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Unsaturated Macrocyclic Compounds. XXII.[1] A Synthesis of Cycloöctadeca-1,3,7,9,13,15-hexaene-5,11,17-triyne (Tridehydro-[18]annulene)[2] from 1,5-Hexadiyn-3-ol

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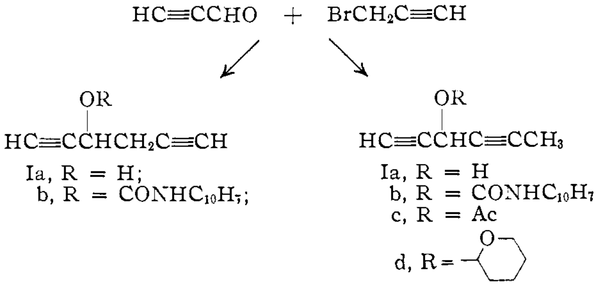
Various procedures for synthesizing 1,5-hexadiyn-3-ol (Ia) from propargylaldehyde and propargyl bromide are described. Under suitable conditions the isomeric 1,4-hexadiyn-3-ol (IIa) is obtained. Oxidative coupling of the alcohol Ia with cupric acetate in pyridine, followed by lithium aluminum hydride reduction and dehydration, leads to the same tridehydro-[18]annulene[2] (VII) as obtained in the preceding paper.[1] The intermediates in this reaction sequence are presumably the hexayne-triol III and the triene-triyne-triol VI, although these were not isolated in pure form. While the yield of tridehydro-[18]annulene was inferior to that obtained before, the present work is of value since it confirms the structure VII previously assigned to this substance.

The discovery that macrocyclic poly-acetylenes are formed by the oxidative coupling of linear α,ω-diacetylenes[3,4] pointed the way to the synthesis of completely conjugated monocyclic large-ring systems, and in the preceding paper[1] one method was reported by which such compounds could in fact be obtained by use of the coupling reaction.[5] We now describe the full details[6] of another route to this type of system, again taking advantage of the coupling of an α,ω-diacetylene for constructing the ring, whereby the same fully conjugated eighteen-membered hexaene-triyne VII (tridehydro-[18]-annulene)[2] was produced as had been obtained by the first method.[1] This substance is of interest not only *per se*, but also because it can be converted by partial hydrogenation to [18]annulene, the corresponding conjugated nonaene.[7]

The α,ω-diacetylene used in the present work was the previously unknown 1,5-hexadiyn-3-ol (ethinyl propargyl carbinol) (Ia). It was expected that oxidative coupling of this substance would lead to cyclic products, since 1,5-hexadiyne (the desoxy analog)[1,3c] as well as hepta-1,6-diyn-4-ol (a higher homolog)[3e] had yielded cyclic poly-acetylenes on oxidation. It was considered possible that dehydration, directly or after partial reduction, might then lead to fully conjugated cyclic polyene-polyynes or polyenes.

The required 1,5-hexadiyn-3-ol (Ia) was obtained in 50% yield by the reaction of propargylaldehyde with allenylmagnesium bromide (prepared from propargyl bromide and magnesium in ether at *ca.* 25°, catalyzed with mercuric chloride, according to Gaudemar[8]). The same alcohol Ia was formed (in *ca.* 55% yield) by a modification of this procedure, which involved the addition of a mixture of propargyl bromide and propargylaldehyde to magnesium in ether at −30° to −10° in the presence of mercuric chloride, the reaction being initiated by means of a small amount of allenylmagnesium bromide.[9] This modification has the advantage that it circumvents the necessity of first converting the propargyl bromide to the magnesium derivative, a reaction which must be carried out with considerable care in order to prevent the formation subsequently of any of the "rearranged" alcohol IIa (see below). The alcohol Ia could also be synthesized (in 55% yield) by allowing propargyl bromide to react with aluminum in the presence of mercuric chloride, and then with propargylaldehyde at −30°.[11]



The structure Ia assigned to the products from all three reactions was confirmed by the infrared spectra (which were identical with each other and showed monosubstituted acetylene bands at 3.03 and 4.69 μ[12] but no disubstituted acetylene or allene bands), as well as by the facts that titration against silver nitrate[13] pointed to the presence of two ethinyl groups and that full hydrogenation furnished 3-hexanol. The alcohol Ia was characterized as the crystalline α-naphthylurethan Ib (m.p. 118–119°), and the liquid acetate Ic and 2′-tetrahydropyranyl ether Id were also prepared.

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[1] For Part XXI, see F. Sondheimer and R. Wolovsky, *J. Am. Chem. Soc.*, **84**, 260 (1962).

[2] For the nomenclature employed, see footnote 1.

[3] F. Sondheimer, *et al.*, *ibid.*, (a) **78**, 4178 (1956); **79**, 5817 (1957); (b) **79**, 6263 (1957); (c) **79**, 4247 (1957); (d) **81**, 4600 (1959); (e) **81**, 6301 (1959).

[4] G. Eglinton, *et al.*, *Chemistry & Industry*, 737 (1956); 699 (1959); 559 (1960); *J. Chem. Soc.*, 889 (1959); 3614 (1960).

[5] For a related route to such systems investigated by us, see F. Sondheimer, R. Wolovsky and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **83**, 1686 (1961).

[6] For a preliminary communication, see F. Sondheimer, Y. Amiel and Y. Gaoni, *ibid.*, **81**, 1771 (1959).

[7] F. Sondheimer and R. Wolovsky, *Tetrahedron Letters*, No. **3**, 3 (1959); F. Sondheimer, R. Wolovsky and Y. Amiel, *J. Am. Chem. Soc.*, **84**, 274 (1962).

[8] (a) M. Gaudemar, *Ann. chim. (Paris)*, [13] 1, 190 (1956); (b) C. Prévost, M. Gaudemar, L. Miginiac, F. Bardone-Gaudemar and M. Andrac, *Bull. soc. chim. France*, 679 (1959).

[9] It is to be noted that no condensation between propargyl bromide and propargylaldehyde could be brought about by means of zinc in a Reformatsky type of reaction, despite the fact that propargyl bromide has been condensed successfully with other aldehydes under these conditions.[10]

[10] H. B. Henbest, E. R. H. Jones and I. M. S. Walls, *J. Chem. Soc.*, 2696 (1949).

[11] Method of Gaudemar.[8a] The aluminum derivative of propargyl bromide, like the magnesium derivative, has been shown to exist in the allenic form.[8b]

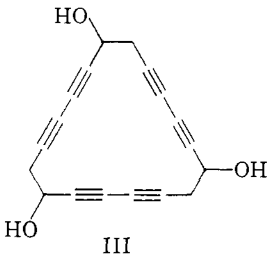
[12] See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 2nd. Edition, 1958, Chapter 4.

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

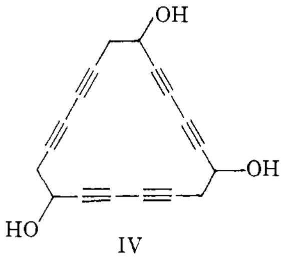
When the mercuric chloride-catalyzed reaction between propargyl bromide and magnesium was carried out in boiling ether, and the mixture was then boiled for a number of hours prior to condensation with propargylaldehyde, the "rearranged" alcohol 1,4-hexadiyn-3-ol (IIa) was the only product to be isolated (35% yield). This result is in accord with the findings of Gaudemar in related reactions.[8a] The structure of IIa was confirmed by the fact that the infrared spectrum exhibited a band at 4.47 μ (disubstituted acetylene)[12] as well as at 3.02 and 4.70 μ (monosubstituted acetylene)[12]; titration against silver nitrate[13] revealed the presence of only one ethinyl group, and one C-methyl group was found to be present by the Kuhn–Roth method.[14] The alcohol IIa, the physical properties of which agreed reasonably well with those reported for the known substance,[15] was characterized as the crystalline α-naphthylurethan IIb (m.p. 116–117°), and the liquid acetate IIc was also made.

1,5-Hexadiyn-3-ol (Ia) was submitted to oxidative coupling with cupric acetate in pyridine under conditions similar to those used with 1,5-hexadiyne.[1,3c] The resulting amorphous poly-ol, which was unstable and at times decomposed explosively on being rubbed in air in the dry state, contained α,γ-diacetylene units as evidenced by the relatively low-intensity ultraviolet maxima at 231, 243, 251 and 257 mμ [*cf.* the maxima of 3,5-octadiyn-2,7-diol ($HOCHMeC{\equiv}CC{\equiv}CCHMeOH$) at 230.5, 242.5 and 256 mμ[16]]. Acetylation yielded a poly-acetate containing a comparatively low ratio of terminal acetylene to α,γ-diacetylene groupings as judged by the relative intensity of the infrared band at 3.03 μ ($-C{\equiv}CH$)[12] to those at 4.42 and 4.62 μ ($-C{\equiv}CC{\equiv}C-$).[3d] This observation is indicative that a considerable part of the coupling product is cyclic and/or that long linear polymers had been formed. Unfortunately we could not settle this point at this stage since chromatography neither of the poly-ol nor of the poly-acetate led to any crystalline materials, nor did the corresponding full hydrogenation products give crystalline substances on chromatography. Coupling of the acetate Ic under the conditions used with Ia gave a poly-acetate similar in properties and infrared spectrum to that obtained previously, and the same type of material was formed when the 2′-tetrahydropyranyl ether Id was subjected to the coupling reaction, followed by acid cleavage of the protecting groups and acetylation. In no case could a crystalline substance be obtained and at times explosive decompositions occurred during attempted purification.

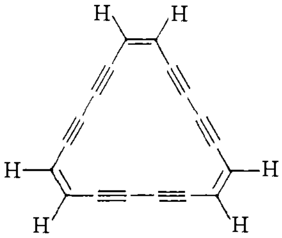
It was assumed at this point that the coupling product from Ia contained the two possible positionally isomeric cyclic trimers III and IV besides higher cyclic polymers, by analogy with the results obtained with 1,5-hexadiyne.[1,3c] Two racemic forms are possible for III, four for IV, and the higher cyclic products can also exist as a mixture of positional as well as stereoisomers. It is the wide scope for isomerism which exists when the coupling is performed with an unsymmetrical α,ω-diacetylene such as Ia which may well be responsible for the failure to isolate a pure substance at this stage. That the mixture of poly-ols in fact contains the symmetrical trimer III follows from the results described below.



III



IV



V

The next experiments were aimed at the synthesis of the fully conjugated eighteen-membered triene-hexayne hexadehydro-[18]annulene (V), formally derivable from both III and IV through loss of water. However, numerous attempts to obtain this substance through dehydration of the crude poly-ol (directly or through the *p*-toluenesulfonate[17]), as well as by loss of acetic acid from the poly-acetate, met with no success and no products with ultraviolet spectral properties compatible with V could be obtained even after careful chromatography. It may be mentioned that we had previously attempted to dehydrate 1,5-hexadiyn-3-ol (Ia) to 3-hexene-1,5-diyne ($HC{\equiv}CCH{=}CHC{\equiv}CH$),[18] the *cis* isomer of which on coupling might have produced V. This approach, however, was also fruitless since the dehydration of Ia to the ene-diyne could not be realized in practice.

We now turned our attention to the partial reduction of the acetylenic bonds of the coupling product of Ia. Partial hydrogenation of the poly-ol in methanol over a Lindlar palladium catalyst[19] proceeded only very slowly and was interrupted after 2 molar equivalents of hydrogen (per C_6 unit) had been absorbed. Attempts were made to dehydrate the product under a variety of conditions, but in no case was there any indication that a fully conjugated cyclic polyene had been formed. The partial hydrogenation of the poly-acetate (in benzene) followed by saponification and attempted dehydration met with a similar lack of success.

It has been shown that lithium aluminum hydride causes reduction of propargylic alcohols to the corresponding *trans*-allylic alcohols, whereas other

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[14] R. Kuhn and H. Roth, *Ber.*, **66**, 1274 (1933). As usual, a low value (76% of theory) was obtained in this determination.

[15] J. Chauvelier and P. Lacombe, *Compt. rend.*, **230**, 2210 (1950).

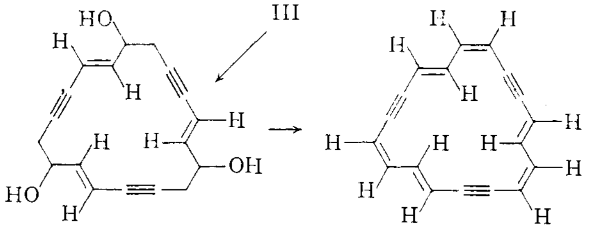
[16] J. B. Armitage, C. L. Cook, N. Entwistle, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 1998 (1952).

[17] See G. Eglinton and M. C. Whiting, *ibid.*, 3650 (1950).

[18] A. Roedig and K. Kiepert, *Ann.*, **593**, 55, 71 (1955).

[19] H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

acetylenes are generally not affected.[20] Consequently the poly-ol derived from the coupling of Ia was subjected to lithium aluminum hydride reduction, whereby the symmetrical trimer III would be expected to yield the triene-triyne-triol VI. The fact that *trans*-ene-yne units had indeed been formed in this step was evident from the ultraviolet properties of the product [λ_{max} 227 mμ (ε 11,300 per C_6 unit), λ_{infl} 236 mμ (ε 9,900 per C_6 unit)][21] and the infrared spectrum (band at 10.44 μ due to the CH out-of-plane deformation of a conjugated *trans*-double bond),[22] although again no crystalline substance could be isolated.



VI VII

Dehydration of the lithium aluminum hydride product was attempted under a number of different conditions. The action of potassium bisulfate in boiling acetic anhydride–acetic acid, as well as of phosphorus oxychloride in pyridine at room temperature, yielded materials which without purification showed the ultraviolet maxima at *ca.* 322, 335, 384 and 399 mμ (isoöctane) typical of tridehydro-[18]annulene (VII).[1] Chromatography on alumina of the product from the potassium bisulfate dehydration then led to the brown compound VII as sole crystalline material to be isolated (0.12% over-all yield from Ia). This substance (m.p. 190–192° dec.) was identified with the previously described one[1] by the complete identity of the infrared and ultraviolet spectra as well as by full hydrogenation to cycloöctadecane.

Tridehydro-[18]annulene (VII) must have been derived from 1,5-hexadiyn-3-ol (Ia) *via* the symmetrical trimer III and the triene-triyne-triol VI. The present synthesis provides additional evidence for the structure VII assigned to tridehydro-[18]annulene in the previous paper,[1] since the symmetrical molecule VII is the only one which can be derived from the symmetrical trimer III by the route employed, there being no reason to assume any isomerization to have taken place during the reduction or the dehydration step. While the unsymmetrical trimer IV could have given rise to another tridehydro-[18]annulene (the unsymmetrical cycloöctadeca-1,3,5,7,11,13-hexaene-9,15,17-triyne), it is hardly likely that the same substance would have been formed by the two routes were this the structure of the compound under discussion.

Although the route to VII described in this paper is of interest in so far as it confirms the structure previously assigned to this substance, the synthesis reported in the preceding paper[1] is a better one from the preparative standpoint since 1,5-hexadiyne is more readily available in quantity than is 1,5-hexadiyn-3-ol and the over-all yield of VII from the former diyne is much superior to that given by the latter.

Experimental[23]

1,5-Hexadiyn-3-ol (Ia) from Propargyl Bromide and Propargylaldehyde. (a) By Use of Magnesium (Two-stage Procedure).—Magnesium (7.3 g., 0.3 mole) was covered with 30 cc. of dry ether in a 3-neck flask equipped with a stirrer, dropping funnel, thermometer and reflux condenser, under nitrogen. Mercuric chloride (*ca.* 0.1 g.) and propargyl bromide (3 g.) were added with stirring and the mixture was heated until reaction commenced. The mixture was then cooled to 23° and a solution of 32.7 g. (total, 0.3 mole) of propargyl bromide in 200 cc. of ether was then added dropwise during 2 hr. with stirring, the internal temperature being kept at 23–25° by ice-water cooling; two layers were apparent and practically all the magnesium had disappeared. The mixture was stirred for a further 10 minutes, was then cooled to −20° (Dry Ice–acetone) and a solution of 10.8 g. (0.2 mole) of freshly distilled propargylaldehyde[24] in 100 cc. of ether was added dropwise during 1 hr. with continued cooling to −20° (internal temperature). The mixture was stirred for a further 1 hr. without cooling. Ice and ammonium chloride solution were added, the aqueous layer was extracted several times with ether and the combined organic extracts were washed with saturated salt solution, dried and evaporated. Rapid distillation under nitrogen yielded the crude alcohol Ia, b.p. *ca.* 70–80° (20 mm.); a dark residue remained which underwent an explosive decomposition when an attempt to continue the distillation was made. Redistillation through a small Vigreux column yielded 9.2 g. (49%) of 1,5-hexadiyn-3-ol as a colorless liquid, b.p. 72–73° (20 mm.), $n^{25}D$ 1.4755; infrared bands (in chloroform) at 2.80(s) and 2.94(s) μ (hydroxyl) and at 3.03(s) and 4.69(m)μ (monosubstituted acetylene), no bands at *ca.* 4.45 μ (disubstituted acetylene) or 5.10 μ (allene). Chromatography of a sample on alumina and infrared examination of the eluates indicated the alcohol to be homogeneous.

Anal. Calcd. for C_6H_6O: C, 76.57; H, 6.43; acetylenic H (2), 2.14. Found: C, 76.26; H, 6.46; acetylenic H, 2.06.[13]

The *α*-**naphthylurethan** Ib after crystallization from petroleum ether (b.p. 60–80°) showed m.p. 118–119°.

Anal. Calcd. for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32; acetylenic H (2), 0.77. Found: C, 77.78; H, 5.13; N, 5.61; acetylenic H, 0.71.[13]

The acetate Ic (acetic anhydride–pyridine, 16 hr. at room temperature) showed b.p. 80–81° (20 mm.), $n^{26}D$ 1.4535; infrared bands (in chloroform) at 3.03(s) and 4.68(m) μ (monosubstituted acetylene) and 5.77(s) μ (acetate).

Anal. Calcd. for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.12; H, 5.66.

(b) **By Use of Magnesium (One-stage Procedure).** A stirred mixture containing 7.3 g. (0.3 mole) of magnesium, 2 g. of propargyl bromide, *ca.* 0.1 g. of mercuric chloride and 30 cc. of dry ether was heated under nitrogen until reaction started. The mixture was then cooled to −30° (Dry Ice–acetone) and a solution containing 33.7 g. (total. 0.3 mole) of propargyl bromide and 10.8 g. (0.2 mole) of freshly distilled propargylaldehyde[24] in 100 cc. of ether was added drop-

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(20) *Inter al.*, J. D. Chanley and H. Sobotka, *J. Am. Chem. Soc.*, **71**, 4140 (1949); R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 3185 (1950); K. R. Bharucha and B. C. L. Weedon, *ibid.*, 1584 (1953); E. B. Bates, E. R. H. Jones and M. C. Whiting, *ibid.*, 1854 (1954).

(21) 3-Decen-5-yn-2-ol ($HOCHMeCH{=}CHC{\equiv}CBu(n)$), containing the same chromophoric system as VI, shows λ_{max} 226 mμ (ε 16,200) and λ_{infl} 235 mμ (ε 15,100) (I. M. Heilbron, E. R. H. Jones and R. A. Raphael, *J. Chem. Soc.*, 264 (1943)).

(22) *Inter al.*, J. L. H. Allan and M. C. Whiting, *ibid.*, 3314 (1953); J. L. H. Allan, G. D. Meakins and M. C. Whiting, *ibid.*, 1874 (1955).

(23) Melting points were taken on a Fisher–Johns apparatus and are uncorrected. Ultraviolet spectra were determined on a Unicam model S.P. 500 spectrophotometer and infrared spectra on a Baird double-beam recording spectrophotometer with sodium chloride optics. Analyses were carried out in our microanalytical laboratory under the direction of Mr. Erich Meier.

(24) Prepared according to F. Wille and L. Saffer, *Ann.*, **568**, 34 (1950).

wise with stirring and continued cooling at −30° under nitrogen at such a rate that the internal temperature did not exceed −10° (exothermic reaction). After being cooled for a further 1 hr. at −30°, the mixture was allowed to reach room temperature and was then set aside overnight. Decomposition and isolation as previously (explosive residue!) furnished 10.1 g. (54%) of 1,5-hexadiyn-3-ol, b.p. 73–75° (21 mm.), $n^{22}\mathrm{D}$ 1.4759. The infrared spectrum was identical in every respect with that of the alcohol obtained by method a.

(c) **By Use of Aluminum.**—The aluminum derivative was prepared from 60 g. (0.5 mole) of propargyl bromide, 9 g. (0.33 mole) of aluminum granules and 2 g. of mercuric chloride, exactly as described by Gaudemar.[8a] After being boiled under reflux in nitrogen for 4 hr., the mixture was cooled to −40° (Dry Ice–acetone). A solution of 16.2 g. (0.3 mole) of propargylaldehyde[24] in 40 cc. of dry ether was then added during *ca.* 30 minutes with vigorous stirring, the internal temperature being kept at −30° to −35° by continued cooling. The temperature was allowed to rise to 5° and the complex was decomposed by addition of ice and water. Isolation as previously (explosive residue!) yielded the alcohol Ia (15.6 g., 55%), b.p. 78–79° (27 mm.), $n^{26}\mathrm{D}$ 1.4746. The infrared spectrum was completely identical with that of the alcohol obtained by method a.

3-Hexanol from 1,5-Hexadiyn-3-ol (Ia).—A solution of 0.476 g. of 1,5-hexadiyn-3-ol in 20 cc. of methanol was shaken in hydrogen over 0.5 g. of a 10% palladium–charcoal catalyst at room temperature and atmospheric pressure. Uptake stopped when 4.1 molar equivalents of hydrogen had been absorbed. Removal of the catalyst and solvent, followed by distillation, produced 3-hexanol, b.p. 134–135°, $n^{21}\mathrm{D}$ 1.4153 (reported b.p. 134.5–135°,[25a] $n^{20}\mathrm{D}$ 1.4168[25b]). The acid phthalate showed m.p. 76–76.5° (reported[25c] m.p. 76–77°).

3-(2′-Tetrahydropyranoxy)-1,5-hexadiyne (Id).—Phosphorus oxychloride (3 drops) was added to a solution containing 0.73 g. of 1,5-hexadiyn-3-ol and 1.22 g. of dihydropyran (freshly distilled over potassium hydroxide). The solution was allowed to stand for 2 hr. at room temperature and was then poured into sodium carbonate solution. Isolation with ether and distillation produced 1.04 g. (75%) of the ether Id as a colorless liquid, b.p. 89–90° (10 mm.), $n^{21}\mathrm{D}$ 1.4748; infrared bands (in chloroform) at 3.03(s) and 4.69(m) μ (monosubstituted acetylene), no hydroxyl bands.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92; acetylenic H(2), 1.13. Found: C, 73.83; H, 7.79; acetylenic H, 1.11.[13]

1,4-Hexadiyn-3-ol (IIa).—The mercuric chloride catalyzed reaction between propargyl bromide (35.7 g., 0.3 mole) and magnesium (7.3 g., 0.3 mole) was carried out as described above for the preparation of Ia (method a), except that the ethereal propargyl bromide solution was added to the magnesium during 2 hr. without external cooling, whereby a steady reflux was maintained. The mixture was stirred at room temperature for 16 hr. and was then boiled for a further 2 hr. A solution of 10.8 g. (0.2 mole) of propargylaldehyde[24] in 50 cc. of ether was added without cooling, which again caused gentle reflux to occur and a brown mass to separate. Stirring at room temperature was continued for 16 hr. and the product was then isolated as previously. Rapid distillation yielded the crude alcohol, b.p. *ca.* 75–85° (20 mm.), which was redistilled through a small Vigreux column. The resulting 1,4-hexadiyn-3-ol (6.8 g., 36%) was obtained as a colorless liquid, b.p. 82–84° (20 mm.), $n^{25}\mathrm{D}$ 1.4765 [reported[15] b.p. 77° (11 mm.), $n^{18}\mathrm{D}$ 1.4813]; infrared bands (in chloroform) at 2.78(s) and 2.92(s) μ (hydroxyl), 3.02(s) and 4.70(w) μ (monosubstituted acetylene) as well as at 4.47(m) μ (disubstituted acetylene), no allene band at *ca.* 5.10 μ. Chromatography of a sample on alumina and infrared examination of the eluates indicated the alcohol to be homogeneous.

Anal. Calcd. for C_6H_6O: C, 76.57; H, 6.43; C–CH_3 (1), 15.97; acetylenic H (1) 1.07. Found: C, 76.57; H, 6.59; C–CH_3, 12.21; acetylenic H, 1.04.[13]

The α-naphthylurethan IIb after crystallization from petroleum ether (b.p. 60–80°) exhibited m.p. 116–117°. There was a considerable m.p. depression on admixture with the derivative Ib derived from 1,5-hexadiyn-3-ol.

Anal. Calcd. for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.88; H, 5.02; N, 5.26.

The acetate IIc (acetic anhydride–pyridine, overnight at room temperature) showed b.p. 87–89° (20 mm.), $n^{23}\mathrm{D}$ 1.4562; infrared bands (chloroform) at 3.03(s) and 4.68(w) μ (monosubstituted acetylene), 4.45(m) μ (disubstituted acetylene) and 5.77(s) μ (acetate).

Anal. Calcd. for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.45; H, 5.94.

Coupling of 1,5-Hexadiyn-3-ol (Ia) **and Derivatives with Cupric Acetate in Pyridine.**—The carbinol Ia (10 g.) was added to a mixture of 150 g. of finely ground neutral cupric acetate monohydrate and 1 l. of pyridine (commercial grade, previously distilled over sodium hydroxide). The mixture was then heated to 40° and stirred vigorously at this temperature under a reflux condenser for 2.5 hr. The mixture was cooled, filtered and the solid was washed very well with ethyl acetate. The pyridine filtrate was evaporated to small volume under reduced pressure, the residue was diluted with the ethyl acetate washings and was then washed with dilute hydrochloric acid and water. The dried extract on evaporation at 20° under reduced pressure in nitrogen yielded 8.6 g. of poly-ol as a red-brown foam, soluble in ethyl acetate, tetrahydrofuran and pyridine but only very sparingly soluble in chloroform, ether or benzene; $\lambda_{\max}^{\text{methanol}}$ 231, 243, 251 and 257 mμ (ϵ 610, 920, 1020 and 1120, per C_6 unit). The infrared spectrum gave little information regarding the amount of terminal acetylene present, owing to the low solubility in chloroform and the presence of a strong hydroxyl band in the 3.0 μ region (measured in tetrahydrofuran solution).

The thoroughly dried poly-ol at times decomposed explosively on being scratched with a spatula in air. The poly-ol on chromatography on alumina (Merck, acid-washed) was eluted mainly with benzene–ethyl acetate (1:1) as a yellow foam which like the total coupling product resisted attempts at crystallization.

Acetylation of the crude coupling product with acetic anhydride in pyridine at room temperature for 16 hr. yielded an amorphous poly-acetate. The infrared spectrum (in chloroform) showed bands at 4.42(w) and 4.62(w) μ (α,γ-diacetylene) and 5.77(s) μ (acetate), but only a relatively weak band at 3.03 μ due to terminal acetylene. On chromatography on alumina most of the poly-acetate was eluted with benzene–ether (1:1), but no crystalline substance could be separated.

A non-crystalline poly-acetate with very similar infrared properties to those of the above-described material was obtained when the cupric acetate coupling was carried out with the acetate Ic. Moreover coupling of the tetrahydropyranyl ether Id, followed by chromatography on alumina, cleavage of the protecting groups with 2 *N* sulfuric acid in dioxane (overnight at room temperature), acetylation and chromatography again resulted in amorphous polyacetate fractions showing similar infrared spectra to those of the previously described materials.

Lithium Aluminum Hydride Reduction of the Coupling Product of 1,5-Hexadiyn-3-ol (Ia).—A solution of 8.5 g. of the crude poly-ol obtained by the coupling of Ia, in 100 cc. of dry tetrahydrofuran, was added rapidly to a suspension of 10 g. of lithium aluminum hydride in 1 l. of tetrahydrofuran, under nitrogen. The mixture was heated at *ca.* 45° for 3.5 hr. and was then boiled under reflux for 0.5 hr. The excess reagent was destroyed by the careful addition of ethyl acetate and a saturated solution of sodium sulfate was then added. The mixture was evaporated to small volume under reduced pressure and ethyl acetate was added to the residue. Washing with water, drying and evaporation of the solvent under reduced pressure yielded 6.1 g. of a red-brown amorphous mass; $\lambda_{\max}^{\text{methanol}}$ 227 mμ (ϵ 11,300 per C_6-unit) and $\lambda_{\text{infl}}^{\text{methanol}}$ 236 mμ (ϵ 9,900 per C_6-unit); infrared band (in tetrahydrofuran) at 10.44(s) (conjugated *trans*-double bond), not present in the precursor. A portion of the reduced poly-ol was acetylated (acetic anhydride–pyridine, overnight at room temperature) and the product was chromatographed on alumina (Merck, acid-washed). Most of the material was eluted with pentane–ether (7:3 to 3:7), but no crystalline substance could be obtained.

Cycloöctadeca-1,3,7,9,13,15-hexaene-5,11,17-triyne (Tridehydro-[18]annulene) (VII) **by Dehydration of the Reduced Poly-ol. (a) With Potassium Bisulfate in Acetic Anhydride –Acetic Acid.**—A mixture containing 5.8 g. of the crude lithium aluminum hydride product, 2 g. of anhydrous potassium bisulfate (freshly fused and then finely ground), 90

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[25] (a) P. M. Ginnings and R. Webb, *J. Am. Chem. Soc.*, **60**, 1388 (1938); (b) A. L. Henne and A. H. Matuszak, *ibid.*, **66**, 1650 (1944); (c) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **103**, 1923 (1913).

cc. of acetic anhydride and 90 cc. of glacial acetic acid was boiled under reflux by means of an oil-bath for 1 hr., moisture being excluded. The cooled mixture was diluted with benzene, washed well with sodium bicarbonate solution and water, and was then dried and evaporated to dryness under reduced pressure. The amorphous residue (3.4 g.) showed $\lambda_{\max}^{\text{isooctane}}$ 322, 335, 384 and 399 mμ, typical of VII. It was dissolved in a little benzene and roughly chromatographed on a column of 170 g. of alumina (Merck, acid-washed), in order to remove hydroxylic substances. The fractions eluted with pentane to pentane–ether (7:3) on evaporation yielded a total of 162 mg. of material, the ultraviolet spectrum of which indicated the presence of 16 mg. of VII (later fractions showed no maxima above 300 mμ on ultraviolet examination). This material was dissolved in *ca.* 1 cc. of benzene and re-chromatographed on a column of 100 g. of alumina (Aluminum Co. of America, grade F-20), which was washed with pentane and then with various mixtures of pentane–ether. The fractions eluted with pentane–ether (4:1), the only ones with ultraviolet maxima above 300 mμ, were combined, evaporated and crystallized from pentane. The resulting hexaene-triyne VII (11.2 mg., 0.12% over-all from Ia) formed brown plates, m.p. 190–192° (dec.; sample placed on block just before). It was identified with the previously described substance[1] by the complete identity of the ultraviolet spectrum (in isoöctane) as well as the infrared spectrum (in KBr). Furthermore, full hydrogenation (in dioxane over platinum), followed by crystallization from ethanol, smoothly yielded cycloöctadecane, m.p. 70–71°, undepressed on admixture with an authentic sample (m p. 71–72°).

(b) With **Phosphorus Oxychloride in Pyridine.**—Freshly distilled phosphorus oxychloride (10 drops) was added to a solution of 28.5 mg. of the crude lithium aluminum hydride product in 1.5 cc. of dry pyridine. The mixture was allowed to stand at room temperature for 20 hr., moisture being excluded, and was then poured on ice and extracted successively with pentane and ethyl acetate. The pentane extract was washed with dilute sulfuric acid, sodium bicarbonate solution and water, and was then dried and evaporated. The residue (1.4 mg.) showed ultraviolet maxima at 323, 335, 384 and 398 mμ (in isoöctane), typical of VII, with intensities indicating a purity of 6% (0.18% over-all yield from Ia). The ethyl acetate extract showed no well-defined ultraviolet maxima above 300 mμ.

Tridehydro-[18]annulene (VII) was also formed (as indicated by the ultraviolet spectrum of the product) when the dehydration with phosphorus oxychloride in pyridine was carried out at 60° for 15 minutes, but the yield appeared to be inferior.

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

Unsaturated Macrocyclic Compounds. XXIII.[1] The Synthesis of the Fully Conjugated Macrocyclic Polyenes Cycloöctadecanonaene ([18]Annulene),[2] Cyclotetracosadodecaene ([24]Annulene), and Cyclotriacontapentadecaene ([30]Annulene)

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Catalytic partial hydrogenation of tridehydro-[18]annulene (I) produces [18]annulene (cycloöctadecanonaene) (II), the first fully conjugated cyclopolyolefin after benzene for which aromatic character was predited. The physical and chemical properties of [18]annulene are described, and it is shown that this substance undergoes addition rather than substitution reactions. Evidence is presented, however, that this cyclopolyolefin in fact represents an aromatic system. Tetradehydro-[24]annulene (III) on similar partial hydrogenation yields [24]annulene (cyclotetracosadodecaene) (IV or V), an unstable substance which is theoretically non-aromatic; in addition a product is formed (apparently also produced by allowing [24]annulene to stand in solution), which is probably no longer monocyclic. The analogous partial hydrogenation of pentadehydro-[30]annulene (VI or an isomer) leads to the theoretically aromatic [30]annulene (VII or an isomer), a compound which proved to be quite unstable.

Introduction.—The synthesis and possible aromatic properties of macrocyclic hydrocarbons formally containing alternating single and double bonds (the annulenes)[2] have often been discussed.[3,4] Current theory predicts that such compounds should be aromatic provided their carbon skeleton can exist in a configuration which is planar or not far from planar, and they contain a closed shell of $(4n + 2)$ π-electrons ("Hückel's rule," met by annulenes made up formally of an odd number of double bonds).[5,6]

It has previously been pointed out by Mislow[7] that [10]annulene and [14]annulene,[8] the two members following benzene which comply with Hückel's rule, presumably cannot be planar in view of the steric interactions of the internal hydrogen atoms in the planar molecules as is evident from the scale drawings A and B.[9] These substances therefore do not meet one of the two criteria for aromaticity. It appeared to us from inspection of scale drawings that [18]annulene (C)[9] is the first member after benzene in which hydrogen–hydrogen interactions are not extreme and consequently in which the deviation of the carbon skeleton from coplanarity would not be great. [18]Annulene also complies with Hückel's rule ($n = 4$) and this substance was therefore the first cyclic polyene after benzene for which we anticipated aromatic character at the outset of our work (see also footnote 3c). This is in contrast to the conclusion of Mislow[7] who considered the interaction of the internal hydrogen atoms in [18]annulene still to

[1] For Part XXII, see F. Sondheimer, Y. Amiel and Y. Gaoni, *J. Am. Chem. Soc.*, **84**, 270 (1962).

[2] For the nomenclature employed, see F. Sondheimer and R. Wolovsky, *ibid.*, **84**, 260 (1962).

[3] For reviews, see (a) W. Baker and J. F. W. McOmie in "Progress in Organic Chemistry," Ed. J. W. Cook, Butterworths Scientific Publications, London, 1955, Vol. 3, Chapter 2; (b) W. Baker in "Perspectives in Organic Chemistry," Ed. Sir A. Todd, Interscience Publishers, Inc., New York, N. Y., 1956, p. 28; (c) W. Baker and J. F. W. McOmie in "Non-benzenoid Aromatic Compounds," Ed. D. Ginsburg, Interscience Publishers, Inc., New York, N. Y., 1959, Chapter 9; (d) M. E. Vol'pin, *Uspekhi Khim.*, **29**, 298 (1960) [English translation: *Russ. Chem. Revs.* (published by The Chem. Soc., London), 129 (1960)].

[4] For recent theoretical discussions of such systems, see O. E. Polansky, *Monatsh.*, **90**, 929 (1959); **91**, 898, 916 (1960).

[5] E. Hückel, *Z. Physik*, **70**, 204 (1931).

[6] E. Hückel, "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938.

[7] K. Mislow, *J. Chem. Phys.*, **20**, 1489 (1952).

[8] F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **82**, 5765 (1960).

[9] The following dimensions have been used in drawing the diagrams A–D, following Mislow: carbon–carbon bond lengths (all equal), 1.40 Å.; carbon–hydrogen bond lengths, 1.10 Å.; hydrogen radii, 1.00 Å.; all angles 120 or 240°.