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Synthesis of Dibenzo[*d,j*]-6,8-bisdehydro-oxa-[13]annulene

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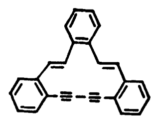
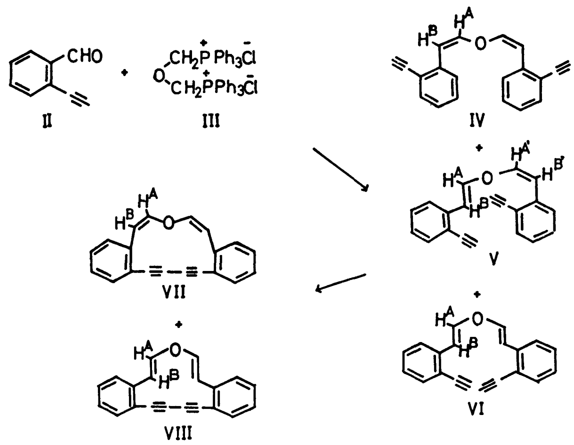
Synopsis. The title compound (VII or VIII) has been synthesized from *o*-ethynylbenzaldehyde (II) by the Wittig reaction with the salt (III) followed by the oxidative coupling. The examination of the NMR spectra suggests that both of VII and VIII are atropic molecules.

In a previous paper, we have reported a synthesis of tribenzo[*a,e,i*]-11,13-bisdehydro[14]annulene (I) by a double Wittig reaction followed by the oxidative coupling starting from *o*-ethynylbenzaldehyde (II).[1] As an extension of our work on benzofused annulenes, we attempted to synthesize a corresponding oxygen analogue, *i.e.*, dibenzo[*d,j*]-6,8-bisdehydro-oxa-[13]annulene according to the same sequence of reactions used in preparation of I.



I

The synthesis of the title compound (VII or VIII) was carried out as follows.



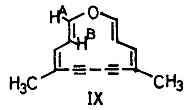
Wittig reaction of II and dimethyl ether-α,α'-bis(triphenylphosphonium chloride) (III)[2] in *N,N*-dimethylformamide by means of ethanolic lithium ethoxide at 80 °C led to, together with the recovered aldehyde, a mixture of acyclic compound in 14% yield from which IV, V, and VI were isolated in a ratio of *ca.* 3: 2: 1, respectively. Configuration of each isomer was confirmed by IR and NMR spectra. Oxidation of the mixture (IV, V, and VI) with copper(II) acetate in pyridine[3] at 60 °C afforded unstable *cis-cis* isomer (VII) and *trans-trans* isomer (VIII) in 6 and 17% yields, respectively.

Wittig reaction between *o*-ethynylcinnamaldehyde[4] and the salt (III) was also attempted to prepare a higher vinylogue of VIII. However, all attempts to obtain the corresponding acyclic compound were unsuccessful in cases using either phenyl lithium in ether or ethanolic lithium ethoxide as a base.[5]

TABLE 1. ^{1}H-NMR DATA OF VII-IX IN $CDCl_3$ (τ-VALUES; INTERNAL STANDARD, TMS; *J* VALUES IN Hz IN PARENTHESES)

	VII[a]	VIII[a]	IX[b]
H^A	3.21d (8)	2.95d (13)	3.87d (13.5)
H^B	3.73d (8)	3.67d (13)[c]	5.09dd (9.5, 13.5)
benzenoid H	1.8—2.4m	2.4—2.7m	

a) At 60 MHz. b) At 100 MHz. c) We assigned the high field signal to H^B proton by reference to the chemical shifts of the related compounds.[7]



IX

The NMR spectral data of the protons of VII and VIII together with those of IX reported by Wife and Sondheimer[7] are summarized in Table 1. The chemical shift of olefinic protons of VII or VIII, particularly of the inner protons, H^B is in normal region. Thus, it is apparent that both of VII and VIII are atropic. Support for this interpretation is given by comparison of the inner H^B proton chemical shift of VII or VIII with that of the closely related annulene IX which was shown to be weakly diatropic (Table 1). The chemical shift of H^B of VII or VIII is at lower field than that of IX.

Experimental

All melting points are not corrected. The alumina used for column chromatography is Brockmann, Act. II—III. The IR and UV spectra were taken on a Hitachi EPI-S2 and a Hitachi 124 spectrophotometers, respectively. Shoulders in UV spectra are indicated by sh. The NMR and mass spectra were taken on JEOL-MH-60 at 60 MHz and JEOL-JMS-OI-SG-2 spectrometers, respectively. The chemical shifts are given in τ-values with respect to TMS as the internal standard, and the coupling constants are given in Hz.

Dimethyl Ether-α,α'-bis(triphenylphosphonium chloride) (III).[2] Triphenylphosphine (52.4 g, 0.2 mol) and α,α'-dichlorodimethyl ether (11.2 g, 0.1 mol)[8] were heated in dry *N,N*-dimethylformamide for 7 h. The mixture was then cooled, the resulting crystals were collected and washed with ether-*N,N*-dimethylformamide. Recrystallization from chloroform and drying *in vacuo* at 80 °C afforded 43.8 g (69%) of III,[2] mp 294—296 °C.

The Isomeric Bis[2-(o-ethylphenyl)vinyl]ether (IV), (V), and (VI). Lithium ethoxide prepared from lithium (0.354 g,

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0.051 g atom) in ethanol (114 ml) was added dropwise with stirring under nitrogen atmosphere at 80 °C for 1 h to *o*-ethynylbenzaldehyde (II, 5.68 g, 0.044 mol) and dimethyl ether-α,α′-bis(triphenylphosphonium chloride) (III, 14.2 g, 0.022 mol) in *N*,*N*-dimethylformamide (437 ml). After completion of addition, the reaction mixture was stirred for further 2 h under an atmosphere of nitrogen at 80—85 °C, and cooled. The mixture was then poured into water (1000 ml) and extracted thoroughly with ether. The ethereal extracts were washed with dilute hydrochloric acid, aqueous sodium hydrogencarbonate and saturated sodium chloride solutions successively, dried over sodium sulfate, and evaporated to give a pale yellow liquid. The oil was dissolved in ether and chromatography on alumina with light petroleum as eluent gave a mixture of acyclic compd (0.82 g, 14, 29% based on consumed II) as an oil from early fractions, Mass: *m/e* 270 (M^+, 25), 160 (100); mol. wt., 270.3. The following fractions eluted with the same solvent afforded the recovered aldehyde (II, 2.98 g). The mixture was again dissolved in ether and absorbed onto alumina (100 g). Careful elution with light petroleum resulted in separation of three isomers. Early fractions gave *cis-cis* isomer (IV) (0.26 g, 4.5%) as an unstable colorless liquid, IR (neat): 3250 (–C≡CH), 2100 (–C≡C–), 1650, 1595 (C=C), 700 cm^{-1} (*cis* C=C), UV (EtOH): λ_{max} 229 sh, 237, 243, 268 sh, 275, 285 sh, 320 sh nm, NMR ($CDCl_3$): 2.4—3.0 (m, 8H, phenyl H), 3.80 (d, *J*=7, 2H, H^A), 4.15 (d, *J*=7, 2H, H^B), 6.73 (s, 2H, –C≡CH). The next material eluted was *cis-trans* isomer (V) (0.163 g, 2.8%) as a colorless oil. IR (neat): 3300 (–C≡CH), 2090 (–C≡C–), 1640, 1595 (C=C), 940 (*trans* C=C), 700 cm^{-1} (*cis* C=C), UV (EtOH): λ_{max} 230 sh, 237, 243, 268 sh, 274, 290 sh, 320 sh nm, NMR ($CDCl_3$): 2.4—3.1 (m, 9H, phenyl H and H^A), 3.77 (d, *J*=13, 1H, H^B), 3.83 (d, *J*=8, 1H, $H^{A'}$), 4.21 (d, *J*=8, 1H, $H^{B'}$), 6.77 (s, 2H, –C≡CH). The last fractions gave *trans-trans* isomer (VI) (0.079 g, 1.34%) as a colorless liquid. IR (neat): 3250 (–C≡CH), 2100 (–C≡C–), 1640, 1600 (C=C), 1000, 940 cm^{-1} (*trans* C=C), UV (EtOH): λ_{max} 230 sh, 237, 243 sh, 273, 290 sh, 320 sh nm, NMR ($CDCl_3$): 2.4—3.1 (m, 10H, phenyl H and H^A), 3.75 (d, *J*=13, 2H, H^B), 6.67 (s, 2H, –C≡CH).

The Isomeric Dibenzo[d,j]*-6,8-bisdehydro-oxa-*[*13*]*annulene (VII), (VIII).* A soln of a mixture of IV, V, and VI (0.6 g, 0.002 mol) in pyridine (15 ml) was added dropwise to a stirred soln of copper(II) acetate monohydrate (5.1 g) in pyridine (20 ml) for 10 min at 50 °C, and the reaction mixture was stirred for further 2 h at 60—65 °C. The precipitate formed on cooling and diluting with benzene (100 ml) was washed with benzene (50 ml×2). Then the filtrate was washed with 6% hydrochloric acid until it was acid to litmus, and saturated sodium chloride solution successively, and dried over sodium sulfate. The residual dark red liquid obtained after evaporation of the solvent was chromatographed on alumina (80 g) with light petroleum as eluent. Early fractions gave *cis-cis* isomer (VII) (35 mg, 6%) as unstable white crystals (mp 104—106 °C) which turned to brownish mixtures when exposed to air and light in neat state, IR (KBr disk): 2100 (–C≡C–), 1640, 1595 (C=C), 705 cm^{-1} (*cis* C=C), UV (EtOH): λ_{max} 248, 264 sh, 275, 308, 328, 355 sh nm, NMR: see Table 1. The following fractions afforded *trans-trans* isomer (VIII) (100 mg, 17%) as relatively stable white needles (from benzene), mp 172 °C (dec), Mass: *m/e* 268 (M^+, 30), 239 (100); mol. wt., 268.3, IR (KBr disk): 2100 (–C≡C–), 1640, 1595 (C=C), 930 cm^{-1} (*trans* C=C), UV (EtOH): λ_{max} (ε) 237 (30800), 258 sh (15500), 277 (20000), 311 (5960), 352 (7250), 353 nm (6790), NMR: see Table 1.

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