# Syntheses and Properties of Methyl-substituted Benzannelated Tetradehydro[13]annulenones

By **Juro Ojima** * and **Masamitsu Fujiyoshi,** Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930, Japan

Syntheses of 6,11-dimethyl- (6) and 8,11-dimethyl-12,13,14,15-tetradehydrobenzocyclotridecen-7-one (7) and 6-methyl-14,15,16,17-tetradehydrodibenzo[a,g]cyclotridecen-7-one (8) are described. The influence of methyl substitution and benzannelation upon the structure and tropicity of the tetradehydro[13]annulenone ring system is discussed in view of the [1]H n.m.r. and u.v. spectra of these annulenones, as well as those of the α-methyl-unsubstituted annulenones (4) and (5).

IN 1972, Howes *et al.* reported a simple general approach to the bis(cyclohexene)-annelated tetradehydro-[13]-(1), -[15]-, and -[17]-annulenones in which the carbonyl group is flanked on both sides by ethylenic bonds.[1] The method involves an aldol condensation of an appropriate aldehyde and ketone containing terminal acetylene groups, followed by intramolecular oxidative

[13]annulenones, (4) and (5) respectively, prepared previously,[2a] might also be conformationally mobile. In order to investigate this possibility, it was decided to re-examine the preparation of (4) and (5), and to synthesize the related methyl-substituted tetradehydro-[13]annulenones (6)—(8). This paper deals with the syntheses and properties of compounds (6)—(8) and
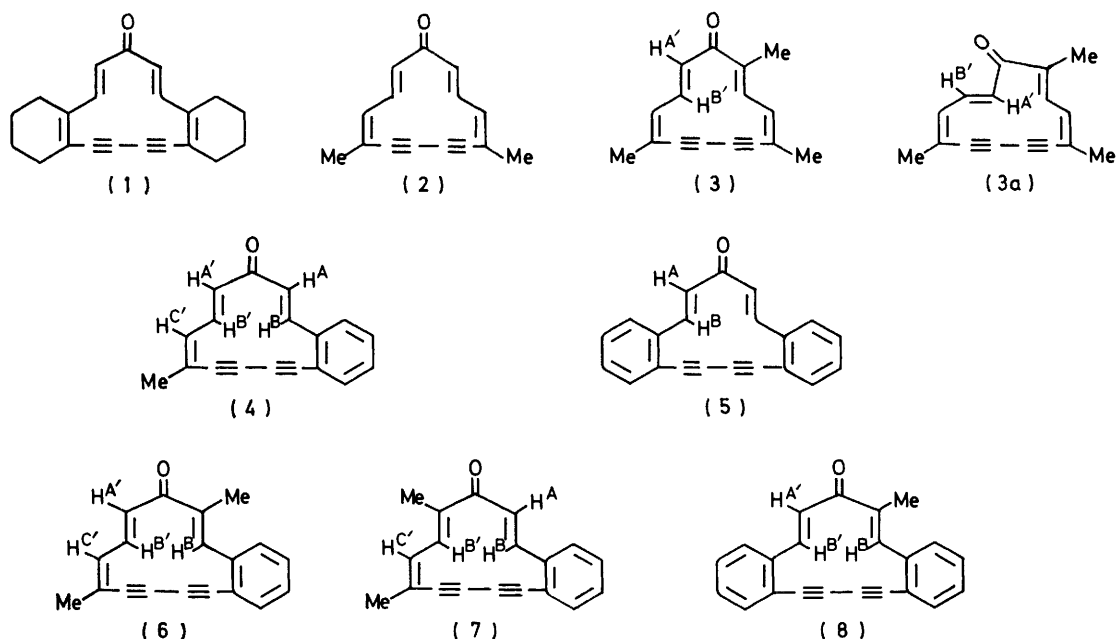
coupling of the resulting acyclic ketone. Since this work was carried out, several syntheses of methylated and/or benzannelated tetradehydroannulenones of type (1) have been accomplished by the above procedure [2] starting from (Z)-3-methylpent-2-en-4-ynal (9) and/or o-ethynylbenzaldehyde (12).

Among these annulenones, Cresp *et al.* examined the properties of the di- and tri-methyl-substituted [13]-annulenones (2) and (3), respectively, which a study on a closely related dimethyltetradehydrothia[13]annulene [3] had suggested to be conformationally mobile. In practice, it was found that, compared with (2), the extra methyl group adjacent to the oxo-group of (3) causes a change of conformation due to a rotation of the H^{A'}=H^{B'} double bond, with (3) existing in the conformation (3a) at −60 °C.[2c]

This suggested that the methylbenz- (4) and dibenz-

further examines the preparation and properties of the α-methyl-unsubstituted annulenones (4) and (5).[4]

The annulenone (4) was prepared by a modification of the reported method.[2a] Aldol condensation of (Z)-3-methylpent-2-en-4-ynal (9) [5] and the ketone (10) [6] in the presence of methanolic sodium methoxide in ether led to a 35% yield of the ketone (11) which was readily separated from other products by column chromatography, in contrast to the case using methanolic potassium hydroxide.[2a] Oxidative coupling of the ketone (11) with anhydrous copper(II) acetate in pyridine and ether [7] at 50 °C afforded the annulenone (4) in 48% yield. Similarly, the dibenzannulenone (5) was also prepared by a modification of the previous method [2a] using anhydrous copper(II) acetate [7] instead of monohydrate in the oxidative coupling reaction. The α,α'-dideuterium-labelled isomer of (5) was prepared *via* condensation

with [²H₆]acetone in a similar manner. These improved yields made the annulenones (4) and (5) relatively readily available substances, and made it desirable to utilize these compounds for the syntheses of fulvalene derivatives.[8]

(18), obtained by condensation between (9) and (14) as reported,[2c] with (12) gave the ketone (19) in 46% yield, which formed the annulenone (7) in 55% yield. The structures of these new compounds were established from their spectral properties and elemental analyses.
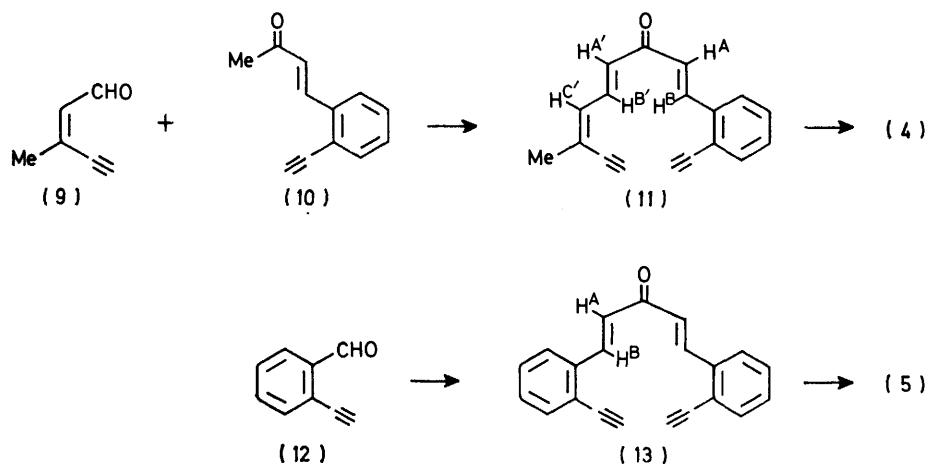
The annulenones (6)—(8) were obtained in relatively good yields. Aldol condensation of butan-2-one (14) with o-ethynylbenzaldehyde (12) in the presence of sulphuric acid in acetic acid gave the ketone (15) (41% yield) which was further condensed with the enyne-

Treatment of the annulenones (4)—(8) with trifluoro-acetic or deuteriotrifluoroacetic acid gave the corresponding carbonyl-protonated or -deuteriated species (4')—(8'), respectively, (6') being dark red, (7') dark red, and (8') yellow. Quenching of (6')—(8') with
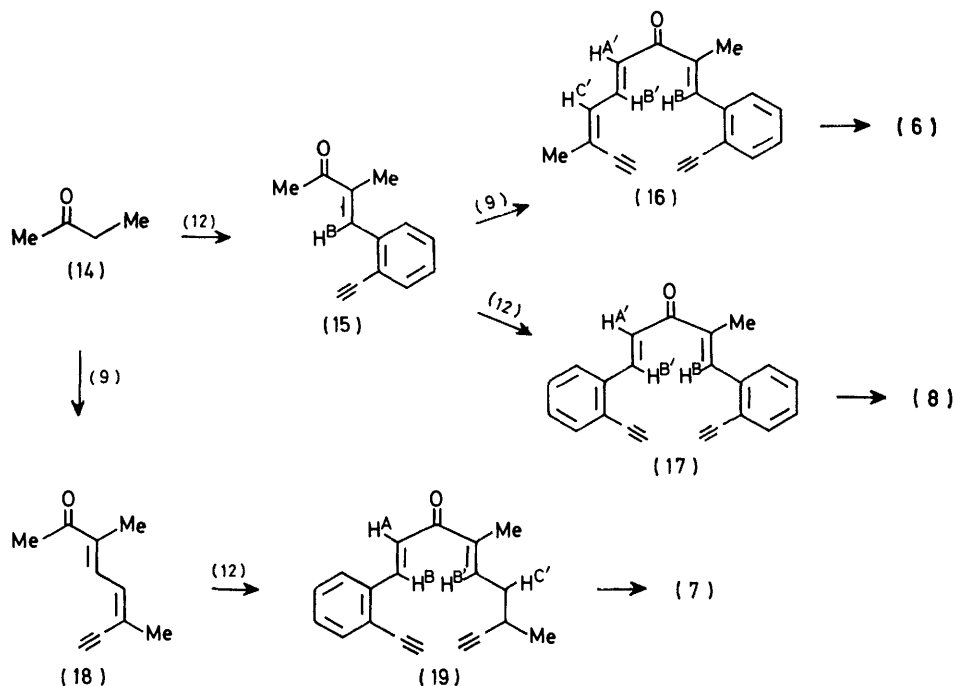
aldehyde (9) by means of ethanolic potassium hydroxide in tetrahydrofuran, affording the acyclic ketone (16) in 40% yield. Oxidative coupling of (16) with anhydrous copper(II) acetate as before gave the annulenone (6) in 50% yield. Similarly, condensation of (15) with (12) gave the ketone (17) (62% yield) which was oxidized to afford the annulenone (8) in 88% yield. The reaction of

aqueous sodium hydrogencarbonate resulted in regeneration of (6)—(8) respectively [see ref. 2a for (4) and (5)].

The electronic absorption maxima (in ether) of the annulenones (2)—(8) are given in Table 1. As expected, the spectra are similar, the medium bands exhibiting an appreciable bathochromic shift with increasing numbers of fused benzene rings, as observed for the related

benzannelated annulenes.[7a] In contrast, the bands of longest wavelength exhibit a considerable hypsochromic shift as the degree of annelation of the benzene ring increases   [(5) = (8) < (4) = (6) = (7) < (2) = (3)],

obtained by dissolving the respective annulenones in deuteriotrifluoroacetic acid. Individual assignments were made on the basis of multiplicity, coupling constant (see Experimental section), and data for closely related

TABLE 1

Electronic absorption maxima of tetradehydro[13]annulenones in ether $[\lambda_{max.}$ $(\varepsilon_{max.})$ values]

(2) [a]	(4)	(5)	(3) [a]	(6) [b]	(7) [b]	(8) [b]
	236 (19 700)	224 (40 200)		232sh (31 100)	235sh (24 800)	222 (34 800)
250sh (25 800)	253sh (30 800)		250sh (24 700)			
262 (37 900)		266sh (29 100)	265 (48 300)	265sh (33 100)		268sh (24 600)
273 (39 900)	273 (34 700)	279 (41 200)	276 (50 300)	276 (39 700)	275 (41 300)	280 (35 200)
	290sh (21 800)	293 (45 400)		290sh (25 300)	290sh (30 200)	295 (38 700)
		354 (3 390)				352 (3 700)
387 (990)	386 (1 830)	364sh (3 330)	390sh (1 400)	378 (3 280)	380 (2 970)	370sh (3 040)

[a] See ref. 2c.   [b] Absorption curve previously given in ref. 4.

suggesting that the skeletons of the annelated annulenones are less delocalized π-electron systems than those of non-annelated ones. The electronic absorption maxima of the annulenones (4)—(8) in trifluoroacetic

compounds.[2a,c] Table 3 shows that the inner proton adjacent to the methyl substituent resonates at lower field than the opposite inner proton, except for the case of (6'), suggesting that the bulky methyl group forces
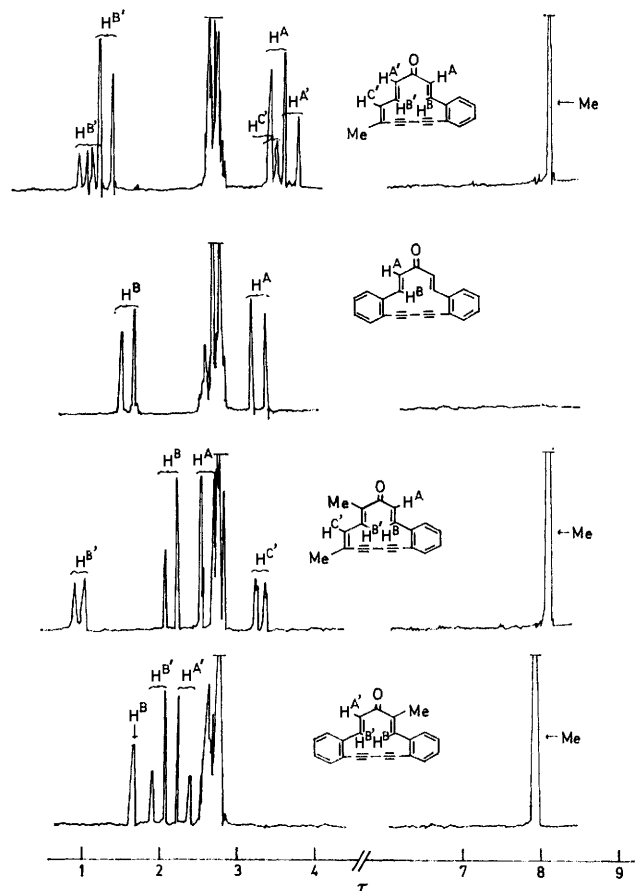
TABLE 2

Electronic absorption maxima of tetradehydro[13]annulenones in trifluoroacetic acid $[\lambda_{max.}$ (relative extinction coefficients)]

(4)	(5) [a]	(6)	(7)	(8)
276sh	288sh	274sh	282sh	289sh
(0.86)	(0.82)	(0.86)	(0.93)	(0.85)
290	301	287	293	300
(1.00)	(1.00)	(1.00)	(1.00)	(1.00)
350sh	348sh	343sh	346sh	348sh
(0.19)	(0.13)	(0.17)	(0.18)	(0.12)
420sh	413sh	410sh	420sh	410sh
(0.10)	(0.02)	(0.11)	(0.06)	(0.03)

[a] See ref. 2a.

this proton into a distinct inner position of the thirteen-membered ring system. Also, if we judge the tropicity[9] of these annulenones from the differences in chemical shift between the various resonances for the cyclic
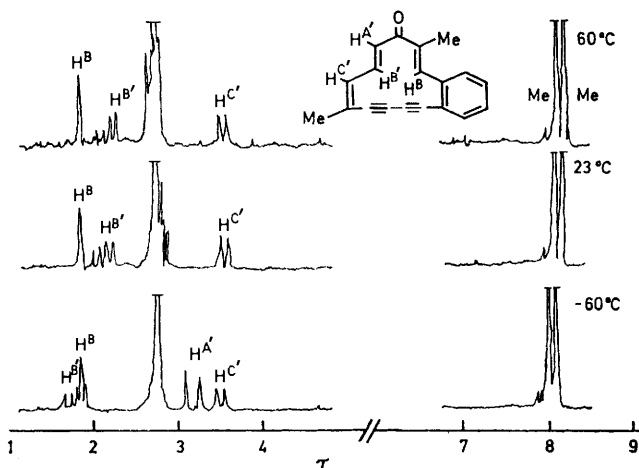

FIGURE 1   100-MHz ¹H N.m.r. spectra of the [13]annulenones (4), (5), (7), and (8) in CDCl₃ at 25 °C

FIGURE 2   100-MHz ¹H N.m.r. spectra of the [13]annulenone (6) in CDCl₃ at various temperatures

acid are given in Table 2. For each annulenone, protonation with this acid resulted in an appreciable bathochromic shift (5—18 nm) of the main maxima.

The chemical shifts of the olefinic, aromatic, and methyl protons of these annulenones and those of the corresponding acyclic ketones are listed in Table 3, together with data for the deuteriated species (4')—(8')

ketone (annulenone) and the corresponding acyclic model (upfield shift for the outer protons and downfield for the inner) (Table 3), the annulenones (4) and (5) are seen to be paratropic molecules, while (6)—(8) are

atropic ones. This observation is more readily seen from Figures 1 and 2 (centre portion of spectrum) which show the ¹H n.m.r. spectra of (4)—(8) at 25 °C. In the spectra of (6)—(8), compared with those of (4) and (5), the high- and low-field shifts of the resonances of the

ring current of macrocyclic systems may reflect a local anisotropic effect of the diacetylene moiety together with small changes of molecular conformation of this tetra-dehydro[13]annulenone ring.

The variable-temperature ¹H n.m.r. spectra of (4)—(8)

TABLE 3

¹H N.m.r. parameters of compounds (4)—(8), (11), (13), (16), (17), and (19) (in CDCl₃) and (4')—(8') (in CF₃CO₂D) at 90 MHz, determined at 35 °C (τ values, internal standard Me₄Si)

	H^A	H^A'	H^B	H^B'	H^C'	ArH	Me	
(11) [a]	2.93	3.45	1.89	2.25	3.49	2.2—2.8	7.97	
(4) [a]	3.50	3.70	1.28	1.08	3.47	2.6—2.8	8.13	
(4') [a]	3.57	3.27	0.45	0.00	3.45	2.6—2.8	8.10	
Δ(4) — (11)	+0.57	+0.25	−0.61	−1.17	−0.02		+0.16	
Δ(4') — (11)	+0.64	−0.18	−1.44	−2.25	−0.04		+0.13	
(13) [a]	2.83 [b]		1.77 [b]			2.3—2.8		
(5) [a]	3.17 [b]		1.47 [b]			2.4—2.8		
(5') [a]	2.89 [b]		0.80 [b]			2.4—2.7		
Δ(5) — (13)	+0.34		−0.30					
Δ(5') — (13)	+0.06		−0.97					
(16)		3.10	2.23	2.20	3.46	2.4—2.8	7.91	7.93
(6)		(2.6—2.8) [c]	1.73	2.05	3.47	2.6—2.8	7.98	8.06
(6')		2.87	1.67	1.37	3.35	2.5—2.7	7.98	8.06
Δ(6) — (16)			−0.50	−0.15	+0.01		+0.05—+0.15	
Δ(6') — (16)		−0.23	−0.56	−0.83	−0.11		+0.05—+0.15	
(19)	(2.2—2.8) [c]		1.90	(2.2—2.8) [c]	3.25	2.2—2.8	7.90	7.97
(7)	2.59		2.12	0.93	3.30	2.6—2.9	8.10	
(7')	2.19		1.77	0.09	3.29	2.6—2.9	8.09	
Δ(7) — (19)			+0.22		+0.05		+0.13—+0.20	
Δ(7') — (19)			−0.13		+0.04		+0.12—+0.19	
(17)		(2.2—2.8) [c]	2.10	1.80		2.2—2.8	7.87	
(8)		2.25	1.58	1.90		2.5—2.7	7.90	
(8')		1.82	1.05	1.55		2.5—2.7	7.80	
Δ(8) — (17)			−0.52	+0.10			+0.03	
Δ(8') — (17)			−1.05	−0.25			−0.07	

[a] Spectra were re-examined by measuring at 90 MHz for purposes of comparison (see ref. 2a). [b] Assignments by preparing α,α'-dideuterio-analogues of (13) and (5). [c] Signals submerged by those of the aromatic protons.

inner and outer protons, respectively, with respect to the aromatic protons are not observed. Also, if only the inductive effect of the methyl group is considered, it may be predicted that the expected paratropicity would decrease in the sequence (4) ≃ (6) ≃ (7) > (5) ≃ (8),

were taken at 100 MHz at −60 to +60 °C, and the chemical shifts are summarized in Table 4. The spectra of the annulenones (4), (5), (7), and (8) were found to be essentially temperature-independent over this temperature range, although the variations of the chemical

TABLE 4

¹H N.m.r. parameters for compounds (4)—(8) in CDCl₃ at 100 MHz (τ values)

Compound	T (°C)	H^A	H^A'	H^B	H^B'	H^C'	ArH	Me	
(4)	60	3.65	3.50	1.38	1.22	3.48	2.6—2.8		8.14
	23	3.78	3.58	1.38	1.16	3.48	2.6—2.8		8.14
	−60	3.96	3.78	1.32	0.98	3.52	2.7—3.0		8.12
(5)	60	3.18		1.60			2.5—2.8		
	23	3.26		1.60			2.5—2.8		
	−60	3.54		1.64			2.6—2.9		
(6)	60		(2.6—2.8) [a]	1.86	2.18	3.54	2.6—2.8	8.04	8.12
	23		(2.6—2.9) [a]	1.82	2.10	3.56	2.6—2.9	8.02	8.12
	−60		3.18	1.86	1.78	3.52	2.6—2.8	8.00	8.10
(7)	60	2.60		2.14	1.00	3.30	2.6—2.9	8.08	8.12
	23	2.62		2.16	0.99	3.33	2.7—2.9	8.10	8.14
	−60	2.64		2.18	0.94	3.32	2.7—2.9		8.12
(8)	60		2.28	1.70	1.98		2.5—2.9		7.92
	23		2.32	1.60	2.00		2.5—2.8		7.92
	−60		2.34	1.62	2.05		2.6—2.8		7.90

[a] Signal submerged by those of the aromatic protons.

i.e. with increasing number of fused benzene rings on the macrocyclic system, as seen for other examples.[10] The data do not, however, show such a trend even though there is such a tendency for the corresponding deuteriated carbonyl species [(4') ≃ (6') ≃ (7') > (5') ≃ (8')]. The observed changes in chemical shift which violate the known recognition of benzannelation effects upon the

shifts are larger for the α-methyl unsubstituted annulenones (4) and (5) than for the substituted ones (7) and (8). On the other hand, as shown in Figure 2, the spectrum of (6) shows the signals for H^A and the aromatic protons as an unresolved multiplet at both 25 and 60 °C. On cooling, the band gradually resolves and the H^B band moves to lower field, the expected first-

order pattern being observed at −60 °C. However, the $J_{B',C'}$ value (10 Hz), pointing to an *s-trans* relationship of $H^{B'}$ and $H^{C'}$, does not vary from −60 to +60 °C, thus excluding a change of conformation of (6) due to rotation of the $H^{A'}=H^{B'}$ double bond over this temperature range, in contrast to the case for the trimethyltetradehydro[13]annulenone (3). Accordingly, it is suggested that the benzannelation, which is formulated by the transformation from (7) to (6), makes this tetradehydro[13]annulenone ring system less mobile. The ^1H n.m.r. spectra of the annulenones (6)—(8) also indicate that (6) is more flexible than (7) and (8), reflecting that the annulenones (7) and (8), in which the ' potentially mobile bond ' ($H^{B'}=H^{C'}$ bond) is flanked by the fused benzene ring, experience the effect of benzannelation more highly than (6).

In conclusion, the results obtained from this study indicate that the extra methyl substituent and fused benzene ring exert a considerable influence on the development of the paratropic character in the tetradehydro[13]annulenone system, which suggests that the skeleton of the [13]annulenone ring system is less planar than that of the [17]annulenone of this type,[11] as is predicted by molecular models.

EXPERIMENTAL

Deoxygenated ether and tetrahydrofuran were used to minimize oxidation of the compounds used for the aldol condensation, and were freed from peroxides by passing through a short column of basic alumina (activity I) followed by flushing with nitrogen immediately before use. M.p.s were determined with a hot-stage apparatus. Mass spectra were recorded with a JEOL JMS-OI-SG-2 spectrometer operating at 75 eV using a direct-inlet system. I.r. and u.v. spectra were taken with a Hitachi EPI-S2 and 124 spectrophotometers respectively. N.m.r. spectra were recorded with Varian EM-390 (90 MHz) or MH-100 (100 MHz) spectrometers (Me₄Si as internal standard). Merck alumina (activity II—III) was used for column chromatography. Most reactions was followed by t.l.c. using Merck pre-coated alumina. Solvents were evaporated under water aspirator pressure.

1-(o-*Ethynylphenyl*)-7-*methylnona*-1,4,6-*trien*-8-*yn*-3-*one* (11).—This compound was prepared by a modification of the previously described method.[2a] A solution of the enyne aldehyde (9) (2.60 g, 28 mmol) in dry ether (27 ml) was added dropwise over 20 min to a cooled (ice-bath) stirred solution of the ketone (10) [6] (2.30 g, 13 mmol) in dry ether (40 ml) containing methanolic sodium methoxide [from sodium (45 mg) and dry methanol (12 ml)]. After stirring for a further 3 h at the same temperature, the reaction was quenched by addition of aqueous oxalic acid. The mixture was poured into water (150 ml) and extracted with benzene. After the usual work-up, the residue was chromatographed over alumina (120 g). Elution with light petroleum–ether (17 : 3) gave the unchanged ketone (0.95 g). Use of light petroleum–ether (4 : 1) afforded the ketone (11) (1.33 g, 35%) as an orange liquid, *m/e* 246 (*M*⁺, 22%) and 155 (100); *M*, 246.3; $\nu_{max.}$ (neat) 3 300 (−C≡CH), 2 100 (−C≡C−), 1 655, 1 620, 1 600 (C=O, C=C), and 980 cm⁻¹ (*trans*-C=C); $\lambda_{max.}$ (ether) 226 (ε 23 500), 247 (21 700), and 332 nm (29 400); τ(CDCl₃; 90 MHz) 1.89 (1 H, d, *J* 16 Hz, H^B), 2.25 (1 H,

dd, *J* 16 and 11 Hz, $H^{B'}$), 2.2—2.8 (4 H, m, ArH), 2.93 (1 H, d, *J* 16 Hz, H^A), 3.45 (1 H, d, *J* 16 Hz, $H^{A'}$), 3.49 (1 H, d, *J* 11 Hz, $H^{C'}$), 6.45 (1 H, s, −C≡CH), 6.51 (1 H, s, −C≡CH), and 7.97 (3 H, s, Me).

11-*Methyl*-12,13,14,15-*tetradehydrobenzocyclotridecen*-7-*one* (4).—This compound was prepared by a modification of the previously described procedure.[2a] A solution of the ketone (11) (0.69 g, 2.8 mmol) in pyridine–dry ether (3 : 1) (69 ml) was added dropwise during 1.5 h to a stirred solution of anhydrous copper(II) acetate (4.1 g) in pyridine–dry ether (3 : 1) (152 ml) at 45—50 °C (bath temperature). The solution was stirred at the same temperature for a further 2 h and then cooled. After addition of benzene (100 ml), the reaction mixture was filtered through Hyflo Super-Cel. The precipitate was washed with benzene (50 ml × 2), and the filtrate poured into 3N-hydrochloric acid (1 l). The organic layer was separated and the aqueous layer extracted with benzene. The combined organic layer and extracts were washed with 3N-hydrochloric acid, water, aqueous sodium hydrogencarbonate, and brine, dried (Na₂SO₄), and concentrated *in vacuo*. The resultant dark red liquid was chromatographed on alumina (120 g); elution with light petroleum–ether (1 : 1) gave the annulenone (4) (0.32 g, 48%) which was recrystallized from benzene to afford yellow *needles*, m.p. *ca.* 170 °C; *m/e* 244 (*M*⁺, 20%) and 215 (100); *M*, 244.3; $\nu_{max.}$(KBr) 2 150 (−C≡C−), 1 630, 1 610, 1 590 (C=O, C=C), and 975 cm⁻¹ (*trans*-C=C); for u.v. data see Table 1; τ(CDCl₃; 90 MHz) 1.08 (1 H, dd, *J* 16 and 11 Hz, $H^{B'}$), 1.28 (1 H, d, *J* 16 Hz, H^B), 2.6—2.8 (4 H, m, ArH), 3.47 (1 H, d, *J* 11 Hz, $H^{C'}$), 3.50 (1 H, d, *J* 16 Hz, H^A), 3.70 (1 H, *J* 16 Hz, $H^{A'}$), 8.13 (3 H, s, CH₃), and see Figure 1; τ(CF₃CO₂D; 90 MHz) 0.00 (1 H, dd, *J* 16 and 11 Hz, $H^{B'}$), 0.45 (1 H, d, *J* 16 Hz, H^B), 2.6—2.8 (4 H, m, ArH), 3.27 (1 H, d, *J* 16 Hz, $H^{A'}$), 3.45 (1 H, d, *J* 11 Hz, $H^{C'}$), 3.57 (1 H, d, *J* 16 Hz, H^A), and 8.10 (3 H, s, CH₃) (Found: C, 88.3; H, 4.7. C₁₈H₁₄O requires C, 88.5; H, 4.95%).

14,15,16,17-*Tetradehydrodibenzo*[a,g]*cyclotridecen*-7-*one* (5).—This compound was prepared as reported [2a] except that anhydrous copper(II) acetate in pyridine and dry ether was employed instead of monohydrate in the oxidative coupling step as in the preparation of (4); the yield was thus improved to 40% [based on (12)].

α,α'-*Dideuterio-isomer of* (13).—To a stirred solution of *o*-ethynylbenzaldehyde (12) (3.6 g, 28 mmol) and [²H₆]-acetone (0.79 g, 14 mmol) in deoxygenated ether (42 ml) was added 20% methanolic potassium hydroxide [from potassium hydroxide (0.2 g) and CD₃OD (1 ml)] at 15—18 °C. After stirring for 2.5 h at the same temperature, the reaction was quenched with acetic acid (1.2 ml). A red liquid, obtained by the usual work-up, was purified by column chromatography over alumina (120 g). The early fractions gave the recovered aldehyde (12) (0.28 g). The following fractions eluted with light petroleum–ether (65 : 35) were collected and evaporated to give the α,α'-dideuterio-isomer of (13) (2.4 g, 60%). Recrystallization from benzene afforded yellow cubes, m.p. 98—100 °C; *m/e* 284 (*M*⁺, 35%), 156 (100); *M*, 284.6; $\nu_{max.}$(KBr) 3 250 (−C≡CH), 2 100 (−C≡C−), 1 650, 1 590 (C=O, C=C), 980, and 965 cm⁻¹ (*trans*-C=C); $\lambda_{max.}$(EtOH) 225 (ε 35 700), 250 (23 800), and 332 nm (25 400); τ(CDCl₃; 90 MHz) 1.78 (2 H, s, H^B), 2.25—2.83 (8 H, m, ArH), and 6.49 (2 H, s, −C≡CH).

α,α'-*Dideuterio-isomer of* (5).—Preparation of the α,α'-dideuterio-isomer of (5) was carried out by the method described for the isolation of (4) from (11), utilizing the

α,α'-dideuterio-isomer of (13) (2.0 g, 7 mmol) in pyridine and dry ether (3 : 1, 160 ml), and anhydrous copper(II) acetate (8.8 g) in pyridine–dry ether (3 : 1, 320 ml). The semi-solid obtained by work-up, was chromatographed on alumina (140 g) with light petroleum–ether (4 : 6) as eluant to give the α,α'-dideuterio-isomer of (5) (1.1 g, 55%), obtained as yellow leaflets from benzene, m.p. 180 °C (decomp.); m/e 282 (M^+, 70%) and 281 (100); M, 282.6; $\nu_{max.}$(KBr) 2 200 (–C≡C–), 1 630, 1 610, 1 590 (C=O, C=C), and 980 cm⁻¹ (trans-C=C); $\lambda_{max.}$(EtOH) 224 (ε 35 800), 282 (41 200), 296 (47 900), 350sh (2 200), and 374sh nm (1 970); τ(CDCl₃; 90 MHz) 1.50 (2 H, s, H^B), and 2.40—2.77 (8 H, m, ArH); τ(CF₃CO₂D; 90 MHz) 0.80 (2 H, s, H^B) and 2.4—2.7 (8 H, m, ArH).

4-[o-Ethynylphenyl)-3-methylbut-3-en-2-one (15).—A solution of o-ethynylbenzaldehyde (12) (8.0 g, 0.061 mol) in acetic acid (39 ml) was added dropwise over 45 min to a stirred solution of butan-2-one (14) (19.0 g, 0.26 mol) and concentrated sulphuric acid (4.8 ml) in acetic acid (236 ml) at room temperature. The resultant dark red solution was stirred for a further 20 h at this temperature, and then cautiously poured into saturated aqueous potassium carbonate. The reaction mixture was extracted with benzene and the benzene extracts were washed with saturated aqueous sodium chloride and dried (Na₂SO₄). After removal of the solvent the residue was chromatographed on alumina (160 g) with light petroleum–ether (95 : 5) to give (15) (4.6 g, 41%) as a liquid which crystallized from ether–hexane to give pale yellow needles, m.p. 33—34 °C; m/e 184 (M^+, 55%) and 169 (100); M, 184.2; $\nu_{max.}$(KBr) 3 300 (–C≡CH), 2 100 (–C≡C–), 1 660 (C=O), and 1 630 cm⁻¹ (C=C); $\lambda_{max.}$ (ether) 238 (ε 14 400) and 277 nm (8 270); τ(CDCl₃; 90 MHz) 2.17 (1 H, s, H^B), 2.36—2.78 (4 H, m, ArH), 6.60 (1 H, s, –C≡CH), 7.55 (3 H, s, CH₃), and 8.01 (3 H, s, CH₃) (Found: C, 85.0; H, 6.6. C₁₃H₁₂O requires C, 84.75; H, 6.6%).

1-(o-Ethynylphenyl)-2,7-dimethylnona-1,4,6-trien-8-yn-3-one (16).—Potassium hydroxide–ethanol (2.5 ml; 10% w/v) was added to a solution of the ketone (15) (1.5 g, 8 mmol) in dry tetrahydrofuran (THF) (24 ml), and a solution of the enyne aldehyde (9) (1.4 g, 15 mmol) in dry THF (9.5 ml) was then added during 10 min with stirring. After 3 h at 23—25 °C, the reaction was quenched by addition of acetic acid (3 ml). The resulting solution was poured into water (200 ml) and the mixture was extracted with benzene. The usual work-up afforded a red liquid which was chromatographed on alumina (150 g). The early fractions gave the recovered (15) (0.64 g). Later fractions, eluted with light petroleum–ether (4 : 1), gave the ketone (16) (0.84 g, 40%) as a partly crystallized liquid. Crystallization from benzene afforded yellow cubes, m.p. 92—93 °C; m/e 260 (M^+, 9%) and 217 (100); M, 260.3; $\nu_{max.}$(KBr) 3 290, 3 240 (–C≡CH), 2 100 (–C≡C–), 1 640, 1 620, 1 585 (C=O, C=C), and 980 cm⁻¹ (trans-C=C); $\lambda_{max.}$ (ether) 225 (ε 23 500), 243 (20 100), and 316 nm (24 800); τ(CDCl₃; 90 MHz) 2.20 (1 H, dd, J 15 and 10 Hz, H^B'), 2.23 (1 H, s, H^B), 2.36—2.75 (4 H, m, ArH), 3.10 (1 H, d, J 15 Hz, H^A'), 3.46 (1 H, d, J 10 Hz, H^C'), 6.50 (1 H, s, –C≡CH), 6.58 (1 H, s, –C≡CH), and 7.91 (3 H, s, CH₃) (Found: C, 87.8; H, 6.2. C₁₉H₁₆O requires C, 87.7; H, 6.2%).

6,11-Dimethyl-12,13,14,15-tetradehydrobenzocyclotridecen-7-one (6).—The annulenone (6) was prepared from (16) (0.91 g, 3.5 mmol) in pyridine–dry ether (3 : 1; 76 ml) with anhydrous copper(II) acetate (4.5 g) in pyridine–dry ether (3 : 1, 164 ml), as described for the preparation of (4).

Chromatography of the residue over alumina (160 g) with light petroleum–ether (8 : 2) gave (6) (0.45 g, 50%), obtained as yellow needles from benzene, m.p. 144—146 °C; m/e 258 (M^+, 93%) and 215 (100); M, 258.3; $\nu_{max.}$(KBr) 2 100 (–C≡C–), 1 655, 1 625 (C=O, C=C), and 985 cm⁻¹ (trans-C=C); for u.v. data see Table 1; τ(CDCl₃; 90 MHz) 1.73 (1 H, s, H^B), 2.05 (1 H, dd, J 16 and 9 Hz, H^B'), 2.55—2.75 (5 H, m, H^A' and ArH), 3.47 (1 H, d, J 9 Hz, H^C'), 7.98 (3 H, s, CH₃), and 8.06 (3 H, s, CH₃) (see also Figure 2); τ(CF₃CO₂D; 90 MHz) 1.37 (1 H, dd, J 16 and 10 Hz, H^B'), 1.67 (1 H, s, H^B), 2.5—2.7 (4 H, m, ArH), 2.87 (1 H, d, J 16 Hz, H^A'), 3.35 (1 H, d, J 10 Hz, H^C'), 7.98 (3 H, s, CH₃), and 8.06 (3 H, s, CH₃) (Found: C, 88.5; H, 5.5. C₁₉H₁₄O requires C, 88.3; H, 5.5%).

1,5-Bis-(o-ethynylphenyl)-2-methylpenta-1,4-dien-3-one (17).—Potassium hydroxide (0.22 g) in absolute ethanol (2.7 ml) was added to a solution of the ketone (15) (1.5 g, 8.1 mmol) in dry THF (24 ml), and a solution of (12) (1.6 g, 12 mmol) in dry THF (8.1 ml) was then added during 10 min, with stirring. After stirring for 4 h at 25 °C, the reaction was quenched by addition of acetic acid (1.7 ml). The resultant solution was poured into water (200 ml) and the mixture extracted with benzene. Work-up as in the preparation of (16) gave a red liquid which was chromatographed on alumina (160 g) with light petroleum–ether (13 : 7) as eluant to give (17) (1.49 g, 62%). Recrystallization from benzene–hexane afforded yellow needles, m.p. 102—104 °C; m/e 296 (M^+, 80%) and 253 (100); M, 296.3; $\nu_{max.}$(KBr) 3 260 (–C≡CH), 2 100 (–C≡C–), 1 650, 1 635, 1 600 (C=O, C=C), and 975 cm⁻¹ (trans-C=C); $\lambda_{max.}$ (ether) 224 (ε 37 500), 245 (33 500), 252sh (29 700), and 305 nm (24 500); τ(CDCl₃; 90 MHz) 1.80 (1 H, d, J 16 Hz, H^B'), 2.10 (1 H, s, H^B), 2.2—2.8 (9 H, m, H^A' and ArH), 6.55 (1 H, s, –C≡CH), 6.62 (1 H, s, –C≡CH), and 7.87 (3 H, s, CH₃) (Found: C, 89.1; H, 5.5. C₂₂H₁₆O requires C, 89.1; H, 5.4%).

6-Methyl-14,15,16,17-tetradehydrodibenzo[a,g]cyclotridecen-7-one (8).—The annulenone (8) was prepared from reaction of the ketone (17) (1.1 g, 3.7 mmol) in pyridine–dry ether (3 : 1; 80 ml) with anhydrous copper(II) acetate (4.7 g) in pyridine–dry ether (3 : 1; 172 ml), by the method described for the preparation of (4). The residue obtained was chromatographed on alumina (130 g) with light petroleum–ether (3 : 7) as eluant to give (8) (0.96 g, 88%) as a solid. Recrystallization from benzene afforded yellow needles, m.p. 176—177 °C; m/e 294 (M^+, 100%); M, 294.3; $\nu_{max.}$(KBr) 2 160 (–C≡C–), 1 665, 1 630, 1 590 (C=O, C=C), and 985 cm⁻¹ (trans-C=C); for u.v. data see Table 1; τ(CDCl₃; 90 MHz) 1.58 (1 H, s, H^B), 1.90 (1 H, d, J 16 Hz, H^B'), 2.25 (1 H, d, J 16 Hz, H^A'), 2.47—2.74 (8 H, m, ArH), and 7.90 (3 H, s, CH₃) (see also Figure 1); τ(CF₃CO₂D; 90 MHz) 1.05 (1 H, s, H^B), 1.55 (1 H, d, J 16 Hz, H^B'), 1.82 (1 H, d, J 16 Hz, H^A'), 2.46—2.70 (8 H, m, ArH), and 7.80 (3 H, s, CH₃) (Found: C, 89.5; H, 4.8. C₂₂H₁₄O requires C, 89.8; H, 4.8%).

3,6-Dimethyl-3,5-octadien-7-yn-2-one (18).—This compound was prepared as reported.[2c]

1-(o-Ethynylphenyl)-4,7-dimethylnona-1,4,6-trien-8-yn-3-one (19). Compound (19) was prepared by the method described for the preparation of (16), using the ketone (18) (1.6 g, 11 mmol) in dry THF (33 ml), potassium hydroxide (0.30 g) in ethanol (3.7 ml), and (12) (2.3 g, 18 mmol) in dry THF (11 ml). Chromatography of the product over alumina (140 g) with light petroleum–ether (3 : 2) gave recovered (18) (0.28 g) from the early fractions. Later

fractions (3 : 2) gave the ketone (19) (1.3 g, 46%) as a solid. Recrystallization from benzene afforded orange *plates*, m.p. 79—80 °C; *m/e* 260 (M^+, 31%) and 218 (100); *M*, 260.3; $\nu_{max.}$(KBr) 3 275 (–C≡CH), 2 100 (–C≡C–), 1 650, 1 590 (C=O, C=C), and 985 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ (ether) 227 (ε 26 200), 249 (30 200), 254 (29 500), and 325 nm (28 900); τ(CDCl$_3$; 90 MHz) 1.90 (1 H, d, *J* 16 Hz, H^B), 2.20—2.77 (6 H, m, H^A, H$^{B'}$, and ArH), 3.25 (1 H, d, *J* 12 Hz, H$^{C'}$), 6.48 (1 H, s, –C≡CH), 6.57 (1 H, s, –C≡CH), 7.90 (3 H, s, CH$_3$), and 7.97 (3 H, s, CH$_3$) (Found: C, 87.7; H, 6.3. C$_{19}$H$_{16}$O requires C, 87.7; H, 6.2%).

8,11-*Dimethyl*-12,13,14,15-*tetradehydrobenzocyclotridecen*-7-*one* (7). A solution of the ketone (19) (2.0 g, 7.7 mmol) in pyridine–dry ether (3 : 1; 160 ml) was added dropwise during 2.5 h to a stirred solution of anhydrous copper(II) acetate (9.6 g) in pyridine–dry ether (3 : 1; 348 ml) at 49—50 °C (bath temperature). The solution was stirred at the same temperature for further 1.5 h. Work-up as in the preparation of (6) gave a red liquid which was chromatographed on alumina (160 g) with light petroleum–ether (7 : 3) as eluant to give (7) (1.1 g, 55%) as a solid. Recrystallization from benzene afforded orange *plates*, m.p. 140—142 °C; *m/e* 258 (M^+, 41%) and 215 (100); *M*, 258.3; $\nu_{max.}$(KBr) 2 150 (–C≡C–), 1 645 (C=O), 1 610 (C=C), and 975 cm^{-1} (*trans*-C=C); for u.v. data see Table 1; τ(CDCl$_3$; 90 MHz) 0.93 (1 H, d, *J* 11 Hz, H$^{B'}$), 2.12 (1 H, d, *J* 16 Hz, H^B), 2.59 (1 H, d, *J* 16 Hz, H^A), 2.63—2.89 (4 H, m, ArH), 3.30 (1 H, d, *J* 11 Hz, H$^{C'}$), and 8.10 (6 H, br s, CH$_3$) (see also Figure 1); τ(CF$_3$CO$_2$D; 90 MHz) 0.09 (1 H, d, *J* 11 Hz, H$^{B'}$), 1.77 (1 H, d, *J* 16 Hz, H^B), 2.19 (1 H, d, *J* 16 Hz, H^A), 2.63—2.85 (4 H, m, ArH), 3.29 (1 H,

d, *J* 11 Hz, H$^{C'}$), and 8.09 (6 H, br s, CH$_3$) (Found: C, 88.6; H, 5.5. C$_{19}$H$_{14}$O requires C, 88.3; H, 5.5%).

REFERENCES

[1] P. D. Howes, E. LeGoff, and F. Sondheimer, *Tetrahedron Letters*, 1972, 3691, 3695.

[2] (a) J. Ojima, Y. Yokoyama, and M. Enkaku, *Bull. Chem. Soc. Japan*, 1977, **50**, 1522; (b) J. Ojima, M. Ishiyama, and A. Kimura, *Bull. Chem. Soc. Japan*, 1977, **50**, 1584; (c) T. M. Cresp, J. Ojima, and F. Sondheimer, *J. Org. Chem.*, 1977, **42**, 2130; (d) J. Ojima, M. Enkaku, and M. Ishiyama, *J.C.S. Perkin I*, 1977, 1548; (e) J. Ojima and Y. Shiroishi, *Bull. Chem. Soc. Japan*, 1978, **51**, 1204.

[3] R. L. Wife and F. Sondheimer, *J. Amer. Chem. Soc.*, 1975, **97**, 640.

[4] Preliminary communication, J. Ojima and M. Fujiyoshi, *Chem. Letters*, 1978 569,

[5] J. Ojima, T. Katakami, G. Nakaminami, and M. Nakagawa, *Bull. Chem. Soc. Japan*, 1976, **49**, 292.

[6] J. Ojima, T. Yokomachi, and A. Kimura, *Bull. Chem. Soc. Japan*, 1976, **49**, 2840.

[7] (a) N. Darby, T. M. Cresp, and F. Sondheimer, *J. Org. Chem.*, 1977, **42**, 1960; (b) J. Ojima, Y. Shiroishi, and M. Fujiyoshi, *Bull. Chem. Soc. Japan*, 1978, **51**, 2112.

[8] T. Asao, N. Morita, J. Ojima, and M. Fujiyoshi, *Tetrahedron Letters*, 1978, 2795.

[9] F. Sondheimer, *Accounts Chem, Res,*, 1972, **5**, 81,

[10] *Inter alia*, M. Iyoda and M. Nakagawa, *Chemistry Letters*, 1975, 815; R. T. Weavers, R. R. Jones, and F. Sondheimer, *Tetrahedron Letters*, 1975, 1043.

[11] J. Ojima, K. Kanazawa, K. Kusaki, and K. Wada, following paper; *Chem. Letters*, 1978, 1099.