

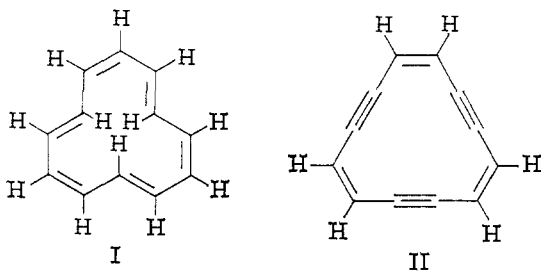
Unsaturated Macrocyclic Compounds. XXXVI.¹ The Synthesis of Two Isomers of Bisdehydro[12]annulene and Biphenylene from 1,5-Hexadiyne²

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The oxidative coupling of 1,5-hexadiyne (III) with oxygen, cuprous chloride, and ammonium chloride, in a solvent system consisting of water, ethanol, and benzene, gave rise to the very unstable cyclic dimer IV besides other substances. Rearrangement of IV with potassium *t*-butoxide yielded biphenylene (VIII), as well as two isomers of bisdehydro[12]annulene (cyclododecatetraenediyne). The 1,5-diyne structure IX is assigned to isomer A, and the 1,7-diyne structure X to isomer B. The nuclear magnetic resonance spectra of the two isomers show no indication of the existence of a ring current. This observation is in agreement with theory, since Hückel's rule is not obeyed and the substances are therefore not expected to be aromatic. The partial hydrogenation of both isomers of bisdehydro[12]annulene to [12]annulene (e.g., I) was studied. It is possible that [12]annulene was obtained, but this was not established unequivocally.

Fully conjugated 12-membered monocyclic systems such as [12]annulene (e.g., I) and related acetylenic analogs (dehydro[12]annulenes, e.g., II) are of considerable theoretical interest. These substances are not expected to be aromatic, since they do not obey Hückel's rule (presence of $(4n + 2)$ out-of-plane π -



electrons).⁴ Moreover, [12]annulene itself presumably cannot exist in a planar configuration, in view of the steric interactions of the internal hydrogen atoms,^{2b,5} although this does not apply to some of the dehydro[12]annulenes.

(1) The paper by Y. Gaoni, A. Melera, F. Sondheimer, and R. Wolovsky, *Proc. Chem. Soc.*, 397, (1964), is considered to be part XXXV of this series, and that by Y. Gaoni and F. Sondheimer, *ibid.*, 299 (1964), to be part XXXIV. For part XXXIII, see F. Sondheimer and A. Shani, *J. Am. Chem. Soc.*, 86, 3168 (1964).

(2) (a) For a preliminary communication, see R. Wolovsky and F. Sondheimer, *ibid.*, 84, 2844 (1962); (b) reviewed in a Congress Lecture presented at the XIXth International Congress of Pure and Applied Chemistry, London, July 1963; see F. Sondheimer, *Pure Appl. Chem.*, 7, 363 (1963).

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

(5) See K. Mislow, *J. Chem. Phys.*, 20, 1489 (1952).

Substances have been reported in the literature for which the [12]annulene structure was tentatively suggested,⁶ but no confirmation for this assignment has been provided subsequently. Theoretical speculations regarding tridehydro[12]annulene (II) have been published,⁷ although this compound was not synthesized. It thus appears that no 12-membered conjugated monocyclic system of the type under discussion has been prepared until now.⁸

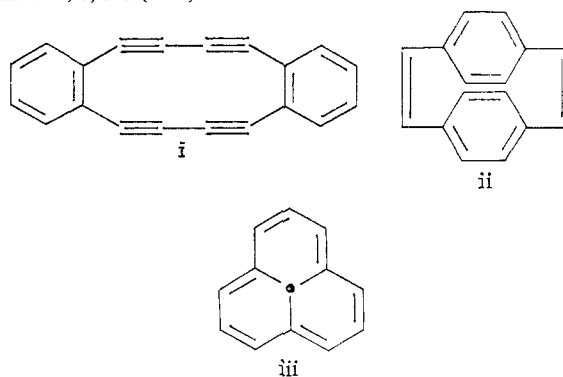
A possible approach to dehydro[12]annulenes appeared to involve the oxidative coupling of 1,5-hexadiyne (III) to the cyclic dimer IV, followed by prototropic rearrangement. Similar rearrangements have already been carried out successfully with higher cyclic oligomers of 1,5-hexadiyne.⁹ This scheme could be realized in practice, as already reported in preliminary form.² We now describe our work in detail.

Previous attempts by us to prepare the cyclic dimer IV from 1,5-hexadiyne (III) had not met with success. Oxidation of III with cupric acetate in pyridine had given the cyclic trimer and higher cyclic compounds, but no IV.⁹ Coupling with oxygen in the presence of cuprous chloride and ammonium chloride in aqueous ethanol (Glaser conditions) had yielded an unusually large amount of brown, insoluble, polymeric material in addition to linear products.¹⁰ By contrast, higher

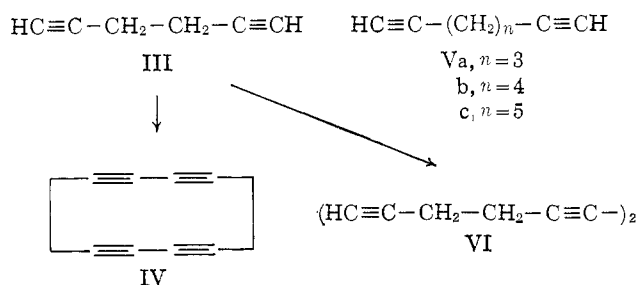
(6) (a) Work of W. Reppe, *et al.*, summarized in ref. 1-4 in A. C. Cope and S. W. Fenton, *J. Am. Chem. Soc.*, 73, 1195 (1951); (b) G. Wilke, *Angew. Chem.*, 69, 397 (1957).

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

(8) On the other hand, several analogs incorporating fused benzene rings are known, *viz.* two tetrabenzo[12]annulenes (G. Wittig, G. Koenig, and K. Clauss, *Ann.*, 593, 127 (1955)), hexabenzo[12]annulene (hexaphenylene) (G. Wittig and G. Lehmann, *Ber.*, 90, 875 (1957)), and the dibenzotetrahydro[12]annulene (i) (O. M. Behr, G. Eglinton, A. R. Galbraith, and R. A. Raphael, *J. Chem. Soc.*, 3614 (1960)). The [2,2]-paracyclopentane diolefin (ii) may also be considered to belong to the [12]-annulene series: K. C. Dewhirst and D. J. Cram, *J. Am. Chem. Soc.*, 80, 3115 (1958). Moreover, the relatively stable perinaphthyl radical (iii) and related compounds presumably possess tricyclic structures derived from [12]annulene: see P. B. Sogo, M. Nakazaki, and M. Calvin, *J. Chem. Phys.*, 26, 1343 (1957); E. Clar, W. Kemp, and D. G. Stewart, *Tetrahedron*, 3, 325 (1958).



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



homologs of 1,5-hexadiyne (1,6-heptadiyne (Va),¹⁰ 1,7-octadiyne (Vb),¹¹ and 1,8-nonadiyne (Vc)¹⁰) had given rise to the corresponding cyclic dimers by use of the Glaser conditions, the yield decreasing as the length of the polymethylene chain increased.

We suspected that the insoluble polymer obtained by Glaser coupling of 1,5-hexadiyne was due to the fact that the cyclic dimer IV had actually been formed, but was not soluble in the aqueous ethanol and had decomposed. Inspection of models shows the dimer IV to be a highly strained compound, containing "bowed" 1,3-diyne rods, and therefore presumably quite unstable.¹² The Glaser coupling of 1,5-hexadiyne therefore was reinvestigated under the conditions used by us previously,¹⁰ but in the presence additionally of a large amount of benzene, in order to keep the products in solution and thus prevent the decomposition of IV. It is possible that the addition of benzene also might be beneficial in increasing the yield of IV, in view of the higher dilution conditions employed.¹³ Use of this technique indeed led to the desired cyclic dimer IV.

Careful chromatography of the reaction product on alumina yielded first the two chloro compounds obtained previously.¹⁰ Then fractions containing the cyclic dimer IV admixed with linear dimeric material (see below) were obtained, as evidenced by the fact that full hydrogenation of representatives led to a mixture of cyclododecane and *n*-dodecane. However, it was not found possible to obtain IV completely free from linear products, even after rechromatography or silver nitrate treatment.

The cyclic dimer IV proved to be a very unstable substance, which could be handled only in solution. It was converted to an insoluble brown-black polymer as soon as its solution was taken to dryness, even when all possible precautions were taken. In fact, this behavior could be used in order to determine which chromatography fractions contained IV (see the Experimental Section). This instability of IV made an exact estimate of yield impossible, but the yield must be at least 9.5% in view of the results of the isomerization experiments described below.¹⁴

(10) F. Sondheimer, Y. Amiel, and R. Wolovsky, *J. Am. Chem. Soc.*, **79**, 6263 (1957).

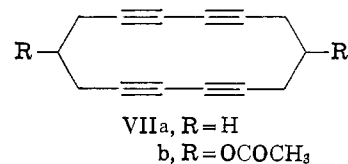
(11) F. Sondheimer and Y. Amiel, *ibid.*, **79**, 5817 (1957).

(12) The 1,3,7,9-cyclododecatetraene ring system (IV) is contained in the cyclic dimer (i) of *o*-diethynynylbenzene (O. M. Behr, *et al.*). Substance i, which has been shown to contain "bowed" 1,3-diyne units (W. K. Grant and J. C. Speakman, *Proc. Chem. Soc.*, 231 (1959)) proved to be a comparatively unstable compound, although the presence of the two fused benzene rings would be expected to increase the stability compared with IV.

(13) It has been shown that when the couplings are carried out with cupric acetate in pyridine, the use of high dilution conditions favor the formation of lower as against higher cyclic oligomers: I. D. Campbell and G. Eglinton, *J. Chem. Soc.*, 1158 (1964); unpublished observations with 1,5-hexadiyne from our laboratory.

(14) The estimate of 5–6% given in the preliminary communication^{2a} is definitely too low.

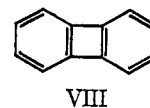
The above-mentioned linear dimeric material accompanying IV proved to be mainly the expected unrearranged linear dimer VI.¹⁰ However, ultraviolet examination revealed the additional presence of smaller amounts of rearrangement products of this dimer, containing five as well as six¹⁵ conjugated multiple bonds (see the Experimental Section for details). These linear impurities made it difficult to obtain accurate ultraviolet data for IV. However, the ultraviolet spectra of the fractions rich in IV, as well as of a sample purified through silver nitrate treatment, indicated that maxima at *ca.* 236, 247, and 263 $m\mu$ (in pentane–ether) were due to this cyclic dimer. By comparison, normal disubstituted 1,3-diyne show ultraviolet maxima at *ca.* 227, 240, and 253 $m\mu$.^{10,11,16} This type of bathochromic shift has already been observed to occur in the cyclic dimer VIIa of 1,6-heptadiyne ($\lambda_{\text{max}}^{\text{isooctane}}$ 226, 238, 246 (infl.), and 263 $m\mu$),¹⁰ as well as in the corresponding 6,13-diacetoxy com-



pound VIIb ($\lambda_{\text{max}}^{\text{MeOH}}$ 225, 237, 247, and 262 $m\mu$).¹⁷ These unusual spectra are presumably due to the proximity of the 1,3-diyne functions, resulting in electronic interaction, although the bending of these chromophores may also be a contributing factor.¹⁸

In view of the instability of the cyclic dimer IV, the chromatography fractions containing this substance (in pentane–ether) were subjected directly to rearrangement by means of a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol. The best experimental conditions were found to involve reaction at room temperature for *ca.* 20 min. These conditions are considerably milder than those found necessary to effect the analogous isomerization of the higher cyclic oligomers of 1,5-hexadiyne with this base,⁹ and this relative ease of rearrangement of IV is presumably a consequence of the strain in the molecule. The resulting material then was chromatographed on alumina, whereby three cyclic compounds were obtained (in addition to linear conjugated substances,¹⁵ derived from the linear dimeric impurities present prior to rearrangement).

The first cyclic compound (m.p. 110–111°) to be eluted formed straw-colored crystals. This substance proved to be biphenylene (VIII), as evidenced by direct comparison with an authentic sample. The over-all



yield from 1,5-hexadiyne was *ca.* 7.4%. Biphenylene

(15) For the base isomerization of the linear dimer VI to a mixture of *n*-dodecatetraenediynes, see F. Sondheimer, D. A. Ben-Efraim, and R. Wolovsky, *J. Am. Chem. Soc.*, **83**, 1682 (1961).

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

(17) F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **81**, 6301 (1959).

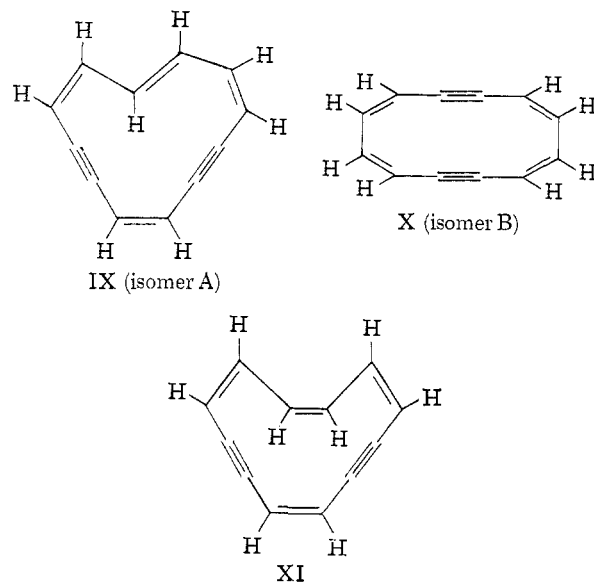
(18) See D. J. Cram and H. Steinberg, *ibid.*, **73**, 5691 (1951); D. J. Cram, N. L. Allinger, and H. Steinberg, *ibid.*, **76**, 6132 (1954).

has been prepared previously by a number of different routes,¹⁹ but this appears to be the first synthesis from a nonbenzenoid precursor. The formation of biphenylene by base treatment of the cyclic dimer (IV) of 1,5-hexadiyne is analogous to the formation of triphenylene (though only as a by-product) from the corresponding cyclic trimer.^{9,20} Other examples of base-catalyzed transformations of polyacetylenes to benzenoid substances have been reported recently.²¹

The next cyclic compound (m.p. 54–55° dec.) was obtained as brown needles, pink-violet in solution. This substance, formed in *ca.* 1.5% over-all yield, was clearly a bisdehydro[12]annulene (isomer A). This follows from the elemental composition, the infrared spectrum (Figure 1) which showed the presence of an acetylene band at 4.60 μ (but no allene bands), and the fact that full hydrogenation in ethyl acetate over a platinum catalyst gave rise to cyclododecane in over 90% yield (small amounts of two unidentified hydrocarbons, presumably formed by a transannular reaction, were also obtained). The ultraviolet spectrum (in isooctane), reproduced in Figure 2, exhibited high-intensity maxima at 244 m μ (ϵ 51,900) and 249 m μ (ϵ 54,800), a low-intensity maximum at 465 m μ (ϵ 183), and absorption above 600 m μ . This substance proved to be very unstable in the solid state, the crystals being almost completely destroyed after being allowed to stand for 1 hr. at room temperature.

The three structures IX, X, and XI can reasonably be considered for a bisdehydro[12]annulene. In our preliminary communication^{2a} we had favored the 1,7-diyne formulation X for the above-described isomer. However, the nuclear magnetic resonance (n.m.r.) spectrum has now been determined (Figure 3). This clearly shows isomer A in fact to possess the 1,5-diyne structure IX, containing three *cis* and one *trans* double bonds in addition to the two acetylenes, the *trans* double bond being perpendicular to the plane of the rest of the ring. This nonplanarity causes the protons marked H¹, H², H³, and H⁴ (see Figure 3) on one side of the molecule to be equivalent to the corresponding H^{1'}, H^{2'}, H^{3'}, and H^{4'} protons on the other side.²²

The H⁴ and H^{4'} protons give rise to a two-proton signal at τ 5.47 (see Figure 3), which has fine structure due to interaction of H⁴ with H³ and H^{3'} (and conversely of H^{4'} with H^{3'} and H³; the same converse relationships of course exist for the couplings described below, but are not specifically mentioned). The H³ and H^{3'} protons produce a two-proton doublet ($J_{3,2} \approx 10.5$ c.p.s.) centered at τ 5.82; additional fine structure arises through interaction of H³ with H⁴ and H^{4'}. The two-proton octet centered at τ 4.97 is assigned to H² and H^{2'} ($J_{2,3} \approx 10.5$ c.p.s., $J_{2,1} \approx 5$ c.p.s.,²³ $J_{2,1'}$



≈ 2.5 c.p.s.). Finally, the two-proton quartet centered at τ -0.90 is assigned to H¹ and H^{1'} ($J_{1,2} \approx 5$ c.p.s., $J_{1,2'} \approx 2.5$ c.p.s.).

The structure IX assigned to bisdehydro[12]annulene (isomer A) is supported by the presence in the infrared spectrum (Figure 1) of a strong band at 10.23 μ , indicative of a conjugated *trans* double bond.²⁵

The third cyclic compound (m.p. 96° dec.) obtained from the chromatogram proved to be a second isomer of bisdehydro[12]annulene (isomer B).²⁶ This substance, obtained in *ca.* 0.65% over-all yield, crystallized as brick-red needles, pink in dilute solution. Full hydrogenation in ethyl acetate over platinum again gave cyclododecane in over 90% yield (in addition, small amounts of the two unidentified hydrocarbons previously obtained as by-products in the hydrogenation of isomer A, were apparently formed). The infrared spectrum (Figure 1) once more showed an acetylene band at 4.60 μ , but was considerably simpler than that of isomer A. In particular, it showed no bands in the 10.0–10.5- μ region, consistent with a formulation lacking the *trans* double bond of isomer A. The ultraviolet spectrum of isomer B (Figure 2) resembled that of isomer A, exhibiting main maxima at 238 m μ (ϵ 36,200) and 247 m μ (ϵ 54,200); however, considerably more fine structure in the higher wave length region was apparent. Isomer B was found to be much more stable in the solid state than isomer A, and could be kept with little change for several hours at room temperature.

The n.m.r. spectrum of bisdehydro[12]annulene (isomer B) is reproduced in Figure 4. Only one band at τ 5.58 is present, which is assigned to all eight protons of the molecule.²⁷ Of the two formulations X and XI (each containing four *cis* double bonds in addition to the two acetylenes) which can be considered for this isomer, the 1,7-diyne structure X possesses two different types of protons, while the 1,5-diyne structure

Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *J. Am. Chem. Soc.*, **84**, 4307 (1962).

(25) Among others see J. L. H. Allan, G. D. Meakins, and M. C. Whiting, *J. Chem. Soc.*, 1874 (1955).

(26) This isomer was not detected in early small-scale experiments, and was not reported in the preliminary communication.^{2a}

(27) The n.m.r. spectrum taken at -60° was found to be essentially identical with that determined at room temperature (see part XXXV of this series¹).

(19) For a review, see W. Baker and J. F. W. McOmie in "Nonbenzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p. 65 ff.

(20) Y. Amiel and F. Sondheimer, *Chem. Ind. (London)*, 1161 (1960), (21) G. Eglinton, R. A. Raphael, R. G. Willis, and J. A. Zabkiewicz, *J. Chem. Soc.*, 2597 (1964), and references cited there.

(22) For a photograph of a molecular model, see Figure 31 in footnote 2b.

(23) The fact that $J_{2,1}$ is lower than the value of *ca.* 12 c.p.s. found for the coupling constant of protons attached to a planar *s-trans* system (10.7 c.p.s. in dimethyl *cis, trans*-muconate, 12.2 c.p.s. in tridehydro[18]annulene)²⁴ is consistent with the nonplanar conformation assigned to substance IX.

(24) See L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim,

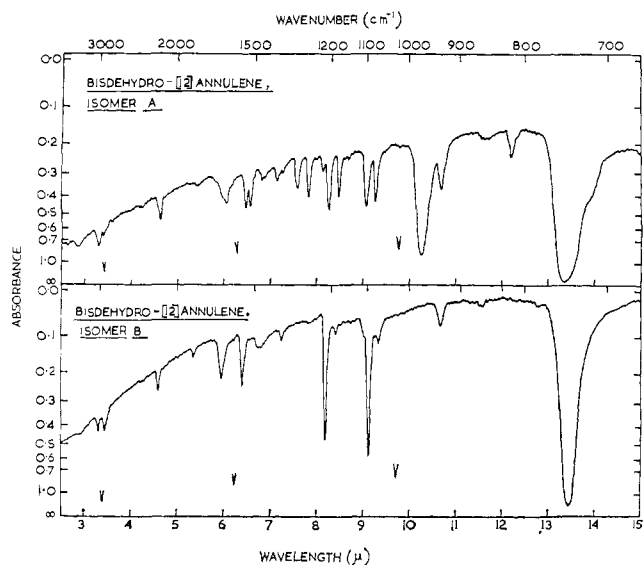


Figure 1. Infrared absorption spectra of bisdehydro[12]annulene, isomer A (IX) and isomer B (X), determined as KBr pellets with a Perkin-Elmer Infracord recording spectrophotometer (calibrated with polystyrene).

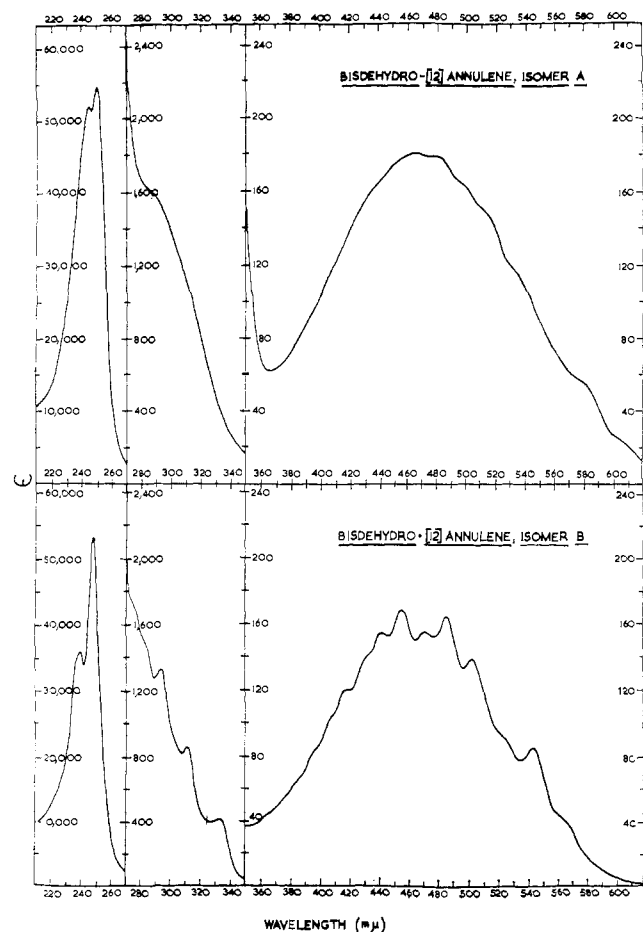


Figure 2. Ultraviolet absorption spectra of bisdehydro[12]annulene, isomer A (IX) and isomer B (X), determined in isoctane with a Cary Model 14 recording spectrophotometer.

XI possesses four different types. The observed n.m.r. spectrum strongly suggests the substance in fact to be the 1,7-diyne X, the single band being due to the identical chemical shifts of both types of protons. Such a

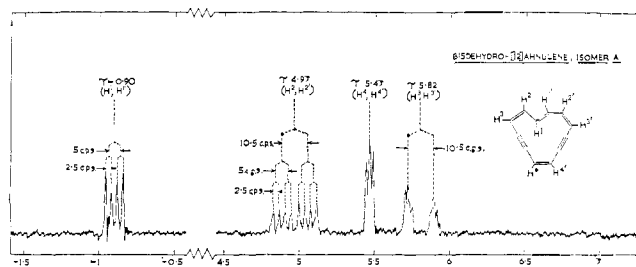


Figure 3. Nuclear magnetic resonance spectrum of bisdehydro[12]annulene, isomer A (IX), determined in carbon tetrachloride with a Varian A-60 spectrometer (tetramethylsilane used as internal reference).

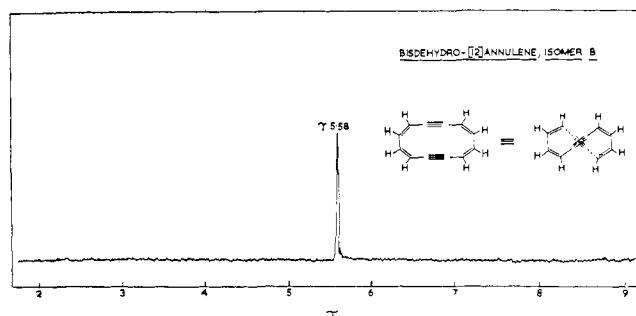


Figure 4. Nuclear magnetic resonance spectrum of bisdehydro[12]annulene, isomer B (X), determined in carbon tetrachloride with a Varian A-60 spectrometer (tetramethylsilane used as internal reference).

merging into a single band is much less likely for the 1,5-diyne XI. It is to be noted that structure X is presumably again not planar, but exists in a twisted form as indicated in Figure 4.

It has been mentioned in the introduction that dehydro[12]annulenes are not expected to be aromatic. This expectation is borne out in practice by the n.m.r. spectra of both isomers A and B, which show no indication of the existence of a ring current.^{24,28} These spectra also indicate that neither of the two substances has a triplet ground state.²⁴ Inspection of a model of structure IX shows that a planar conformation is possible for bisdehydro[12]annulene (isomer A) without serious distortions. The observed nonplanarity of this substance is presumably a consequence of the fact that no aromatic system would result if it were planar, and that the hydrogen-hydrogen interactions are less in the nonplanar than in the planar conformation.

The over-all combined yield of the three cyclic compounds VIII, IX, and X from 1,5-hexadiyne (III) was *ca.* 9.5%. This is therefore the minimum value for the yield in the conversion of 1,5-hexadiyne to the cyclic dimer IV, and the actual value is presumably significantly higher than this figure.¹⁴

Treatment of either isomer of bisdehydro[12]annulene with potassium *t*-butoxide under the conditions

(28) It may be noted that the H¹ and H^{1'} protons in isomer A (Figure 3) appear at unusually *low* field ($\tau = 0.90$), whereas the "inner" protons are known to appear at unusually *high* field when a ring current exists.^{2b,24} The unusual low-field position of the H¹ and H^{1'} protons may well be due to deshielding by the acetylenic bonds. Similarly, the nonaromatic bisdehydro[16]annulene and tetrahydro[24]annulene show n.m.r. bands due to the protons corresponding to H¹ and H^{1'} at unusually low field (τ 2.25 and 1.80, respectively),^{2b,24} presumably for the same reason.

used for the rearrangement resulted in the recovery of starting material (and some decomposition product), but no detectable amounts of the other isomer or of biphenylene were produced. These experiments show that the two isomers are formed from the cyclic dimer IV by independent paths, and that the bisdehydro[12]-annulenes are not intermediates in the conversion of IV to biphenylene.

The partial hydrogenation of both isomers of bisdehydro[12]annulene was studied, in order to obtain [12]annulene (e.g., I). Unfortunately, the results were not completely clear-cut, and it has not yet been established unequivocally whether [12]annulene is in fact formed by this route. Nevertheless, it appears worthwhile briefly to report the outcome of these experiments at this stage.

Partial hydrogenation of bisdehydro[12]annulene (isomer A) in pentane solution over a Lindlar lead-poisoned palladium-calcium carbonate catalyst,²⁹ or a palladium-charcoal catalyst, resulted in the appearance of a new ultraviolet maximum at *ca.* 296 m μ . The intensity of this band was highest when approximately 3-4 molar equiv. of hydrogen had been absorbed, although a considerable amount of starting material was still present. Careful chromatography on alumina into about 250 fractions then gave yellow solutions showing ultraviolet maxima in the 295-299-m μ region, eluted before the unchanged bisdehydro[12]-annulene. These yellow solutions appeared to consist mainly of two compounds, as shown by thin layer chromatography. It is possible that they contain [12]annulene, since evaporation led to an unstable yellow oil, which no longer exhibited the acetylene band at *ca.* 4.6 μ in the infrared, while full hydrogenation gave about equal amounts of cyclododecane and another unidentified hydrocarbon (gas chromatographic analysis). The yellow material responsible for the ultraviolet maximum at *ca.* 296 m μ was also unstable in solution, as shown by the fact that the intensity of this band steadily decreased as the chromatography fractions were allowed to stand. Full hydrogenation after various periods of standing revealed that the ratio of unidentified hydrocarbon to cyclododecane increased. This may be due to [12]annulene undergoing a transannular reaction, or merely decomposing.

The partial hydrogenation of bisdehydro[12]annulene (isomer B) over a palladium-charcoal catalyst gave very similar results to those obtained with isomer A (see the Experimental Section for details). An investigation of the partial hydrogenation of both isomers in greater detail is planned, in order to find out unequivocally whether [12]annulene is in fact formed.

Experimental Section

General Procedures. Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Ultraviolet spectra were measured on a Unicam Model S.P. 500 as well as on a Cary Model 14 recording spectrophotometer (sh = shoulder); the ultraviolet spectra of chromatography fractions were determined against pentane. Infrared spectra were measured as potassium bromide pellets on a Perkin-Elmer Model 137 infrared recording spectrophotometer with sodium chloride optics (s = strong, m = medium, w = weak). Anal-

(29) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

yses were carried out in our microanalytical department under the direction of Mr. Raoul Heller. All solvents were evaporated under reduced pressure, the bath temperature being kept below 40°.

Full hydrogenations of chromatography fractions were carried out by shaking in hydrogen over a pre-reduced platinum oxide catalyst at room temperature and atmospheric pressure for *ca.* 1 hr. Hydrogenations of pure substances were performed similarly in ethyl acetate solution. The resulting solutions were filtered, evaporated to small volume, and analyzed by gas chromatography.

Gas chromatograms were carried out with a Research Specialties Model 600 instrument (Argon ionization detector), using a glass column (6 ft. \times 0.25 in. outer diameter) filled with 5% SE 30 silicone rubber on Chromosorb W operated at 100°; and an argon flow rate of 62 ml./min. Under these conditions, the retention time of *n*-dodecane was 6.6 min., and of cyclododecane 12.1 min.

Thin layer chromatograms were carried out on Kieselgel G (Merck AG, Darmstadt) plates, the thickness of absorbent being *ca.* 0.25 mm. The eluents used were pentane or pentane-ether mixtures, and the plates were developed by spraying with cupric acetate-permanganate reagent (prepared by dissolving 0.5 g. of potassium permanganate in 100 ml. of a saturated aqueous cupric acetate solution).

Oxidative Coupling of 1,5-Hexadiyne (III). A three-necked, 3-l. flask equipped with an efficient mechanical stirrer, gas inlet tube, and reflux condenser (on top of which was attached a cold finger filled with Dry Ice-acetone to prevent loss of the diacetylene during the reaction) was placed in a water bath. Ammonium chloride (48 g.), cuprous chloride (30 g.), water (127 ml.), concentrated hydrochloric acid (0.3 ml.), and benzene (1.5 l.) were introduced, and the water bath was heated to 55°. A vigorous stream of oxygen (*ca.* 2.5 l./min.) was then bubbled through the mixture, which was stirred vigorously.³⁰ A solution of 1,5-hexadiyne (15 g.)³¹ in ethanol (30 ml.) was then added in one portion. The blue-green mixture turned into a yellow suspension, which gradually became bright green as the reaction continued. The reaction was allowed to proceed at 55° for 2 hr., with continued vigorous stirring and passing in of oxygen. A small amount of a brown-black precipitate due to polymerized IV was formed at the rim of the flask and in the gas inlet tube (due to evaporation of benzene) toward the end of the reaction. The mixture was cooled to room temperature, the yellow benzene layer was separated, and the aqueous layer was washed twice more with benzene. The combined benzene extracts were filtered, washed with water, and dried over anhydrous sodium sulfate.

The oxidation was then repeated in the same way with another 15 g. of 1,5-hexadiyne, and the dried benzene extracts from both experiments were concentrated under reduced pressure to a volume of *ca.* 700 ml. (this volume was found to be the optimum, since further

(30) Strong agitation and a vigorous stream of oxygen appeared to be essential. Experiments in which stirring was not very efficient, or in which only a slow stream of oxygen was passed in, resulted in a greatly decreased yield of the cyclic dimer IV.

(31) Prepared according to R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 120 (1950).

concentration resulted in appreciable separation and spontaneous decomposition of the cyclic dimer IV, while more dilute solutions could not be chromatographed efficiently). This concentrate was then chromatographed as soon as possible, since a yellow decomposition product derived from IV gradually separates on standing.

For analytical purposes, 23 ml. of the 700-ml. concentrate was chromatographed on a column of 500 g. of alumina (Merck, acid-washed), prepared with pentane. The column was washed with pentane, which eluted first the benzene, and then the two previously mentioned liquid chloro compounds.¹⁰ The column was then washed with increasing amounts of ether in pentane, 25-ml. fractions being collected. Fractions 17–51 (eluted with 10–20% ether in pentane) all contained the linear dimer VI as well as rearranged linear products (see the ultraviolet spectra), while fractions 23–29 in addition were rich in the cyclic dimer IV (color test and full hydrogenation, see below). The ultraviolet spectra of representative fractions were (relative optical densities in parentheses): fraction 17, λ_{\max} 225, 229, 241, 254, 305, 316, and 326 $m\mu$ (0.428, 0.430, 0.510, 0.352, 0.490, 0.560, and 0.455); fraction 19, λ_{\max} 232, 240, 254, 306, 315, and 326 $m\mu$ (0.226, 0.291, 0.232, 0.620, 0.705, and 0.560); fraction 23, λ_{\max} 235, 242, 247, 263, 305, 314, and 327 $m\mu$ (0.298, 0.360, 0.400, 0.295, 0.370, 0.415, and 0.325); fraction 25, λ_{\max} 236, 247, 263, 304, 316, and 326 $m\mu$ (0.275, 0.383, 0.270, 0.182, 0.195, and 0.158); fraction 27, λ_{\max} 235, 247, 263, 303, 314, and 326 $m\mu$ (0.317, 0.423, 0.310, 0.378, 0.412, and 0.305); fraction 29, λ_{\max} 228, 247, 264, 304, 315, 326, and 354 $m\mu$ (0.285, 0.360, 0.287, 0.588, 0.644, 0.460, and 0.105); fraction 31, λ_{\max} 227, 240, 303, 314, 325, and 354 $m\mu$ (0.410, 0.412, 1.160, 1.320, 1.000, and 0.205); fraction 35, λ_{\max} 230, 239, 303, 317, 334, and 354 $m\mu$ (0.470, 0.360, 1.07, 1.320, 1.215, and 0.690); fraction 43, λ_{\max} 233, 244, 324, 337, and 354 $m\mu$ (0.280, 0.242, 0.707, 0.856, and 0.642); fraction 51, λ_{\max} 233, 244, 255, 326, 338, and 354 $m\mu$ (0.175, 0.235, 0.180, 0.320, 0.356, and 0.278).

The ultraviolet data point to the formation of rearrangement products of the linear dimer VI, containing five conjugated multiple bonds (*n*-decatetraenyne show λ_{\max} 300–308, 313, and 327–329 $m\mu$),¹⁵ as well as six multiple bonds (*n*-dodecatetraendiynes obtained by base isomerization of VI show the highest wave length maximum at 352 $m\mu$).¹⁵ Representatives of fractions 17–51 were evaporated to dryness, allowed to stand for 1 hr., separated from polymerized IV, and fully hydrogenated in ethyl acetate solution. Gas chromatographic analysis then showed essentially only *n*-dodecane, indicating the rearrangement products to contain the *n*-dodecane carbon skeleton.

Direct crystallization of the combined fractions 35–51 from pentane led to the linear dimer VI, m.p. 97–99°, identified by direct comparison with an authentic sample (m.p. 99–100°).¹⁰

Parts of fractions 23, 25, 27, and 29 on full hydrogenation and subsequent analysis by gas chromatography in each case yielded a mixture of cyclododecane and *n*-dodecane. These hydrocarbons were identified by the fact that the retention times were identical with those of authentic samples, and there was no separation on admixture. The proportion of the cyclic:normal

saturated hydrocarbon varied from *ca.* 1:0.8 for fraction 23 to *ca.* 1:2 for fraction 29.

A more convenient method for locating the fractions containing the cyclic dimer IV consisted in evaporating a few drops to dryness on a watch glass on a steam bath. The formation of a brown-black polymeric residue then indicated the presence of IV, while linear products gave rise to a white or yellow residue (when the proportion of cyclic to linear dimer was small, then evaporation led to a brown residue embedded in white or yellow material). An even simpler test involved dipping strips of filter paper in the different fractions, and drying them rapidly in a stream of warm air blown from a hair dryer. Formation of a black-brown color on the strip then indicated the relevant fraction to contain IV. By use of these tests, it was shown that the above-described fractions 23–29 were rich in IV.

The combined fractions 23–29 gradually deposited a yellow precipitate due to polymerized IV on being allowed to stand at room temperature. All attempts to isolate IV free of solvent (*e.g.*, by evaporation of the solvent in nitrogen under reduced pressure at –60°) only led to brown-black polymeric material. It was not even possible to prepare a concentrated solution suitable for measurement of the infrared or n.m.r. spectrum. Attempted thin layer chromatography also resulted in polymerization.

An aliquot of the combined fractions 23–29 on being shaken with a solution of silver nitrate in aqueous ethanol (in order to remove material containing a free ethynyl group), followed by removal of the resulting precipitate, showed λ_{\max} 236, 247, 303, 314, and 326 $m\mu$ (relative optical densities, 0.52, 0.60, 0.49, 0.50, 0.56, and 0.38).

For preparative purposes, the remaining 677 ml. of the benzene concentrate (derived from 29 g. of 1,5-hexadiyne) was chromatographed on 3.2 kg. of alumina (Merck, acid-washed), which was then developed a before, 200-ml. fractions being collected. Application of the above-described color test showed that fractions 29–48 (eluted with 15–20% ether in pentane) were rich in the cyclic dimer IV. These fractions were combined and used directly for the rearrangement.

Rearrangement of 1,3,7,9-Cyclododecatetrayne (IV) to Biphenylene (VIII) and Bisdehydro[12]annulene (Isomers A and B). A saturated solution of potassium *t*-butoxide in *t*-butyl alcohol (1 l.) was added to the combined fractions 29–48 (4 l.) from the above-described preparative chromatogram (derived from the coupling of 29 g. of 1,5-hexadiyne). The solution, which immediately became red-violet, was then allowed to stand at room temperature for 20 min. Water was added and the organic layer was separated and washed repeatedly with water until the washings were no longer alkaline. The red-violet solution was then concentrated under reduced pressure to a volume of *ca.* 500 ml. The solution was again washed several times with water, in order to remove the small amount of *t*-butyl alcohol which remained and would have interfered in the subsequent chromatographic separation. The solution was dried over anhydrous sodium sulfate and filtered. A concentrated benzene solution was obtained by addition of *ca.* 50 ml. of this solvent and evaporation under reduced pressure to *ca.* 30 ml.

This concentrate was then chromatographed into 110 fractions on 1.2 kg. of alumina (Alcoa activated, grade F-20, reactivated through 4 hr. of heating at 200–210°), prepared with pentane.

Fractions 1 and 2 were eluted with pentane, while the succeeding fractions were eluted with increasing amounts of ether in pentane. The volume of fractions 1–11 was 2.5 l. each, and all the others were 250 ml. each. During the chromatogram, the two isomers of bisdehydro[12]annulene could be seen to move down the column as separate, colored bands. Ultraviolet examination and thin layer chromatography³² of each fraction showed that the following separation had been achieved: fractions 6–11 (3.5% ether) contained pure biphenylene, fractions 12–17 (6% ether) contained a mixture of biphenylene and isomer A, fractions 18–52 (6–10% ether) contained pure isomer A, fractions 53–69 (10–12% ether) contained a mixture of isomers A and B as well as an unidentified conjugated (presumably linear) material, while fractions 70–88 (12–20% ether) contained pure isomer B. Subsequently colorless fractions with different ultraviolet spectra were obtained, which were not further investigated. Rechromatography of the combined fractions 12–17 on Alcoa alumina gave further quantities of pure biphenylene and of isomer A, while rechromatography of the combined fractions 53–69 led to further amounts of pure isomer A and of isomer B.

The combined biphenylene fractions on evaporation to dryness yielded 2.084 g. (7.4% over-all) of this hydrocarbon as straw-colored crystals, m.p. 108–110°. Crystallization from methanol led to the analytical sample, m.p. 110–111°; $\lambda_{\text{max}}^{\text{pentane}}$ 239 m μ (ϵ 59,600), 248 (114,000), 325 (2730), 330 (2930), 338 (5860), 343 (5350), ca. 348 sh (3400), and 358 (8900). The melting point was undepressed on admixture with an authentic sample (m.p. 110–111°), and the characteristic infrared and ultraviolet spectra, as well as the retention times on gas chromatography, were completely identical.

Anal. Calcd. for C₁₂H₈: C, 94.70; H, 5.30. Found: C, 94.51; H, 5.25.

The combined fractions containing bisdehydro[12]annulene, isomer A, were shown to be homogeneous, as determined by thin layer chromatography. The yield of this isomer, estimated spectroscopically, was 0.43 g. (1.5% over-all). Parallel experiments showed that the spectroscopic yield corresponded approximately to that which could actually be obtained in crystalline form, but the substance was best estimated and kept in solution in view of its instability in the solid state. Evaporation of an aliquot to small volume under reduced pressure (outside temperature ca. 20°) and cooling to –50° yielded the crystalline isomer A as brown-violet needles, m.p. 54–55° dec.³³; infrared bands at 3.29 (w), 3.40 (w), 4.60 (w), 6.00 (m), 6.43 (m), 6.54 (m), 6.78 (w), 6.85 (w), 7.10 (w), 7.23 (w), 7.54 (m), 7.78 (m), 8.10 (w), 8.23 (m), 8.44 (m), 9.05 (m), 9.24 (m), 10.23 (s) 10.66 (m), 12.16 (m), and 13.35 (s) μ (see Figure 1); $\lambda_{\text{max}}^{\text{isopentane}}$ 244 m μ (ϵ 51,900), 249 (54,800), ca. 285 sh (1620), 465 (183), ca. 479 sh (180),

(32) The spot due to biphenylene became visible only a few minutes after spraying. The relative R_f values were: biphenylene (0.65), isomer A (0.46), isomer B (0.19).

(33) Put on block between two cover slides just below this temperature. Only polymerization occurred when the melting point was determined in the usual way.

ca. 500 sh (163), ca. 517 sh (146), ca. 536 sh (116), ca. 580 sh (57), and ca. 605 sh (25) (see Figure 2)³⁴; for the n.m.r. spectrum see Figure 3. A pentane–ether solution was red when concentrated and pink-violet when more dilute. The compound was quite soluble in pentane, ether, benzene, etc. It could be kept in pentane–ether solution with only little decomposition for several months at ca. –15°. However, on being allowed to stand in the solid state at room temperature, it had partially decomposed after 10 min., and almost completely after 1 hr., an insoluble yellow-brown polymer being formed.

Anal. Calcd. for C₁₂H₈: C, 94.70; H, 5.30. Found³⁵: C, 94.30; H, 5.46.

Full hydrogenation of isomer A, followed by gas chromatographic analysis, yielded cyclododecane (retention time 12.1 min., identical with that of an authentic sample) in over 90% yield. In addition, small peaks with retention times of 8.5 and 13.4 min. were observed, but these were not identified.

The combined fractions containing bisdehydro[12]annulene (isomer B) were homogeneous, as determined by thin layer chromatography. The yield of this isomer, estimated spectroscopically, was 0.187 g. (0.66% over-all). Evaporation to small volume under reduced pressure in a bath kept at ca. 40°, and cooling, afforded 0.171 g. of isomer B (in two crops) as brick-red needles, m.p. 96° dec.³³; infrared bands at 3.28 (w), 3.40 (w), 4.60 (w), 5.35 (w), 5.99 (m), 6.43 (m), 6.80 (w), 7.25 (w), 8.20 (s), 8.42 (w), 9.01 (w), 9.12 (s), 9.33 (w), 10.68 (w), and 13.43 (s) μ (see Figure 1); $\lambda_{\text{max}}^{\text{isopentane}}$ 238 m μ (ϵ 36,200), 247 (54,200), ca. 276 sh (1710), ca. 282 sh (1520), 293 (1340), 311 (843), 332 (405), ca. 395 sh (81), ca. 408 sh (102), 417 (121), ca. 431 sh (139), 442 (155), 457 (168), 472 (155), 487 (165), 505 (138), ca. 522 sh (94), 544 (85), and ca. 563 sh (42) (see Figure 2); for the n.m.r. spectrum see Figure 4. A pentane–ether solution was red when concentrated and pink when more dilute. The substance showed the same type of solubility behavior as isomer A. It could be kept in pentane–ether solution at ca. –15° for several months essentially without change. It proved to be considerably more stable than isomer A in the solid state at room temperature, but even with isomer B a small amount of insoluble decomposition product had been formed after 4 hr. of standing.

Anal. Calcd. for C₁₂H₈: C, 94.70; H, 5.30. Found³⁵: C, 95.02; H, 5.01.

Full hydrogenation of isomer B, and subsequent gas chromatographic analysis, again led to over 90% of cyclododecane (retention time 12.1 min.), as well as to small amounts of two substances with retention times of 8.5 and 13.4 min. (presumably identical with the two by-products obtained previously by hydrogenation of isomer A).

*Treatment of Bisdehydro[12]annulene (Isomers A and B) with Potassium *t*-Butoxide.* A saturated solution of potassium *t*-butoxide in *t*-butyl alcohol (12.5 ml.) was added to a solution of 10 mg. of bisdehydro[12]annulene (isomer A) in 50 ml. of pentane. The solution was allowed to stand at room temperature for 20

(34) The ϵ values may well be too low, owing to some decomposition having occurred during the weighing process.

(35) For the precautions taken during the elemental analysis, see F. Sondheimer, Y. Amiel, and R. Wolovsky, *J. Am. Chem. Soc.*, **81**, 4600 (1959).

min., and the product was isolated as previously. The ultraviolet spectrum was identical with that of the starting material, and thin layer chromatography showed that only this substance was present, in addition to some decomposition product (no trace of isomer B or of biphenylene could be detected).

Identical treatment of bisdehydro[12]annulene (isomer B) with potassium *t*-butoxide also resulted in no change (except for some decomposition), no trace of isomer A or of biphenylene being detected.

Partial Hydrogenation of Bisdehydro[12]annulene (Isomer A). The following experiments are representative of the many which were carried out.

A suspension of *ca.* 40 mg. of Lindlar lead-poisoned palladium-calcium carbonate catalyst²⁹ in 30 ml. of pentane was stirred in hydrogen at room temperature and atmospheric pressure until equilibrium was reached. A solution of 40 mg. of bisdehydro[12]annulene (isomer A) in 20 ml. of pentane then was added through a side arm, and the mixture was stirred very gently. Aliquots were removed with a syringe at intervals, and the ultraviolet spectra were determined. It was found that a broad new peak at *ca.* 296 $m\mu$ appeared, at the expense of the 244- and 249- $m\mu$ bands of the starting material. The highest intensity of the 296- $m\mu$ band was reached when the 249- and 296- $m\mu$ bands were of about equal height (corresponding to the absorption of approximately 3-4 molar equiv. of hydrogen); further hydrogenation resulted in the decrease of the 296- $m\mu$ maximum, as well as of the maxima due to starting material. The optimum point corresponded to a certain lightening of the intense pink-violet color of the solution, and this color change could be used in preparative experiments for estimating when to terminate the reaction.

Another experiment on the same scale as above was interrupted at the optimum point. The hydrogen was removed immediately by passing in nitrogen and the catalyst was filtered off. Examination of the filtrate by thin layer chromatography revealed two major new spots (more mobile than starting material), besides that due to starting material. The solution was concentrated under reduced pressure to *ca.* 20 ml. and chromatographed on 100 g. of alumina (Alcoa activated, grade F-20). All elutions were made with pentane, about 250 50-ml. fractions being collected. The ultraviolet spectra of representatives were examined. Fractions 64-178 all showed broad maxima in the 295-300- $m\mu$ region, a small bathochromic shift from *ca.* 295 $m\mu$ for the earlier fractions to *ca.* 299 $m\mu$ for the later fractions being apparent. Unchanged starting material was eluted subsequently in fractions 223-233.

Representatives of the fractions 64-178 on thin layer chromatography showed the above-mentioned two new spots, but no starting material. Fractions 64-178 were combined, and a part was evaporated under reduced pressure to small volume, giving a light yellow solution, λ_{\max} 296 $m\mu$. Evaporation to dryness gave

an unstable yellow oil, which on immediate infrared examination (neat or in chloroform) showed no acetylene band at *ca.* 4.6 μ .

Another part of the combined fractions 64-178 was concentrated and then fully hydrogenated on the same day that it had been obtained. Gas chromatographic analysis of the product gave approximately equal amounts of cyclododecane (retention time 12.1 min.) and a substance with retention time 8.5 min. (presumably identical with the by-product with retention time 8.5 min. obtained previously by full hydrogenation of either isomer of bisdehydro[12]annulene). A further part of the combined fractions was allowed to stand at room temperature without protection from diffuse daylight for 1 week, and was then similarly concentrated and fully hydrogenated. Gas chromatographic analysis then showed that the ratio of the substance with retention time 8.5 min. to cyclododecane was *ca.* 5:1. After 6 weeks of standing, the ratio was *ca.* 20:1. Ultraviolet examination of the combined fractions 64-178 revealed that the intensity of the 296- $m\mu$ maximum steadily decreased on standing.

The partial hydrogenation of bisdehydro[12]annulene (isomer A) was also carried out with a 10% palladium-charcoal catalyst, whereby very similar results to those described for the Lindlar catalyst were obtained.

Partial Hydrogenation of Bisdehydro[12]annulene (Isomer B). A solution of 24 mg. of bisdehydro[12]annulene (isomer B) in 40 ml. of pentane was partially hydrogenated over *ca.* 40 mg. of a 10% palladium-charcoal catalyst (previously equilibrated by being stirred in hydrogen), essentially as described above for isomer A. The reaction was terminated when the intense color of the solution had become light pink-yellow, corresponding to the uptake of *ca.* 3.5 molar equiv. of hydrogen. The product was isolated and chromatographed on 90 g. of alumina (Alcoa activated, grade F-20) as before. Fractions 104-144 (25 ml. each) eluted with pentane to pentane-ether (99:1 to 49:1) all showed maxima in the range 296-298 $m\mu$. Unchanged starting material was eluted subsequently with pentane-ether (49:1 to 97:3). The combined fractions 104-144 on thin layer chromatography apparently gave the same two spots as obtained from isomer A. Evaporation to dryness under reduced pressure also led to an unstable yellow oil. Full hydrogenation of a part of the combined fractions 104-144 after about 4 weeks of standing, followed by gas chromatographic analysis, gave mainly the peak with retention time 8.5 min.

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