had 96.5% d_1 composition, was labeled 76.4% at C-3 (2-Cl) and 20.1% at C-7 (3-Cl).[15] The composition of this mixture did not change substantially during two passes through the preparative gas chromatography separation procedures.

(15) The propensity of benzonorbornenyl radicals to rearrange has been noted previously.[16]

(16) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, 32, 3727 (1967).

The Synthesis of 1,2-Diethynylcyclohexene and Its Oxidation to a Tetradehydro[12]annulene Derivative[1]

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Contribution from the University Chemical Laboratory, Cambridge, England. Received August 10, 1970

Abstract: Two syntheses of 1,2-diethynylcyclohexene (1) are described. The first method involves the conversion of 1,2-cyclohexanedione (3) to 1,2-diethynyl-1,2-cyclohexanediol (4) by means of sodium acetylide, followed by reduction with diphosphorus tetraiodide. The second method, the preferred one, uses 2-isopropoxymethylene-cyclohexanone (9) as starting material; treatment with lithium acetylide and acid hydrolysis gave 2-ethynyl-1-cyclohexenecarboxaldehyde (15), which was converted to 1 by Wittig reaction with chloromethylenetriphenylphosphorane (17) and subsequent dehydrochlorination of the resulting chloromethylene compound (18, trans and cis isomers) with sodamide or potassium *tert*-butoxide. Oxidative coupling of 1 with cupric acetate in pyridine led to the corresponding cyclic "dimer" 2, a tetraalkylated tetradehydro[12]annulene, in ~50% yield. The properties of 2 have been investigated, and there is some nmr evidence for the existence of a paramagnetic ring current. The oxidative coupling of 1 with oxygen, cuprous chloride, and ammonium chloride has also been studied, and it was found that this reaction gives rise to a variety of cyclic and "linear" chloro compounds.

The fully conjugated macrocyclic polyenynes (dehydroannulenes) obtained by our group in recent years have been prepared from nonconjugated α,ω-diacetylenes by oxidative coupling to large-ring polyacetylenes, and subsequent formation of the conjugated systems.[3] An attractive alternative involves the direct synthesis of dehydroannulenes by the coupling of conjugated α,ω-diacetylenes, but this approach had not been investigated by us before the presently described work was initiated in 1965 since no suitable starting materials (except for certain benz-fused derivatives[4]) were known.[5] An appropriate conjugated diacetylene appeared to be 1,2-diethynylcyclohexene (1). The

fused cyclohexene ring in this substance ensures that the double bond is held in the required cis configuration, while its presence in the final conjugated systems should not seriously disturb the π-electron distributions. In this paper we describe the synthesis of 1 by two routes,[8]

1   2
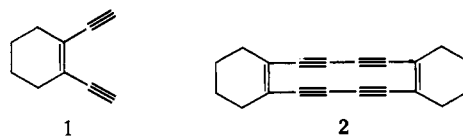
and its oxidative coupling to the cyclic "dimer" 2, a tetraalkylated tetradehydro[12]annulene. In the following paper[9] the syntheses of 13-membered ring systems from 1 are reported.

Syntheses of 1,2-Diethynylcyclohexene (1). The starting material for the first synthesis of 1 was 1,2-cyclohexanedione (3), which was prepared most conveniently from cyclohexanone *via* 2-chlorocyclohexanone in 26% overall yield by the method of McEntee, *et al.*[10] Treatment of 3 (which exists largely in the enolic form[11]) with ~2.5 mol equiv of sodium acetylide in liquid ammonia for 24 hr gave 1,2-diethynyl-1,2-cyclohexanediol (4)[12] in 66% yield as a mixture of the trans

(1) Unsaturated Macrocyclic Compounds. LXXIII. [For part LXXII, see R. M. McQuilkin and F. Sondheimer, *J. Amer. Chem. Soc.*, 92, 6341 (1970).] Taken from the Ph.D. Dissertation of G. M. Pilling, Cambridge University, Aug 1968.

(2) Author to whom inquiries should be addressed at the Chemistry Department, University College, London W.C.1, England.
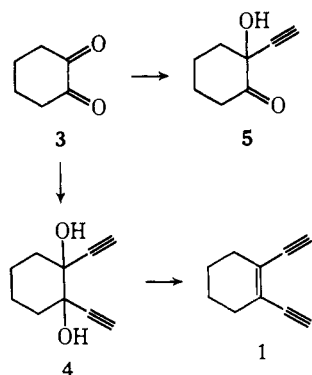
(3) For reviews, see F. Sondheimer, *Pure Appl. Chem.*, 7, 363 (1963); *Proc. Roy. Soc., Ser. A*, 297, 173 (1967); *Proc. Robert A. Welch Found. Conf. Chem. Res.*, 12, 125 (1968).

(4) (a) Synthesis and coupling of *o*-diethynylbenzene: O. M. Behr, G. Eglinton, A. R. Galbraith, and R. A. Raphael, *J. Chem. Soc.*, 3614 (1960); (b) synthesis and coupling of 1,8-diethynylanthracene: S. Akiyama, S. Misumi, and M. Nakagawa, *Bull. Chem. Soc. Jap.*, 33, 1293 (1960); (c) synthesis and coupling of 1,8-diethynylnaphthalene: R. H. Mitchell and F. Sondheimer, *Tetrahedron*, 24, 1397 (1968); (d) synthesis and coupling of 2,2'-diethynylbiphenyl: H. A. Staab, H. Mack, and E. Wehinger, *Tetrahedron Lett.*, 1465 (1968).

(5) The synthesis and coupling of other suitable conjugated α,ω-diacetylenes (*cis*-3-hexene-1,5-diyne,[6] *cis,cis*- and *cis,trans*-3,5-octadiene-1,7-diyne[7]) have now been carried out.

(6) W. H. Okamura and F. Sondheimer, *J. Amer. Chem. Soc.*, 89, 5991 (1967).

(7) G. H. Mitchell and F. Sondheimer, *ibid.*, 91, 7520 (1969); G. P. Cotterrell, G. H. Mitchell, and F. Sondheimer, unpublished experiments.

(8) Preliminary communication: G. M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.*, 90, 5610 (1968).

(9) G. M. Pilling and F. Sondheimer, *ibid.*, 93, 1977 (1971).

(10) M. E. McEntee, A. R. Pinder, H. Smith, and R. E. Thornton, *J. Chem. Soc.*, 4699 (1956).

(11) See G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta*, 30, 663 (1947); G. Hesse and G. Krehbiel, *Justus Liebigs Ann. Chem.*, 593, 35 (1955); R. Bakule and F. A. Long, *J. Amer. Chem. Soc.*, 85, 2309, 2313 (1963).

(12) W. Ried and H. J. Schmidt, *Chem. Ber.*, 90, 2499 (1957).

and cis isomers (~7:1), in addition to small amounts of 2-ethynyl-2-hydroxycyclohexanone (5).[10,12,13] The trans isomer, previously characterized by Ried and Schmidt,[12] could be obtained by direct crystallization as crystals, mp 80–81°.[15] Chromatography of the mother liquors then afforded the cis isomer, mp 63–64°.

Conversion of the diol 4 to 1,2-diethynylcyclohexene (1) was achieved, using a modification of the Kuhn–Winterstein reduction of 1,2-diols to olefins with diphosphorus tetraiodide.[16] Inhoffen, et al.,[17] have shown that this reduction can be applied to 1,2-diols containing terminal acetylene groups, by careful choice of experimental conditions.[18] Specifically, they converted the diol 6 (either the meso or the racemic form) to the trans olefin 7 in 43% yield, only a trace of the cis
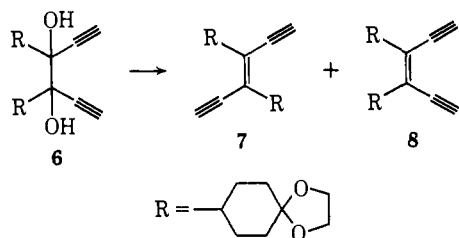
isomer 8 being formed.[17] In our case, only the cis olefin 1 is possible, and this substance was obtained in ~20% yield from the diol 4 (trans isomer or mixture of trans and cis isomers) by use of the Inhoffen experimental conditions.[18]

The enediyne 1 proved to be a rather unstable liquid, showing spectral properties in agreement with the assigned structure. Thus, the electronic spectrum showed maxima at 256 and 269 nm, close to those of the similarly constituted 7 (261.5 and 271 nm) and 8 (260 and 272 nm).[17] The nmr spectrum of 1 in carbon tetrachloride, reproduced in Figure 1 (upper curve), consisted of a 2 H singlet at τ 7.02 (acetylenic protons), a 4 H multiplet at 7.65–7.95 (allylic methylene protons), and a 4 H multiplet at 8.20–8.50 (nonallylic methylene protons).

(13) Ried and Schmidt[12] have shown that a prolonged reaction time is necessary for 4 to be formed from 3 and sodium acetylide in liquid ammonia, the usual reaction time (3–4 hr) giving rise to 5 as the main product. Similarly, we have found that treatment of 3 with an excess of ethynylmagnesium bromide[14] in tetrahydrofuran for 4 hr led mainly to 5.

(14) E. R. H. Jones, L. Skattebøl, and M. C. Whiting, J. Chem. Soc., 4765 (1956); Org. Syn., 39, 56 (1959).

(15) Ried and Schmidt[12] reported mp 105°. The difference may be due to polymorphism.

(16) R. Kuhn and A. Winterstein, Helv. Chim. Acta, 11, 87 (1928).

(17) H. H. Inhoffen, K. Radscheit, U. Stache, and V. Koppe, Justus Liebigs Ann. Chem., 684, 24 (1965).

(18) The diol, in anhydrous pyridine, was added to a supersaturated solution of diphosphorus tetraiodide in carbon disulfide, obtained by Soxhlet extraction of the solid reagent prior to the reaction.
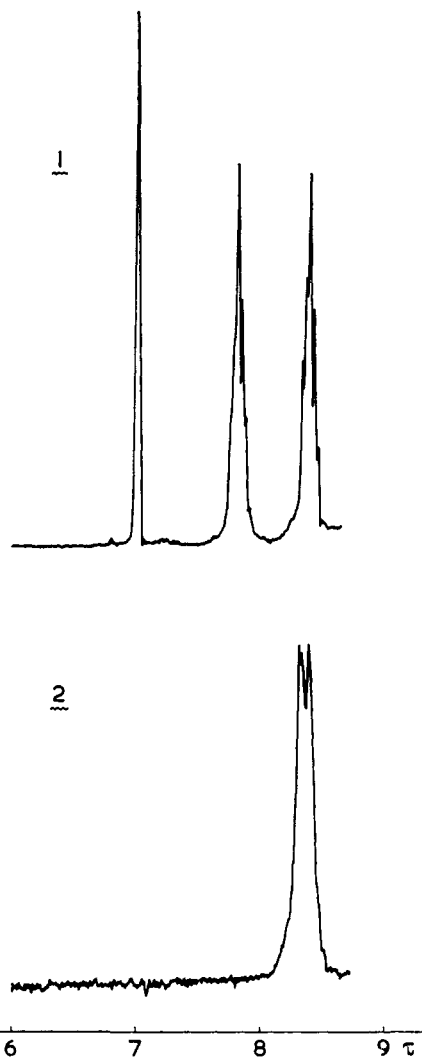
Figure 1. Nmr spectra (100 MHz) of 1,2-diethynylcyclohexene (1) (upper curve, CCl₄, 35°) and the tetradehydro[12]annulene 2 (lower curve, CDCl₃, −20°).

The overall yield of 1 from cyclohexanone by this route was rather poor (~3%), and only relatively small amounts (1–2 g) could be obtained conveniently in one run. An alternative synthesis of 1 was therefore investigated. This proceeded from 2-isopropoxymethylenecyclohexanone (9), which was prepared from cyclohexanone via 2-hydroxymethylenecyclohexanone, as described previously,[19] in 57% overall yield.
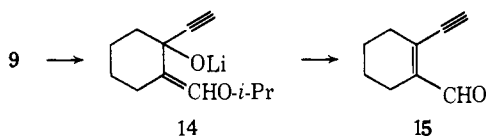
Dreiding and Nickel[19c] have shown that the reaction of 9 with organometallic reagents can lead to products derived from both 1,2 and 1,4 addition to the α,β-unsaturated carbonyl system, the relative amounts being influenced by the type of reagent used. Thus, treatment of 9 with methylmagnesium iodide and then with dilute acid gave 67% 2-ethylidenecyclohexanone (11), derived from the 1,4 addition product 10. On the other hand, methyllithium led mainly (53%) to 2-methyl-1-cyclohexenecarboxaldehyde (13), derived from the 1,2 addition product 12, although 23% of 11 was also obtained.[19c]

In view of these observations, it appeared possible that reaction of 9 with lithium acetylide would result

(19) See (a) W. S. Johnson and H. Posvic, J. Amer. Chem. Soc., 69, 1361 (1947); (b) R. B. Woodward and W. M. McLamore, ibid., 71, 379 (1949); (c) A. S. Dreiding and S. N. Nickel, ibid., 76, 3965 (1954).
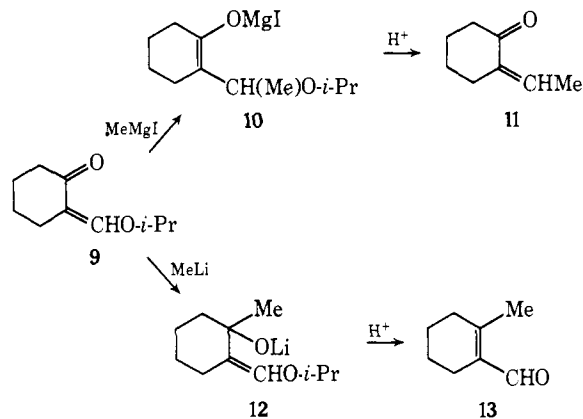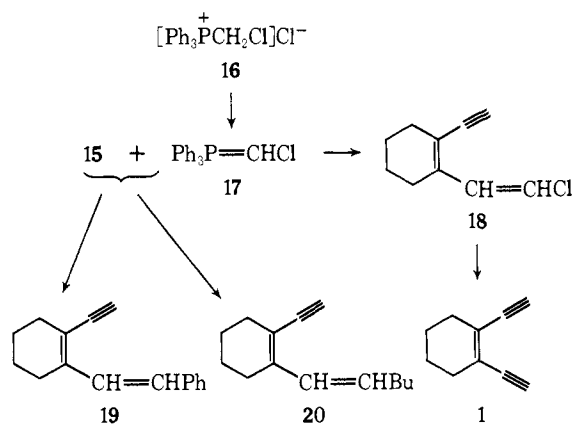
in 1,2 addition, and this indeed proved to be the case. Treatment of 9 with lithium acetylide–ethylenediamine[20] and subsequent hydrolysis with dilute sulfuric acid gave 2-ethynyl-1-cyclohexenecarboxaldehyde (15, mp 49.5–50°) in 39% yield, presumably via the inter-

mediate 14.[21,22] The presence of both an ethynyl and a carboxaldehyde group in 15 was clearly indicated by the infrared and nmr spectra (see Experimental Section).

Wittig reaction of the aldehyde 15 with chloromethylenetriphenylphosphorane [17, generated by treatment of (chloromethyl)triphenylphosphonium chloride (16) with n-butyllithium in tetrahydrofuran at −70°[23]] led to ~55% of the very unstable chloromethylene compound 18 as a mixture of trans and cis isomers

(~2:1). The presence of both isomers, in the indicated proportion, follows from the nmr spectrum and glc analysis, described in the Experimental Section. The isomers were not separated on a preparative scale, in view of their instability, similar glc retention times, and

the fact that both were expected to give 1 on dehydrochlorination.

By-products in the reaction of 15 and 17 proved to be the phenyl compound 19 and the butyl compound 20; both substances were mixtures of trans and cis isomers, in a ratio of ~2:1 and ~3:1, respectively (each isomer of 20 was obtained pure, but separation could not be effected in the case of 19). The yield of 19 was ~2%, while that of 20 was variable (0–13% in different experiments).[24] The formation of 20 was not surprising, but that of the phenyl derivative 19 was unexpected. The phenyl group in 19 must originate from the (chloromethyl)triphenylphosphonium chloride (16) used to generate the ylide 17 by some form of ligand exchange reaction. For example, a possible mechanism involves the reaction of 16 with butyllithium to form the salt 21 and phenyllithium, and it is the last-mentioned substance which then gives rise to the phenyl compound 19. A similar mechanism, involving the reaction of methyltriphenylphosphonium bromide (22) with methyllithium to form the salt 23 and phenyllithium, has previously been considered in order to explain the formation of benzene when 22 is treated with methyllithium.[25]

$$[\text{Ph}_3\text{P}^+\text{CH}_2\text{Cl}]\text{Cl}^- + \text{BuLi} \longrightarrow [\text{Ph}_2\text{BuP}^+\text{CH}_2\text{Cl}]\text{Cl}^- + \text{PhLi}$$
$$\quad\quad 16 \quad\quad\quad\quad\quad\quad\quad\quad\quad 21$$

$$[\text{Ph}_3\text{P}^+\text{Me}]\text{Br}^- + \text{MeLi} \longrightarrow [\text{Ph}_2\text{P}^+\text{Me}_2]\text{Br}^- + \text{PhLi}$$
$$\quad\quad 22 \quad\quad\quad\quad\quad\quad\quad 23$$

Dehydrochlorination of 18 (isomeric mixture) to the enediyne 1 was achieved by treatment with sodamide in liquid ammonia (60% yield), or with potassium tert-butoxide in boiling ether (46% yield). This route to 1 was preferred to the firstly described one, since the overall yield from cyclohexanone was better (~7.5%) and it could be more easily adapted to the synthesis of larger amounts of 1 (~10 g per run).

Oxidative Coupling of 1,2-Diethynylcyclohexene (1). The availability of 1 makes possible, in principle, the synthesis of a variety of dehydroannulene derivatives. The simplest route to such derivatives appeared to involve direct oxidative coupling, and this type of reaction was therefore investigated first.

Oxidative coupling of 1 with cupric acetate in pyridine (Eglinton conditions[26]) at 55° for 3 hr led to ~50% of the cyclic dimer 2 [5,6:11,12-bis(tetramethyl-

ene)-1,3,7,9-tetradehydro[12]annulene] as orange-red needles, but none of the cyclic trimer 24. The crystals

(20) Supplied by Foote Mineral Co., Exton, Pa.; see O. F. Beumel and R. F. Harris, J. Org. Chem., 28, 2775 (1963); 29, 1872 (1964).
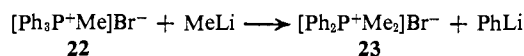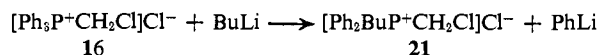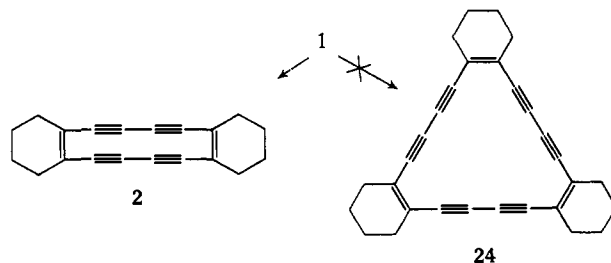
(21) No substance derived from 1,4 addition was identified. Although tlc analysis of the crude reaction mixture after acid hydrolysis indicated the presence of another product (with a similar R_f value to that of 15), this substance proved to be rather unstable and its structure was not elucidated.

(22) P. Schiess, H. L. Chia, and C. Suter [Tetrahedron Lett., 5747 (1968)] have independently synthesized 15 (mp 52–53°) by essentially the same method.

(23) G. Wittig and M. Schlosser, Chem. Ber., 94, 1373 (1961); G. Köbrich, H. Trapp, K. Flory, and W. Drischel, ibid., 99, 689 (1966).

(24) Separation between 18 and 20 was difficult, and it was found most convenient to isolate 20 after the mixture had been dehydrochlorinated in order to convert 18 to 1.

(25) D. Seyferth, W. B. Hughes, and J. K. Heeren, J. Amer. Chem. Soc., 87, 2847 (1965).

(26) (a) See (a) G. Eglinton and A. R. Galbraith, J. Chem. Soc., 889 (1959); (b) F. Sondheimer, Y. Amiel, and R. Wolovsky, J. Amer. Chem. Soc., 81, 4600 (1959).

or **2** rapidly decomposed on being exposed to air and light at room temperature, but a dilute ether solution proved to be relatively stable.

The structural assignment **2** was based on spectral and microanalytical data. Thus, the mass spectrum (70 eV) of **2** showed the expected molecular ion at m/e 256 (100%), with very few fragmentation peaks. The infrared spectrum (chloroform) exhibited maxima at 2175 (m) and 2100 (w) cm^{-1} due to the 1,3-diyne groupings, but no maximum at $\sim$3300 cm^{-1} due to a terminal acetylene. The nmr spectrum of **2** in deuterio-chloroform at $-20°$,[27] reproduced in Figure 1 (lower curve), consisted of a multiplet at τ 8.15–8.55 assigned to both the allylic and the nonallylic methylene protons.

The electronic spectrum of **2** in ether (Figure 2) showed main maxima at 234 (ϵ 23,200), 242 (23,600), and 247 sh nm (21,700), with lower intensity maxima extending into the visible region. As expected, the spectrum resembled that of the previously described 1,5,9-tridehydro[12]annulene **(25)** [main $\lambda_{max}^{isooctane}$ 238 (ϵ 36,200) and 247 nm (54,200)][28-30] and 1,5-bisdehydro-

25   **26**
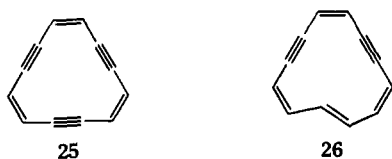
[12]annulene **(26)** [main $\lambda_{max}^{isooctane}$ 244 (ϵ 51,900) and 249 nm (54,800)].[28] The fact that the ϵ values of the main maxima of **2** are lower than those of **25** and **26** may be due to the larger number of acetylenes in **2**, and may perhaps also be a reflection of the strained nature of the 12-membered ring in this substance (see below).

The tetradehydro[12]annulene **2**, like the previously reported dibenz analog **27**,[4a,31] is presumably a highly strained compound. An X-ray crystallographic analysis of **27** has shown that it contains "bowed" 1,3-diacetylenic linkages,[32] and it is reasonable to assume that

27   **28**
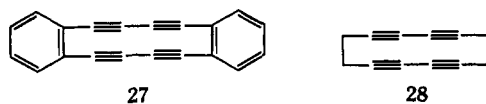
2 will possess a similar geometry. The fact that the infrared diyne bands in **2** ($\nu_{max}^{CHCl_3}$ 2175 and 2100 cm^{-1}), like those in **27** ($\nu_{max}^{CCl_4}$ 2187 and 2116 cm^{-1}),[4a] occur at shorter wavelengths and are of higher intensity than usual is presumably due to the same effect. Substance **2** does not possess the stabilizing fused benzene groups of **27**, and we find the comparative stability of **2** (e.g., the fact that it can be obtained as a crystalline solid) quite surprising. By comparison, 1,3,7,9-cyclododeca-tetrayne **(28)**, which presumably possesses a similar geometry, cannot be obtained in the neat state.[28]

The tetradehydro[12]annulene **2** contains $4n$ out-of-plane π electrons ($n = 3$). It is therefore expected

(27) The spectrum was determined at $-20°$, since appreciable decomposition occurred at room temperature.

(28) R. Wolovsky and F. Sondheimer, *J. Amer. Chem. Soc.*, **87**, 5720 (1965).

(29) F. Sondheimer, R. Wolovsky, P. J. Garratt, and I. C. Calder, *ibid.*, **88**, 2610 (1966).

(30) K. G. Untch and D. C. Wysocki, *ibid.*, **88**, 2608 (1966).

(31) O. M. Behr, G. Eglinton, I. A. Lardy, and R. A. Raphael, *J. Chem. Soc.*, 1151 (1964).

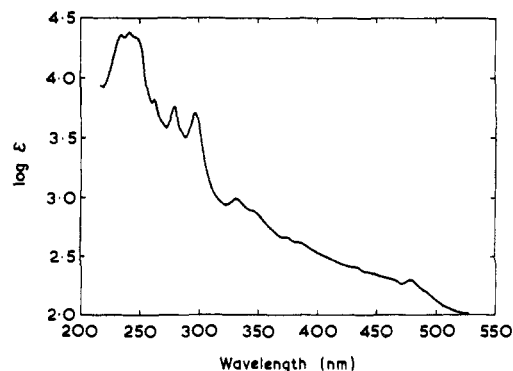(32) W. K. Grant and J. C. Speakman, *Proc. Chem. Soc.*, 231 (1959).

Figure 2. Electronic spectrum, in ether, of the tetradehydro[12]-annulene **2**.

to be nonaromatic and sustain an induced paramagnetic ring current in an applied magnetic field.[33] Unfortunately, the lack of protons bound directly to the macrocyclic ring of **2** made the determination of ring-current effects by nmr spectrometry less clear than in the other dehydroannulenes studied by us.[3] However, the fact that there is an upfield shift of τ 0.5–0.6 of the allylic methylene protons in **2** (τ 8.15–8.55) compared with those in the precursor **1** (τ 7.65–7.95; see Figure 1) is probably due to the existence of a paramagnetic ring current. By comparison, the diamagnetic ring current in the aromatic tetramethyltetradehydro[18]annulene **(29)**[34] causes the methyl proton nmr signals to be shifted downfield by $\sim\tau$ 0.6 from the normal position.

29
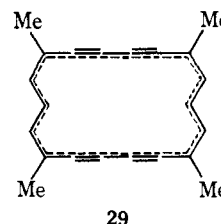
Hydrogenation of **2** in ethyl acetate and acetic acid over a platinum catalyst yielded $\sim$45% of the saturated tricyclic compound **30** as a liquid (presumably a mixture of stereoisomers), the mass spectrum of which showed it to possess the expected molecular weight (276). The hydrogenation also gave rise to $\sim$40% of another liquid substance (probably also a mixture of stereoisomers) which was assigned a pentacyclic benzenoid structure of type **31** on the basis of its spectral properties. The mass spectrum showed the molecular

**2** →   **30**   +   **31**

27 →   **32**   +   **33**
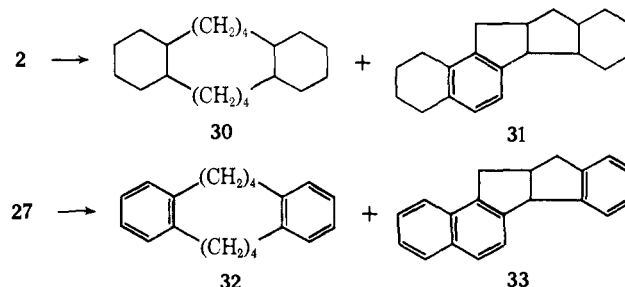
(33) See J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966); F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch. A*, **22**, 103 (1967); H. C. Longuet-Higgins, *Chem. Soc. Spec. Publ.*, No. 21, 109 (1967).

(34) J. Ojima, T. Katakami, G. Nakaminami, and M. Nakagawa, *Tetrahedron Lett.*, 1115 (1968).

weight to be 266, and the electronic and nmr spectra (see Experimental Section) were compatible with structure **31**. Although no definite confirmation of this formulation was obtained, it is a likely one in view of the finding of Behr, *et al.*,[4a] that catalytic hydrogenation of the dibenzotetradehydro[12]annulene **27** in tetrahydrofuran over a palladium/charcoal catalyst had given rise to 38% of the related pentacyclic compound **33** in addition to 50% of the normal tricyclic product **32**.

Partial hydrogenation of **2** in ethyl acetate over a 10% palladium/charcoal or a 10% palladium/strontium carbonate catalyst led to a number of substances. These were shown to be transannular reaction products by examination of their electronic, nmr, and mass spectra, but their exact structures were not elucidated. No evidence for the presence of the tetraalkylated [12]annulene among the reaction products was obtained, and this is not surprising in view of the instability of [12]annulene at room temperature which has now been demonstrated.[35]

It is of interest to compare the results obtained in the oxidative coupling of the four 1,5-diynes **34, 35, 1**, and **36** under Eglinton conditions. The nonfused diynes **34**[36] and **35**[6] give the respective cyclic trimers (and

34   **35**   **1**   **36**
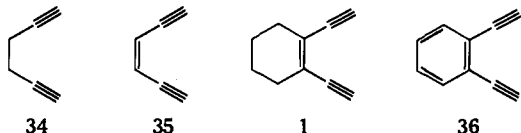
higher oligomers in the case of **34**) but no cyclic dimers, while the fused diynes **1** and **36**[4a] give the cyclic dimers in relatively high yield[37] but no cyclic trimers. The preferential formation of the highly strained cyclic dimers from **1** and **36** is surprising, since it is the corresponding cyclic trimers which should be strain-free systems. It is presumably the presence of the fused six-membered rings in **1** and **36** which accounts for the different results obtained in their coupling under Eglinton conditions as compared with **34** and **35**, but the exact reason for this difference is unknown.

The oxidative coupling of **1** with oxygen, cuprous chloride, and ammonium chloride (Glaser conditions) in aqueous ethanol and benzene[28] was also investigated. This reaction gave rise to six crystalline products (each containing at least two chlorine atoms[38]), which could be isolated by chromatography on alumina. The mass spectra showed these products, in order of elution, to have the following compositions: (a) $C_{20}H_{16}Cl_2$; (b) $C_{30}H_{24}Cl_6$; (c) $C_{20}H_{17}Cl_3$; (d) $C_{30}H_{24}Cl_2$; (e) $C_{30}H_{26}Cl_2$; (f) $C_{30}H_{26}Cl_2$. These spectra, as well as other spectra given in the Experimental Section, indicate the following partial structural assignments: (a) cyclic dimer + Cl_2; (b) cyclic trimer + Cl_6 (or linear trimer + Cl_4, both terminal acetylenes replaced by Cl); (c) linear dimer + Cl_2, one terminal acetylene replaced

by Cl; (d) cyclic trimer + Cl_2; (e) and (f) linear trimer + Cl_2. Only the linear products c (16.5% yield) and f (7.5% yield) were obtained in more than trace quantities, and the reaction was not investigated further. The result obtained in the coupling of **1** under Glaser conditions is in contrast to that obtained with the 1,5-diyne **34**, which had given rise to the corresponding cyclic dimer **28** in at least 10% yield.[28]

Experimental Section

General Procedures. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were measured on a Perkin-Elmer 257 or 21 spectrophotometer (s = strong, m = medium, w = weak); only significant maxima are reported. Electronic spectra were determined on a Cary 14M or a Unicam SP 800 spectrophotometer (sh = shoulder). Nmr spectra were measured on a Perkin-Elmer R-10 (60 MHz) or a Varian HA-100 (100 MHz) spectrometer, tetramethylsilane being used as an internal standard. Mass spectra were determined on an AEI MS-9 spectrometer operating at 70 eV. Glc was carried out on an F & M 720 instrument. Tlc was performed on Kieselgel G (Merck) plates; the solvents were pentane or pentane-ether mixtures, and the plates were developed by spraying with a 5% solution of phosphomolybdic acid in ethanol and then placing under an ultraviolet lamp for several minutes. A mixture (3:1) of silicic acid (Mallinckrodt, 100 mesh) and Hyflo Supercel (Johns-Manville) was used for column chromatography, unless stated otherwise.

trans- and *cis-***1,2-Diethynylcyclohexane-1,2-diol (4).**[13] Cyclohexane-1,2-dione[10] (**3**, 20 g, 0.178 mol) in dry toluene (50 ml) was allowed to react for 24 hr with sodium acetylide [from sodium (10 g, 0.44 g-atom)] in liquid ammonia ($\sim$500 ml), essentially as described by Ried and Schmidt.[12] Isolation as before[12] and distillation through a short-path apparatus yielded first 2-ethynyl-2-hydroxycyclohexanone (**5**, 0.60 g, 2.5%) as a colorless oil, bp 55–60° (0.75 mm); it solidified on standing and on recrystallization from pentane formed needles: mp 50.5–51.5° (lit. mp 51.5–52.5°,[10] 50–52°[39]); infrared spectrum (CHCl$_3$), bands at 3660 (w), 3440 (m) (OH), 3300 (s) ($\equiv$CH), 2105 (w) (RC$\equiv$CH), and 1724 cm^{-1} (s) (C$=$O); nmr spectrum (CCl$_4$), 1 H singlet at τ 5.98 (hydroxyl, disappears on addition of D$_2$O), 1 H singlet at 7.45 (acetylenic), and 8 H multiplet at 6.90–7.30, 7.55–7.80, and 7.80–8.55 (methylene); mass spectrum, peaks at m/e 138 (M, 18%), 112 (M − 26, 25%), and 94 (M − 44, 100%).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.25. Found: C, 69.96; H, 7.60.

Further distillation then gave a very viscous liquid, bp 80–90° (0.75 mm), which failed to crystallize on standing. It was mixed with an equal volume of benzene, and pyridine was added slowly, with scratching. The resulting crystalline *trans*-1,2-diethynylcyclohexane-1,2-diol (*trans*-**4**) on recrystallization from ether–pentane weighed 16.3 g (56%), and showed mp 80–81°;[15] infrared spectrum (CHCl$_3$), bands at 3570 (s) (OH), 3315 (s) ($\equiv$CH), and 2120 cm^{-1} (w) (RC$\equiv$CH); nmr spectrum (CDCl$_3$), 2 H singlet at τ 7.38 (hydroxyl, disappears on addition of D$_2$O), 2 H singlet at 7.40 (acetylenic), and 8 H multiplet at 7.85–8.20 and 8.20–8.55 (methylene); mass spectrum, peaks at m/e 164 (M, 0.5%), 138 (M − 26, 5.5%), and 112 (M − 52, 100%).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.23; H, 7.06.

The mother liquors after removal of *trans*-**4** were chromatographed on silicic acid–Supercel (500 g). Pentane–ether (9:1) eluted an oil (2.0 g) consisting mainly of 2-ethynyl-2-hydroxycyclohexanone (**5**). Elution with pentane–ether (4:1) and crystallization from pentane–ether then gave *cis*-1,2-diethynylcyclohexane-1,2-diol (*cis*-**4**, 2.4 g, 8%): mp 63–64°; infrared spectrum (CHCl$_3$), bands at 3550 (s) (OH), 3295 (s) ($\equiv$CH), and 2120 cm^{-1} (w) (RC$\equiv$CH); nmr spectrum (CDCl$_3$), 2 H singlet at τ 7.17 (hydroxyl, disappears on addition of D$_2$O), 2 H singlet at 7.43 (acetylenic), and 8 H multiplet at 7.85–8.20 and 8.20–8.55 (methylene); mass spectrum, peaks at m/e 164 (M, 0.5%), 138 (M − 26, 3%), and 112 (M − 52, 100%).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.10; H, 7.05.

Finally, elution of the column with pentane–ether (3:1) furnished

(35) J. F. M. Oth, H. Röttele, and G. Schröder, *Tetrahedron Lett.*, 61 (1970).

(36) F. Sondheimer and R. Wolovsky, *J. Amer. Chem. Soc.*, 84, 260 (1962).

(37) It is of interest to note that our conversion of **1** to the cyclic dimer **2** in $\sim$50% yield was effected without use of high dilution conditions, whereas such conditions were employed by Behr, *et al.*,[4a] for the oxidation of **36** to the cyclic dimer **27** in 43% yield.

(38) The formation of chloro compounds in the oxidation of terminal acetylenes under Glaser conditions has been observed before (*e.g.*, F. Sondheimer, Y. Amiel, and R. Wolovsky, *J. Amer. Chem. Soc.*, 79, 6263 (1957)).

(39) R. H. Jaeger and H. Smith, *J. Chem. Soc.*, 646 (1955).

a further amount (0.5 g, 1.7%) of *trans*-**4**. The total yield of *trans*- and *cis*-**4** was 19.2 g (66%).

1,2-Diethynylcyclohexene (1) from 1,2-Diethynylcyclohexane-1,2-diol (4). Diphosphorus tetraiodide (Koch-Light; 50 g, 88 mmol) was finely ground in a mortar, and extracted with dry carbon disulfide (2.5 l.) for 3 hr in a Soxhlet extractor. *trans*-1,2-Diethynylcyclohexane-1,2-diol (*trans*-**4**, 10 g, 61 mmol) in dry pyridine (BDH Chemicals, 500 ml) was added with stirring during 10 min. The solution immediately turned brown, and was then stirred at room temperature for 2 hr. The carbon disulfide was removed under reduced pressure, and the residue was extracted with ether. The ether extract was washed successively with 2 N sodium hydroxide solution, 12% sodium thiosulfate solution, 1.5 N sulfuric acid, water, saturated sodium bicarbonate solution, and saturated sodium chloride solution. The extract was dried (MgSO₄) and evaporated, and the resulting brown residue (1.8 g) was chromatographed on silicic acid-Supercel (200 g). Pentane eluted 1,2-diethynylcyclohexene (**1**, 1.48 g, 19%) as a colorless liquid: bp 52–53° (18 mm) (under nitrogen; extensive decomposition occurred during distillation), homogeneous on tlc; infrared spectrum (film), bands at 3310 (s) (≡CH), 2110 (m) (RC≡CH), and 1610 cm⁻¹ (w) (C=C); λ_{max} (95% EtOH) 249 sh (ϵ 10,200), 256 (12,400), 260 sh (11,100), and 269 nm (9700); nmr spectrum, see Discussion and Figure 1 (upper curve); mass spectrum, peaks at m/e 130 (M, 100%), 128 (M − 2, 44%), 115 (M − 15, 47%), and 102 (M − 28, 24%).

Anal. Calcd for C₁₀H₁₀: C, 92.30; H, 7.70. Found: C, 92.31; H, 8.01.

Substance **1** rapidly decomposed on exposure to air and light at room temperature, becoming red and viscous. Samples stored under nitrogen in the dark at −30° suffered only slight decomposition after several days, and ether solutions of **1** in the dark at 0° were also relatively stable.

Reduction of an isomeric mixture of **4** under exactly the same conditions led to **1** in 20% yield.

2-Ethynyl-1-cyclohexenecarboxaldehyde (15). Dry tetrahydrofuran (800 ml) was saturated with acetylene. Lithium acetylide-ethylenediamine[20] (75 g, 0.75 mol) was added, and the suspension was heated to 35°. A solution of 2-isopropoxymethylenecyclohexanone[19] (9, 126 g, 0.75 mol) in dry tetrahydrofuran (100 ml) was then added with stirring during 15 min, an internal temperature of 35° being maintained by ice cooling. The cooling bath was removed, and the mixture was stirred for 3 hr in an atmosphere of acetylene. Water (200 ml) was added slowly, and the mixture was boiled gently under reflux for 1 hr to remove all the acetylene. The mixture was cooled, the organic layer was separated, and the aqueous layer was extracted with ether (two 100-ml portions). The combined organic extracts were then stirred with 1.5 N sulfuric acid (2 l.) for 2 hr at room temperature. The organic layer was separated, and the aqueous layer was extracted thoroughly with ether. The combined organic extracts were washed with saturated sodium chloride solution, dried (MgSO₄), and evaporated under reduced pressure. Rapid distillation under nitrogen through a short-path apparatus gave a pale yellow liquid, bp 58–62° (0.4 mm), which immediately solidified. Crystallization from light petroleum (bp 40–60°) yielded 2-ethynyl-1-cyclohexenecarboxaldehyde (**15**, 38.8 g 39%)[22] as colorless crystals, mp 49.5–50°, having a characteristic odor: infrared spectrum (CCl₄), bands at 3320 (s) (≡CH), 2710 (w) (CHO), 2100 (w) (RC≡CH), 1675 (vs) (C=O), and 1605 cm⁻¹ (s) (C=C); λ_{max} (95% EtOH) 272 nm (ϵ 13,400); nmr spectrum (CCl₄), 1 H singlet at τ −0.17 (aldehydic), 1 H singlet at 6.58 (acetylenic), 4 H multiplet at 7.40–7.95 (allylic methylene), and 4 H multiplet at 8.10–8.45 (nonallylic methylene); mass spectrum, peaks at m/e 134 (M, 95%), 133 (M − 1, 63%), 105 (M − 29, 54%), and 91 (M − 43, 100%).

Anal. Calcd for C₉H₁₀O: C, 80.56; H, 7.51. Found: C, 80.30; H, 7.86.

Reaction of 2-Ethynyl-1-cyclohexenecarboxaldehyde (15) with Chloromethylenetriphenylphosphorane (17). Dry powdered (chloromethyl)triphenylphosphonium chloride[23] (16, 24.9 g, 71.5 mmol) was suspended in dry tetrahydrofuran (300 ml), and cooled to −70° in a Dry Ice-acetone bath. *n*-Butyllithium (Fluka, ~2 N hexane solution, 71.5 mmol) was added during 10 min under nitrogen, with stirring and continued cooling, and the cooled mixture was stirred for 30 min. A solution of 2-ethynyl-1-cyclohexenecarboxaldehyde (**15**, 9.6 g, 71.5 mmol) in dry ether (200 ml) was then added to the deep red ylide **17** during 10 min, the cooling bath was removed, and the mixture was stirred at room temperature under nitrogen for 4 hr. Water (200 ml) was added, the aqueous layer was washed well with ether, and the combined organic extracts were evaporated almost to dryness, and diluted with ether. The

solution was shaken with water and saturated sodium chloride solution, dried (MgSO₄), and evaporated to ~50 ml. The precipitated triphenylphosphine oxide was removed by filtration, the filtrate was preadsorbed on silicic acid, and chromatographed on silicic acid-Supercel (800 g). Elution with pentane gave 1-(β-chlorovinyl)-2-ethynylcyclohexene [**18**, trans–cis mixture (~2:1), 6.85 g, 57%], free of **20**, as an unstable colorless liquid with a pungent odor: infrared spectrum (CCl₄), bands at 3315 (s) (≡CH), 3080 (m) (=CH), 2090 (m) (RC≡CH), 1605 (w) (cis C=C), 1574 (m) (trans C=C), 942 (s) (trans C=C), and 702 cm⁻¹ (m) cis C=C); λ_{max} (95% EtOH) 265 sh (ϵ 19,600), 272 (21,200), and 283 sh nm (14,700); nmr spectrum (CCl₄), 2 H band consisting of two AB quartets (ratio ~2:1) at τ 3.00, 3.95 (J_{trans} = 14 Hz) (trans vinyl) and 3.30, 4.19 (J_{cis} = 8 Hz) (cis vinyl), 1 H band consisting of two singlets (ratio ~2:1) at 6.98 (trans acetylenic) and 7.00 (cis acetylenic), 4 H multiplet at 7.38–7.60 and 7.60–8.06 (allylic methylene), and 4 H multiplet at 8.30–8.55 (nonallylic methylene); mass spectrum, peaks at m/e 168, 166 (M, 19, 58%), 140, 138 (M − 28, 20, 59%), and 131 (M − Cl, 100%). The analytical sample of **18** was prepared by glc (2 ft × 0.25 in. column; Apiezon L, 85°), which showed peaks due to both isomers (ratio ~2:1, cis isomer eluted first); the resolution was too poor for separation to be effected preparatively, and the mixture was collected in a Dry Ice-acetone trap and immediately submitted to microanalysis. The colorless sample became a red viscous oil within seconds at room temperature, but could be kept for short periods at −70° under nitrogen in the dark, and was best stored in ether solution at 0°.

Anal. Calcd for C₁₀H₁₁Cl: C, 72.07; H, 6.65; Cl, 21.28. Found: C, 71.92; H, 6.60; Cl, 21.02.

Elution of the column with pentane-ether (99:1) yielded β-(2-ethynylcyclohexenyl)styrene [**19**, trans–cis mixture (~2:1), 0.35 g, 2.3%] as a colorless liquid: infrared spectrum (CCl₄), bands at 3315 (s) (≡CH), 2085 (m) (RC≡CH), 1600 (w) (cis C=C), 1585 (w) (trans C=C), 963 (s) (trans C=C), and 715 (w) (cis C=C); λ_{max} (95% EtOH) 234 (ϵ 14,000), 303 (20,500), 315 (21,400), and 328 sh nm (13,800); nmr spectrum (CCl₄), 2 H band consisting of two AB quartets (ratio ~2:1) at τ 3.51 (J_{trans} = 14.5 Hz) (trans vinyl) and 3.57 (J_{cis} = 7 Hz) (cis vinyl), the lower two doublets of each AB system being superimposed on a 5 H multiplet at τ 2.42–3.00 (aromatic), 1 H band consisting of two singlets (ratio ~2:1) at 6.84 (trans acetylenic) and 7.00 (cis acetylenic), 4 H multiplet at 7.56–7.90 (allylic methylene), and 4 H multiplet at 8.20–8.55 (nonallylic methylene); mass spectrum, peaks at m/e 208 (M, 100%), 180 (M − 28, 98%), and 165 (M − 43, 44%). Substance **19** slowly darkened on exposure to light and air at room temperature, but it could be kept with little change for several days at 0° under nitrogen in the dark, or for longer periods in ether solution at 0°.

Anal. Calcd for C₁₆H₁₆: C, 92.26; H, 7.74. Found: C, 92.40; H, 7.82.

In some experiments, the chloromethylene compound **18** was contaminated with *trans*- and *cis*-1-(1′-hexenyl)-2-ethynylcyclohexene (**20**). Isolation of **20** was best effected after the mixture had been dehydrochlorinated with sodamide in order to convert **18** to **1** (see next experiment). Chromatography on silicic acid-Supercel and elution with pentane gave firstly *trans*-**20** as a colorless fairly stable liquid, which was homogeneous on tlc: infrared spectrum (film), bands at 3315 (s) (≡CH), 3025 (m) (=CH), 2085 (m) (RC≡CH), 1585 (w) (trans C=C), and 967 cm⁻¹ (s) (trans C=C); λ_{max} (ether) 265 nm (ϵ 26,400); nmr spectrum (CCl₄), 2 H band (vinyl) consisting of an ABX₂ system at τ 3.03, 3.30 (doublet, J_{AB} = 16 Hz, 1 H) and 4.12, 4.40 (two triplets, J_{AB} = 16 Hz, J_{BX} = 7 Hz, 1 H), 1 H singlet at 6.92 (acetylenic), 4 H multiplet at 7.55–7.95 (ring allylic methylene), 10 H multiplet at 8.10–8.90 (other methylene), and 3 H triplet at 9.06 (J = 6.5 Hz) (methyl); mass spectrum, peaks at m/e 188 (M, 0.7%), 174 (M − 14, 7.5%), 159 (M − 29, 1%), 145 (M − 43, 13.5%), 132 (M − 56, 60%), 131 (M − 57, 42%), 117 (M − 71, 38%), 104 (M − 84, 100%), and 91 (M − 97, 84%).

Anal. Calcd for C₁₄H₂₀: C, 89.29; H, 10.71. Found: C, 89.37; H, 10.60.

Further elution of the column with pentane gave *cis*-**20** as a colorless fairly stable liquid, which was homogeneous on tlc: infrared spectrum (film), bands at 3315 (s) (≡CH), 3000 (m) (=CH), 2085 (m) (RC≡CH), 1620 (w) (cis C=C), and 702 cm⁻¹ (w) (cis C=C); λ_{max} (ether) 260 nm (ϵ 14,500); nmr spectrum (CCl₄), 2 H band (vinyl) consisting of an ABX₂ system at τ 3.64, 3.84 (doublet, J_{AB} = 12 Hz, 1 H) and 4.53, 4.73 (two triplets, J_{AB} = 12 Hz, J_{BX} = 7 Hz, 1 H), 1 H singlet at 7.04 (acetylenic), 6 H multiplet at 7.50–8.00 (allylic methylene), 8 H multiplet at 8.10–8.90 (non-

allylic methylene), and 3 H triplet at 9.07 ($J = 6.5$ Hz) (methyl); mass spectrum, peaks at m/e 188 (M, 13%), 174 (M $-$ 14, 59%), 159 (M $-$ 29, 100%), 145 (M $-$ 43, 91%), and 131 (M $-$ 57, 17%).

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.05; H, 10.74.

The ratio of the trans-cis isomers of **20** was ~3:1, and the total yield varied from 0 to 13% in different experiments.

In a typical preparative experiment to obtain **18**, **16** (85.8 g, 0.246 mol) in tetrahydrofuran (1 l.) was treated with *n*-butyllithium (0.246 mol) and then with **15** (33 g, 0.246 mol) in ether (660 ml), exactly as described above. Isolation and chromatography, as before, then gave a colorless liquid (23.5 g) consisting of *trans*- and *cis*-**18** contaminated with *trans*- and *cis*-**20** (1.1 g) (yield of **18**, 22.4 g, 55%). This mixture was used directly in the next step.

1,2-Diethynylcyclohexene (1) from 1-(β-Chlorovinyl)-2-ethynylcyclohexene (18). A. By Dehydrochlorination with Sodamide. The mixture of *trans*- and *cis*-**18** (22.4 g, 0.135 mol) and *trans*- and *cis*-**20** (1.1 g) from the previous experiment in dry ether (100 ml) was added during 10 min under nitrogen to a stirred suspension of sodamide [prepared from sodium (25.3 g, 1.1 g-atom) as described by Vaughn, *et al.*[40]] in liquid ammonia (~3 l.), cooled in a Dry Ice-acetone bath. The bath was removed, and the mixture was stirred for 3 hr in a slow stream of nitrogen. Ammonium chloride (100 g) and ether (500 ml) were added, and the ammonia was allowed to evaporate overnight. Water (300 ml) was added to the residue, followed by ether (500 ml). The ether layer was washed successively with water and saturated sodium chloride solution, and was then dried (MgSO₄). Evaporation gave a brown oil, which was preadsorbed on silicic acid, and chromatographed on silicic acid-Supercel (800 g). Pentane eluted first unchanged *trans*- and *cis*-**20** (1.1 g). Further elution with pentane then gave **1** (10.5 g, 60%) as a colorless liquid, the infrared, electronic, nmr, and mass spectra of which were identical with those of the substances prepared from **4**.

B. By Dehydrochlorination with Potassium *tert*-Butoxide. A solution of *trans*- and *cis*-**18** (1 g, 6.0 mmol, uncontaminated with **20**) in dry ether (50 ml) was added to freshly prepared potassium *tert*-butoxide (2.8 g, 25 mmol). The flask was flushed with nitrogen, tightly stoppered, and allowed to stand at room temperature with occasional shaking. After 2 days, starting material was still present (tlc), and the mixture was then heated gently under reflux for 12 hr in a very slow stream of nitrogen, the volume being maintained by periodic additions of ether. The mixture was cooled, diluted with ether (100 ml), and water (50 ml) was added. The ether layer was washed successively with dilute sulfuric acid, water, and saturated sodium chloride solution, and was then dried (MgSO₄). Evaporation of the solvent gave a yellow oil, which was chromatographed on silicic acid-Supercel (100 g). Pentane eluted unchanged **18** (460 mg, 46%), followed by **1** (360 mg, 46%). The last-mentioned substance showed spectral properties identical with those of the substance prepared from **4**.

Oxidative Coupling of 1,2-Diethynylcyclohexene (1) with Cupric Acetate in Pyridine. A solution of 1,2-diethynylcyclohexene (**1**, 1 g) in pyridine (technical, dried over calcium hydride and distilled from potassium hydroxide, 8 ml) was added to a suspension of finely ground neutral cupric acetate monohydrate (16 g) in pyridine (100 ml), previously heated to 55°. The mixture was stirred for 3 hr at a bath temperature of 55°, cooled, and filtered, and the solid was washed well with warm benzene. The combined organic extracts were washed successively with water, dilute hydrochloric acid, water, and saturated sodium chloride solution. The solution was dried (MgSO₄), and concentrated to ~20 ml by evaporation under reduced pressure on a rotary evaporator (bath temperature ~20°). The insoluble polymeric material was removed by filtration, and the red filtrate was chromatographed on alumina (Spence H, 200 g). Pentane eluted the tetradehydro[12]annulene **2** (510 mg, 52%, estimated from the electronic spectrum), which crystallized from pentane at $-70°$ to give unstable orange-red needles, which became black at ~100° on attempted melting point determination: infrared spectrum (CHCl₃), bands at 2950 (s), 2885 (m), 2870 (m), 2840 (m), 2175 (m), 2100 (w), 1537 (m), 1454 (m), 1437 (m), 1355 (w), 1302 (w), 1150 (w), and 1125 cm⁻¹ (w); λ_{max} (ether) 234 (ϵ 23,200), 242 (23,600), 247 sh (21,650), 262 (6660), 268 sh (4200), 279 (5770), 285 (3570), 296 (5040), 330 (990), 349 sh (760), 373 (460), 382 (425), 408 sh (315), 433 (250), 445 sh (230), 479 (200), 491 sh (160), and 525 sh nm (100) (see Figure 2); nmr spectrum,

see Discussion and Figure 1 (lower curve); mass spectrum, see Discussion.

Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.33; H, 6.53 (analysis performed as rapidly as possible after crystallization).

Substance **2** was soluble in ether, benzene, chloroform, carbon tetrachloride, and ethyl acetate, moderately soluble in pentane, and insoluble in ethanol. The crystals rapidly decomposed on standing in light and air at room temperature (after standing for 24 hr, a sample had become black and no longer dissolved in ether), but could be stored for several days with little deterioration at $-30°$ in the dark under nitrogen. Pentane or carbon tetrachloride solutions of **2** on standing in the dark at 0° gradually deposited a yellow polymeric material. The compound was usually stored in dilute ether or ethyl acetate solution in the dark at 0°.

Further elution of the column with pentane and ether-pentane mixtures gave no appreciable amounts of any other products.

Catalytic Hydrogenation of the Tetradehydro[12]annulene 2. A solution of **2** (10 mg) in ethyl acetate (5 ml) was added to platinum (from 100 mg of platinic oxide) in glacial acetic acid (50 ml), and the mixture was stirred under hydrogen for 2.5 hr. The catalyst was removed by filtration, and the filtrate was diluted with ether. The solution was washed successively with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution, and was then dried (MgSO₄) and evaporated. The resulting pale yellow oil, which showed two main spots on tlc, was chromatographed on silicic acid-Supercel (100 g). Pentane eluted first the tricyclic hydrocarbon **30** (4.9 mg, 45%), presumably a mixture of stereoisomers, as a colorless liquid; electronic spectrum, end absorption only; mass spectrum, molecular ion peak at m/e 276. Pentane then eluted another colorless liquid (4.1 mg, 39%), assigned a pentacyclic structure of type **31**: λ_{max} (pentane) 264 sh (ϵ 1150), 271 (1320), 277 sh (1060), and 287 nm (690); nmr spectrum (CCl₄), 2 H multiplet at 3.00–3.40 (aromatic), 1 H multiplet at 6.20–6.60, and ~6 H multiplet at 7.00–7.70 (benzylic), ~3 H multiplet at 7.75–8.00 (methine), and ~14 H multiplet at 8.10–8.80 (methylene); mass spectrum, peaks at m/e 266 (M, 100%) and 223 (M $-$ 43, 40%).

Oxidative Coupling of 1,2-Diethynylcyclohexene (1) with Oxygen, Cuprous Chloride, and Ammonium Chloride. A solution of **1** (1.52 g) in ethanol (25 ml) was added to a mixture of cuprous chloride (40 g), ammonium chloride (64 g), water (170 ml), and concentrated hydrochloric acid (0.4 ml). The stirred mixture was placed in a water bath at 60°, and after 5 min more ethanol (25 ml) and benzene (100 ml) were added. A vigorous stream of oxygen was then bubbled for 1.5 hr into the well-stirred mixture at 60°, the volume being maintained by periodic additions of benzene. The cooled mixture was diluted with ether, and the organic layer was washed successively with dilute hydrochloric acid and water. The resulting brown solution was dried (MgSO₄), evaporated almost to dryness under reduced pressure on a rotary evaporator (bath temperature ~20°), and chromatographed on neutral alumina (Woelm, activity IV, 300 g). Pentane-ether (99:1) eluted an orange oil (~50 mg), which was a mixture of two compounds (tlc examination). On standing at 0°, this mixture partially crystallized, and each component could be obtained by fractional crystallization from pentane-ether. The major component, a cyclic dimeric dichloride, formed orange-red prisms: λ_{max} (ether) 266 (relative optical density 1.28) and 276 nm (1.86); mass spectrum, molecular ion peaks at m/e 330 (11.5%), 328 (61%), and 326 (100%) (calcd for $C_{20}H_{16}Cl_2$: m/e 330–326). The minor component, a cyclic or linear trimeric hexachloride, formed pale yellow needles: mass spectrum, molecular ion peaks at m/e 606 (0.2%), 604 (1.7%), 602 (10%), 600 (37%), 598 (82%), 596 (100%), and 594 (52%) (calcd for $C_{30}H_{24}Cl_6$: m/e 606–594).

Elution of the column with pentane-ether (99:1) and crystallization from pentane-ether gave a linear dimeric trichloro compound (350 mg, 16.5%) as stable colorless prisms: mp 121.5–122° dec; infrared spectrum (KBr), bands at 3300 (s) ($\equiv$CH), 2185 (w) (RC$\equiv$CR'), 2090 (w) (RC$\equiv$CH), and 742 cm⁻¹ (s) (C–Cl); λ_{max} (ether) 234 (ϵ 20,400), 248 sh (16,150), 262 (6600), 298 (18,800), 310 (27,550), 317 sh (24,000), and 331 nm (28,950); nmr spectrum (CCl₄), 1 H singlet at τ 6.94 (acetylenic), 4 H multiplet at 7.00–7.40 and 4 H multiplet at 7.50–7.85 (allylic methylene), and 8 H multiplet at 8.05–8.45 (nonallylic methylene); mass spectrum, molecular ion peaks at m/e 368 (4.5%), 336 (34%), 364 (99%), and 362 (100%) (calcd for $C_{20}H_{17}Cl_3$: m/e 368–362).

Anal. Calcd for $C_{20}H_{17}Cl_3$: C, 66.03; H, 4.68; Cl, 29.29. Found: C, 66.33; H, 4.93; Cl, 29.00.

Elution with pentane-ether (49:1) and crystallization from

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(40) T. H. Vaughn, R. R. Vogt, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **56**, 2120 (1934).

pentane–ether yielded a cyclic trimeric dichloro compound (25 mg) as fairly stable pale yellow prisms, which decomposed at ~225–230° on attempted melting point determination: infrared spectrum (KBr), bands at 2185 (w), 2120 (w) (RC≡CR'), and 1555 cm⁻¹ (w) (C=C); λmax (ether) 248 (ε 9550), 298 sh (47,500), 303 (56,000), 317 (94,300), 337 sh (10,300), 344 (9500), 361 (7200), 372 (6850), 389 (5700), 415 sh (800), and 440 nm (485); nmr spectrum (CDCl₃), 2 H multiplet at τ 6.80–7.00, 6 H multiplet at 7.00–7.25, and 4 H multiplet at 7.30–7.55 (allylic methylene), and 12 H multiplet at 8.00–8.35 (nonallylic methylene); mass spectrum, molecular ion peaks at m/e 458 (10.5%), 456 (65%), and 454 (100%) (calcd for C₃₀H₂₄Cl₂: m/e 458–454).

Further elution with pentane–ether (49:1) gave a mixture of two isomeric linear trimeric dichloro compounds, which were separated by rechromatography on alumina (Woelm, activity IV). The first isomer to be eluted (50 mg, 3.1%) crystallized from ether–pentane as rather unstable yellow crystals, which showed a blue fluorescence in solution, and became black at ~120–130° on attempted melting point determination: infrared spectrum (KBr), bands at 3305 (m), 3285 (m) (≡CH), 2185 (w) (RC≡CR'), and 2085 cm⁻¹ (w)

(RC≡CH); λmax (ether) 271 (ε 17,900), 300 (32,600), 315 (25,900), 330 (24,200), and 385 sh nm (815); mass spectrum, molecular ion peaks at m/e 460 (26.5%), 458 (77.5%), and 456 (100%) (calcd for C₃₀H₂₆Cl₂: m/e 460–456). The second isomer to be eluted (120 mg, 7.5%) crystallized from ether–pentane as yellow needles, which also showed a blue fluorescence in solution, and became black at ~150–160° on attempted melting point determination: infrared spectrum (KBr), bands at 3300 (m), 3280 (m) (≡CH), 2185 (w) (RC≡CR'), and 2085 cm⁻¹ (w) (RC≡CH); λmax (ether) 242 sh (ε 23,500), 271 (18,700), 290 sh (25,400), 300 (33,700), 325 sh (21,850), and 335 nm (23,300); mass spectrum, molecular ion peaks at m/e 460 (25.5%), 458 (77.5%), and 456 (100%) (calcd for C₃₀-H₂₆Cl₂: m/e 460–456).

The Synthesis and Reactions of 4,5:10,11-Bis(tetramethylene)-4,10-cyclotridecadiene-2,6,8,12-tetrayn-1-one, a Derivative of [13]Annulenone[1]

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Abstract: 1,2-Diethynylcyclohexene (**12**) has been converted to 1,5-di(2'-ethynylcyclohexenyl)-1,4-pentadiyn-3-ol (**13**) by reaction of the mono-Grignard derivative with ethyl formate. Oxidative coupling of **13** gave the corresponding cyclic "monomer" **14**, which was oxidized to 4,5:10,11-bis(tetramethylene)-4,10-cyclotridecadiene-2,6,8,12-tetrayn-1-one (**15**). Alternatively, **13** was oxidized to the corresponding ketone **17**, which was coupled to give **15**. The ketone **15** is a tetraalkylated tetradehydro[13]annulenone, and is the first derivative of a macrocyclic annulenone (fully unsaturated monocarbocyclic ketone) to be reported. Some evidence for the nonaromatic nature of **15** could be obtained from the nmr spectrum, which gave an indication of a paramagnetic ring current. Some reactions of **15** have been investigated. Of most interest is its condensation with cyclopentadiene to give 1-cyclopentadienylidene-4,5,10,11-bis(tetramethylene)-4,10-cyclotridecadiene-2,6,8,12-tetrayne (**33**), a derivative of pentatridecafulvalene (**32**).

Fully conjugated monocarbocyclic ketones are an interesting class of compounds, for which we have proposed the generic name "annulenones."[3] Related ketones in which one or more of the ethylenic bonds have been replaced by an acetylenic linkage are named dehydroannulenones. If the carbonyl group is polarized in the usual way, an annulenone or dehydroannulenone containing a (4n + 3)-membered ring should represent a (4n + 2) π-electron system and be aromatic. Well-known examples are cyclopropenone (**1**) (n = 0)[4] and tropone (**2**) (n = 1).[5,6] Conversely,

1   2
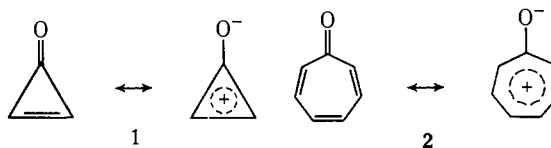
such compounds containing a (4n + 1)-membered ring should represent a 4n π-electron system and be non-aromatic.[7] An example is cyclopentadienone (**3**) (n = 1),[8] which is unstable and readily undergoes self-condensation. Moreover, the relatively high-field positions of the ring-proton resonances in the nmr spectrum of 2,4-di-*tert*-butylcyclopentadienone (**4**)[9] may

(1) Unsaturated Macrocyclic Compounds. LXXIV. [For part LXXIII, see G. M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.*, **93**, 1970 (1971).] Taken from the Ph.D. Dissertation of G. M. Pilling, Cambridge University, Aug 1968.

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(3) G. M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 5610 (1968).

(4) See R. Breslow, G. Ryan, and J. T. Groves, *ibid.*, **92**, 988 (1970), and references cited there.

(5) *Inter al.*, see A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 279; L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1963, p 383; D. Lloyd, "Carbocyclic

Non-benzenoid Aromatic Compounds," Elsevier, Amsterdam, 1966, Chapter VI; G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, London, 1969, p 85.

(6) The aromatic nature of tropone has been questioned recently: D. Bertelli and T. G. Andrews, *J. Amer. Chem. Soc.*, **91**, 5280 (1969); D. Bertelli, T. G. Andrews, and P. O. Crews, *ibid.*, **91**, 5286 (1969).

(7) See F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, *Chem. Soc., Spec. Publ.*, No. 21, 75 (1967).

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(9) E. W. Garbisch and R. F. Sprecher, *J. Amer. Chem. Soc.*, **88**, 3433 3434 (1966); **91**, 6785 (1969).