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The Synthesis of Benzannelated Annulenes. Dibenzo-tetrakisdehydro[18]annulene, and Tribenzo-bisdehydro[14]annulene

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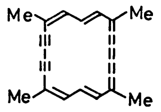
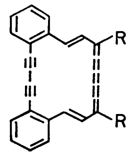
In order to establish the effect of the annelation of benzene rings on $[4n+2]$annulenes, the syntheses of benzannelated dehydroannulenes were attempted. Dibenzo-tetrakisdehydro[18]annulenes (IIa and IIb) were prepared according to the reaction sequence developed in the synthesis of tetramethyltetrakisdehydro-[18]annulene (I) from *o*-ethynylbenzaldehyde (VIII); both of them proved to be unstable. Tribenzo-bisdehydro[14]annulene (XVII) was also prepared from VIII by a double Wittig reaction, followed by oxidative coupling. An examination of the NMR spectrum indicated that XVII is atropic.

The effect on the ring current of diatropic macrocyclic $(4n+2)\pi$-electron systems produced by the annelation of one or more benzenoid rings seems to be of considerable interest.[1]

In 1968, one of the present authors (J. O.) reported the synthesis of 1,5,10,14-tetramethyl-6,8,15,17-tetrakisdehydro[18]annulene (I).[2] The strong diatropicity observed in I prompted us to synthesize the corresponding dibenzo analogue, 11,16-dimethyldibenzo-[*a*,*g*]-3,5,12,14-tetrakisdehydro[18]annulene (IIa), in order to examine the effect of the annelation of the benzene nuclei on the conjugated eighteen-membered ring system containing formal diacetylene and hexapentaene linkages.[3] To this end, a synthesis of *o*-ethynylbenzaldehyde (VIII) was required. VIII appeared to be a valuable intermediate for the synthesis of other conjugated macrocycles with fused benzene nuclei. Related experiments designed along similar lines have been reported in preliminary form by several workers after the completion of this work.[4]



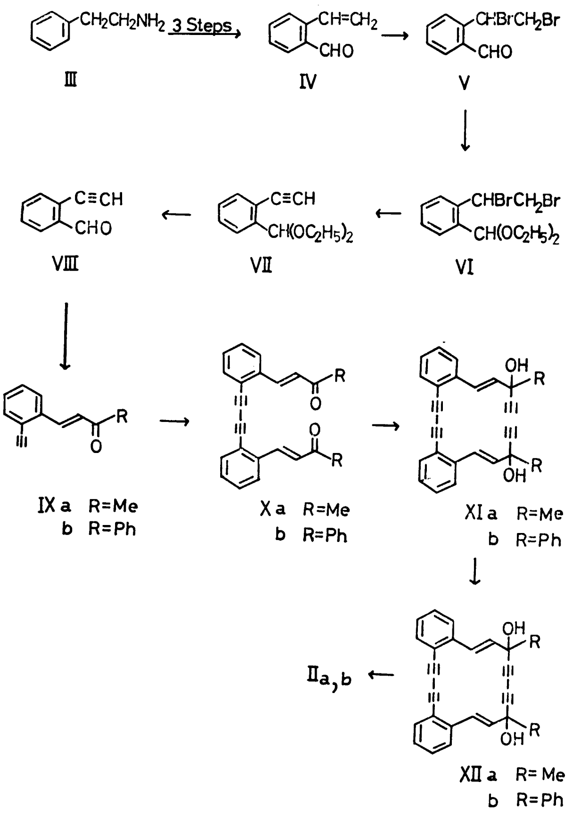
I



IIa R=Me
b R=Ph

Recently, Weavers and Sondheimer have reported the synthesis of benzo-1,3-bisdehydro[14]annulene (XIX) and showed that the fusion of one benzene ring reduces the diatropicity of the 1,3-bisdehydro[14]-annulene series.[41] By the use of *o*-ethynylbenzaldehyde (VIII), we have prepared the corresponding tribenzo analogue, XVII, in order to examine the relative magnitude of the ring current in the "1,3-bisdehydro[14]annulene" system. In this paper, we wish to report the syntheses and properties of 11, 16-dimethyldibenzo[*a*,*g*]-3, 5, 12, 14-tetrakisdehydro[18]annulene (IIa), the diphenyl derivative (IIb), and tribenzo[*a*,*e*,*i*,]-11,13-bisdehydro[14]annulene (XVII).

The key compound, *o*-vinylbenzaldehyde (IV), was prepared from phenethylamine (III) as has been described by Dale *et al.*[5] The reaction of *o*-vinylbenzaldehyde (IV) with a 1 molar equivalent of bromine in carbon tetrachloride gave *o*-(1,2-dibromoethyl)-benzaldehyde (V) in a 74% yield; this substance was converted with triethyl orthoformate into diethyl acetal (VI) in an 88% yield. The dehydrobromination of VI was effected by means of potassium hydroxide in boiling methanol to give *o*-ethynylbenzaldehyde diethyl acetal (VII). VIII was obtained in a good yield after the hydrolysis of the VII with dilute hydrochloric acid. The over all yield of VIII in the seven-step synthesis from I was *ca.* 20%.



The conversion of VIII to IIa and IIb was performed according to the reaction sequence developed for the synthesis of tetramethyltetrakisdehydro-[18]annulene (I). The condensation of VIII with acetone gave the ketone (IXa) in a 52% yield; the ketone was oxidatively coupled to afford the diketone (Xa) in an 82% yield by the use of copper(II) acetate in a mixture of pyridine and methanol.[6] The reaction of IXa with the lithium acetylide–ethylenediamine complex[7] in tetrahydrofuran gave the glycol (XIa) as a yellow, viscous liquid in a 63% yield. The intramolecular oxidative coupling of XIa was per-

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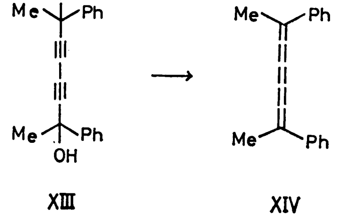
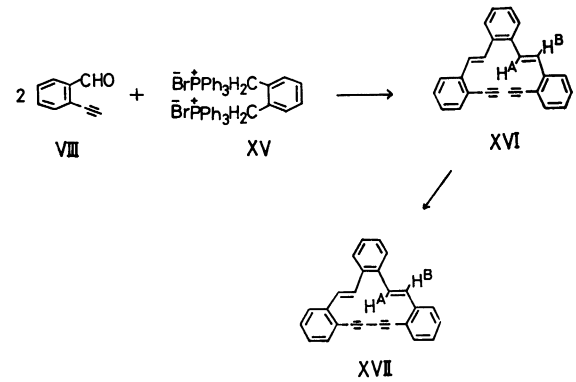
formed under high-dilution conditions, using ether as the entraining agent, by Eglinton's method.[6] The dehydroxylation of cyclic glycol XIIa could be effected by tin(II) chloride in concentrated hydrochloric acid. The rapid color change of the resulting oil seemed to suggest the unstable nature of the dibenzannelated annulene (IIa). The substance could be kept at room temperature in a relatively dilute solution for less than half an hour. As all attempts to obtain IIa in the neat state or in a concentrated solution resulted in decomposition, we were unable to determine the well-defined IR, UV, NMR and mass spectra. The UV spectrum [$\lambda_{max}^{benzene}$ (>300 nm) 350, 418, 437, 510 sh nm] was similar to that of 1,6-dimethyl-1, 6-diphenylhexapentaene (XIV) [$\lambda_{max}^{benzene}$ 352, 419, 443 nm]. Consequently, it seemed that the product obtained was IIa. XIV was prepared from 2,7-diphenyl-3,5-octadiyne-2,7-diol (XIII) on treatment with tin(II) chloride in concentrated hydrochloric acid.[8] Since it was expected that the unstability of IIa might be reduced by the introduction of a substituent group bulkier than a methyl group, the synthesis of the diphenyl derivative was attempted by the same route. The oxidative coupling of IXb gave the diketone, Xb, in a 65% yield. However, as Xb was poorly soluble in usual solvents, XIb could be obtained only in a low yield by the bisethynylation of Xb. Therefore, the conversion of XIb to IIb was performed by using crude products. The IIb thus obtained proved to be as unstable as IIa.

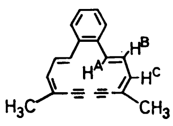


Recently, Weavers and Sondheimer have reported the synthesis of benzobisdehydro[14]annulene (XIX) by the oxidative coupling of the acyclic compound (XVIII), which has been synthesized by a double Wittig reaction between *cis*-3-methyl-2-penten-4-ynal and the salt XV.[41] In order to examine the relative magnitude of the ring current in 1,3-bisdehydro[14]-annulene system, we decided to prepare the corresponding tribenzo analogue of this type, tribenzo[*a*,*e*,*i*]-11,13-bisdehydro[14]annulene (XVII), by using *o*-ethynylbenzaldehyde (VIII) according to the route developed for the synthesis of XIX. The Wittig reaction of 2 molar equivalents of *o*-ethynylbenzaldehyde (VIII) and 1 molar equivalent of α,α′-bis(triphenylphosphonio)-*o*-xylene dibromide[9] (XV) in *N*,*N*-dimethylformamide with ethanolic lithium ethoxide led to a mixture of geometrical isomers which, upon chromatography on alumina, gave the di-*trans* isomer (XVI) in a 16% yield. The oxidative coupling of XVI with copper(II) acetate monohydrate in pyridine afforded the desired XVII in a 33% yield.

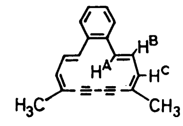
The chemical shifts of the protons of the XVI and XVII thus obtained are summarized in Table 1, along with those of XVIII and XIX reported by Weavers and Sondheimer.[41] As is shown in Table 1, there is not much difference in the NMR spectra between XVI and XVII, particularly on the chemical shift of the inner proton, H^A. That is, the observed chemical shift of H^A of XVII is in the normal region of the olefinic proton. Therefore, it is apparent that XVII is not diatropic, but atropic.



On the other hand, a comparison of the NMR spectra of XVIII and XIX suggests that compound XIX is diatropic, because the H^A resonance has moved to a higher field, and the H^B, H^C, and CH_3 resonances, to a lower field, as compared with the resonances of XVIII.



XVIII



XIX

From these results, it may be concluded that the diatropic nature, which is revealed in the monobenzo-fused compound, XIX, is completely suppressed in the tribenzo-fused compound, XVII.

Table 1. ^{1}H-NMR parameters of XVI, XVII, XVIII, and XIX in $CDCl_3$
(τ-values; TMS as the internal standard)

Proton	XVI[a,c]	XVII[a,d]	XVIII[b]	XIX[b]
H^A	3.42[e]	3.33[e]	3.12	5.01
H^B	f)	f)	2.85	2.56
benzenoid	2.45—3.15	2.37—2.70		
H^C			3.51	2.92
CH_3			8.10	7.64

a) At 60 MHz. b) At 100 MHz. c) In addition, a singlet at 6.70 (-C≡CH). d) The ^{1}H-NMR spectrum of XVII was essentially temperature-independent in the range from −60 °C to 25 °C. e) We assigned the high-field signal to the H^A proton by referring to the chemical shifts of the related compound.[4e,f,h] However, some ambiguity remains because we do not have data definitely supporting this assignment. f) This proton signal is submerged by those of the benzenoid protons.

Experimental

All the melting and boiling points are uncorrected. Brockmann alumina (Act. II—III) was used for column chromatography. The IR and UV spectra were taken on Hitachi EPI-S2 and Hitachi 124 spectrophotometers respectively. The shoulders in the UV spectra are indicated by sh. The NMR and mass spectra were taken on JEOL-C-60A and JEOL-JMS-OI-SG-2 spectrometers respectively. The chemical shifts are given in τ-values with respect to TMS as the internal standard, while the coupling constants are given in Hz.

o-*Vinylbenzaldehyde (IV).* *o*-Vinylbenzaldehyde was prepared by the reported method,[5] with slight modifications.

o-*[1,2-Dibromoethyl]benzaldehyde (V).* Bromine (43.2 g, 0.27 mol) was added, in one portion, to a solution of the aldehyde (IV, 34.1 g, 0.26 mol) in chloroform (280 ml) over a period of 1 h at 0 °C, after which the solution was stirred for a further 3 h at room temperature. After the addition of an aqueous sodium carbonate solution (150 ml) to the cooled mixture, the organic and benzene extracts of the aqueous layer were combined and worked up in the usual way. The dark red liquid thus obtained gave a solid mass of crystals (V, 70.4 g, 74%) on cooling. Recrystallization from light petroleum-benzene afforded pure V as colorless cubes; mp 74.5—75.1°C. IR (KBr disk): 1700 cm^{-1} (CHO), NMR (CCl_4): −0.18 (s, 1H, -CHO), 2.1—2.5 (m, 4H, phenyl H), 3.36 (t, $J=8$, 1H, -CHBr), 5.97 (d, $J=8$, 2H, $-CH_2Br$).

Found: C, 37.17; H, 2.69%. Calcd for $C_9H_8OBr_2$: C, 37.02; H, 2.76%.

o-*Ethynylbenzaldehyde (VIII).* A solution of dibromide (V, 82.6 g, 0.28 mol), triethyl orthoformate (55 g, 0.37 mol), and *p*-toluenesulfonic acid (1.6 g) in absolute ethanol (126 ml) was refluxed for 5 h. After pouring into 3M-aqueous ammonia, the mixture was extracted with ether. The extracts were then washed successively with 3M-aqueous ammonia (2 times) and a saturated sodium chloride solution (3 times), dried over potassium carbonate, and evaporated to give a dark red liquid (VI, 91 g). The liquid shows no IR absorption due to an aldehyde group, but it does show that due to an acetal group, IR (neat): 1100, 1070, 1050 cm^{-1} (C–O–C).

The crude product (VI, 91 g, 0.25 mol) in methanol (35 ml) was stirred into a solution of potassium hydroxide (159 g, 2.83 mol) in boiling methanol (247 ml) for 1 h. Crystals of potassium bromide deposited soon. The mixture was then heated under reflux for an additional 3 h, poured into water (1500 ml), and extracted with ether. The extracts were washed with a saturated sodium chloride solution and dried over potassium carbonate. The dark red liquid after the evaporation of the solvent was distilled under reduced pressure to give ethynyl acetal as a colorless liquid (VII, bp 85—97°C/2 Torr, 26.5 g, 52%); IR (neat): 3350 (-C≡CH), 2150 (-C≡C-), 1100, 1040 cm^{-1} (C-O-C).

The ethynyl acetal (VII, 26.5 g, 0.13 mol) in ether (82 ml) was stirred with 3M-hydrochloric acid (165 ml) at room temperature for 2 h. The organic and ethereal extracts from the aqueous layer were combined and worked up in the usual way. A partly crystallized liquid thus obtained was dissolved in benzene and absorbed on alumina (200 g).

Elution with light petroleum gave VIII (9.3 g, 55%).

Recrystallization from hexane afforded pure VIII as colorless needles; mp 62.5—63.5 °C, IR (KBr disk): 3250(–C≡CH), 2100 (–C≡C–), 1695 cm^{-1} (CHO), UV: $\lambda_{\max}^{\text{EtOH}}$ 250 (8800), 255 (9210), 305 (2370), 314 (2410), NMR ($CDCl_3$): −0.43 (s, 1H, -CHO), 2.0—2.7 (m, 4H, phenyl H), 6.54 (s, 1H, -C≡CH).

Found: C, 82.80; H, 4.58%. Calcd for C_9H_6O: C, 83.06; H, 4.65%.

*4-(*o*-Ethynylphenyl)-1-buten-2-one (IXa).* An ice-cooled mixture of 12% aqueous sodium hydroxide (16 ml) and ethanol (8 ml) was added to a stirred and ice-cooled solution of the aldehyde (VIII, 5.2 g, 0.04 mol) in acetone (5 ml). After being stirred for 90 min at the same temperature, the reaction was quenched with 1M-sulfuric acid (8 ml). A dark red liquid obtained from the ethereal extracts was chromatographed on alumina (200 g) with light petroleum–ether (8:2) to afford a pale yellow liquid (IXa, 3.5 g, 52%). Crystallization from hexane gave pure IXa as yellow plates; mp 64—65°C,[10] Mass: *m/e* 170 (M$^+$, 35%), 120 (base); mol. wt, 170.20, IR (KBr disk): 3250 (–C≡CH), 2100 (–C≡C–), 1700, 1615, 1595 (C=O, C=C), 990, 970 cm^{-1} (*trans* C=C), UV: $\lambda_{\max}^{\text{EtOH}}$ 230 sh (14400), 242 (17700), 247 (16200), 291 (13800), NMR ($CDCl_3$): 2.02 (d, $J=16$, 1H, olefinic H), 2.3—2.8 (m, 4H, phenyl H), 3.33 (d, $J=16$, 1H, olefinic H), 6.57 (s, 1H, –C≡CH), 7.59 (s, 3H, Me).

Found: C, 84.77; H, 6.21%. Calcd for $C_{21}H_{10}O$: C, 84.68; H, 5.92%.

*1,4-Bis[*o*-(3-oxo-1-butenyl)phenyl]-1,3-butadiyne (Xa).* A solution of the ketone (IXa, 8.4 g, 0.049 mol) in methanol (126 ml) and pyridine (210 ml) was stirred, drop by drop over a 2 h period at room temperature, into a solution of copper(II) acetate monohydrate (19 g, 0.095 mol) in methanol (660 ml) and pyridine (660 ml). The mixture was then stirred for an additional 3 h at the same temperature, concentrated under reduced pressure to a quarter volume, poured into 2M-sulfuric acid (1800 ml), and extracted with ether. The ethereal extracts were washed successively with water, aqueous sodium hydrogencarbonate, and saturated sodium chloride solutions, and dried over sodium sulfate. The dark red liquid obtained by evaporating the solvent was chromatographed on alumina (100 g) with benzene to give Xa (6.82 g, 82%). Recrystallization from methanol gave pure Xa as yellow needles; mp 144.0—145.5°C, IR (KBr disk): 2200 (–C≡C–), 1670—1630 (triplet, C=O), 995, 975 cm^{-1} (*trans* C=C), NMR ($CDCl_3$): 1.92 (d, $J=16$, 2H, olefinic H), 2.15—2.65 (m, 8H, phenyl H), 3.16 (d, $J=16$, 2H, olefinic H), 7.56 (s, 6H, Me).

Found: C, 84.93; H, 5.21%. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36%.

*1,4-Bis[*o*-(3-hydroxy-3-methyl-1-penten-4-ynyl)phenyl]-1,3-butadiyne (XIa).* To a mixture of the lithium acetylide-ethylenediamine complex (14.1 g, 0.153 mol) and tetrahydrofuran (500 ml) saturated with acetylene we added a solution of the diketone (IXa, 24.1 g, 0.14 mol) in the same solvent (150 ml) for 5 hr at 35°C under stirring and bubbling with acetylene. After the reaction mixture had been stirred vigorously for an additional 2 h under the slow introduction of acetylene, a cold saturated sodium chloride solution (200 ml) was added to the cooled reaction mixture. The organic layer, combined with ethereal extracts, was washed successively with 2M-hydrochloric acid, aqueous sodium hydrogencarbonate, and saturated sodium chloride solutions, and dried over sodium sulfate. After the solvents had been removed under reduced pressure, a dark red liquid thus obtained was chromatographed on alumina (500 g) with benzene–ether to give XIa (17.4 g, 63%) as a yellow liquid. All attempts to crystallize the liquid failed; the IR (neat) (3300 (–OH), 3250 (–C≡CH), 2200, 2100 (–C≡C–), 965 cm^{-1} (*trans* C=C)) and the NMR ($CDCl_3$) (2.5—3.0 (m, 8H, phenyl H), 3.04 (d, $J=16$, 2H, olefinic H), 3.87 (d, $J=16$, 2H, olefinic H), 6.8 (broad s, 2H, -OH), 7.42 (s, 2H, –C≡CH), 8.37 (s, 6H, Me)) were found to be in accord with the structure of XIa.

1,6-Dimethyl-9,10 : 15,16-dibenzocyclooctadeca-7,17-diene-2,4,11, *13-tetrayne-1,6-diol (XIIa).* A high-dilution apparatus was used in this experiment. A solution of the acyclic glycol (XIa, 4.66 g, 0.012 mol) in ether (60 ml), methanol (72 ml), and pyridine (290 ml) was stirred, over a 15-h period, into a refluxing mixture of copper(II) acetate monohydrate (13.1 g, 0.066 mol) in ether (300 ml), methanol (360 ml) and pyridine (1400 ml). The reaction mixture was refluxed for an additional 1 h, concentrated to 300 ml under reduced pressure, and then poured into 2M-hydrochloric acid (1800 ml). The ethereal extracts from the aqueous layer were worked up in the usual way. The dark red liquid thus obtained was chromatographed on alumina (700 g) with ether-ethyl acetate to give XIIa (1.54 g, 33%). Recrystallization from acetone yielded pure XIIa as pale yellow plates; mp 160°C (dec). Although a satisfactory elemental analysis is not obtained, the IR (KBr disk) (3350 (-OH), 2200, 2140 (-C≡C-), 1595 (C=C), 965 cm^{-1} (*trans* C=C)), the NMR (DMSO-d_6) (2.65 (d, J=16.5, 2H, olefinic H), 2.05—2.75 (m, 8H, phenyl H), 3.48 (d, J=16.5, 2H, olefinic H), 6.40 (broad s, 2H, -OH), 8.40 (s, 6H, Me), and the mass (*m/e* 388 (M$^+$); mol. wt., 388.4) were found to be consistent with the assigned structure.

11,16-Dimethyldibenzo[a,g]*-3,5,12,14-tetrakisdehydro*[*18*]*annulene (IIa).* Into a suspension of cyclic glycol (XIIa, 550 mg, 1.4×10^{-3} mol) in pentane (20 ml) benzene (10 ml), we stirred at room temperatuer a solution of tin(II) chloride dihydrate (730 mg, 3.2×10^{-3} mol) in concentrated hydrochloric acid (8 ml). After 10 min, benzene (30 ml) was added in 5-ml portions for 15 min. The reddish reaction mixture was then poured into water (100 ml), and the layers were separated. The organic layer and ethereal extracts were combined, washed successively with water, aqueous sodium hydrogencarbonate and saturated sodium chloride solutions, dried over sodium sulfate, and evaporated under reduced pressure. The residue was chromatographed on alumina with light petroleum-benzene to give a reddish fraction which was concentrated to one-third its original volume. After the addition of benzene, this fraction was subjected to UV measurement. UV: $\lambda_{\max}^{\text{benzene}}$ (>300 nm) 350 (relative optical density, 0.50), 418 (0.93), 437 (1.00), 510 sh nm. The further concentration of this eluent gave yellow substances which were insoluble in benzene.

3-(o*-Ethynylphenyl)-1-phenyl-2-propen-1-one (IXb).* To a stirred and ice-cooled solution of the aldehyde (VIII, 2.5 g, 0.019 mol) in ethanol (13 ml), we added, drop by drop, a 40% aqueous potassium hydroxide solution (10 ml) and acetophenone (2.3 g, 0.019 mol) simultaneously over a 15-min period; then the mixture was stirred for a further 3 h at room temperature. The reaction mixture was then poured into 3M-hydrochloric acid (100 ml) and extracted with ether. The ethereal extracts were worked up in the usual way. The dark red liquid thus obtained was chromatographed on alumina (200 g) with light petroleum-ether (8:2) to give Xb (1.1 g, 25%). Recrystallization from cyclohexane gave pure Xb as pale yellow cubes; mp 55.0—55.5°C, IR (KBr disk): 3300 (-C≡CH), 2100 (-C≡C-), 1660 (C=O), 1605, 1600 (C=C), 1020, 985 cm^{-1} (*trans* C=C), UV: $\lambda_{\max}^{\text{EtOH}}$ 249 (16300), 254 (16800), 308 (18200), NMR (CDCl$_3$): 1.57 (d, J=17, 1H, olefinic H), 1.8—2.6 (m, 10H, phenyl and olefinic H), 6.33 (s, 1H, -C≡CH), Mass: *m/e* 232 (M$^+$, 45%), 203 (base); mol. wt., 232.27.

Found: C, 87.72; H, 5.28%. Calcd for $C_{17}H_{12}O$:C, 87.90; H, 5.21%.

1,4-Bis[o*-(2-benzoylvinyl)phenyl*]*-1,3-butadiyne (Xb).* A solution of the ketone (IXb, 4.7 g, 0.021 mol) in methanol (19 ml) and pyridine (19 ml) was stirred, over a period of 30 min at room temperature, into a solution of copper(II) acetate monohydrate (12.2 g, 0.06 mol) in methanol (77 ml) and pyridine (77 ml), and then the mixture was stirred for a further 3 h at the same temperature. The reaction mixture was then poured into 3M-hydrochloric acid (600 ml). The resulting solids (Xb, 3.0 g, 65%) were collected on a filter and washed with water (300 ml). Recrystallization from benzene gave an analytical specimen; mp 192—194°C, IR (KBr disk): 1660 (C=O), 1600—1580 (triplet, C=C), 1010, 990 cm^{-1} (*trans* C=C), UV: $\lambda_{\max}^{\text{THF}}$ 267 (28700), 290 (21600), NMR (AsCl$_3$): 1.62 (d, J=16, 2H, olefinic H), 1.8—2.8 (m, 20H, phenyl and olefinic H), Mass: *m/e* 463 (M$^+$, 75%), 357 (base); mol. wt., 462.52.

Found: C, 88.26; H, 4.80%. Calcd for $C_{34}H_{22}O_2$: C, 88.29; H, 4.79%.

11,16-Diphenyldibenzo[a,g]*-3,5,12,14-tetrakisdehydro*[*18*]*annulene (IIb).* This experiment was carried out by almost the same procedure as that used in the preparation of IIa. However, as the Xb diketone was poorly soluble in usual solvents and was, hence, converted to XIb in only a very low yield, the crude products were used for the preparation of IIb as well as XIIb. The UV spectrum of IIb is as follows: $\lambda_{\max}^{\text{benzene}}$ 417 (relative optical density, 1.00), 498 (0.46), 530 (0.48), 550 nm (0.45).

2,7-Diphenyl-3,5-octadiyne-2,7-diol (XIII). XIII was prepared by the ethynylation of acetophenone, followed by oxidative coupling; mp 194—195°C (lit, 194°C)[11] NMR (CDCl$_3$): 2.3—2.8 (m, 10H, phenyl H), 6.69 (broad s, 2H, -OH), 8.15 (s, 6H, Me).

Found: C, 82.61; H, 6.27%. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%.

1,6-Dimethyl-1,6-diphenylhexapentaene (XIV). XIV was prepared like IIa. The UV spectrum of XIV is as follows: $\lambda_{\max}^{\text{benzene}}$ 352 (relative optical density, 0.27), 419 (0.60), 443 nm (1.00).

o*-Bis*[trans*-2-(*o*-ethynylphenyl)vinyl*]*benzene (XVI).*

Lithium ethoxide prepared from lithium (323 mg, 0.046 gatm) in ethanol (120 ml) was stirred, drop by drop under a nitrogen atmosphere at 80—85 °C for 1 h, into *o*-ethynylbenzaldehyde (VIII, 6.0 g, 0.046 mol) and α,α′-bis(triphenylphosphonio)-*o*-xylene dibromide[9] (XV, 18.6 g, 0.023 mol) in dry *N,N*-dimethylformamide (460 ml). After the completion of the addition, the reaction mixture was stirred under a nitrogen atmosphere at 80—85°C for further a 2 h; then it was poured into water (1500 ml) and extracted with ether (500 ml × 3). The ethereal extracts were worked up in the usual way to give a dark red liquid. The liquid was passed through a column of alumina (200 g) with light petroleum to give a mixture of XVI and other geometrical isomers (4.5 g, 59%) as a dark red liquid. Repeated chromatography on alumina (100 g) with light petroleum afforded the *trans-trans* isomer, XVI (1.2 g, 16%). Recrystallization from hexane gave pure XVI as white needles; mp 107—108°C, IR (KBr disk): 3300 (-C≡CH), 2120 (-C≡C-), 1615, 1600 (C=C), 945 cm^{-1} (*trans* C=C), UV: $\lambda_{\max}^{\text{THF}}$ 259 (26500), 315 (20500), mass: *m/e* 330 (M$^+$, 100%); mol. wt., 330.40, NMR (CDCl$_3$): 3.42 (d, J=14.5, 2H, H_A) 2.45—3.15 (m, 14H, phenyl and H), and see Table 1.

The elementary analyses of XVI always afforded low values of carbon, but the spectral properties clearly support the structure of XVI.

Tribenzo[a,e,i]*-11,13-bisdehydro*[*14*]*annulene (XVII).*

A solution of XVI (2.0 g, 0.006 mol) in pyridine (45 ml) was stirred, drop by drop over a 20 min period, into a solution of copper(II) acetate monohydrate (18 g) in pyridine (60 ml) kept at 50 °C; the mixture was then stirred for a further 2 h at 60—65 °C. Then the mixture was chilled, diluted with benzene (200 ml), and poured into 6% hydrochloric acid (1000 ml). The layers were separated, and the aqueous layer was extracted with ether (150 ml×2). The organic and ethereal extracts were combined, washed successively with aqueous sodium hydrogencarbonate and saturated sodium chloride solutions, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on alumina (200 g) with light petroleum-ether (8:2) to give XVII (650 mg, 33%). Recrystallization from hexaene-benzene gave pure XVII as colorless cubes; mp 202—203°C, IR (KBr disk): 2200 (-C≡C-), 950 cm^{-1} (*trans* C=C), UV: $\lambda_{\max}^{\text{THF}}$ 237 (24800), 256 (21400), 291 (34700), 330 (22800), 356 (11300), mass: *m/e* 328 (M$^+$, 100%); mol wt, 328.39, NMR (CDCl$_3$): 3.33 (d, J=14.5, 2H, H$^{\text{A}}$), 2.3—2.7 (m, 14H, phenyl and H$^{\text{A}}$), and see Table 1.

Found: C, 95.25; H, 5.01%. Calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91%.

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References

1) K. Endo, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, **1970**, 2557; *Bull. Chem. Soc. Jpn.*, **44**, 2465 (1971).

2) J. Ojima, T. Katakami, G. Nakaminami, and M. Nakagawa, *Tetrahedron Lett.*, **1968**, 1115; *Bull. Chem. Soc. Jpn.*, **49**, 292 (1976).

3) For a preliminary report, see J. Ojima, T. Yokomachi, and T. Yokoyama, *Chem. Lett.*, **1972**, 633.

4) a) M. Iyoda, M. Morigaki, and M. Nakagawa, *Tetrahedron Lett.*, **1974**, 817, 3677; b) A. Yasuhara, T. Satake, M. Iyoda, and M. Nakagawa, *ibid.*, **1975**, 895; c) M. Iyoda and M. Nakagawa, *Chem. Lett.*, **1975**, 815; d) A. Yasuhara, M. Iyoda, T. Satake, and M. Nakagawa, *Tetrahedron Lett.*, **1975**, 3931; e) J. Ojima, Y. Yokoyama, and T. Yokoyama, *Chem. Lett.*, **1974**, 1261; f) J. Ojima, A. Kimura, and T. Yokoyama, *ibid.*, **1975**, 207; g) R. T. Weavers, R. R. Jones, and F. Sondheimer, *Tetrahedron Lett.*, **1975**, 1043; h) J. Ojima, M. Ishiyama, A. Kimura, and Y. Yokoyama, *ibid.*, **1975**, 1909; i) R. T. Weavers and F. Sondheimer, *Angew. Chem. Int. Ed. Engl.*, **13**, 141 (1974).

5) W. J. Dale, L. Starr, and C. W. Strobel, *J. Org. Chem.*, **26**, 2225 (1961).

6) G. Eglinton and A. R. Galbraith, *Chem. Ind.*, **1956**, 737; *J. Chem. Soc.*, **1959**, 889.

7) D. F. Beumel, Jr., and R. F. Harris, *J. Org. Chem.*, **28**, 2775 (1963); *ibid.*, **29**, 1872 (1964).

8) R. Kuhn and H. Krauch, *Chem. Ber.*, **88**, 309 (1955); F. Bohlmann and K. Kieslich, *ibid.*, **88**, 1211 (1955).

9) C. E. Griffin, K. R. Martin, and B. E. Douglas, *J. Org. Chem.*, **27**, 1627 (1962); C. E. Griffin and J. A. Peters, *ibid.*, **28**, 1715 (1963).

10) The melting point of IXa given in the preliminary report (Ref. 3) was erroneous.

11) J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, **1954**, 44.