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The Synthesis of Benzannelated Annulenes. Tribenzo[*a*,*g*,*m*]-15,17-bisdehydro[18]annulene, and Bis[dibenzo[1,2:9,10]-11,13-bisdehydro[14]annuleno][5,6-*a*:5′,6′-*d*]benzene[1]

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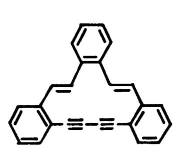
The Wittig reaction between *o*-ethynylcinnamaldehyde (II) and α,α′-bis(triphenylphosphonio)-*o*-xylene dibromide (III) gave the corresponding acyclic compound (IV and V) in a good yield, while that between *o*-ethynylbenzaldehyde (VII) and α,α′,α″,α‴-tetrakis(triphenylphosphonio)durene tetrabromide (VIII) similarly afforded an acyclic compound (IX) in a moderate yield. The title compounds, VI and X, were obtained by the oxidative coupling of V (or, IV and V) and IX, respectively. The examination of the NMR spectra indicated that VI and tribenzo-fused, fourteen-membered periphery on the sides of the benzene nucleus of X are atropic.

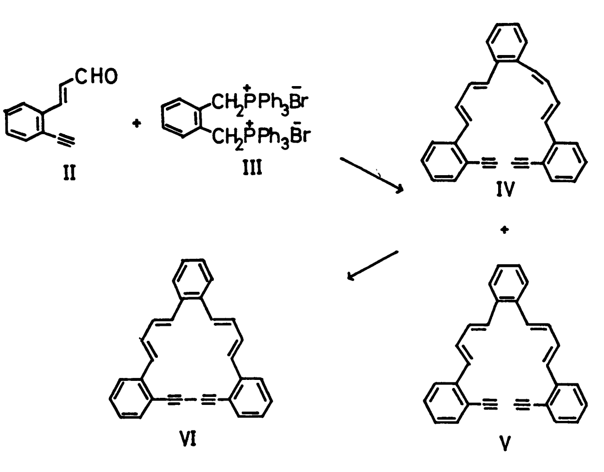
The Wittig reaction has been used to synthesize many unsaturated cyclic compounds.[2]



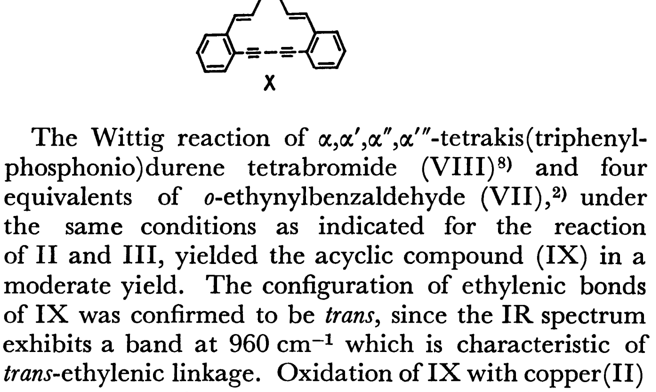
I

In the previous work, we reported the preparation of the tribenzo[*a*,*e*,*i*]-11,13-bisdehydro[14]annulene (I) from the *o*-ethynylbenzaldehyde (VII) by the Wittig reaction with α,α′-bis(triphenylphosphonio)-*o*-xylene dibromide (III) followed by the oxidative coupling.[3] In connection with our works on benzo-fused annulenes,[4] the present paper deals with syntheses of a higher vinylogue of I, *i.e.*, tribenzo[*a*,*g*,*m*]-15,17-bisdehydro[18]annulene (VI), and bis[dibenzo[1,2:9,10]-11,13-bisdehydro[14]annuleno][5,6-*a*:5′,6′-*d*]benzene (X), formally derived from I by the fusion of the second benzannelated fourteen-membered ring system on the opposite side of one benzene nucleus.

The preparation of VI and X was carried out according to the same procedure as used in that of I.



The double Wittig reaction of 2 molar equivalents of *o*-ethynylcinnamaldehyde (II)[5] and 1 molar equivalent of α,α′-bis(triphenylphosphonio)-*o*-xylene dibromide (III)[6] in *N*,*N*-dimethylformamide with ethanolic lithium ethoxide at 80 °C afforded an acyclic stereoisomeric mixture in a 53% yield, which, upon chromatography on alumina, yielded the *cis-trans* isomer (IV) and the *trans-trans* isomer (V) in a ratio of *ca.* 1 : 1. The structure of IV was assigned to the compound based on the following evidence. The two signals due to acetylenic protons were observed in the NMR spectrum of IV, whereas only one signal was observed in that of V (Table 1). In addition, the longest wavelength maximum of IV in the electronic spectrum appeared at a lower wave length than that of V (Experimental). Furthermore, the IR spectrum of IV exhibited a band at 660 cm^{-1} which is characteristic of *cis*-ethylene linkage. The oxidation with copper(II) acetate in pyridine[7] gave the desired VI in a 34% yield. The Dreiding molecular model of VI suggested that VI should be an almost strainless molecule.



The Wittig reaction of α,α′,α″,α‴-tetrakis(triphenylphosphonio)durene tetrabromide (VIII)[8] and four equivalents of *o*-ethynylbenzaldehyde (VII),[2] under the same conditions as indicated for the reaction of II and III, yielded the acyclic compound (IX) in a moderate yield. The configuration of ethylenic bonds of IX was confirmed to be *trans*, since the IR spectrum exhibits a band at 960 cm^{-1} which is characteristic of *trans*-ethylenic linkage. Oxidation of IX with copper(II) acetate in pyridine[7] gave X in a 16% yield, together with an unidentified substance. Under the oxidation conditions employed, it seems likely that the IX also provides the alternative product, XI, arising from the coupling of 2-(*o*-ethynylphenyl)vinyl moieties at 1

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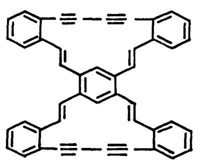
and 3 positions of the central benzene nucleus of IX. However, inspection by the use of the molecular model revealed that this possibility is presumably precluded, since the molecular model corresponding to the structure of X can be constructed more readily, as compared with that for XI, which can be done only with difficulty. Thus, the structure of X rather than XI was assigned to the oxidation product from IX, although the available spectral properties, such as NMR, UV, and IR, did not give a sufficient reason for such an assignment.



XI

Table 1. ^{1}H-NMR DATA OF IV—VI AND IX—X IN $CDCl_3$ AT 100 MHz
(τ-values, TMS as an internal standard)

	IV	V	VI[a)]	IX	X
Olefinic and Phenyl H	2.25—3.42	2.20—3.05	2.31—3.29	2.10—2.84	2.14—3.76
-C≡CH	6.65 6.67	6.64		6.73	

a) The NMR spectra of VI were found to be essentially temperature independent over the range from −60 to 25 °C.

The chemical shifts on the protons of the obtained compounds IV—VI and IX—X are given in Table 1. The signals due to olefinic protons could not be located precisely, because the signals due to phenyl protons were also observed in almost the same region as those of olefinic protons. Consequently, it is difficult to compare the chemical shifts between each proton of the acyclic compound (IV and V) and the corresponding proton of the cyclic one (VI). The same is true for the comparison of the NMR spectra between IX and X. However, the chemical shifts of all protons of VI and X are in the normal region. Therefore, it appears from this result that VI and tribenzo-fused, fourteen-membered periphery on both sides of the central benzene nucleus of X are atropic.

Experimental

All the melting points are uncorrected. Brockmann alumina (Act. II—III) was used for column chromatography. The IR and UV spectra were taken on a Hitachi EPI-S2 and a Hitachi 124 spectrophotometer respectively. Shoulders in the UV spectra are indicated by sh. The NMR spectra were recorded on a Varian XL-100 spectrometer. The mass spectra were measured using a JEOL-JMS-OI-SG-2 spectrometer operating at 75 eV.

The Isomeric o-*Bis[4-(*o*-ethynylphenyl)-1,3-butadienyl] benzene (IV) and (V).* Lithium ethoxide prepared from lithium (224 mg, 0.032 gatm) in ethanol (84 ml) was added drop by drop with stirring under a nitrogen atmosphere at 80—85°C over a period of 1 h to *o*-ethynylcinnamaldehyde (II, 5.0 g, 0.032 mol)[5)] and α,α′-bis(triphenylphosphonio)-*o*-xylene dibromide (III, 12.9 g, 0.0165 mol)[6)] in dry *N,N*-dimethylformamide (320 ml). After completion of the addition, the reaction mixture was stirred under a nitrogen atmosphere at the same temperature for 2 more hours; then it was poured into water (1000 ml) and extracted with ether (300 ml × 3). The ethereal extracts were washed successively with dilute hydrochloric acid, sodium hydrogencarbonate, and saturated sodium chloride solutions, and dried over sodium sulfate. After the solvent had been evaporated, the residual dark red liquid obtained was chromatographed on alumina (100 g) with light petroleum–ether (92: 8—96: 4) to give a mixture of acyclic isomers as a partly crystallized liquid (3.2 g, 53%). The mixture was dissolved in ether and absorbed on alumina (75 g). Careful elution with solvents with increasing polarity resulted in the separation of stereoisomers. Fractions eluted with light petroleum–ether (97: 3) yielded *cis-trans* isomer, IV. Recrystallization from hexane–benzene gave pure IV as pale yellow cubes: mp 149.5—150.5 °C; IR (KBr disk): 3250 (–C≡CH), 2100 (–C≡C–), 990, 970, 950 (*trans* C=C), 660 cm^{-1} (*cis* C=C); UV: $\lambda_{\max}^{\mathrm{THF}}$ 250 (28000), 260 sh (27200), 268 (23200), 287 sh (26100), 310 sh (38600), 325 (44000), 354 nm (53600); Mass: *m/e* 382 (M$^+$, 10), 253 (100); mol wt, 382.5; NMR: see Table 1.

Found: C, 93.93; H, 5.77%. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80%.

The following fractions eluted with light petroleum–ether (96: 4—95: 5) gave *trans-trans* isomer, V. Recrystallization from hexane–benzene afforded pure V as yellow cubes: mp 185 °C (dec); IR (KBr disk): 3280 (–C≡CH), 2100 (–C≡C–), 975 cm^{-1} (*trans* C=C); UV; $\lambda_{\max}^{\mathrm{THF}}$ 260 (28700), 269 sh (25300), 314 sh (51500), 325 (56000), 364 nm (54100); Mass: *m/e* (M$^+$, 25), 253 (100); mol wt, 382.5; NMR: see Table 1.

Found: C, 94.03; H, 6.06%. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80%.

Tribenzo[a,g,m]*-15,17-bisdehydro[18]annulene (VI).* A solution of V (0.6 g, 0.0016 mol) dissolved in pyridine (13 ml) was added dropwise to a vigorously stirred solution of copper(II) acetate monohydrate (4.9 g) in pyridine (16 ml) for 45 min at 50 °C, and the reaction mixture was stirred for an additional 2 h at 60—65 °C. The mixture, after had been chilled to room temperature and diluted with benzene (300 ml), was filtered through Hyflo Super-Cel,[9)] and the resulting precipitate was further washed with benzene (100 ml × 2). Then the filtrate was washed with 5% hydrochloric acid until it was acid to litmus, and then with a saturated sodium chloride solution, and dried over sodium sulfate. The dark red liquid obtained after evaporation of the solvent was chromatographed on alumina (130 g) with light petroleum–ether (8: 2) to give VI (0.2 g, 34%). Recrystallization from hexane–benzene afforded pure VI as yellow needles: mp 248 °C (dec); IR (KBr disk): 980 cm^{-1} (*trans* C=C); UV: $\lambda_{\max}^{\mathrm{THF}}$ 275 sh (29700), 292 (42600), 328 (64100), 378 sh nm (14100); Mass *m/e* 380 (M$^+$, 100); mol wt, 380.5; NMR: see Table 1.

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

In a run performed under similar conditions using a mixture of IV and V, VI was obtained in a 23% yield.

*1,2,4,5-Tetra[*trans*-2-(*o*-ethynylphenyl)vinyl]benzene (IX).* Lithium ethoxide prepared from lithium (441 mg, 0.063 gatm) in ethanol (160 ml) was added dropwise, with stirring under a nitrogen atmosphere at 82—85 °C for 2 h, to *o*-ethynylbenzaldehyde (VII, 8.0 g, 0.062 mol) and α,α′,α″,α‴-tetrakis(triphenylphosphonio)durene tetrabromide (VIII, 19.4 g, 0.013 mol) in dry *N,N*-dimethylformamide (634 ml).

After completion of the addition, the reaction mixture was stirred maintaining the same temperature under a nitrogen atmosphere for an additional 2 h; then it was poured into water (1000 ml) and extracted with ether (500 ml × 3). The ethereal extracts were worked up in the usual manner to give a dark red liquid. The liquid was chromatographed on alumina (150 g) with light petroleum–ether (8: 2) to give IX (1.3 g, 17%) as a partly crystallized liquid. Recrystallization from hexane–benzene afforded pure IX as yellow needles: mp 186 °C (dec); Mass: m/e 583 (M^+, 5), 149 (100); mol wt, 582.7; IR (KBr disk): 3300 ($-C\equiv CH$), 2100 ($-C\equiv C-$), 1600 (C=C), 960 cm^{-1} (*trans* C=C); UV: $\lambda_{\max}^{\text{THF}}$ 221 (56800), 240 sh (45000), 254 sh (41000), 344 (60400), 376 sh nm (48700); NMR: see Table 1.

Found: C, 94.29; H, 5.07%. Calcd for $C_{46}H_{30}$: C, 94.81; H, 5.19%.

Bis[dibenzo[1, 2:9, 10]-11, 13-bisdehydro[14]annuleno][5, 6-a: 5′,6′-d]benzene (X). A solution of IX (1.82 g, 0.0031 mol) in pyridine (52 ml) was added dropwise to a stirred solution of copper(II) acetate monohydrate (18.0 g) in pyridine (37 ml) for 25 min at 55 °C, and the reaction mixture was stirred for an additional 3 h at 60—65 °C. Then the mixture was chilled, diluted with benzene (200 ml), and filtered through a Hyflo Super-Cel. The precipitate formed was washed with benzene (100 ml × 3). Then the filtrate was washed with 5% hydrochloric acid until it was acid to litmus, and with saturated sodium chloride solution, and dried over sodium sulfate. The dark red liquid obtained after evaporation of the solvent was chromatographed on alumina (200 g). The fractions eluted with light petroleum–ether (7: 3—6: 4) gave X (0.29 g, 16%) as a partly crystallized liquid. Recrystallization from benzene afforded pure X as yellow cubes: mp 216 °C (dec). Although a satisfactory elemental analysis is not obtained, the Mass (*m/e* 579 (M^+, 57), 576 (100); mol. wt., 578.7), the IR (KBr disk) (2200 ($-C\equiv C-$), 965, 950 cm^{-1} (*trans* C=C)), the UV ($\lambda_{\max}^{\text{THF}}$ 224 (60200), 260 sh (32000), 307 (48400), 324 sh (38300), 352 sh (17200), 393 sh (6150)), and the NMR (see Table 1) were found to be consistent with the assigned structure.

The following fractions with the same solvents afforded crystals (0.15 g) which, on recrystallization from benzene, yielded yellow cubes, mp 206 °C (dec). The structure of the material is not established. Its spectral properties are as follows: Mass: *m/e* 280 (70), 254 (100); IR (KBr disk): 2200, 1635, 1620, 975 cm^{-1}; UV (THF): $\lambda_{\max}$ 228, 281, 296, 354, 376, sh nm; NMR ($CDCl_3$): 1.54[a] (d, $J=16$), 2.44—2.82[b] (m), 3.21[c] (d, $J=16$); The integral ratio of each signal (a, b, and c) is 1: 5: 1.

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9) Hyflo Super-Cel was obtained from Wako Pure Chemicals Co., Ltd.