing at ca. 15° in light and air, Ib became cream-coloured after 1–2 min and then pale brown. An ether–pentane solution gradually deposited a brown insoluble polymer, even at −15°.

Fractions 226–230, eluted with pentane–ether (92 : 8 to 84 : 16), on concentration and cooling gave crude Id (770 mg, 4·3%) as pale brown crystals. This material was rechromatographed on Al_2O_3 (Merck, 100 g); elution with pentane–ether (98 : 2) and recrystallization from pentane yielded pure Id as colourless glittering leaflets, m.p. 73–74° (placed on block at 60°); IR λ_{max} (KBr)μ: 3·03(s), 4·70(w) (HC$\equiv$C), 4·30(w) (C$\equiv$C); UV (EtOH): end absorption only. (Found: C, 93·97; H, 5·64; acetylenic H, 1·07.[10] $C_{14}H_{10}$ requires: C, 94·34; H, 5·66; acetylenic H (2), 1·13%). Id was reasonably stable, and remained unchanged after standing at room temp for 2 days without protection from light or air. Catalytic hydrogenation of Id in dioxane over Pt, followed by filtration in pentane through Al_2O_3 (F-20), gave n-tetradecane, m.p. 4·5–5°, undepressed on admixture with an authentic sample (m.p. 5·5°).

Fraction 237, eluted with pentane–ether (70 : 30), on concentration and cooling yielded crude Ie (230 mg, 1·4%) as yellow crystals. This compound was rechromatographed on Al_2O_3 (Merck, 100 g); elution with pentane–ether (60 : 40) and recrystallization from ether then gave pure Ie as colourless crystals, m.p. 112–113·5° (sample placed on block at 110°); IR λ_{max} ($CHCl_3$)μ: 3·02(s), 4·70(w) (HC$\equiv$C), 4·31(w) (C$\equiv$C); UV (pentane): end absorption only. (Found: C, 94·84; H, 5·30. $C_{20}H_{14}$ requires: C, 94·45; H, 5·55%). Ie became yellow-brown after standing at room temp for 2 days without protection from light or air. Catalytic hydrogenation of Ie in dioxane over Pt, followed by crystallization from EtOH, gave n-eicosane, m.p. 35–36°, undepressed on admixture with an authentic sample (m.p. 36–36·5°).

Two identical experiments were carried out, each involving the condensation of III [from 47·5 g (1·95 g atoms) Mg][8] with XIII[22] (53 g, 0·25 mole) in THF (3·25 l.) containing CuCl (5 g) (6 hr reflux). Isolation with ether and distillation of the combined products under N_2 gave Ib as a colourless liquid, b.p. ca. 50–60° (4 mm). However, the black viscous residue decomposed explosively while being cooled at the end of the distillation and contaminated the distillate with black material. Filtration of the distillate in pentane–ether (1 : 1) through Al_2O_3 (Merck, 200 g) gave Ib (14·7 g, 29%), which solidified on cooling to 0°, and exhibited essentially the same IR spectrum ($CHCl_3$) as the analytical specimen. One crystallization from pentane of a sample gave pure Ib, m.p. 21–21·5°.

2,4,6-*Octatriyne* (XVII)

(a) *By rearrangement of the reaction product from* XIII *and* III *with alkaline alumina.* A soln of XIII[22] (66·7 g, 0·31 mole) in dry THF (170 ml) was added during 15 min to III [from 60 g (2·47 g atoms) Mg][8] in THF (2·5 l.) containing CuCl (8 g) at 45°. The temp was then raised to reflux during 105 min, and the mixture was boiled for 50 min. Isolation with ether as previously led to a viscous brown oil showing no allene band at ca. 5·1 μ in the IR spectrum ($CHCl_3$). This material was chromatographed on Al_2O_3 (F-20, 2·5 kg). Most of the fractions eluted with pentane and pentane–ether (95 : 5 to 90 : 10) now showed terminal allene bands at ca. 5·15(s), 5·85(m) and 11·70(s) μ[27] in the IR spectrum (neat or $CHCl_3$). The partially crystalline fractions eluted with pentane on crystallization from pentane gave XVII as colourless crystals (1·56 g, 4·9% based on XIII), m.p. 130° (placed on block just below this temp); IR λ_{max} ($CHCl_3$)μ: 4·49(s), 4·91(w) (C$\equiv$C); UV λ_{max} (EtOH) mμ (ε): 207 (110,000), 239 (77), 252 (127), 262 (114), 268 (169), 277 (128), 286 (175), 294 (95), 305 (102). The properties and spectra agree with those reported for XVII.[9b, 17c, 23]

(b) *By rearrangement of* Ib *with alkaline alumina.* Al_2O_3 (F-20, 20 g) was added to a soln of Ib (300 mg) in pentane (45 ml), and the mixture was stirred at room temp for 36 hr. The resulting mixture contained XVII, as evidenced by the IR and UV spectra. Material containing a terminal allene was also formed, since the IR spectrum (neat) showed λ_{max} 5·16(s), 5·85(m) and 11·75 (s) μ.[27]

(c) *By rearrangement of* Ib *with potassium* t-*butoxide*. A satd soln of KOBu^t in Bu^{t}OH (15 ml) was added to a soln of Ib (450 mg) in ether (5 ml). The black mixture was stirred at room temp for 70 min, and then poured into ice-H_2O. The product was extracted with pentane, and the pentane layer was washed with H_2O, dried (Na_2SO_4) and evaporated. The resulting pale yellow solid (191 mg, 42%) consisted of crude XVII (ca. 60% purity, estimated from the UV spectrum; yield of XVII, ca. 25%). Chromatography on Al_2O_3 (Merck, 100 g), elution with pentane, and crystallization from pentane led to pure XVII, m.p. 130°, exhibiting identical IR and UV spectra as the sample obtained by method (a).

2-*Ethoxy*-2-*octene*-4,6-*diyne* (XVIIIa)

(a) *From* Ib. A soln of KOH (15 g) in 95% EtOH (75 ml) was added to a soln of Ib (1·5 g) in 95% EtOH (15 ml). The soln was boiled under reflux for 45 min, cooled and poured into ice-H_2O. The product was extracted with pentane and chromatographed on Al_2O_3 (Merck, 300 g). The crystalline material eluted with pentane on crystallization from pentane yielded XVIIIa (294 mg, 13·5%) as colourless prisms, m.p. 42·5–43°; IR λ_{max} ($CHCl_3$) μ: 4·48(m), 4·66(m), 4·89(w) (C≡C), 6·17(s), 12·17(m) (trisubst C=C), 7·80(s), 8·18(s) $(=\overset{|}{C}-OR)$, 9·40(s) (—OR); UV λ_{max} (EtOH) mμ (ε): 222 (29,000), 251 sh (7,600), 263 (11,000), 276 (14,800), 292 (11,600) (the IR and UV spectra are very similar to those of XVIIIb[24]); NMR (V-4300-B, $CDCl_3$) τ: broad band at 5·43 $(-C\underline{H}{=}\overset{|}{C}-O-)$,[25] q ($J$ = 7 cps) at 6·31 $(-C\underline{H}_2-O-)$, s at 8·00 $(C\underline{H}_3-C{\equiv})$*, unresolved d (?) at 8·05 $(C\underline{H}_3-\overset{|}{C}{=})$* and *t* ($J$ = 7 c/s) at 8·72 $(C\underline{H}_3-CH_2-O-)$. (Found: C, 81·24; H, 8·20. $C_{10}H_{12}O$ requires: C, 81·04; H, 8·16%).

(b) *From* XVII. The triyne XVII (5 mg) was added to a soln of KOH (240 mg) in 95% EtOH (6 ml), and the soln was boiled under reflux for 1 hr. Isolation with pentane then yielded a soln showing the typical UV spectrum of XVIIIa [λ_{max} (pentane) mμ (rel opt dens): 222 (0·58), 251 sh (0·15), 264 (0·23), 276 (0·28), 292 (0·22)].

2-t-*Butoxy*-2-*octene*-4,6-*diyne* (XVIIIc)

The triyne Ib (1·5 g) was added to a satd soln of KOBu^t in Bu^{t}OH (30 ml), and the soln was heated at 75–80° (bath temp) for 20 min under N_2, using a reflux condenser. Isolation with pentane gave a partially crystalline material (1·19 g), which was now heated with a satd soln of KOBu^t in Bu^{t}OH (70 ml) at 100–110° (bath temp) for 70 min under N_2. The product was isolated with pentane and chromatographed on Al_2O_3 (F-20, 250 g). Elution with pentane–ether (85 : 15 to 72 : 25) gave crude XVIIIc (418 mg, 16%) as a colourless liquid, which solidified at 0°; UV λ_{max} (pentane) mμ (rel opt dens): 222 (1·08), 251 sh (0·31), 263 (0·51), 275 (0·67), 291 (0·55). Two further chromatographic separations on Al_2O_3 (Merck) led to a sample of XVIIIc as crystals, m.p. ca. 22–33°; IR λ_{max} ($CHCl_3$) μ: 4·46 (m), 4·67(m), 4·89(w) (C≡C), 6·18(s), 12·20(m) (trisubst C=C), 7·79(s), 8·04(s) $(=\overset{|}{C}-OR)$, 9·67(s) (—OR); UV λ_{max} (pentane) mμ (ε): 221 (28,600), 252 sh (7,900), 263 (11,300), 275 (15,800), 291 (12,900). (Found: C, 82·12; H, 9·22. $C_{12}H_{16}O$ requires: C, 81·77; H, 9·15%).

1,4,7,10-*Undecatetrayne* (Ic)

III [from 36·5 g (1·5 g atoms) Mg][8] was allowed to react with II (59·5 g, 0·5 mole) in the presence of CuCl to give Ia and Ib, as described above. The reaction mixture obtained after standing for 16 hr consisted of a brown liquid and a solid. Half of the liquid was then transferred (N_2 pressure, H_2O exclusion) into another flask, and a soln of EtMgBr [from 19·5 g (0·8 g atom) Mg] in THF (250 ml) was added dropwise during 40 min with stirring, the internal temp being kept below 30° by cooling with ice-H_2O. THF (200 ml) and CuCl (2 g) was then added, followed by a soln of II (77 g, 0·65 mole) in THF (80 ml). More CuCl (2 g) was added, and the mixture was stirred at room temp for 20 min. Since no exothermic reaction occurred, the mixture was placed in a water bath at 50° and stirred at this temp for 2·5 hr (the internal temp rose to 55° during this time). The mixture was allowed to stand for 16 hr, and was then poured into ice-H_2O. Isolation with ether gave a brown liquid (20·5 g) consisting of a least 7 components (TLC). A sample (ca. 0·1 g) in ether (20 ml) was shaken in H_2 over pre-reduced PtO_2 (ca. 50 mg) until absorption stopped. Filtration,

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* The assignments of the τ 8·00 and 8·05 bands to the acetylenic and olefinic methyl protons, respectively, are based on the similarity of the spectrum to that of the related 2-ethoxy-2-hexen-4-yne, in which the expected splittings of the olefinic methyl protons and the olefinic proton are clearly observed (see following paper).

evaporation, and filtration of the brown residue in pentane through Al_2O_3 (F-20) yielded a colourless liquid. GLC analysis (column S, 20–100°) indicated the presence of n-undecane and n-tetradecane as major components (comparison of retention times with authentic samples), as well as ca. 10 additional substances.

The brown reaction product (20·4 g) was chromatographed on Al_2O_3 (Merck, 2·3 kg), 100 ml fractions being collected. Fractions 158–173, eluted with pentane–ether (92 : 8), contained C_{11} and C_{14} hydrocarbons (GLC analysis after catalytic hydrogenation). These combined fractions were evaporated, and the residue (1·56 g brown liquid) was chromatographed on SiO_2 (300 g). The crystalline fractions eluted with pentane–ether (97 : 3) on crystallization from pentane–ether gave Ic (92 mg, 0·25% based on II used originally) as pale cream-coloured leaflets, homogeneous by TLC, m.p. 44–45°; IR λ_{max} ($CHCl_3$) μ: 3·01(s), 4·69(w) ($HC{\equiv}C$), 4·31(w) ($C{\equiv}C$); UV (EtOH): end absorption only. (Found: C, 93·94; H, 6·00; acetylenic H, 1.33.[10] $C_{11}H_8$ requires: C, 94·25; H, 5·75; acetylenic H (2), 1·44%). Ic was unstable; e.g., a brown insoluble polymer had formed after an ether–pentane soln had been allowed to stand in the dark at − 15° for 10 days. Catalytic hydrogenation of Ic in ether over Pt gave n-undecane as sole product (GLC comparison with authentic sample; column S, 100°).

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