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The Benzannelated Annulenones. Syntheses and Properties of 10-Methylbenzo[*d*]- and Dibenzo[*d*,*j*]-6,8-bisdehydro[13]annulenone

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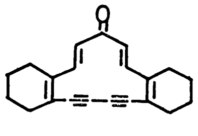
In order to examine the paratropic nature expected for a thirteen-membered ring system arising from polarization of the carbonyl group, the two benzannelated bisdehydro[13]annulenones, VI and IX, were prepared respectively by the aldol condensation of an appropriate aldehyde and an appropriate ketone followed by the oxidative coupling of the resulting acyclic ketone containing terminal acetylene groups. The NMR spectra indicate that both of VI and IX, as well as the respective protonated species, VII and X, are paratropic and paratropicities decrease in the sequence of VI>IX with the increasing number of fused benzene ring. The dibenzannelated annulenone (IX) and its precursor (VIII) were converted into the corresponding alcohols or ethers (XIIa, XIIb and XIa, XIb), respectively, to test the presence of the paratropic nature of IX. The NMR spectra of XIa, XIb and XIIa, XIIb, in addition to those of VIII and IX, suggested that IX seemed to be weakly paratropic. An attempt made to prepare the dibenzannelated bisdehydro[13]annulenyl anion (XIII) was unsuccessful.

A series of fully conjugated monocyclic monoketones (annulenones) are expected to be diatropic or paratropic owing to polarization of a carbonyl group provided they contain a $(4n+3)$-membered ring or $(4n+1)$-membered ring, respectively.1)

In connection with the studies to confirm this prediction Howes *et al.* have reported a simple general approach to bisdehydro[13]- (I), [15]-, and [17]-annulenones in which the carbonyl group is flanked by ethylenic bonds on both sides.2) The method consists in employing an aldol condensation of an appropriate aldehyde and ketone, containing terminal acetylene group, followed an intramolecular oxidative coupling of the resulting acyclic ketone.



I

We have now applied with advantage the method to the synthesis of benzannelated bisdehydro[13]annulenones (VI and IX) by using *o*-ethynylbenzaldehyde (II) as the starting material and essentially by the same approach as that of Howes *et al.* It is now established3) that the annelated benzenoid nuclei such as benzene or naphthalene reduce the diatropic nature of a $(4n+2)$-membered annulene. However, when this work was commenced, little reports had yet appeared concerning the effect of annelation of benzene nuclei on annulenones.4) Some aspect of this work have appeared in the preliminary form.5) In this paper, we present a full account of our investigation on the synthesis and properties of monobenzo and dibenzo analogues of I, *i.e.*, 10-methylbenzo[*d*]- (VI) and dibenzo[*d*,*j*]-6,8-bisdehydro[13]annulenone (IX).

The preparation of VI and IX was carried out as follows. The ketone (III) was obtained by treatment of *o*-ethynylbenzaldehyde (II) with excess acetone in the presence of aqueous sodium hydroxide as previously

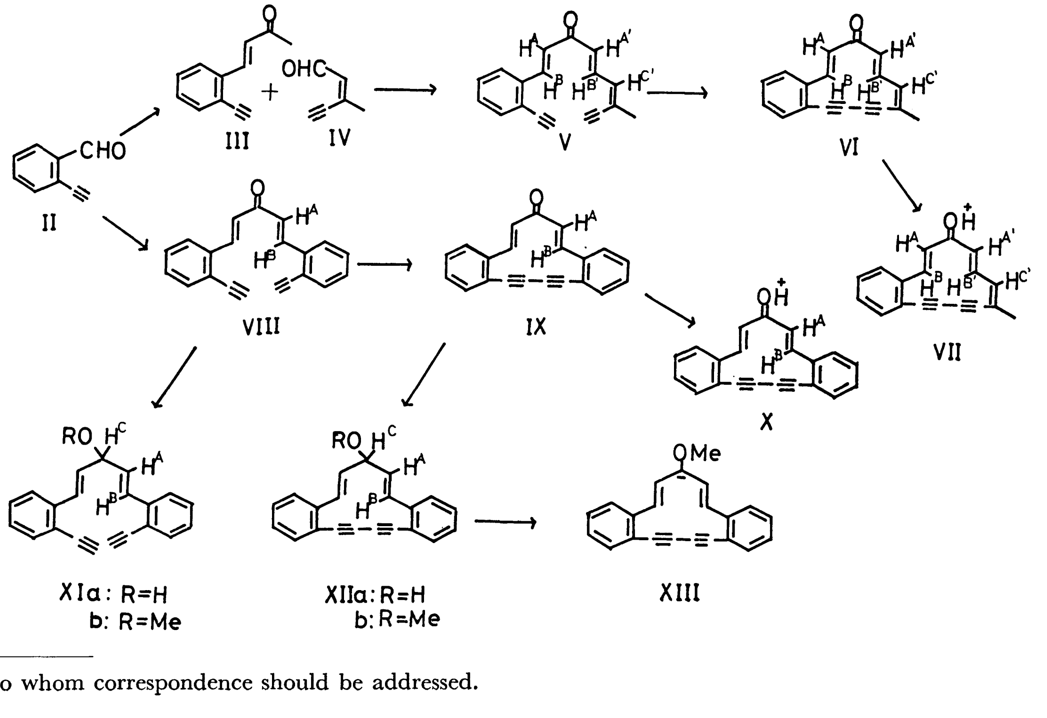


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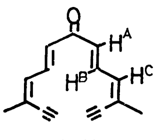
Table 1. ^{1}H-NMR parameters of V, VI, VIII, IX, XIV, and XV in CDCl$_3$ at 60 MHz (τ-values; Internal standard, TMS; *J* values in Hz in parentheses)

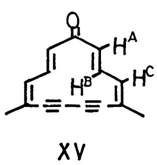
Proton	V[a]	VI	VIII[b]	IX	XIV[b]	XV	ΔVI−V[c]	ΔIX−VIII[c]	ΔXV−XIV[c]
H^A	3.68d(17)[d]	3.90d(16)[e]	2.84d(16)	3.24d(16)	3.55d(16)	3.90d(17)	+0.22	+0.40	+0.35
H^B	1.98d(17)	1.45d(16)	1.82d(16)	1.53d(16)	2.32dd(16,11)	0.61dd(17,10)	−0.53	−0.29	−1.71
H^C	—	—	—	—	3.54d(11)	3.71d(10)	—	—	+0.17
$H^{A'}$	3.42d(17)[d]	3.68d(16)[e]	—	—	—	—	+0.26	—	—
$H^{B'}$	2.13dd(17,11)	1.26dd(16,10)	—	—	—	—	−0.87	—	—
$H^{C'}$	3.32d(11)	3.60d(10)	—	—	—	—	+0.28	—	—
CH_3	8.07s	8.17s	—	—	7.98s	8.26s	+0.10	—	+0.28
Benzenoid H	2.47—3.10m	2.73—2.92m	2.22—2.76m	2.5—2.8m	—	—			

a) In addition, a singlet at 6.87 (–C≡CH). b) In addition, a singlet at 6.54 (–C≡CH). c) This shows the chemical shift differences. d), e) These assignments may be reversed in each group. However, most probable values are given in Table 1 by referring to the chemical shifts of the related compounds.[9]

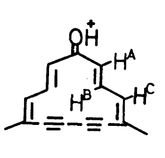
reported.[6] Aldol coupling of III and *cis*-3-methyl-2-penten-4-ynal (IV)[7] by methanolic potassium hydroxide gave the acyclic ketone (V) in a 10% yield, upon chromatographic purification of the product over alumina, as an unstable orange liquid. Both of the aldehyde (IV) and the ketone (V) were unstable at room temperature. Oxidative coupling of V, under Eglinton's conditions using copper(II) acetate in pyridine,[8] gave the cyclic ketone, the desired annulenone (VI), in a 20% yield as relatively stable crystals. While, condensation of 2 molar equivalents of II with 1 molar equivalent of acetone, under the same conditions as indicated for the reaction of III and IV, afforded a 44% yield of the acyclic ketone (VIII). Oxidation of VIII with copper(II) acetate as before, gave the dibenzannelated annulenone (IX) in a 61% yield. The assigned conformations were given to the annulenones (VI) and (IX) in analogy with the compound (I) which was shown to have the conformation based on NMR spectroscopy of dideutrio compound of I.[2] Treatment of VI or IX with trifluoroacetic acid gave the corresponding carbonyl protonated species, VII (dark red; λ_{max} 277 sh, 292, 350 sh, with absorption>700 nm) or X (yellow brown; λ_{max} 285 sh, 301, 348, 413 sh, with absorption>700 nm), respectively.



XIV



XV



XVI

The ^{1}H-NMR parameters of the obtained compounds, V and VI, are listed in Table 1, as well as the chemical shift differences for various resonances on passing from V to VI, indicating the magnitude of the upfield shift of the outer proton signals and the downfield shift of the inner proton signals.

The comparison of the NMR spectra of V and VI (Table 1) reveals the compound VI to be paratropic, as expected for a potential 12π-electron system by the polarization of the carbonyl group, since the inner proton (H^B, $H^{B'}$) resonances of VI have moved to a lower field, the outer (H^A, $H^{A'}$, $H^{C'}$) and methyl proton resonances to a higher field, as compared with those of the corresponding proton of V.

In order to obtain an approximate measure regarding the effect of benzannelation on thirteen-membered ring system, the NMR spectral data of VIII and IX, and the chemical shift differences are also given in Table 1, together with those of XIV and XV which were prepared by Ojima and Sondheimer.[9] The data (Table 1) suggests that IX is also paratropic as VI, because the inner proton (H^B) signal has moved to a lower field, and the outer proton (H^A) signal to a higher field as compared with that of the respective proton of VIII.

As indicated in Table 1, an examination of the NMR spectra demonstrated that the thirteen-membered ring system in dimethyl compound XV is paratropic, in monobenzo-fused compound VI, it is less paratropic, in dibenzo-fused compound IX, it is at most weakly paratropic. This can be seen in particular by the downfield shifts, as compared with the respective models (XV, VI, IX), of the inner proton (H^B, $H^{B'}$) bands [−1.71, (−0.53 and −0.87), −0.29 ppm, respectively],

Table 2. ^{1}H-NMR parameters of XVI, VII, and X in CF$_3$COOD at 60 MHz (τ-values; Internal standard, TMS; *J* values in Hz in parentheses)

	XVI	VII	X	ΔXVI−XIV	ΔVII−V	ΔX−VIII
H^A	3.85 d(16)	3.75[a] d(17)	3.00 d(16)	+0.30	+0.07	+0.16
H^B	−0.79 dd(16,10)	0.65 d(17)	0.98 d(16)	−3.11	−1.33	−0.84
H^C	3.88 d(10)			+0.34		
$H^{A'}$		3.47[a] d(17)			+0.05	
$H^{B'}$		0.19 dd(17,11)			−1.94	
$H^{C'}$		3.42 d(11)			+0.10	
CH_3	8.33s	8.20s		+0.35	+0.13	
Benzenoid H		2.80—2.97m	2.6—2.8m			

a) These assignments may be reversed in this group, as described in Table 1.

Table 3. ^{1}H-NMR parameters of XIa, XIb, XIIa, and XIIb in $CDCl_3$
(τ-values; Internal standard, TMS; J values in Hz in parentheses)

	XIa[a)]	XIb[b)]	XIIa[b)]	XIIb[a)]	ΔIX−VIII	ΔXIIa−XIa	ΔXIIb−XIb
H^{A}	3.87	3.85	4.10	4.23	+0.40	+0.23	+0.38
	dd(16,6)	dd(16,7)	dd(16,6)	dd(17,7)			
H^{B}	3.07	2.95	3.27	3.18	−0.29	+0.20	+0.23
	d(16)	d(16)	d(16)	d(17)			
H^{C}	5.65	6.08	4.91	5.43			
	t (6)	t (7)	t (6)	t (7)			
-OH	7.13		8.10				
	broad s		broad s				
-OMe		6.69 s		6.50 s			
-C≡CH	6.80 s	6.70 s					
Benzenoid H	2.6—2.9 m	2.40—2.85 m	2.50—2.87 m	2.4—2.8 m			

a) At 60 MHz. b) At 100 MHz.

and the chemical shifts [0.61, (1.45 and 1.26), 1.53 τ, respectively].

Furthermore, the result analogous to the above is also obtained by the comparison of the NMR spectra in CF_3COOD (Table 2); the same trend is observed in the downfield shifts and the chemical shifts of the inner proton (H^{B}, H$^{B'}$) bands [−3.11, (−1.94 and −1.33), −0.84 ppm], [−0.79, (0.65 and 0.19), 0.98 τ] of the respective models (XVI, VII, X).[9,10]

As described above, it was concluded that the dibenzannelated [13]annulenone (IX) is paratropic. This conclusion was derived by comparing the chemical shifts of H^{A} and H^{B} protons of IX with those of the acyclic ketone (VIII) which is an atropic compound. However, the chemical shift differences between VIII and IX are so small that we attempted to examine these differences in the corresponding atropic models.[11] Along this line we undertook to prepare the alcohols (XIa, XIIa) and the methyl ethers (XIb, XIIb) which are the corresponding atropic models of VIII and IX.

Reduction of the acyclic ketone (VIII) in ether with sodium borohydride gave a 57% yield of the alcohol (XIa) as a pale yellow liquid. The methylation of XIa with methyl iodide and silver oxide gave fruitless results. However, methylation of XIa could be effected with methy iodide and sodium hydride[12] to afford a 51% yield of the ether (XIb) as a pale yellow liquid. The cyclic ketone (IX) was reduced more readily than the acyclic ketone (VIII) by sodium borohydride to afford alcohol (XIIa) in a 91% yield. Methylation of XIIa with methyl iodide and silver oxide in ether gave a 67% yield of the ether (XIIb) as crystals.

The ^{1}H-NMR data of the compounds thus obtained are given in Table 3, as well as the chemical shift differences. As illustrated in Table 3, we can see the chemical shift differences between XIa and XIIa, or between XIb and XIIb, which are definitely atropic. The chemical shift differences of H^{A} proton between XIa and XIIa, and that between XIb and XIIb, respectively, (+0.23 and +0.38) are smaller than that of H^{A} between VIII and IX (+0.40). Whereas, as for H^{B} proton the reverse is observed (+0.20 and +0.23, −0.29).

This result seems to suggest that the compound IX is weakly paratropic although the differences in chemical shifts of both H^{A} and H^{B} are small.

We have also attempted without success to prepare the dibenzannelated [13]annulenyl anion (XIII) by abstraction of ^{1}H from XIIb with dimsyl sodium in DMSO,[13] as reported by LeGoff and Sondheimer.[14] Under conditions performed, XIIb afforded a deep green solution, however all attempts to obtain a satisfactory NMR spectrum were failed owing to the unstability of the product.

Experimental

Freshly deoxygenated ether, methanol, and acetone were used to minimize an oxidation of the compounds used for aldol condensation. The ether was freed from a peroxide by passing through a short column of basic alumina (Act. I) followed by flushing with nitrogen. The methanol and acetone were flushed by nitrogen. All 20% methanolic potassium hydroxide solutions were prepared by dissolving 10 g of potassium hydroxide in 50 ml of methanol and by flushing the solution with nitrogen immediately prior to use. All the melting points are uncorrected. Brockmann alumina (Act. II—III) was used for column chromatography. The ^{1}H-NMR, IR, UV, and mass spectra were taken using the instruments JEOL-JNM-MH-60 or Varian XL-100, Hitachi EPI-S2, Hitachi-124, and JEOL-MS-OI-SG-2, respectively. Shoulders in UV spectra are denoted by sh.

o-Ethynylbenzaldehyde (II) and 4-(o-Ethynylphenyl)-1-buten-2-one (III). The aldehyde (II) and the ketone (III) were prepared as reported previously.[6]

cis-3-Methyl-2-penten-4-ynal (IV). The aldehyde (IV) was obtained by the reported method.[7]

9-(o-Ethynylphenyl)-3-methyl-3,5,8-nonatrien-1-yn-7-one (V). A mixture of the ketone (III, 3.6 g, 21.2 mmol) and the aldehyde (IV, 2.0 g, 21.3 mmol) in deoxygenated ether (85 ml) was treated with a 20% methanolic potassium hydroxide (3.1 ml). The mixture was further stirred at room temp for 2 h. Neutralization with acetic acid (4.0 ml) followed by addition of water (100 ml), and extraction with ether, and work up in the usual manner gave a dark red liquid. Chromatography of the liquid over alumina (80 g) with light petroleum–ether (8:2) as eluent gave the desired ketone (V, 0.5 g, 10%) as an unstable organge liquid: MS: m/e 246 (M^+, 40), 149 (100); mol wt, 246.29; IR (neat): 3250 (-C≡CH), 2100 (-C≡C-), 1660, 1615, 1600 (C=O, C=C), 980 cm^{-1}

(*trans* C=C); UV: $\lambda_{\max}^{\mathrm{EtOH}}$ 226 (11000), 248 (9230), 321 nm (8830); NMR: see Table 1.

10-Methylbenzo[d]*-6,8-bisdehydro*[*13*]*annulenone (VI).* A soln of V (0.5 g, 2.0 mmol) in pyridine (11 ml) was added dropwise to a stirred soln of copper(II) acetate monohydrate (5.5 g) in pyridine (19 ml) for 10 min at 50—55 °C, and the reaction mixture was stirred for further 2 h at 55—65 °C. The ppt 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 slightly acidic, saturated aq sodium hydrogencarbonate, and sodium chloride solutions 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–ether (7: 3) to afford VI (0.1 g, 20%) as relatively stable solid. Recrystallization from hexane gave pure VI as orange needles: mp *ca.* 160 °C (dec); IR (KBr disk): 2150 (–C≡C–), 1630, 1610, 1590 (C=O, C=C), 980 cm^{-1} (*trans* C=C); UV: $\lambda_{\max}^{\mathrm{EtOH}}$ 236 (9880), 258 (15800), 388 nm (2100); MS: *m/e* 244 (M$^+$, 20), 215 (100); mol wt, 244.28; NMR: see Table 1.

*1,5-Bis(*o*-ethynylphenyl)-1,4-pentadien-3-one (VIII).* To a stirred soln of *o*-ethynylbenzaldehyde (II, 4.0 g, 0.031 mol) and acetone (0.94 g, 0.016 mol) in deoxygenated ether (48 ml) was added a 20% methanolic potassium hydroxide soln (1.5 ml) at 15—16 °C. After stirring for 3 h at the same temp, the reaction was quenched with acetic acid (1.5 ml). A dark red liquid obtained by usual work up of the ethereal extracts was purified by chromatography over alumina (150 g) using light petroleum–ether (95: 5—90: 10) as eluent. The fractions containing VIII were collected and evaporated, yielding the ketone (1.9 g, 44%) as a partly crystalline oil. Crystallization from light petroleum–benzene formed yellow cubes: mp 101.3—101.7 °C; MS: *m/e* 282 (M$^+$, 20), 155 (100); mol wt, 282.32; IR (KBr disk): 3250 (–C≡CH), 2100 (–C≡C–), 1660 (C=O), 1595 (C=C), 985, 965 cm^{-1} (*trans* C=C); UV: $\lambda_{\max}^{\mathrm{EtOH}}$ 250 (24400), 332 nm (24500); NMR: see Table 1.

Found: C, 89.18; H, 4.76%. Calcd for $C_{21}H_{14}O$: C, 89.33; H, 5.00%.

Dibenzo[d,j]*-6,8-bisdehydro*[*13*]*annulenone (IX).* A soln of the ketone (VIII, 1.15 g, 4.07 mmol) dissolved in pyridine (25 ml) was added dropwise to a stirred soln of copper(II) acetate monohydrate (12.0 g) in pyridine (40 ml) for 10 min at 50 °C, and the reaction mixture was stirred for further 3 h at 60—65 °C. The mixture was cooled, diluted with benzene (300 ml), and the resulting mixture was filtered through Hyflo Super-Cel and washed with benzene (100 ml × 2). Work up of the filtrate, as described for the isolation of VI, gave a dark red solid. The solid was chromatographed on alumina (70 g) and the ketone (IX, 0.7 g, 61%) was eluted with light petroleum–ether (9: 1—8: 2). Recrystallization from benzene gave pure IX as yellow cubes: mp 194 °C (dec); MS: *m/e* 280 (M$^+$, 100); mol wt, 280.31; IR (KBr disk): 2150 (–C≡C–), 1640, 1620, 1590 (C=O, C=C), 975 cm^{-1} (*trans* C=C); UV: $\lambda_{\max}^{\mathrm{EtOH}}$ 284 (39000), 298 (46000), 379 sh (3820), 468 sh (1380), NMR: see Table 1.

Found: C, 90.03; H, 4.59%. Calcd for $C_{21}H_{12}O$: C, 89.98; H, 4.32%.

*1,5-Bis(*o*-ethynylphenyl)-1,4-pentadien-3-ol (IXa).* To a stirred soln of the ketone (VIII, 3.5 g, 0.012 mol) in dry ether (300 ml) was added a soln of sodium borohydride (8.5 g, 0.22 mol) in absolute ethanol (400 ml). After stirring at 20—23 °C for 20 h the reaction mixture was poured into water (900 ml) containing acetic acid (6 ml). The organic layer combined with the ethereal extracts was washed with dilute acetic acid, water, saturated aq sodium hydrogencarbonate, and sodium chloride successively, and dried over sodium sulfate. The residual yellow liquid obtained after evaporation of the solvent was chromatographed on alumina (100 g) and the fractions eluted with light petroleum–ether (4: 6—2: 8) gave the desired alcohol (XIa, 2.0 g, 56%) as a pale yellow liquid: MS: *m/e* 284 (M$^+$, 10), 129 (100); mol wt, 284.34; IR (neat): 3300 (–OH), 3250 (–C≡CH), 2100 (–C≡C–) 1700, 1640, 1595 (C=C), 965 cm^{-1} (*trans* C=C); UV: $\lambda_{\max}^{\mathrm{EtOH}}$ 226 sh (12100), 233 (15000), 239 (12800), 249 (8550), 264 (8430), 276 nm (6350); NMR: see Table 3.

4,5 : 10,11-Dibenzocyclotrideca-2,12-diene-6,8-diyn-1-ol (XIIa). To a stirred soln of the ketone (IX, 0.60 g, 2.14 mmol) in dry ether (600 ml) was added a soln of sodium borohydride (900 mg, 0.024 mol) in absolute ethanol (120 ml) at room temp, and the reaction mixture was allowed to stir at the same temp for 2 h. Then the mixture was poured into water (450 ml) containing acetic acid (3 ml) and worked up as described for the isolation of XIa. The residual, partly crystallized, pale yellow liquid was chromatographed on alumina (100 g) with benzene–chloroform (1: 1) to give the alcohol (XIIa, 0.55 , 91%). Recrystallization from benzene formed white needles: mp *ca.* 150 °C (dec); MS: *m/e* 282 (M$^+$, 25), 253 (100); mol wt, 282.32; IR (KBr disk): 3350, 3250 (–OH), 2150 (–C≡C–), 1640 (C=C), 975, 965 cm^{-1} (*trans* C=C); UV: $\lambda_{\max}^{\mathrm{EtOH}}$ 257 (20700), 268 (20000), 297 (13200), 322 (16500), 343 (17500), 368 sh nm (3310); NMR: see Table 3.

*1,5-Bis(*o*-ethynylphenyl)-3-methoxy-1,4-pentadiene (XIb).* To a slurry of sodium hydride (derived from washing 0.065 g of 53% NaH in oil) was added a soln of the alcohol (XIa, 0.24 g, 0.85 mmol) in dry tetrahydrofuran (20 ml) and methyl iodide (5 ml) at room temp under a nitrogen atmosphere. The reaction mixture was stirred at the same temp and the reaction was monitored at appropriate intervals by TLC. After stirring for 20 h additional methyl iodide (2 ml) and sodium hydride (30 mg) was added. After stirring for a total 26 h, the mixture was poured into water (200 ml) and extracted with ether. The extracts were washed with saturated aq sodium chloride soln and dried over sodium sulfate. The residue obtained after the evaporation of the solvent was chromatographed on alumina (130 g) with light petroleum to give the ether (XIb, 0.13 g, 51%) as a pale yellow liquid: IR (neat): 3300 (–C≡CH), 2100 (–C≡C–), 1145, 1110, 1080 (C–O–C), 970 cm^{-1} (*trans* C=C); UV: $\lambda_{\max}^{\mathrm{EtOH}}$ 231 (59900), 238 (47900), 256 (33900), 265 (35300), 274 nm (23100); NMR: see Table 3.

1-Methoxy-4,5: 10,11-dibenzocyclotrideca-2,12-diene-6,8-diyne (XIIb). To a stirred soln of the alcohol (XIa, 0.25 g, 0.90 mmol) in dry ether (40 ml) was added methyl iodide (10 ml) and silver oxide (2 g), and the mixture was allowed to stir for 7 h at the same temp. A second silver oxide (2 g) was added and stirring was continued for another 8 h at the same temp. Then the mixture was filtered and the filtrate was concentrated under reduced pressure to give a pale yellow liquid. Chromatography of the liquid on alumina (100 g) with light petroleum–ether (95: 5—90: 10) afforded the ether (XIIb, 0.15 g, 57%) as yellow liquid which gave white crystals (mp 79—82 °C) on strong cooling. Attempts to recrystallize this material were failed. MS: *m/e* 296 (M$^+$, 40), 266 (100); mol wt, 296.35; IR (KBr disk): 2200 (–C≡C–), 1105, 1080 (C–O–C), 970 cm^{-1} (*trans* C=C); UV: $\lambda_{\max}^{\mathrm{EtOH}}$ 231 (40200), 257 (19000), 268 (17900), 300 (8730), 320 (13100), 342 nm (13400); NMR: see Table 3.

Attempts to Prepare the Anion XIII. To a soln of the ether (XIIb, 252 mg) in dimethyl-d_6 sulfoxide (4 ml) was added a dimsyl anion (0.6 ml, prepared from dimethyl-d_6 sulfoxide and sodium hydride)[13] with stirring at room temp. A deep green color developed. However, no satisfactory

NMR spectrum could be obtained although we performed several runs under similar conditions for various elapse of time.

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