



which, for some years, have been the subject of an extensive and detailed investigation by Cram, *et al.*¹⁴ Such reactions differ in principle from the proton exchange reactions because an additional leaving group, $Y = Z$, is involved. Without reviewing Cram's extensive and pioneering stereochemical studies, suffice it to say that solvents are classifiable experimentally as "inversion" or "retention" depending on the predominant stereochemistry of the product, RH. Glycols are in the inversion class; amines and higher alcohols are in the retention class. To the extent that these reactions are related to the simple proton exchanges, our present results find a prior analogy to Cram's "retention" solvents.

(14) D. J. Cram, J. Allinger and A. Langemann, *Chemistry & Industry*, 919 (1955); D. J. Cram, A. Langemann, J. Allinger and K. R. Kopecky, *J. Am. Chem. Soc.*, **81**, 5740 (1959); and numerous papers following.

TABLE I

Time, min.	α_D	$10^4 k_{\text{ras}}$, min. ⁻¹	$\log I_0/I$	$10^4 k_{D,\text{exp}}$, min. ⁻¹
0	0.405°		0.619	
150	.330	14	.559	6.1
450	.172	19	.461	6.8
800	.102	17	.376	6.7
1330	.036	18	.269	7.1
7500	.002		.052	

Experimental

Kinetics.—Optically active ethylbenzene- α -d⁴ was allowed to exchange at 49.9° as a 0.71 *M* solution in cyclohexylamine, 0.049 *M* in lithium cyclohexylamide according to procedure (A) described previously.⁵ Samples of ethylbenzene were isolated at intervals, distilled and examined for deuterium (infrared) and polarimetrically (1-dm. semi-micro tube). The results are summarized in Table I. Although more accurate rate constants are determined graphically, the instantaneous constants obtained by the usual first-order equation are given in Table I to illustrate the quality of the data.

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Unsaturated Macrocyclic Compounds. XXI.¹ The Synthesis of a Series of Fully Conjugated Macrocyclic Polyene-polyynes (Dehydro-annulenes) from 1,5-Hexadiyne

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The oxidative coupling of 1,5-hexadiyne (I) with cupric acetate in pyridine yields the cyclic trimer II, tetramer III, pentamer IV, hexamer V and heptamer X. The cyclic trimer is rearranged smoothly by means of potassium *t*-butoxide in *t*-butyl alcohol to the fully conjugated eighteen-membered ring monocyclic hexaene-triynene XIII (tridehydro-[18]annulene), a reaction which also produces some triphenylene. Similar rearrangements of III, IV and V give rise to the corresponding conjugated monocyclic polyene-polyynes tetradecahydro-[24]annulene, pentadecahydro-[30]annulene and hexadecahydro-[36]annulene (XIV, XV and XVI, or isomers), respectively. The synthesis of these conjugated substances is carried out most conveniently by the coupling of 1,5-hexadiyne followed by direct rearrangement, without isolation of intermediates. The properties of the novel conjugated polyene-polyynes are discussed briefly, especially in relation to their possible aromatic nature.

Introduction.—Completely conjugated monocyclic large-ring systems are of very considerable interest from a theoretical as well as possibly from a practical standpoint. In Part XIX of this series² we described an attempt to prepare such systems making use of the fact that the oxidative coupling of aliphatic α,ω -diacetylenes may give rise to large-ring poly-acetylenes^{3,4} and that the prototropic rearrangement of linear 1,5-enynes with potassium *t*-butoxide in *t*-butyl alcohol produces the corresponding conjugated polyenes.⁵ It was anticipated that large-ring hydrocarbons made up of 1,5-enyne units could be constructed by the coupling of a suitable α,ω -diacetylene and that subsequent rearrangement would then lead to completely conjugated cyclic polyenes. In the event, the desired prototropic shifts did not proceed smoothly and no clear-cut results were obtained.²

It has been shown by us that linear 1,5-diyne are rearranged by means of potassium *t*-butoxide to conjugated polyen-yne,⁶ a reaction which is analogous to the rearrangement of 1,5-enynes to polyenes but which proceeds with considerably greater facility. An alternative approach to completely conjugated monocyclic systems therefore appeared to involve the synthesis of large-ring compounds consisting of 1,5-diyne units through oxidative coupling of an appropriate α,ω -diacetylene, followed by prototropic rearrangement. This type of approach has been found to be realizable in practice, and in this paper we describe by its use the synthesis of fully conjugated macrocyclic polyene-polyynes containing 18, 24, 30 and 36 carbon atoms in the ring.^{7,8}

Nomenclature.—The work described in this and subsequent papers⁹⁻¹⁰ has made available a con-

(1) For Part XX, see F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **83**, 1259 (1961).

(2) F. Sondheimer, R. Wolovsky and D. A. Ben-Efraim, *ibid.*, **83**, 1686 (1961).

(3) (a) F. Sondheimer and Y. Amiel, *ibid.*, **75**, 5817 (1957); (b) F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **79**, 6263 (1957); (c) F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **81**, 4600 (1959).

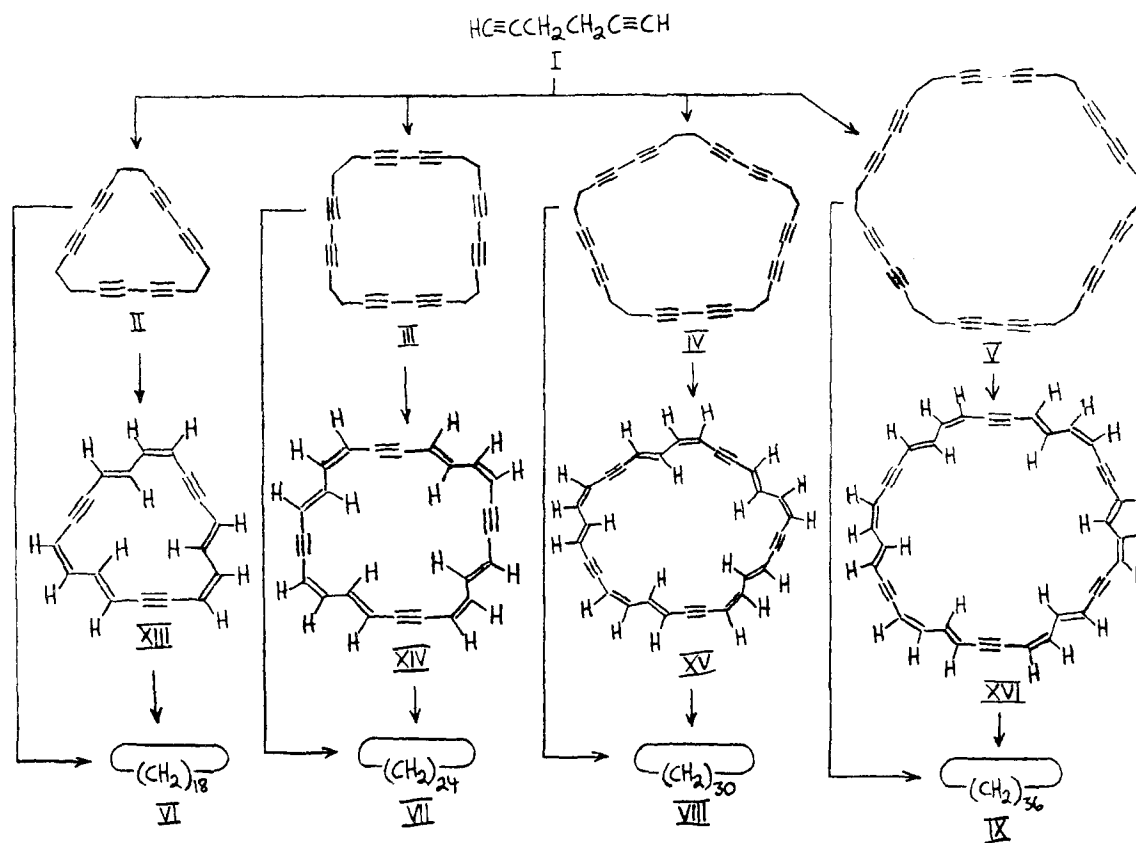
(4) G. Eglington and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959).

(5) F. Sondheimer, D. A. Ben-Efraim and R. Wolovsky, *J. Am. Chem. Soc.*, **83**, 1675 (1961).

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

(7) For preliminary communications, see (a) F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **79**, 4247 (1957); (b) F. Sondheimer and R. Wolovsky, *ibid.*, **81**, 1771 (1959); (c) F. Sondheimer and R. Wolovsky, *ibid.*, **81**, 4755 (1959); (d) F. Sondheimer, R. Wolovsky and Y. Gaoni, *ibid.*, **82**, 754 (1960).

(8) For the synthesis of related compounds by use of the same type of approach, see F. Sondheimer and Y. Gaoni, Part XXV, *ibid.*, in press (for preliminary communications, see footnotes 1 and 7d).



siderable number of monocyclic large-ring hydrocarbons containing a completely conjugated system of double bonds, as well as double and triple bonds. The systematic naming of these substances is lengthy and clumsy. We therefore propose the trivial name "annulene" (annulus = ring, Latin) for a monocyclic fully conjugated polyene, the ring size being indicated by a number in parentheses. The conjugated polyene-polyynes then become "dehydro-annulenes," e.g. the compound XIII described below is named tridehydro-[18]annulene or more specifically 1,7,13-tridehydro-[18]annulene. Although the proposed nomenclature of course does not fully define the compounds under discussion in view of the possibility of stereoisomerism about the double bonds, this is not a serious disadvantage especially since the stereochemistry of the double bonds is not known with certainty for the majority of the conjugated systems prepared.

Oxidative Coupling of 1,5-Hexadiyne.—The simplest method for constructing large-ring compounds made up of 1,5-diyne units appeared to involve the oxidative coupling of 1,5-hexadiyne (dipropargyl) (I).¹¹ It has been shown previously that oxidation of this diyne with oxygen in the presence of cuprous chloride and ammonium chloride in aqueous ethanol leads only to linear products,^{3b} unlike the higher homologs which give rise to cyclic

as well as to linear poly-acetylenes.^{3a,b} We therefore carried out the coupling of I by the cupric acetate-pyridine method,^{2,3c,4} which in the case of the higher homologs had been found to result in a variety of cyclic poly-acetylenes.^{3c}

1,5-Hexadiyne (I)¹¹ was oxidized with cupric acetate in pyridine at 55° for 3 hr., the dilution (1 part of diyne in 100 parts of pyridine) being the same as used by us previously.^{3c} The total product showed an infrared band at 3.03 μ of medium intensity, indicative of the presence of a reasonable amount of terminal acetylene groupings, in contrast to the behavior of the higher homologs of I studied previously.^{3c} The product was then chromatographed very carefully on *ca.* 500 parts of alumina into over 700 fractions, the result of a previous chromatogram having pointed to the necessity for this type of procedure.

The first compound to be eluted from the column (9% yield) showed m.p. 98–99° and was shown to be the linear dimer 1,5,7,11-dodecatetrayne, identical with that obtained by the oxygen-cuprous chloride method.^{3b} Then followed four crystalline substances which proved to be, in order of elution, the cyclic trimer II, the cyclic tetramer III, the cyclic pentamer IV and the cyclic hexamer V.¹² Each of these compounds decomposed explosively at *ca.* 170° on attempted melting point determination, unlike almost all of the monocyclic hydro-

(9) (a) F. Sondheimer, Y. Amiel and Y. Gaoni, *J. Am. Chem. Soc.*, **84**, 270 (1962); (b) F. Sondheimer, R. Wolovsky and Y. Amiel, **84**, 274 (1962).

(10) For preliminary communications, see F. Sondheimer and Y. Gaoni, *ibid.*, **82**, 5765 (1960); Part XXIV, *ibid.*, in press.

(11) R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 120 (1950), and references cited there.

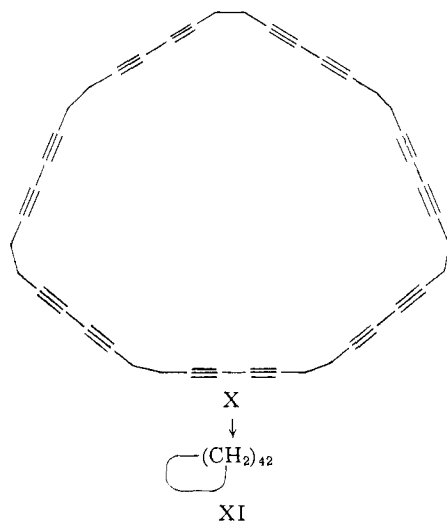
(12) In addition, a linear substance was eluted together with the cyclic tetramer III and pentamer IV, as evidenced by the presence of a terminal acetylene band at 3.03 μ in the infrared. This compound was not obtained in the pure state (remaining in the mother liquors when III and IV were crystallized) and was not identified.

carbons containing α,γ -diacetylene groupings prepared by us previously³ which were generally found to exhibit normal melting point behavior. The structures of the four cyclic products follow from the elemental analyses [indicating the formula $(C_6H_4)_n$ for each substance], the infrared spectra (α,γ -diacetylene present, terminal acetylene absent) and the fact that full hydrogenation yielded, respectively, cyclooctadecane (VI), cyclotetracosane (VII), cyclotriacontane (VIII) and cyclohexatriacontane (IX), identified in each case by direct comparison with the corresponding cycloalkane obtained from a previous coupling experiment.^{3c}

It must be pointed out that the separation between the cyclic compounds II, III, IV and V was not completely clear-cut. Practically all the eluates between fraction 170 (consisting of II) and fraction 650 (consisting of V) contained small quantities of crystalline solids which decomposed explosively on attempted melting point determination and which showed similar infrared properties. Consequently the individual cyclic compounds had to be located through full hydrogenation of representative fractions and identification of the resulting cycloalkane (see Experimental section), although some indication of the locations of the cyclic poly-acetylenes was provided by the fact that each one crystallized in a characteristic form.

It was estimated that the cyclic poly-acetylenes II, III, IV and V had been formed in yields of *ca.* 6, 6, 6 and 2%, respectively (*cf.* the preliminary communication),^{7a} although the properties and chromatographic behavior of these substances did not permit an accurate determination of yields to be made at this stage. However the results of the isomerization experiments described below subsequently confirmed the estimated yields.

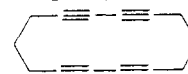
In one experiment in which 1,5-hexadiyne was oxidized under conditions essentially identical to those used above, the results paralleled those obtained previously except that the cyclic heptamer X^{7a} was obtained (in *ca.* 2% yield) in place of the



cyclic hexamer V. The structure of the new substance is based on the fact that its infrared spectrum was similar to that of the other cyclic polymers of I, while full hydrogenation yielded the previously

unknown cyclodotetracontane (XI). The latter hydrocarbon, which suffered a melting point depression on admixture with cyclohexatriacontane (IX) (m.p. 70–71°), showed a melting point (75–76°) in reasonably good agreement with the value 78° predicted for XI from the curve relating the melting points of cycloalkanes to their ring size,^{3c} and the molecular weight (determined by the Rast method in camphene) was close to the theoretical value for XI. The cyclic heptamer X is the highest cyclic polymer derived from the oxidation of an aliphatic α,ω -diacetylene to be identified so far, although corresponding compounds had been formed most probably by the previously described oxidation of higher homologs of 1,5-hexadiyne.^{3c}

The above-described 1,3,7,9,13,15-cyclooctadecahexayne (II) may be considered as cyclohexane in which every second carbon-carbon bond has been elongated by the insertion of an α,γ -diacetylene grouping. Like 1,3,8,10-cyclotetradecatetrayne (XII),^{3b} which is derived formally by the insertion of α,γ -diacetylene groupings into two opposite



XII

bonds of cyclohexane, the hexayne II can in principle exist either in a chair or a boat conformation. While it had been shown that XII in the crystalline state exists in the chair rather than the boat form,^{3b} it has not yet been determined which is the configuration of II. The ultraviolet spectrum of the tetrayne XII had been found to be abnormal, presumably because of the proximity of the two α,γ -diacetylene chromophores.^{3b} No such proximity effect would be anticipated in the hexayne II, and in fact the ultraviolet spectrum of this compound is normal.

Prototropic Rearrangements with Potassium *t*-Butoxide.—The above-described coupling of 1,5-hexadiyne has made available a series of cyclic substances made up of 1,5-diyne units, the prototropic rearrangement of which was now studied.

The cyclic trimer II in benzene on being boiled for 30 minutes with a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol gave a red-brown solution showing a characteristic ultraviolet spectrum with the main maxima at 329 and 342 $m\mu$ (in benzene). Purification by chromatography on alumina then led to a substance, isomeric with the starting material, which crystallized as light-brown plates melting at 190–192° dec. This substance, formed in *ca.* 50% yield (determined spectroscopically), is assigned the fully conjugated unstrained presumably planar tridehydro-[18]annulene structure XIII [cyclooctadeca-1,7,13-(*cis*)-triene-3,9,15-(*trans*)-triene-5,11,17-tri-yne]. The latter is derived from II by prototropic rearrangement of each 1,5-diyne to a 1-(*trans*)-ene-3-(*cis*)-ene-5-yne unit, analogous to the previously described rearrangement of 1,5-hexadiyne to 1,3-hexadien-5-yne consisting mainly of the *cis* isomer.⁶ The reasons for the structural assignment XIII are given in the sequel.

The ultraviolet spectrum, presented in Table I and Fig. 1, shows a multiplicity of maxima. The

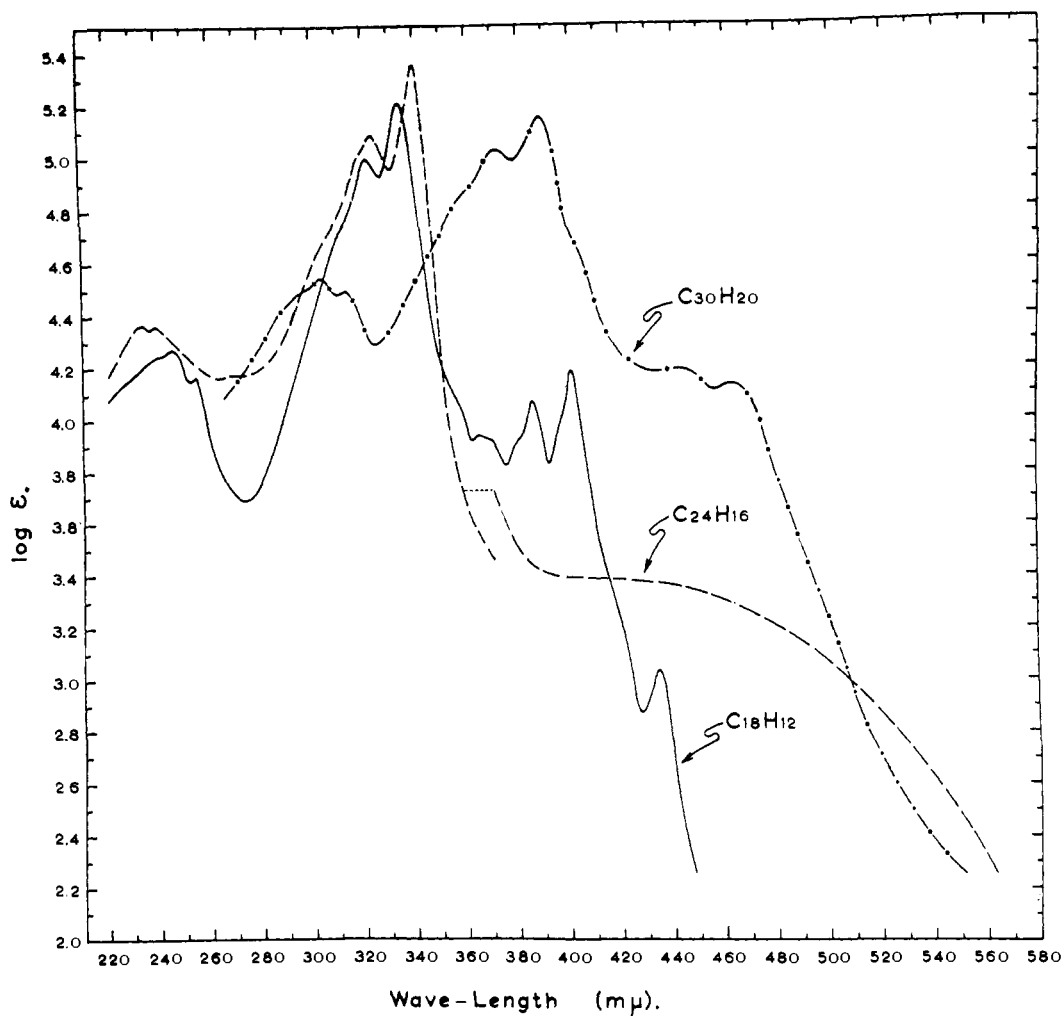


Fig. 1.—Ultraviolet absorption spectra of tridehydro-[18]annulene ($C_{18}H_{12}$), tetradecydro-[24]annulene ($C_{24}H_{16}$) and pentadecydro-[30]annulene ($C_{30}H_{20}$), determined with a Cary model 14 recording spectrophotometer; all spectra in isoöctane, except that the spectrum of the C_{24} -compound in the 370–560 $m\mu$ region has been performed in benzene.

high intensity of the main maximum (ϵ 160,000) points to a highly conjugated system, and the position of the highest wave length maximum (at 441 $m\mu$, in benzene) is consistent with 9 ethylenic and/

TABLE I
ULTRAVIOLET ABSORPTION MAXIMA OF DEHYDRO-ANNULENES

Tridehydro-[18]annulene		Tetradecydro-[24]annulene		Pentadecydro-[30]annulene	
—Isoöctane—	—Benzene—	—Isoöctane—	—Benzene—	—Isoöctane—	—Benzene—
λ_{max} , $m\mu$	ϵ	λ_{max} , $m\mu$	ϵ	λ_{max} , $m\mu$	ϵ
245	18,700	233	23,300	303	34,800
254	14,700	238	23,000	313	31,100
322	98,400	324	122,000	320	40,700
334	160,000	340	225,000	372	107,000
365	8,700	350	232,000	389	141,000
385	11,700	391	12,000	443	15,500
400	15,200	407	15,200	463	13,600
434	1,080	441	1,100	473	16,700

or acetylenic bonds being in conjugation [cf. the linear conjugated nonaene $CH_3(CH=CH)_9CH_3$, which exhibits the highest wave length maximum at 454 $m\mu$ (in benzene)¹³]. The infrared spectrum

(Fig. 2)¹⁴ indicates the presence of acetylenic bonds (weak band at 4.63 μ)¹⁵ as well as of conjugated *cis-trans*-diene groupings (strong bands at 10.27 and 10.80 μ),^{15b,16} while allene functions are clearly absent.¹⁷ Full hydrogenation of XIII in dioxane over platinum smoothly yielded cycloöctadecane (VI), showing that it was still monocyclic.

The isomerization product derived from II is clearly a tridehydro-[18]annulene. From symmetry considerations it was anticipated that the rearrangement would lead to the 1,7,9-tridehydro compound XIII with the three acetylenic groupings symmetrically arranged, and the correctness of this formulation was confirmed later through an independent synthesis reported in the succeeding paper.^{9a}

(13) F. Bohlmann and H. J. Mannhardt, *Ber.*, **89**, 1307 (1956).

(14) A theoretical discussion of the infrared spectrum of this and of related conjugated macrocyclic systems prepared by us will be published subsequently.

(15) *Inter al.*, see (a) J. H. Wotiz and F. A. Miller, *J. Am. Chem. Soc.*, **71**, 3441 (1949); (b) J. L. H. Allan, G. D. Meakins and M. C. Whiting, *J. Chem. Soc.*, 1874 (1955).

(16) *Inter al.*, see W. D. Celmer and I. A. Solomons, *J. Am. Chem. Soc.* **75**, 3430 (1953).

(17) See J. H. Wotiz and D. E. Mancuso, *J. Org. Chem.*, **22**, 207 (1957).

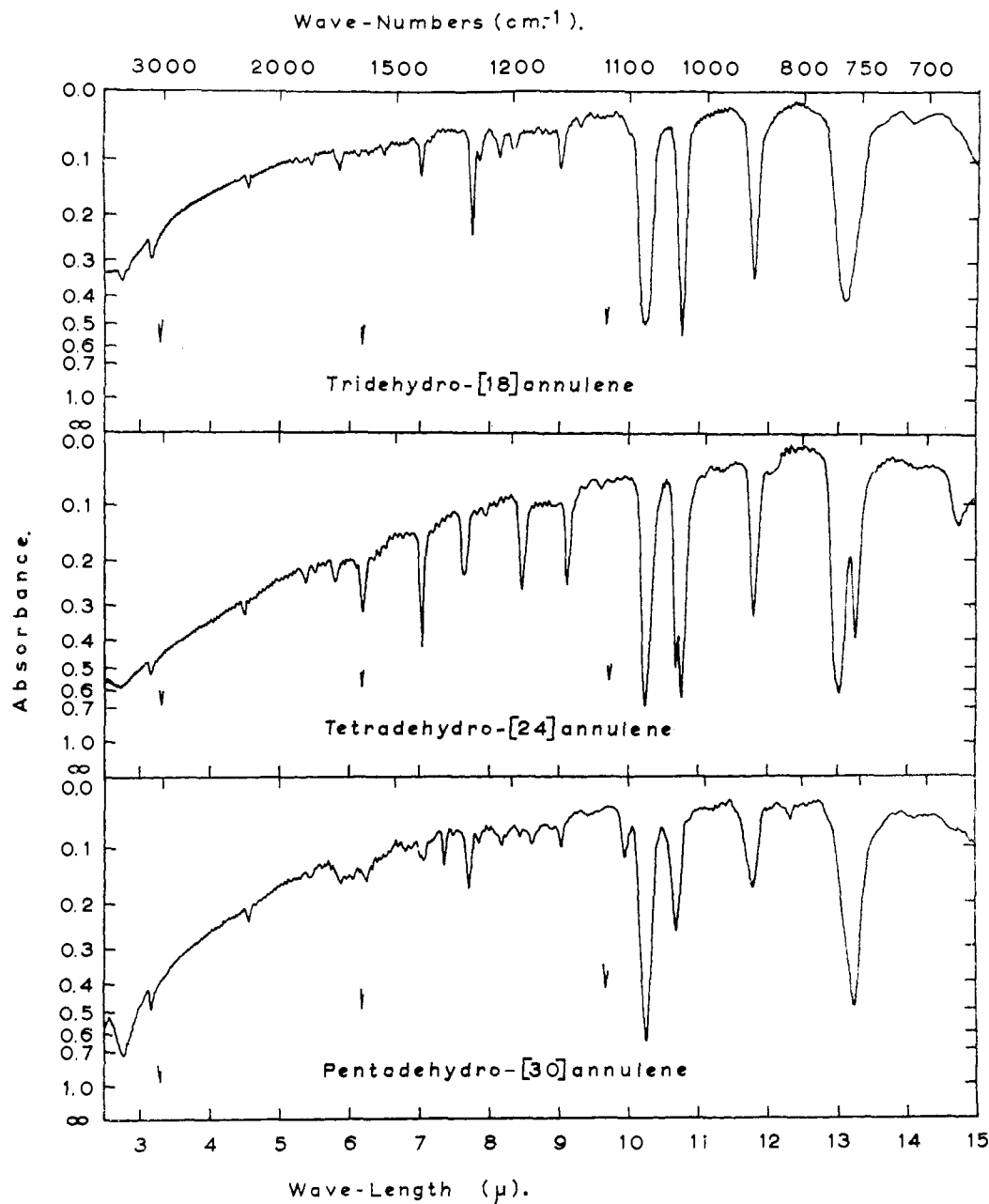


Fig. 2.—Infrared absorption spectra of dehydro-annulenes, determined as KBr pellets with a Perkin-Elmer "Infracord" recording spectrophotometer (calibrated with polystyrene).

It was found subsequently by Dr. Y. Amiel in the course of preparing larger quantities of tridehydro-[18]annulene from 1,5-hexadiyne by coupling, rearrangement of the total product and chromatography (see below), that triphenylene was obtained as a minor product. This polycyclic aromatic hydrocarbon was evidently derived from the cyclic trimer II, and a repetition of the above-described isomerization of II with potassium *t*-butoxide did indeed yield *ca.* 7% of triphenylene (determined spectroscopically after full hydrogenation of the product) in addition to tridehydro-[18]annulene. This transannular reaction has been discussed by us previously in a communication¹⁸ and it therefore suffices in the present paper only

to give the experimental details (see Experimental section).

The cyclic tetramer III in benzene on treatment with potassium *t*-butoxide in *t*-butyl alcohol under the same conditions used with the cyclic trimer II underwent an analogous rearrangement. The resulting isomer, formed in *ca.* 35% yield (determined spectroscopically), crystallized as dark purple prisms resembling potassium permanganate, which decomposed without melting on attempted melting point determination. This isomerization product showed behavior consistent with its formulation as a tetradehydro-[24]annulene (*e.g.*, XIV).

(18) Y. Amiel and F. Sondheimer, *Chemistry & Industry*, 1162 (1960).

The ultraviolet spectrum (Table I and Fig. 1) resembles that of tridehydro-[18]annulene in the 220–360 $m\mu$ region, the main double maxima being shifted by *ca.* 5 $m\mu$ toward higher wave length and increased in intensity; however a marked difference is apparent in the region above 360 $m\mu$, the C_{24} -compound not showing any further maxima but continuous absorption beyond 550 $m\mu$ in contrast to the C_{18} -compound. The infrared spectrum (Fig. 2)¹⁴ is similar to that of tridehydro-[18]annulene, a weak band at 4.62 μ (acetylene¹⁵) and strong bands at 10.25 and 10.79 μ (conjugated *cis-trans*-diene^{15b,16}) being apparent. Full hydrogenation readily produced cyclotetracosane (VII), confirming that the substance was still monocyclic.

Although the exact structure of the tetradecydro-[24]annulene is not known with certainty, symmetry considerations make the 1,7,13,19-tetradecydro formulation XIV most likely, derived from III by rearrangement of each 1,5-diyne to a 1-(*trans*)-ene-3-(*cis*)-ene-5-yne unit as had occurred in the C_{18} -series. Unless the bond angles are unusual, the structure XIV would not be expected to be completely planar in view of the presence of four *cis*-double bonds. The facts that the ultraviolet spectrum of the C_{24} -compound differs from that of the presumably planar C_{18} -compound XIII in not showing any maxima above 360 $m\mu$ and that the difference in the positions of the main ultraviolet maxima of the two compounds is only *ca.* 5 $m\mu$ may well be a reflection of the non-planarity of XIV.

The cyclic pentamer IV on rearrangement with potassium *t*-butoxide under the conditions used with II and III gave a crude product showing main ultraviolet maxima at 382 and 399 $m\mu$ (in benzene), consistent with the formation of a pentadecydro-[30]annulene structure (*e.g.*, XV). The cyclic hexamer V on similar rearrangement furnished a product with ultraviolet maxima at 386 and 406 $m\mu$ (in benzene), consistent with a hexadecydro-[36]annulene structure (*e.g.*, XVI). However, insufficient amounts of the C_{30} and C_{36} conjugated systems were obtained to permit their purification and characterization. In order to prepare larger quantities of these as well as of the C_{18} - and C_{24} -compounds XIII and XIV, the procedure described in the sequel was employed.

1,5-Hexadiyne was subjected to oxidative coupling with cupric acetate in pyridine, as previously, and the total product in benzene was then rearranged directly with potassium *t*-butoxide in boiling *t*-butyl alcohol, followed by careful chromatography on alumina. This procedure has the advantage over the one involving chromatographic separation before rearrangement in that each conjugated macrocyclic substance can be identified as it is eluted from the column by its characteristic ultraviolet spectrum and generally even by its color.

The almost colorless fractions eluted at the beginning were not studied at first. Subsequently, ultraviolet examination showed the earlier ones to contain the conjugated linear dodecatetraenediynes which are known⁶ to be formed by the potassium *t*-butoxide rearrangement of the linear dimer of 1,5-hexadiyne, one of the products of the coupling

reaction (see above). The later colorless fractions exhibited the typical ultraviolet spectrum of triphenylene, and on purification yielded this crystalline aromatic hydrocarbon.

The first colored substance to be eluted proved to be tridehydro-[18]annulene (XIII); the spectroscopic yield based on 1,5-hexadiyne was 3.3% (2.8% was actually isolated in pure form), confirming the previous estimate that *ca.* 6% of the trimer II had been formed in the coupling reaction. The next colored substance to be eluted, well separated from the first, was tetradecydro-[24]annulene (XIV); the over-all spectroscopic yield was 2.0% (1.3% was isolated in pure form), indicative of a *ca.* 6% yield of the precursor III in the coupling reaction, as estimated before. Then followed a considerable number of bright red fractions, well separated from the previously eluted compound, which on ultraviolet examination (see Experimental section) proved to consist of incompletely separated pentadecydro-[30]annulene and hexadecydro-[36]annulene. These fractions on rechromatography were resolved into the separate components.

Pentadecydro-[30]annulene (*e.g.*, XV) was obtained as small orange-red prisms which decomposed without melting on attempted melting point determination. The smooth hydrogenation of this substance to cyclotriacontane (VIII) proved its carbon skeleton. The ultraviolet spectrum (Table I and Fig. 1) is of the same general type as that of the C_{18} -compound XIII, with the main doublet shifted by *ca.* 50 $m\mu$ toward the visible and showing the highest wave length maximum at 463 $m\mu$ (in isoöctane). The infrared spectrum (Fig. 2)¹⁴ is similar to those of the corresponding C_{18} - and C_{24} -compounds, exhibiting an acetylene band at 4.63 μ ¹⁵ and conjugated diene bands at 10.28 and 10.73 μ .^{15b,16}

The yield of the conjugated C_{30} -compound based on 1,5-hexadiyne was 1.0%, while the yield in the above-described rearrangement of the cyclic pentamer IV was 18% (both yields determined spectroscopically). The yield of the pentamer IV produced by the coupling of 1,5-hexadiyne is therefore *ca.* 5.5%. It must be pointed out that the yield of crystallized pentadecydro-[30]annulene was only *ca.* 20% of the amount that appeared to be present in the chromatography fractions as determined by ultraviolet spectroscopy, despite the fact that the ultraviolet spectra of these fractions were almost identical to that of the crystallized product. We are inclined to the view that this phenomenon is due to the formation of more than one isomer of pentadecydro-[30]annulene in the rearrangement of IV. It is to be expected that the chances for different isomers to be formed in this type of rearrangement (both as regards the positions of the acetylenic bonds as well as the stereochemistry of the ethylenic bonds) become greater the more complex the precursor. In view of these considerations it is not possible to say whether the crystalline conjugated substance possesses the structure XV (derived from IV by rearrangement of each 1,5-diyne to a 1-(*trans*)-ene-3-(*cis*)-ene-5-yne unit, as previously) or an isomeric one. In fact the pentade-

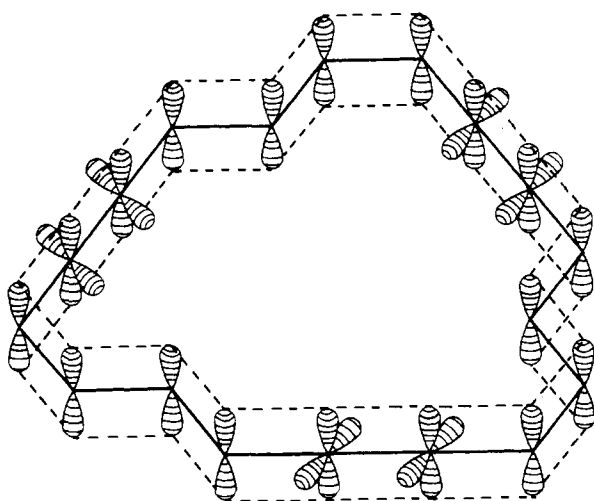


Fig. 3.—Molecular orbital diagram of tridehydro-[18]annulene.

hydro-[30]annulene was not obtained as large regular crystals like the corresponding C_{18} - and C_{24} -compounds, and the possibility that even the crystalline substance consists of a mixture of isomers cannot be excluded with certainty.

Hexadehydro-[36]annulene (XVI or an isomer) was obtained from the re-chromatography as an orange-red microcrystalline powder, which decomposed without melting on attempted melting point determination. The nature of the carbon skeleton was demonstrated by full hydrogenation to cyclohexatriacontane (IX). The ultraviolet spectrum shows only one maximum at $396\text{ m}\mu$ (ϵ 63,200; in isoöctane). The infrared spectrum resembles those of the other conjugated systems, showing an acetylene band at $4.63\text{ }\mu^{15}$ and conjugated diene bands at 10.30 and $10.77\text{ }\mu^{15b,16}$. The compound was clearly not pure, as indicated by the relatively low intensity value of the ultraviolet maximum and the fact that unlike the other conjugated cyclic polyene-polyynes it gave unsatisfactory elemental analytical results. Unfortunately, no further purification could be achieved by recrystallization or rechromatography.

The above-described chromatography of the material derived from 1,5-hexadiyne by coupling and direct rearrangement was carried out with considerable care in order to separate the various products as efficiently as possible. This procedure, however, was wasteful in time and materials (*e.g.*, *ca.* 120 l. of solvents was used for the chromatography of material derived from 15 g. of 1,5-hexadiyne). Consequently for preparative purposes the experience gained by us was utilized in order to simplify the chromatographic separation method, and in the Experimental section a preparative experiment is described whereby 60 g. of 1,5-hexadiyne are converted *inter al.* to 1.6 g. of crystalline tridehydro-[18]annulene (XIII) and 0.75 g. of crystalline tetrahydro-[24]annulene (XIV).

In view of the importance of the fully conjugated cyclic substances described above, it is of interest to determine whether the yields can be increased by modifying the conditions of the coupling of 1,5-hexadiyne and of the prototropic rearrangements.

Such experiments are in progress and will be reported subsequently.

Discussion.—The dehydro-annulenes described in this paper are the first examples of fully conjugated monocyclic systems made up of ethylenic and acetylenic bonds to be synthesized. Benzynes, the existence of which as an unstable intermediate in various reactions has been demonstrated,¹⁹ may be considered as belonging to this class, while other examples have been discussed by Sworski.²⁰

The dehydro-annulenes contain a continuous molecular orbital, as indicated for tridehydro-[18]annulene in Fig. 3. Theoretically such systems should possess aromatic character provided they contain a closed shell of $(4n + 2)$ π -electrons²¹ and they can take up a planar or not far from planar configuration. On this basis aromatic properties would be predicted for tridehydro-[18]annulene and pentadehydro-[30]annulene (if this compound is planar) but not for tetrahydro-[24]annulene and hexadehydro-[36]annulene. It will be of considerable interest to investigate whether these predictions in fact apply, *e.g.*, by determination of the energy content (through the heat of combustion or hydrogenation), the nuclear magnetic resonance (n.m.r.) spectrum, the diamagnetic anisotropy, and of the bond lengths (by X-ray methods). Already it has been shown by the n.m.r. spectrum (determined by Dr. L. M. Jackman, Imperial College of Science, London) that tridehydro-[18]annulene (XIII) can sustain an induced ring current of π -electrons,²² and is therefore the first example of a monocyclic aromatic compound to contain more than the classical sextet of π -electrons.²³

In connection with the present discussion it is relevant to point out that it is not justified to equate "aromaticity" with "stability" as has frequently been done.²⁴ In fact none of the dehydro-annulenes described in this paper proved to be particularly stable, although they could be kept with little change in the solid state for several days at room temperature (see Experimental section for further details).

It was obviously of interest to carry out the partial reduction of the dehydro-annulenes to the corresponding annulenes, and the realization of this type of transformation is the subject of a subsequent paper.^{9b}

Experimental²⁵

Preparation of the Cyclic Trimer II, Tetramer III, Pentamer IV, Hexamer V and Heptamer X from 1,5-Hexadiyne

(19) For a review, see R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

(20) T. J. Sworski, *J. Chem. Phys.*, **16**, 550 (1948).

(21) E. Hückel, *Z. Physik*, **70**, 204 (1931); "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938.

(22) The n.m.r. spectra of the dehydro-annulenes described in this paper will be discussed in detail together with those of related conjugated monocyclic systems in a separate publication.

(23) See also T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960).

(24) For further discussion on this point, see Part XXIII of this series.^{9b}

(25) Melting points were taken on a Fisher-Johns apparatus and are uncorrected. "Petroleum ether" refers to a fraction of b.p. 60–80°. All chromatograms were carried out with Alcoa activated alumina, grade F-20 (Aluminum Co. of America, Pittsburgh, Pa.). Ultraviolet spectra were taken on a Unicam model S.P. 500 as well as on a Cary model 14 recording spectrophotometer (where intensity

(I).—A solution of 15 g. of freshly distilled 1,5-hexadiyne (I)¹¹ in 100 cc. of pyridine was added to a suspension of 225 g. of finely ground neutral cupric acetate monohydrate in 1.4 l. of pyridine (technical grade, dried and then distilled over sodium hydroxide), previously heated to 55°. The mixture was then stirred vigorously at this internal temperature under a reflux condenser for 3 hr. After being cooled to room temperature, the mixture was allowed to stand overnight and was then filtered; the solid was washed well with warm benzene, the washings being kept separately. The filtrate was concentrated almost to dryness under reduced pressure (outside temperature not above 45°), the benzene washings were added and the solution was washed well with water dilute hydrochloric acid and again with water. The solution was then dried and evaporated to ca. 80 cc. under reduced pressure at an outside temperature of ca. 50°. Evaporation of a small aliquot to dryness indicated that 6.42 g. of brown non-volatile product was present, containing some terminal acetylene groupings (medium intensity band at 3.03 μ in the infrared, in chloroform).

The combined aliquot and concentrated solution were then chromatographed on a column of 3 kg. of alumina, prepared with petroleum ether. Fractions 1-100 were eluted with petroleum ether-benzene (1:1), fractions 101-400 with petroleum ether-benzene (2:3), fractions 401-630 with petroleum ether-benzene (1:3) and fractions 631-720 with pure benzene; each fraction contained 80 cc. and was evaporated to dryness under reduced pressure.

Fractions 105-132 consisted of the linear dimer 1,5,7,11-dodecatetrayne (1.31 g., 8.8%), m.p. 92-96°, raised to m.p. 98-99° on crystallization from pentane. It was identified with the previously described compound (m.p. 99-100°)^{3b} through non-depression of the m.p. on admixture and the identity of the infrared spectra.

Infrared examination of representatives indicated that practically all the eluates between fractions 170 and 650 contained cyclic substances (only certain eluates between fraction 300 and 500 showed a terminal acetylene band at 3.03 μ in the infrared).¹²

Aliquots of the combined fractions 170-175, 190-196 and 221-225 on crystallization from benzene, followed by full hydrogenation and crystallization from ethyl acetate-methanol, separately yielded cyclooctadecane (VI) with m.p. in the 69-72° range, undepressed on admixture with a sample (m.p. 71-72°) derived from 1,8-nonadiyne^{3c} or with each other. Fractions 170-225 were therefore combined, evaporated and crystallized from benzene. The resulting cyclic trimer 1,3,7,9,13,15-cyclooctadecahexayne (II) formed colorless hexagonal plates which decomposed explosively at ca. 175-180°²⁶; $\lambda_{\text{max}}^{\text{isoctane}}$ 227, 241 and 255 μ ²⁷; infrared bands at 4.44(w) and 4.64(w) μ (α,γ -diacetylene),^{3c} no terminal acetylene band at ca. 3.03 μ . The substance became yellow-brown on being allowed to stand in light and air. The estimated yield of II was ca. 6%.

Anal. Calcd. for C₁₈H₁₂: C, 94.70; H, 5.30. Found: C, 94.83; H, 5.18.²⁸

Aliquots of the combined fractions 290-294 and 310-319 on separate successive crystallization from benzene, full hydrogenation and crystallization from ethyl acetate-methanol gave cyclotetracosane (VII) with m.p. 45-46° and 46-47°, respectively; neither m.p. was depressed on admixture with a sample (m.p. 46-47°) derived from 1,7-octadiyne^{3c} or with each other, but there was a depression on admixture with cyclotriacontane (VIII) (m.p. 57-58°).^{3c} Fractions 290-319 were therefore combined, evaporated and crystallized from benzene. The cyclic tetramer 1,3,7,9,13,15,19,21-

cyclotetracosaoctayne (III) thus obtained formed colorless prisms which decomposed explosively at ca. 170-180°²⁶; infrared bands at 4.43(w) and 4.63(w) μ (α,γ -diacetylene),^{3c} no terminal acetylene band at ca. 3.03 μ . A saturated iso-octane solution showed no well-defined ultraviolet maxima.²⁹ The substance became pink-red on being allowed to stand for several hr. in light and air. The estimated yield of III was ca. 6%.

Anal. Calcd. for C₂₄H₁₆: C, 94.70; H, 5.30. Found: C, 94.82; H, 5.28.²⁸

Aliquots of the combined fractions 502-512 and 568-579 on successive crystallization from benzene, full hydrogenation and crystallization from ethyl acetate-methanol yielded cyclotriacontane (VIII) with m.p. 56-57° and 55-56°, respectively; neither m.p. was depressed on admixture with a sample (m.p. 57-58°) derived from 1,9-decadiyne^{3c} or with each other, but there was a depression on admixture with cyclotetracosane (VII) or with cyclohexatriacontane (IX) (m.p. 70-71°).^{3c} Fractions 502-579 were therefore combined, evaporated and crystallized from benzene. The resulting cyclic pentamer 1,3,7,9,13,15,19,21,25,27-cyclotriacontadecayne (IV) formed long colorless needles which decomposed explosively at ca. 165°²⁶; infrared bands at 4.43(w) and 4.63(w) μ (α,γ -diacetylene),^{3c} no terminal acetylene band at ca. 3.03 μ . A saturated iso-octane solution showed no ultraviolet maxima.²⁹ The substance gradually became red on being allowed to stand in light and air. The estimated yield of IV was ca. 6%.

Anal. Calcd. for C₃₀H₂₀: C, 94.70; H, 5.30. Found: C, 94.90; H, 5.11.²⁸

Aliquots of the combined fractions 622-630 and 646-650 on successive crystallization from benzene, full hydrogenation and crystallization from ethyl acetate afforded cyclohexatriacontane (IX) with m.p. 67-68° and 68-69°, respectively; neither m.p. was depressed on admixture with a sample (m.p. 70-71°) derived from 1,8-nonadiyne^{3c} or with each other, but there was a depression on admixture with cyclotriacontane (VIII). Fractions 622-650 were therefore combined, evaporated to small volume and cooled. The cyclic hexamer 1,3,7,9,13,15,19,21,25,27,31,33-cyclohexatriacontadodecayne (V) thus obtained formed long colorless needles which decomposed explosively at ca. 180°²⁶; infrared bands at 4.43(w) and 4.63(w) μ (α,γ -diacetylene),^{3c} no terminal acetylene band at ca. 3.30 μ . A saturated iso-octane solution showed no ultraviolet maxima.²⁹ The substance rapidly became bright red on being allowed to stand in light and air. The estimated yield of V was ca. 2%.

Anal. Calcd. for C₃₆H₂₄: C, 94.70; H, 5.30. Found: C, 94.83; H, 5.27.²⁸

No higher cyclic polymers of 1,5-hexadiyne could be obtained in the pure state from later fractions in this experiment. A previous experiment carried out apparently in the same way had yielded, instead of the cyclic hexamer V, a substance in ca. 2% yield (eluted with benzene) which appears to be the cyclic heptamer 1,3,7,9,13,15,19,21,25,27,31,33,37,39-cyclodotetracontatetradecayne (X).^{7a} This compound formed colorless feathery needles from benzene, which decomposed explosively at ca. 180°²⁶ and rapidly turned red in light; infrared bands at 4.43(w) and 4.63(w) μ (α,γ -diacetylene),^{3c} no terminal acetylene band at ca. 3.03 μ . Full hydrogenation and crystallization from ethyl acetate yielded what is most probably slightly impure cyclodotetracontane (XI), m.p. 75-76°, depressed on admixture with a sample of cyclohexatriacontane (IX) (m.p. 70-71°).^{3c}

Anal. Calcd. for C₄₂H₃₄: C, 85.63; H, 14.37; mol. wt., 589. Found: C, 85.42; H, 14.26; mol. wt., 598 (Rast method, in camphene).

Tridehydro-[18]annulene (XIII), Tetradehydro-[24]annulene (XIV), Pentadehydro-[30]annulene (e.g., XV) and Hexadehydro-[36]annulene (e.g., XVI) from 1,5-Hexadiyne (I) without Isolation of Intermediates.—The coupling of 15 g. of 1,5-hexadiyne (I) with 225 g. of cupric acetate in 1.5 l. of pyridine was carried out exactly as described above, except that the final benzene solution was concentrated only to ca. 250 cc. A saturated solution of potassium *t*-butoxide in *t*-butyl alcohol (250 cc.) was then added and the solution was gently boiled under reflux on a boiling water-bath for 30

(29) This indicates that no chromophore with high intensity maxima is present. The low solubility of the substance in iso-octane is doubtless responsible for the comparatively low-intensity maxima of the α,γ -diyne chromophore not being apparent.

values differ from those given in the preliminary communications, the present values are the more accurate ones); the ultraviolet spectra of chromatography fractions were determined against pentane. Infrared spectra were measured as KBr pellets on a Baird double-beam as well as on a Perkin-Elmer "Infracord" recording spectrophotometer (sodium chloride optics). Unless mentioned otherwise, full hydrogenations were carried out in dioxane over platinum as described previously.^{3,30} Analyses were performed in our microanalytical laboratory under the direction of Mr. Erich Meier.

(26) Put on block on an open cover-slide just below this temperature; only polymerization occurred when the m.p. was determined in the usual way.

(27) No accurate intensity values could be obtained in view of the low solubility of the substance in iso-octane.

(28) For the analytical precautions which were taken, see footnote 6 in ref. 3c.

minutes, moisture being excluded. The resulting intense red-brown mixture was cooled in ice and was then filtered in order to remove a dark insoluble material. The solid was washed with benzene, more benzene was added to the filtrate which was then washed well with water, dried and evaporated to *ca.* 100 cc. under reduced pressure at an outside temperature not exceeding 50°. The resulting clear dark red solution was poured on a column of 3 kg. of alumina, prepared with pentane. The column was washed successively with pentane, various mixtures of pentane-ether, ether, ether-chloroform and finally with chloroform, 500-cc. fractions being collected.

During the chromatography five separate colored bands (I-V) were observed to move down the column. The progress of the chromatogram was followed through measurement of the ultraviolet spectra of representatives of the colored eluates.

Representatives of fractions 33-46 (band I, red-brown solutions), eluted with pentane-ether (17:3 to 4:1), all showed the typical ultraviolet spectrum of XIII (maxima at *ca.* 322, 334, 385 and 400 μ), the spectroscopic yield being 485 mg. (3.3% based on I). These fractions on evaporation and crystallization from pentane afforded 410 mg. (2.8%) of tridehydro-[18]annulene (XIII) in two crops (both spectroscopically pure) as large light-brown plates, m.p. 190-192° dec.²⁶ The ultraviolet spectrum (Table I and Fig. 1) was completely unchanged on recrystallization. The infrared spectrum (Fig. 2) showed bands at 3.30(w), 4.63(w), 5.89(w), 7.06(w), 7.79(m), 7.89(w), 8.17(w), 8.39(w), 9.05(w), 10.27(s), 10.80(s), 11.82(s) and 13.12(s) μ .³⁰ A benzene solution was dark red-brown when concentrated and yellow-orange when dilute. The substance XIII was soluble in chloroform, benzene and ether, but only moderately soluble in pentane. It could be kept with little change for 48 hr. in the solid state at room temperature without protection from light, or for 7 days at -15° in the dark, as evidenced by the essentially unchanged ultraviolet intensities; however only *ca.* 60% remained after 30 days at -15° and 20% after 60 days at -15° (in the dark). A benzene solution (1.4 mg./l.) on being allowed to stand at room temperature without protection from diffuse day-light was essentially unchanged after 10 days, 91% remained after 30 days and 86% remained after 60 days.

Anal. Calcd. for C₁₈H₁₂: C, 94.70; H, 5.30. Found: C, 94.71; H, 5.06.²⁸

Full hydrogenation of XIII followed by crystallization from ethyl acetate-methanol smoothly yielded cyclooctadecane (VI), m.p. 72-73°, undepressed on admixture with an authentic sample (m.p. 71-72°).

Representatives of fractions 55-81 (band II, wine-red solutions), eluted with pentane-ether (4:1 to 3:1), all showed the typical ultraviolet spectrum of XIV (main maxima at *ca.* 324 and 340 μ , no maxima in the 380-400 μ region), the spectroscopic yield being 295 mg. (2.0%). These fractions on evaporation to small volume and cooling yielded 190 mg. (1.3%) of tetradecydro-[24]annulene (XIV) as large dark purple prisms which decomposed on attempted m.p. determination. The ultraviolet spectrum (Table I and Fig. 1) was completely unchanged on recrystallization from chloroform, benzene or ether. The infrared spectrum (Fig. 2) showed bands at 3.29(w), 4.62(w), 5.48(w), 5.88(w), 6.26(m), 7.09(m), 7.69(m), 8.52(m), 9.15(m), 10.25(s), 10.70(s), 10.79(s), 11.81(m), 13.05(s) and 13.28(m) μ .³⁰ A benzene solution was intense dark red when concentrated and orange-red when dilute. The compound was soluble in chloroform, tetrahydrofuran and benzene, less in ether and almost insoluble in pentane. It suffered little change on being kept for 48 hr. in the solid state at room temperature without protection from light, as indicated by the essentially unchanged ultraviolet intensities; however, after 30 days it had partly decomposed since it was then no longer completely soluble in benzene.

Anal. Calcd. for C₂₄H₁₆: C, 94.70; H, 5.30. Found: C, 94.65; H, 5.20.²⁸

Full hydrogenation of XIV followed by crystallization from ethyl acetate-methanol smoothly furnished cyclotetacosane (VII), m.p. 46-47°, undepressed on admixture with an authentic sample (m.p. 46-47°).

(30) The spectrum was determined with a Perkin-Elmer Infracord spectrophotometer, while the infrared spectra recorded in the preliminary communications^{30,31} were measured with a Baird spectrophotometer.

Fractions 137-187 (band III, bright red solutions), which were eluted with pentane-ether (1:1) to pure ether, consisted of incompletely separated pentadecydro-[30]annulene and hexadecydro-[36]annulene, the ultraviolet characteristics of representative fractions gradually changing from a double maximum at 371 and 387 μ (due to the C₃₀-compound) to a single maximum at 395 μ (due to the C₃₆-compound) without any definite break. Fractions 198-209 (band IV, dark red solutions), eluted with ether-chloroform (3:1), showed one single ultraviolet maximum in the 397-402 μ region (possibly due to rearranged X). Finally, fractions 217-231 (band V, dark red solutions), showing no characteristic ultraviolet maxima in the 300-600 μ region, were eluted with chloroform. The nature of bands IV and V was not elucidated.

The combined fractions 137-187 (consisting of the conjugated C₃₀- and C₃₆-compounds) were evaporated to dryness and the resulting red oil, dissolved in *ca.* 10 cc. of benzene, was re-chromatographed on a column of 500 g. of alumina. As previously, the column was developed with pentane and then with various mixtures of pentane and ether. Pentane-ether (2:3) eluted first the conjugated C₃₀-compound, then a mixture of the C₃₀- and C₃₆-compounds and finally the C₃₆-compound, as indicated by the ultraviolet spectra.

The least polar fractions [ultraviolet maxima at 371 and 387 μ (beginning) up to 373 and 389 μ (end)] were combined, evaporated to small volume and cooled. Filtration yielded 31 mg. (0.21%) of pentadecydro-[30]annulene (XV or an isomer) (the spectroscopic yield before crystallization was 145 mg., 1.0%). This substance formed small orange-red prisms which decomposed on attempted m.p. determination. The ultraviolet spectrum (Table I and Fig. 1) was unchanged on recrystallization from ether. The infrared spectrum (Fig. 2) showed bands at 3.30(w), 4.63(w), 6.33(w), 7.15(w), 7.41(w), 7.75(m), 7.93(w), 8.21(w), 8.66(w), 9.08(w), 9.98(w), 10.28(s), 10.73(m), 11.83(m), 12.38(w) and 13.28(s) μ .³⁰ A benzene solution was red in concentrated solution and yellow-orange in dilute solution. The compound was soluble in chloroform and benzene, less soluble in dioxane and ether, and insoluble in pentane. It was essentially unaffected on being allowed to stand for 48 hr. in the solid state or for 12 days in dilute benzene solution (5.4 mg./l.), both at room temperature without protection from light (determined by the intensities of the ultraviolet maxima). After 30 days standing, a solid sample had partly decomposed, as it was then no longer completely soluble in benzene.

Anal. Calcd. for C₃₀H₂₀: C, 94.70; H, 5.30. Found: C, 94.18; H, 5.42.²⁸

Full hydrogenation of XV followed by one crystallization from ethyl acetate-methanol yielded cyclotriacontane (VIII), m.p. 55-57°, undepressed on admixture with an authentic sample (m.p. 57-58°), but depressed on admixture with cyclohexatriacontane (IX) (m.p. 70-71°).

The next fractions, consisting of mixtures of the C₃₀- and C₃₆-compounds [ultraviolet maxima at 374 and 390 μ (beginning) to 382 (inflection) and 394 μ (end)] were kept for re-chromatography.

The most polar fractions containing the C₃₆-compound (showing a single ultraviolet maximum, located at 394-395 μ), were combined, evaporated to small volume and cooled. Filtration yielded 35 mg. of the impure hexadecydro-[36]annulene (XVI or an isomer) as an orange-red powder (darker than the C₃₀-compound) which decomposed without melting on attempted m.p. determination. The ultraviolet spectrum showed $\lambda_{\text{max}}^{\text{benzene}}$ 396 μ (ϵ 63,200), $\lambda_{\text{max}}^{\text{benzene}}$ 407 μ (ϵ 60,300). The infrared spectrum showed bands at 3.29(w), 4.63(w), 6.32(w), 7.09(w), 7.75(m), 8.67(w), 10.05(m), 10.30(s), 10.77(m), 11.84(w) and 13.34(s) μ . A benzene solution was red in concentrated solution and orange in dilute solution. The substance was soluble in chloroform and benzene, to some extent in ether, but insoluble in pentane. It showed the same type of stability as the C₃₀-compound. No satisfactory analysis could be obtained.

Anal. Calcd. for C₃₆H₂₄: C, 94.70; H, 5.30. Found: C, 88.55; H, 5.25.

Full hydrogenation of XVI, followed by crystallization from ethyl acetate, yielded cyclohexatriacontane (IX), m.p. 69-71°, undepressed on admixture with an authentic sample (m.p. 70-71°).

The following procedure was employed subsequently when larger amounts of the various dehydro-annulenes had to be

prepared. 1,5-Hexadiyne (60 g.) was coupled and then rearranged as previously, the coupling being performed in 4 separate batches of 15 g. each, followed by combination and rearrangement together. The resulting benzene extract was evaporated under reduced pressure to ca. 100 cc., the warm solution was filtered to remove a dark precipitate, and the filtrate was chromatographed on 3 kg. of alumina. Elution with various mixtures of petroleum ether-ether and spectroscopic examination of representatives of the resulting colored fractions showed that first mixtures of triphenylene (see below) and XIII were obtained, then pure XIII, then mixtures of XIII and XIV and finally pure XIV. As soon as no more XIV was eluted, the column was stripped with chloroform. Re-chromatography of the mixtures of triphenylene and XIII³¹ as well as of the mixtures of XIII and XIV³¹ on 1 kg. of alumina each resulted in reasonably effective separation between the individual substances. Similarly, rechromatography of the material from the chloroform strippings (after evaporation of the chloroform) on 1.5 kg. of alumina effected the same type of separation between XV and XVI as had been obtained in the above-described re-chromatogram of the fractions containing a mixture of these substances. In this way comparable yields of the four dehydro-annulenes to those obtained previously were realized (in particular after crystallization 1.61 g. of XIII and 0.75 g. of XIV were obtained), while a considerable saving in solvents resulted.

Triphenylene. (Experiments Performed by Dr. Y. Amiel).—The almost colorless fractions eluted at the beginning of the above-described chromatogram of the product derived from 1,5-hexadiyne by coupling and direct rearrangement were examined after several months standing. The first fractions, eluted with pentane and pentane-ether (19:1), showed ultraviolet maxima at ca. 241, 250, 259, 270, 289, 310, 327 and 351 m μ , typical of the conjugated linear dodecatetraene-diyne⁹ known to be formed by the rearrangement of the linear dimer of 1,5-hexadiyne. The next fractions, eluted with pentane-ether (9:1 to 17:3) and coming out of the column directly before tridehydro-[18]annulene,³¹ showed sharp ultraviolet maxima at ca. 248, 257, 273 and 283 m μ . Evaporation of these fractions and crystallization of the residue from ethanol-ethyl acetate yielded triphenylene as long cream-colored needles, m.p. 198–199°; $\lambda_{\text{max}}^{\text{ether}}$ 248, 257, 273, 283, 319, 326 and 333 m μ (ϵ 86,700, 149,000, 20,200, 18,200, 810, 630 and 830) [reported³² m.p. 199°; $\lambda_{\text{max}}^{\text{ethanol}}$ 248, 256, 274, 284, 320, 326 and 334 m μ (ϵ 89,100, 151,000, 21,900, 18,200, 850, 790 and 710)]. The m.p. was undepressed on admixture with an authentic sample (m.p. 198–199°; kindly provided by the late Dr. Y. Hirshberg) and the infrared spectra were identical in every respect.

To determine the over-all yield of triphenylene from 1,5-hexadiyne, 350 mg. of the latter was coupled and rearranged directly as usual and the total product, dissolved in 20 cc. of dioxane, was hydrogenated over 0.5 g. of a 10% palladium-charcoal catalyst at room temperature and atmospheric pressure until uptake stopped. Removal of the catalyst and dilution of the filtrate to known volume gave a solution showing the typical ultraviolet maxima of triphenylene, the spectroscopic yield being 1.9 mg. The yield was therefore 0.54% based on 1,5-hexadiyne or 9% based on the cyclic trimer II (assuming a 6% yield of II from 1,5-hexadiyne). This experiment also demonstrated that no other polycyclic aromatic hydrocarbon had been formed in appreciable amounts.

(31) It was our experience that XIII could be obtained pure by simple crystallization if XIV was the impurity, but it was difficult to separate XIII from triphenylene except by chromatography since the two substances tend to come out of solution together.

(32) For references see V. Prelog, V. Boarland and S. Polyak, *Helv. Chim. Acta*, **38**, 434 (1955); C. M. Buess and D. D. Lawson, *Chem. Revs.*, **60**, 313 (1960).

The cyclic trimer II (50 mg.) on potassium *t*-butoxide rearrangement as before, followed by isolation with benzene, evaporation and hydrogenation of the total product in 10 cc. of dioxane over 0.1 g. of a 10% palladium-charcoal catalyst, gave a solution which again showed the typical ultraviolet maxima of triphenylene. The spectroscopic yield of the latter was 3.6 mg. (7.2% based on II).

In a blank experiment in which the cyclic trimer II itself was hydrogenated as before, no trace of triphenylene could be detected by ultraviolet spectral examination of the resulting solution. The same result was obtained when tridehydro-[18]annulene was first treated with potassium *t*-butoxide under the conditions used for its formation, followed by full hydrogenation of the product as before.

Rearrangement of the Cyclic Trimer II to Tridehydro-[18]annulene (XIII).—A solution containing 50 mg. of the cyclic trimer II, 15 cc. of benzene and 15 cc. of a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol was gently boiled under reflux for 30 minutes, moisture being excluded. The resulting red-brown solution was cooled, diluted with benzene and the organic layer was washed well with water. Ultraviolet examination of an aliquot of the dried benzene extract showed the maxima at 329, 342, 391 and 407 m μ (against benzene) typical of tridehydro-[18]annulene, the spectroscopic yield being 52%. Evaporation of the solvent under reduced pressure, followed by chromatography on 50 g. of alumina and elution of the yellow band with pentane-ether, yielded orange solutions which on evaporation and crystallization from pentane furnished 17 mg. of tridehydro-[18]annulene with properties identical to those described in the preparative experiment.

Rearrangement of the Cyclic Tetramer III to Tetrahydro-[24]annulene (XIV).—The cyclic tetramer III (9.3 mg.) in 10 cc. of benzene was rearranged with 10 cc. of a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol, and the product was then isolated with benzene, as described directly above for the trimer II. The resulting red benzene solution showed the maxima at 333 and 350 m μ (but none in the 390–410 m μ region) typical of tetrahydro-[24]annulene, the spectroscopic yield being 36%. Chromatography on 10 g. of alumina, followed by elution with pentane-ether, evaporation to small volume and cooling yielded 1.5 mg. of the pure substance with properties identical to those described in the preparative experiment.

Rearrangement of the Cyclic Pentamer IV to Pentadecahydro-[30]annulene (e.g., XV).—Isomerization of 3.6 mg. of the cyclic pentamer IV in 5 cc. of benzene with 5 cc. of potassium *t*-butoxide in *t*-butyl alcohol as before, followed by extraction with benzene, yielded a red solution with maxima at 320, 382 and 399 m μ (shoulder at ca. 310 m μ), typical of pentadecahydro-[30]annulene (see preparative experiment and Table I); the spectroscopic yield was 18%.

Rearrangement of the Cyclic Hexamer V to Hexadecahydro-[36]annulene (e.g., XVI).—Rearrangement of 2.65 mg. of the cyclic hexamer V in 10 cc. of benzene with 10 cc. of potassium *t*-butoxide in *t*-butyl alcohol for 30 minutes on the steam-bath, followed by extraction with benzene, gave a red solution with ultraviolet maxima at 386 and 406 m μ (ϵ 29,200 and 27,100, based on the weight of V). The 406 m μ band appears to be due to the hexadecahydro-[36]annulene described above, while the 386 m μ band may be due to an isomer.

Acknowledgments.—We are greatly indebted to Drs. Y. Amiel and Y. Gaoni for carrying out certain experiments in connection with the identification of triphenylene and the preparation of the various dehydro-annulenes in quantity, as well as to Dr. D. A. Ben-Efraim for providing certain spectral data.