The hydroxy ketal (**18**) in 100 ml. of acetone and 100 ml. of 3 N aqueous hydrochloric acid was warmed on the steam bath for 10 min. Most of the acetone was removed at reduced pressure and the resulting oil isolated by ether extraction. On trituration with petroleum ether b.p. (60–75°) this oil crystallized; recrystallization from the same solvent afforded 2.0 g. (61%; 46% over-all) of the hydroxy ketone (**19**), m.p. 112–114°. After two further crystallizations from petroleum ether (b.p. 60–75°) the analytical sample melted at 113–114°.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.30; H, 9.85.

9-Methyl-*trans*-decal-1,6-dione (20).—An ice-cooled solution of 60 mg. (0.33 mmole) of the hydroxy ketone (**19**) in 2 ml. of acetone was oxidized with 0.08 ml. of Jones reagent.[37] Chromatography of the resulting oil on 3 g. of alumina afforded 46 mg. (78%) of the dione, m.p. 54–57°, eluted with 200 ml. of 50% benzene petroleum ether (b.p. 40–60°). Recrystallization of this dione from ether-petroleum ether (b.p. 40–60°) afforded 34 mg., m.p. 56.5–57.5° alone or on admixture with the authentic sample.[38]

Acknowledgment.—It is a pleasure to acknowledge the financial support of the National Institutes of Health through a research grant RG-9067.

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(38) Prepared from 10-methyl-$\Delta^{1(9)}$-octal-2,5-dione by the method of A. J. Birch, E. Pridie, and H. Smith, *J. Chem. Soc.*, 4688 (1958).

Synthesis of a Macrocycle by Application of the Wittig Reaction

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A model macrocycle 1,2,5,6,9,10,13,14-tetrabenzocyclohexadeca-1,3,5,7,9,11,13,15-octaene (I) has been successfully synthesized by a five-step process employing Wittig reactions for the preparation of intermediates and final ring closure. This sequence appears to be preferable to classical approaches for macrocyclic syntheses. Evidence derived from absorption spectra indicates (I) to exist in an all-*trans* configuration and a nonconjugated conformation.

In recent years, applications of the extremely versatile Wittig reaction[1] have been extended beyond the preparation of acyclic olefins to the synthesis of medium ring compounds. Intermolecular processes have been employed by Wittig and co-workers in the synthesis of 1,2-benzocyclohepta-1,3,6-triene and 1,2-benzocycloocta-1,3,7-triene from phthaldehyde and the ylides, $Ph_3P{=}CH(CH_2)_nCH{=}PPh_3$ ($n = 1,2$)[2] and by Dimroth in a similar synthesis of 3-benzoxepin.[3] Recently, Bieber[4] has reported the first successful intramolecular Wittig reaction; the ylide derived from (5-oxo-5-phenylpentyl)-triphenylphosphonium bromide readily cyclizes to 1-phenylcyclopentene.

This study was designed to test the feasibility of extending the Wittig olefin formation procedure to macrocyclic compounds. Many of the known methods for the formation of macrocycles involve multistep processes giving low yields and often introducing elements of structural ambiguity. Application of the Wittig reaction in this area might be of more general synthetic utility since the reaction is structurally unequivocal and more direct synthetic routes may be derived. The macrocycle, 1,2,5,6,9,10,13,14-tetrabenzocyclohexadeca-1,3,5,7,-9,11,13,15 - octaene (I) was chosen as the synthetic objective of this study because it had previously been synthesized in an unambiguous fashion by Bergmann[5] by a typical multistep process; this material was also of interest as a possible coordinating agent for metal ions.

The general method employed for the synthesis of I is patterned after that of previous workers[2,3] and is shown in the sequence of reactions 1–4.

The phosphonium salt (V), the precursor of the required diylide, is an *o*-distyrylbenzene structure and is consequently amenable to synthesis by Wittig techniques. Wittig[2] showed that *o*-divinylbenzene could be synthesized in good yield by reaction of *o*-phthalaldehyde with a methylene ylide and a related synthesis of a 2,2′-divinylbiphenyl derivative has been reported.[6] More recently, Campbell and McDonald demonstrated convincingly that the Wittig reaction is a superior method for the synthesis of *p*-distyrylbenzenes[7]; the general experimental techniques employed in the Wittig reactions (reactions 1,4) in this study are modifications of established procedures.[7,8]

In a preliminary study, the synthesis of 1,2-distyrylbenzene (IVa) was carried out as a model for the synthesis of IVb. The *o*-xylylene bisphosphonium salt (II) was prepared in good yield by quaternization of triphenylphosphine with *o*-xylyl-

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(1) For recent reviews, see: U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959); S. Trippett in "Advances in Organic Chemistry: Methods and Results," Vol. I, R. A. Raphael, E. C. Taylor, and H. Wynberg, eds., Interscience Press, New York, 1960, pp. 83–102.

(2) G. Wittig, H. Eggers, and P. Duffner, *Ann*, **619**, 10 (1958).

(3) K. Dimroth and G. Pohl, *Angew. Chem.*, **73**, 436 (1961).

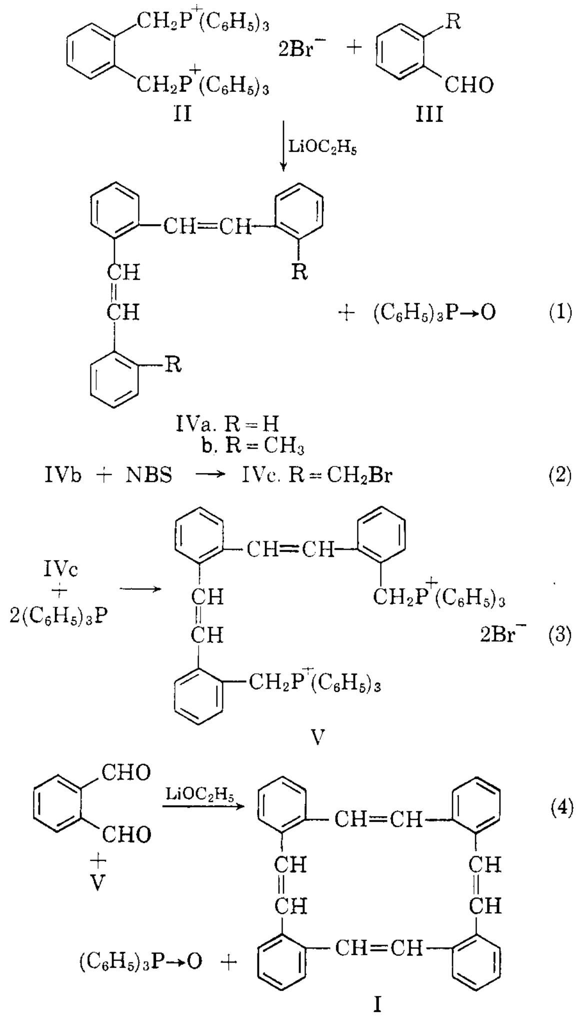
(4) T. I. Bieber, private communication and paper presented at the Southeastern Regional Meeting, American Chemical Society, Birmingham, Ala., November 3–5, 1960.

(5) E. D. Bergmann and Z. Pelchowicz, *J. Am. Chem. Soc.*, **75**, 4281 (1953).

(6) G. Wittig and W. Stilz, *Ann.*, **598**, 93 (1956).

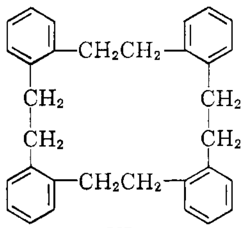
(7) T. W. Campbell and R. N. McDonald, *J. Org. Chem.*, **24**, 1246 (1959).

(8) (a) R. N. McDonald and T. W. Campbell, *J. Org. Chem.*, **24**, 1969 (1959); (b) R. N. McDonald and T. W. Campbell, *J. Am. Chem. Soc.*, **82**, 4669 (1960).



ene dibromide in dimethylformamide. Benzene was employed as solvent in this reaction in one instance but proved to be unsatisfactory; the monophosphonium salt, (*o*-bromomethylbenzyl)triphenylphosphonium bromide, was insoluble and failed to give the bisphosphonium salt. In the presence of lithium ethoxide, II was converted readily to the corresponding diylide; reaction of the diylide with benzaldehyde gave 1,2-distyrylbenzene[9] (IVa) in 84% yield. Experimentally, the only difficulties observed were in the separation of IVa and the by-product, triphenylphosphine oxide; however, separation could be achieved readily by either column chromatographic or extraction techniques. A parallel reaction of II with *o*-tolualdehyde (III. R = CH_3) led to the formation of 1,2-bis(*o*-methylstyryl)benzene (IVb) in 53% yield. IVb was successfully brominated to the bisbromomethyl derivative (IVc) with *N*-bromosuccinimide following established procedures.[10] The bromomethyl compound was not isolated but treated directly with two molar equivalents of triphenylphosphine in dimethylformamide; the bisphosphonium salt (V) separated during the course of the reaction and was obtained in 56% yield (based on the starting material, IVb).

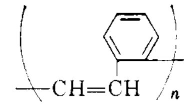
The final cyclization step (4) was carried out in the same manner as the 1,2-distyrylbenzene formation (step 1). The bisphosphonium salt V was converted, by the action of lithium ethoxide, to the corresponding bisylide which was then treated with *o*-phthaldehyde. Upon completion of reaction, the crude octaene (I) was separated from triphenylphosphine oxide by extraction and purified by alumina chromatography and recrystallization. The physical constants for this material agreed with those reported by Bergmann and Pelchowicz[5] and acceptable analytical data were obtained. For substantiation of structure, I was catalytically reduced to the saturated material, 1,2,5,6,9,10,13,14-tetrabenzocyclohexadeca-1,5,9,13-tetraene (VI); this material proved to be identical in all respects with an authentic sample of VI.



VI

Starting with the readily accessible *o*-xylylene dibromide, the five-step sequence reported here gave I in an over-all yield of 8.5% (step 4 in this reaction sequence proceeded in 34% yield). The previously reported synthesis of I[5] involved a ten-step procedure from readily available starting materials; after eight steps, a 10.4% over-all yield was reported (no yield data were reported for the final two steps). Thus it appears that the application of Wittig procedures to certain macrocyclic syntheses may be more advantageous than classical procedures with respect to yield and experimental facility.

In addition to I, reaction 4 gave a dark resinous material; oxidation of this material gave phthalic acid in essentially quantitative yield. Since reaction 4 can lead to polycondensation as well as bimolecular ring closure, it seems probable that the resin obtained is a poly-*o*-xylylidene VII. Similar polycondensations leading to *para* and *meta* analogs of VII have been reported previously by McDonald and Campbell.[8b] The infrared spectrum of VII showed the presence of *o*-disubstituted benzene, olefinic, and both *cis*- and *trans*-1,2-disubstituted olefinic groupings.



VII

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(9) P. L. Ecuyer and F. Turcotte, *Can. J. Research*, **25B**, 575 (1947).

(10) G. A. R. Kon, *J. Chem. Soc.*, 224 (1948).

Bergmann and Pelchowicz[5] indicated I to be a completely strainless, slightly puckered ring and commented upon the colorless nature of the compound; these authors showed by means of infrared spectra that the four stilbene double bonds have *trans* configurations.[11] Confirmation of the all-*trans* configuration for I was obtained in this study; I showed a strong band in the infrared at 961 cm.$^{-1}$,[1,12] and was transparent in the region near 690 cm.$^{-1}$. The former region has been shown to be characteristic of *trans*-1,2-disubstituted alkenes (C—H out-of-plane deformation) while absorption in the latter region is attributed to the corresponding *cis* isomer.[13] Thus, *cis*- and *trans*-2,2′-dichlorostilbene absorb at 695 and 964 cm.$^{-1}$, respectively.[14] Similarily, the 1,2-distyrylbenzenes (IVa and IVb) showed strong absorptions at 962–963 cm.$^{-1}$; IVb was transparent in the 690-cm.$^{-1}$ region, while IVa showed a band of moderate intensity at 686 cm.$^{-1}$ ascribable to a monosubstituted phenyl group.[15] Thus the presence of 960–970 cm.$^{-1}$ and the absence of 690-cm.$^{-1}$ absorptions for I and IVb indicate these structures to possess the all-*trans* and *trans-trans* configurations. In all probability, IVa is the *trans-trans* isomer, although the presence of small amounts of the *cis-cis* or *cis-trans* isomer cannot be ruled out since the 686-cm.$^{-1}$ monosubstituted phenyl band would mask any absorptions arising from *cis* C—H out-of-plane deformations. Samples of I, IVa, and IVb were recrystallized from benzene in the presence of a trace of iodine; this treatment has been routinely employed for the isomerization of *cis*- to the thermodynamically more stable *trans*-styrenes.[7] The spectra of I, IVa, and IVb taken before and after this treatment were superimposable, providing further evidence that the compounds were all-*trans* isomers and not contaminated by *cis* structures. Previously reported studies[1,7,16] have indicated the formation of olefins by the Wittig reaction to be generally nonstereospecific with one notable exception[8]; the apparent stereospecificity observed in the formation of I, IVa, and IVb is probably, as in the case of the diarylbutadienes,[8] as a result of thermodynamic control.

Information regarding the conformation of the all-*trans* isomer I was provided by an examination of the ultraviolet spectrum of the compound: I showed only benzenoid end group absorption ($\lambda_{\max} < 200$ mμ) and B band absorption at 278 mμ (ϵ 3200). If any real degree of coplanarity and orbital overlap were present in I, a styrene or stilbene type spectrum (see Table I) would be expected.[17] The observed spectrum thus indicates an absence of phenyl-ethylenic conjugation and a completely noncoplanar conformation for I. Confirmation of this assignment was provided by an examination of the spectrum of VI, the reduced form of I; the spectrum of this compound was almost identical to that of I [$\lambda_{\max}$ 274 mμ (ϵ 3100) and < 200 mμ]. In VI no possibility of conjugation exists and thus the absorbing chromophores of I and VI must be the same—*i.e.*, *o*-disubstituted phenyl.

TABLE I

ABSORPTION BANDS FOR DISTYRYLBENZENES AND RELATED STRUCTURES[a]

	$\lambda_{\max}$	ϵ	$\lambda_{\max}$	ϵ	Ref.
1,2-Distyrylbenzene IVa	278	43,100	316	29,700	b
1,2-Di(*o*-methylstyryl)benzene IVb	279	52,500	303	47,500	b
1,3-Distyrylbenzene	298	53,700	316	43,700	c
1,4-Distyrylbenzene[d]	294	58,000	...	...	e
trans-Stilbene	295	27,000	310	25,000	f
cis-Stilbene	280	13,500	...	...	f
Styrene	248	14,000	282 291	750 500	f

[a] Spectra recorded in alcohol unless otherwise noted. [b] This study. [c] E. R. Blout and V. W. Eager, *J. Am. Chem. Soc.*, **67**, 1315 (1945). [d] In heptane. [e] E. Hertel and U. Siegal, *Z. phys. Chem.*, **B52**, 167 (1942). [f] Ref. 18.

Disruption of planarity in styrene and stilbene systems by *ortho* substituents is a well known phenomenon[18]; the results of this effect are a hypsochromic shift and a reduction in K-band intensity relative to the unsubstituted compound. The ultraviolet spectra (Table I) of the 1,2-distyrylbenzenes (IVa and IVb) show this effect (*i.e.*, a 15–16-mu hypsochromic shift relative to the planar 1,4-distyrylbenzene). Since infrared studies have indicated IVa and IVb to exist most probably in *trans-trans* configurations, the magnitude of the observed hypsochromic shifts indicates the degree of coplanarity to be quite low in IVa and IVb. It appears that not one but both styryl groups lie somewhat

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[11] Molecular models indicate the all-*cis* and any partially *cis* isomers of I to be markedly less stable than the all-*trans* isomer due to severe phenyl-phenyl crowding.

[12] Bergmann and Pelchowicz report a band at 955 cm.$^{-1}$.

[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, New York, 1958, pp. 34, 45–49.

[14] C. E. Griffin, unpublished results. For the spectra of the parent structures, *cis*- and *trans*-stilbene, see D. S. Brachman and P. H. Plesch, *J. Chem. Soc.*, 2188 (1952).

[15] Ref. 13, pp. 65, 75–77.

[16] J. P. Dusza, *J. Org. Chem.*, **25**, 93 (1960).

[17] Examination of molecular models of the all-*trans* isomer of I shows four conformational possibilities: a tetrastyryl conformer with each styryl system noncoplanar with the others; a distyryl conformer in which the remaining two phenyls and ethylenic groups are noncoplanar; a bis-*o*-distyrylbenzene conformer; and a conformer with no elements of coplanarity (ethylenic and phenyl planes at angles of 40°). Models indicate vinylic hydrogen–nuclear hydrogen interactions to be strong in the tetrastyryl and bis-*o*-divinylbenzene conformers; the distyryl and noncoplanar conformers appear to be most likely on steric grounds.

[18] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," 2nd ed., Edward Arnold Ltd., London, 1957, pp. 276–277.

[19] Melting points are uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Ultraviolet spectra were determined as dilute solutions (c = 1–1.5 × 10^{-5} M) in 95% ethanol and were recorded by a Cary Model 14 spectrophotometer; infrared spectra were recorded by a Perkin-Elmer Model 21 spectrophotometer. The spectrophotometers were provided by generous grants from the National Institutes of Health and the National Science Foundation.

out of the plane of the 1,2-disubstituted benzene ring—*i.e.*, above and below the plane.

Experimental[19]

***o*-Xylylenebis(triphenylphosphonium Bromide) (II).**—A solution of 66.1 g. (0.25 mole) of *o*-xylylene dibromide and 142.5 g. (0.55 mole) of triphenylphosphine in 500 ml. of dimethylformamide was heated at reflux for 3 hr. A colorless, crystalline solid began to separate from the reaction mixture after 10–15 min. The mixture was allowed to cool to room temperature, and the product was filtered and washed successively with dimethylformamide and ether. Air-drying gave 175.9 g. (89.4%) of uncontaminated product, m.p. > 340°. A sample was recrystallized from chloroform for analysis.

Anal. Calcd. for $C_{44}H_{38}Br_2P_2$: C, 67.02; H, 4.86; Br (ionic), 20.27. Found: C, 67.30; H, 4.79; Br (ionic), 20.41.

(*o*-Bromomethylbenzyl)triphenylphosphonium Bromide.—The addition of a solution of 160.5 g. (0.61 mole) of triphenylphosphine in 585 ml. of benzene to a solution of 71.0 g. (0.27 mole) of *o*-xylylene dibromide in 370 ml. of benzene led to an immediate reaction with the formation of a colorless, crystalline product. After addition was completed, the reaction mixture was refluxed for 8 hr. and then allowed to cool to room temperature. The crystalline product was removed by filtration and washed thoroughly with ether. After drying over phosphorus pentoxide at 30 mm. pressure, the weight was 130.6 g. (92%). Recrystallization of a sample from 95% ethanol gave a constant melting point of 253–256°. *Anal.* Calcd. for $C_{26}H_{23}Br_2P$: C, 59.01; H, 4.40; Br (ionic), 15.17, Br (total), 30.37. Found: C, 59.01; H, 4.59; Br (ionic), 15.41; Br (total), 30.64.

The monophosphonium salt could be converted readily to the bisphosphonium salt in essentially quantitative yield by treatment with triphenylphosphine in refluxing dimethylformamide.

1,2-Distyrylbenzene (IVa).—A solution of 42.5 g. (0.054 mole) *o*-xylylenebis(triphenylphosphonium bromide) (II) and 12.6 g. (0.119 mole) of benzaldehyde in 150 ml. of absolute ethanol was treated with 500 ml. of 0.4 *M* lithium ethoxide in ethanol. The solution was allowed to stand at room temperature for 30 min. and was refluxed for 2 hr. to yield a red-orange solution. The ethanolic solution was concentrated under reduced pressure to a volume of 100 ml.; addition of 300 ml. of water led to the precipitation of a yellow oil which was extracted with ether. The ethereal extract was reduced in volume to yield a mobile oil which could not be crystallized directly but was purified by chromatography in portions on an alumina column (Fisher A540, 2.5 × 55 cm.). Elution with low-boiling petroleum ether (250–300 ml.) gave an oily fraction which crystallized on evaporation of solvent. The combined solids were recrystallized from aqueous ethanol to give 12.7 g. (84%) of colorless needles melting at 117–119°. An analytical sample was recrystallized from aqueous ethanol to give a constant melting point of 117.5–119° (lit.,[9] m.p. 120–122°).

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.43; H, 6.45.

IVa absorbed in the infrared at 1495, 1451, 1318, 963, 758, and 686 cm.$^{-1}$ (CCl_4 solution and Nujol mull) and in the ultraviolet showed maxima at 278 (ϵ 43,100) and 316 mμ (ϵ 29,700) and minima at 243 (ϵ 8550) and 303 mμ (ϵ 27,600).

Further elution of the column with benzene led to the isolation of triphenylphosphine oxide (73%), which was identified by the lack of mixture melting point depression with an authentic sample.

The product could also be isolated from the crude yellow oil by the following procedure. Treatment of an acetone solution of the yellow oil with petroleum ether led to the precipitation of a yellow semisolid. The mother liquor was removed by decantation, and the precipitate was redissolved in acetone and again treated with petroleum ether. After a number of repetitions of this procedure, the precipitate was a colorless, crystalline material identified as triphenylphosphine oxide. The combined mother liquors were reduced in volume to give a thick yellow oil; crystallization from a 95% ethanol solution by slow evaporation gave 1,2-distyrylbenzene. Product recovery by this method compared favorably with the chromatographic separation.

1,2-Bis(*o*-methylstyryl)benzene (IVb).—A solution of 10.8 g. (0.09 mole) of *o*-tolualdehyde and 32.0 g. (0.041 mole) of the bisphosphonium salt (II) in 100 ml. of absolute ethanol was treated with 400 ml. of 0.4 *M* lithium ethoxide and, after standing at room temperature for 30 min., was refluxed for 4 hr. On cooling to room temperature, the solvent was evaporated under reduced pressure to yield a pale yellow oil which was washed thoroughly with water and dissolved in ether. The ethereal solution was extracted with saturated sodium bisulfite, washed thoroughly with water, and dried over sodium sulfate. Evaporation of the ether gave an almost colorless oil which was chromatographed on an alumina column (2 5 × 55 cm.); 250 ml. of low-boiling petroleum ether solution were collected and evaporated to give a colorless oil. Slow evaporation of a 95% ethanolic solution of the oil gave a crystalline material, m.p. 57–59°; repeated recrystallizations from 95% ethanol gave colorless crystals, 6.8 g. (53%), m.p. 72–74°.

Anal. Calcd. for $C_{24}H_{22}$: C, 92.85; H, 7.15. Found: C, 93.06; H, 7.16.

IVb absorbed in the infrared at 1608, 1497, 1475, 1383, and 962 cm.$^{-1}$ (CCl_4 solution) and at 1656, 1590, 1477, 1468, 1368, 1348, 1305, 1285, 1248, 1095, 1026, and 955 cm.$^{-1}$ ($CHCl_3$ solution). Maxima in the ultraviolet were observed at 279 (ϵ 52,500) and 303 mμ (ϵ 47,500) and a minimum at 246 mμ (ϵ 26,700).

1,2-Bis(*o*-triphenylphosphoniummethylstyryl)benzene Dibromide (V).—A mixture of 6.5 g. (0.021 mole) of 1,2-bis(*o*-methylstyryl)benzene, 7.5 g. (0.042 mole) of *N*-bromosuccinimide, 50 mg. of dibenzoyl peroxide, and 50 ml. of dry redistilled carbon tetrachloride was refluxed for 36 hr. The precipitated succinimide was removed by filtration and washed with carbon tetrachloride. The combined carbon tetrachloride solutions were washed with water, dried over sodium sulfate, and evaporated to give the crude dibromide as a pale yellow, semicrystalline mass. A solution of the crude dibromide and 11.0 g. (0.042 mole) of triphenylphosphine in 250 ml. of dimethylformamide was heated at reflux for 16 hr. A colorless, crystalline material began to separate from the reaction mixture after 1 hr. After cooling to 0°, the product was removed by filtration and washed successively with dimethylformamide and petroleum ether. Air-drying gave 11.6 g. (56%) of product melting at 310–314°; a sample was recrystallized from chloroform to a constant melting point of 314–316°. Analysis indicated the material to be essentially uncontaminated by starting material or monophosphonium salt.

Anal. Calcd. for $C_{60}H_{40}Br_2P_2$: C, 72.57; H, 5.08; Br (ionic), 16.10; P, 6.24. Found: C, 72.64, 72.71; H, 5.10, 5.22; Br (ionic), 16.20, 16.31; P, 6.08, 6.17.

1,2,5,6,9,10,13,14-Tetrabenzocyclohexadeca-1,3,5,7,9,11,-13,15-octaene (I).—A mixture of 26.5 g. (0.027 mole) of the bisphosphonium salt (V), 3.6 g. (0.027 mole) of *o*-phthaldehyde and 700 ml. of 0.1 *M* lithium ethoxide in ethanol was heated at reflux for 16 hr. Upon cooling, the solution was removed by decantation from a dark resinous material adhering to the sides of the flask. The ethanolic solution was evaporated to give a yellow semisolid, which was extracted repeatedly with hot petroleum ether to leave colorless crystals (12.4 g. 82%) which were identified as triphenylphosphine oxide by mixture melting point. On cooling to room temperature, the combined petroleum ether extracts deposited colorless crystals, m.p. 230–238°; concentration of the mother liquor to approximately one half the original volume and further cooling gave additional material of the same melting point. The combined crystalline material was dissolved in benzene and passed through an alumina column; evaporation of solvent at reduced pressure gave 3.7 g. (34%) of colorless prisms, m.p. 264–267°. Recrystallization from hexane gave a constant melting point of 266–267.5° (lit.,[5] m.p., 267–268°).

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 94.22, 93.97; H, 5.97, 6.02.

The dark, resinous, ethanol-insoluble material (approximately 7.5 g.) could not be crystallized from common solvents and was only slightly soluble in dimethylformamide and dimethyl sulfoxide. Its infrared spectrum (Nujol mull) was extremely simple, showing bands characteristics of *o*-disubstituted benzene (746), olefin (1624), and both *cis*- and *trans*-1,2-disubstituted olefins (685, 1305, and 968 cm.$^{-1}$).[15,16] Oxidation of a 1.1-g. sample of the resin with excess potassium permanganate led to the formation of phthalic acid (1.4 g.).

Reduction of I.—A solution of 1.0 g. of I in dimethylformamide was hydrogenated over palladium. After the catalyst was removed by filtration, the colorless product was isolated by precipitation with water. Repeated recrystallization from benzene gave 0.72 g. of 1,2,5,6,9,10,13,14-tetrabenzocyclohexadeca-1,5,9,13-tetraene (VI), m.p. 204–205° (lit.,[5] m.p. 205°). This material was identical in all respects (mixture melting point, ultraviolet and infrared spectra) to an authentic sample of VI.

Acknowledgment.—This study was supported by grants from the National Science Foundation (G-11280) and the Atomic Energy Commission [Contract AT(30-1)2274]. We are indebted to Professor E. D. Bergmann for a generous sample of the tetraene VI.

Synthesis of 1,3,5-Hexatriene

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A new and convenient synthesis of 1,3,5-hexatriene is described.

1,3,5-Hexatriene (I) has been previously synthesized *via* the pyrolysis of the diformate ester of 1,5-hexadien-3,4-diol,[4] condensation of allyl chloride with sodamide,[5] dehydration of 1,5-hexadien-3-ol with phthalic anhydride,[6] debromination of 3,4-dibromo-1,5-hexadiene,[7] and the vapor phase dehydration of 1,3-hexadien-5-ol[8,9] and 2,4-hexadien-1-ol.[10] Kiun-Houo[11] attempted to synthesize I by vapor phase dehydration of 1,5-hexadien-3-ol but obtained only resins. Prevost and Bidon[12] dehydrated 1,4-hexadien-3-ol in an attempt to synthesize I but obtained 1,3-cyclohexadiene. In most cases the yields were low and the purity questionable. In other cases the sample was purified[4,8] but no spectroscopically pure material was isolated.

Recently, Hwa, de Benneville, and Sims[13] prepared I by the quaternization of isomeric bromohexadienes followed by Hofmann elimination. This work gave two hydrocarbon fractions which were identified as *cis* and *trans* isomers of I. This was the first authentic sample of the *cis* isomer of I to be isolated.

We have synthesized I from easily available starting materials, *via* a four-step reaction, involving the synthesis of 4-hexen-1-yn-3-ol (II) from sodium acetylide and crotonaldehyde. Reduction of the en-yn-ol to the corresponding 1,4-hexadien-3-ol (III) and vapor phase dehydration over alumina gave I in an over-all yield of *ca.* 60%, *i.e.*

$$\mathrm{Na{-}C{\equiv}CH + CH_3{-}CH{=}CH{-}CHO \xrightarrow[-80^\circ]{NH_3} CH_3{-}CH{=}CH{-}CHONa{-}C{\equiv}CH} \qquad (1)$$

$$\mathrm{CH_3{-}CH{=}CH{-}CHONa{-}C{\equiv}CH + NH_4Cl \longrightarrow \underset{(II)}{CH_3{-}CH{=}CH{-}CHOH{-}C{\equiv}CH} + NaCl + NH_3} \qquad (2)$$

$$\mathrm{CH_3{-}CH{=}CH{-}CHOH{-}C{\equiv}CH + H_2 \xrightarrow{Pd} \underset{(III)}{CH_3{-}CH{=}CH{-}CHOH{-}CH{=}CH_2}} \qquad (3)$$

$$\mathrm{CH_3{-}CH{=}CH{-}CHOH{-}CH{=}CH_2 \xrightarrow[300^\circ]{alumina} \underset{(I)}{CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2} + H_2O} \qquad (4)$$

Compound I was purified by crystallization from methanol. It had a freezing temperature of −8.46°. The calculated purity was 98.8% based upon an estimated freezing temperature for pure I of −8.06° (method of Taylor and Rossini[14]). A cryoscopic constant of 2.9 mole per cent/degree and cyclohexene as an impurity were used in obtaining this

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