Syntheses and Properties of α-Ethyl-substituted Bisdehydro-[13]annulenone and Its Benzo-annelated Derivatives

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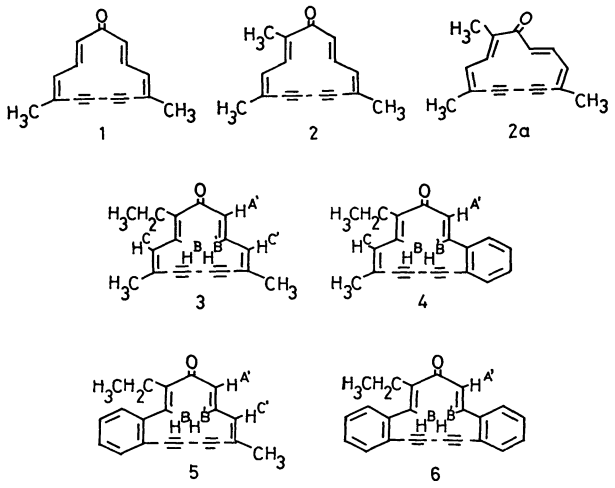
2-Ethyl-5,10-dimethyl-, 13-ethyl-10-methyl-4,5-benzo-, 2-ethyl-10-methyl-4,5-benzo-, and 2-ethyl-4,5:10,11-dibenzo-6,8-bisdehydro[13]annulenone were synthesized. Influence of α-ethyl substitution upon the skeleton of the bisdehydro[13]annulenone ring system is discussed on the basis of ^{1}H NMR and UV spectra of these annulenones and their corresponding α-methyl-substituted derivatives.

In a previous paper[1] the synthesis of the paratropic 5,10-dimethyl- **1** and 2,5,10-trimethyl-6,8-bisdehydro-[13]annulenone **2** was reported and it was shown that α-methyl-unsubstituted annulenone **1** exists in the conformation indicated and, in contrast, the extra α-methyl group of trimethylbisdehydro[13]annulenone **2** causes a change of conformation due to rotation of the opposite double bond, **2** existing in the conformation of **2a** at −60 °C. The benzo-annelated derivatives of **1** and **2** were also prepared and it was shown that the extra α-methyl substituent and fused benzene ring(s) exert a considerable influence on the development of paratropic character and conformational mobility in the bisdehydro[13]annulenone system, as compared with that in the case of α-methyl-unsubstituted compounds.[2]

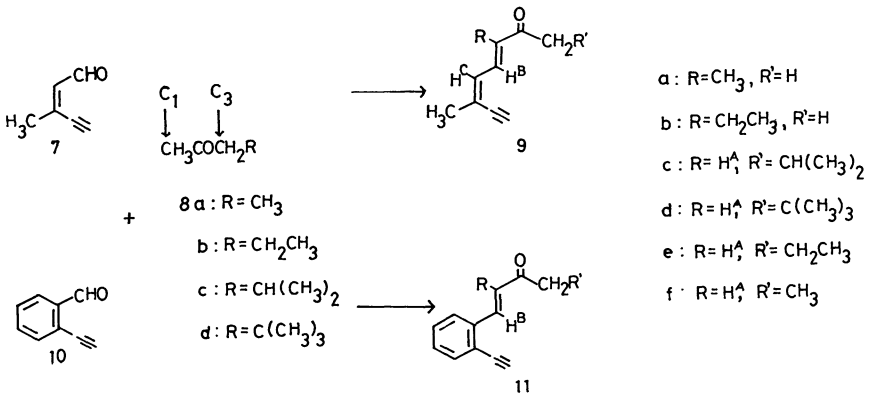


In view of these results, we investigated effects of different steric bulks of α-alkyl groups on the molecular skeleton of the bisdehydro[13]annulenone ring system. It required the preparation of 3-alkyl-2-alkanones of types **9** and **11** (R=alkyl, R′=H). In practice, we could obtain only 3-ethyl-2-alkanones **9b** and **11b** by acid-catalyzed aldol condensation from aldehydes **7** and **10** (Scheme 1). Thus we could prepare α-ethyl-substituted bisdehydro[13]annulenones **3**—**6**.

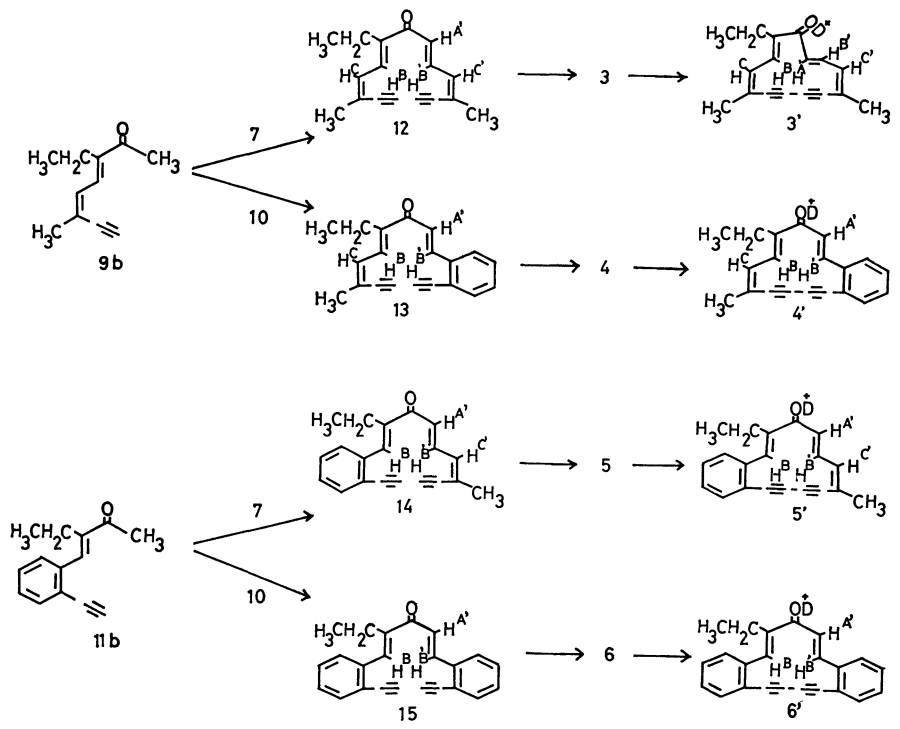
Results and Discussion

Synthesis. It is known that reaction of 2-butanone **8a**, an unsymmetrical aliphatic ketone, with aldehydes shows regioselectivity, depending on conditions used; base-catalyzed aldol condensation of 2-butanone **8a** favors C_1 of ketone as the position of attack, in contrast to C_3 favored by acid-catalyzed reaction.[3] In practice, reaction of 3-methyl-2-penten-4-ynal **7**[4] or *o*-ethynylbenzaldehyde **10**[5] with **8a** yielded **9a**[1] or **11a**[2] under acidic conditions but **9f**[1] or **11f** under basic conditions, respectively.

We examined aldol condensations of aldehydes **7** and **10** with 2-pentanone **8b** and its branched isomers **8c** and **8d**, as illustrated in Scheme 1. The results obtained demonstrate that only 2-pentanone **8b** shows regioselectivity for aldehydes **7** and **10**, as 2-butanone **8a** does. Under acidic conditions (acetic acid–sulfuric acid) **8b** yielded C_3-products, while both 4-methyl-**8c** and 4,4-dimethyl-2-pentanone **8d** yielded C_1-products. On the other hand, under basic conditions (sodium hydroxide in aqueous ethanol) all of **8b**—**d** gave C_1-products usually in higher yields than under



Scheme 1.



Scheme 2.

Table 1. Electronic absorption maxima of bisdehydro[13]annulenones in ether

λ_{max}/nm (ε_{max})

3		4		5		6	
210	(22900)	234 sh	(22700)	232 sh	(22800)	223	(36300)
250 sh	(15800)	276	(33900)	263	(25400)	268 sh	(23800)
263	(27100)	290 sh	(26400)	275	(30600)	281	(37600)
274	(28700)	388	(2980)	290 sh	(15700)	295	(39000)
390	(1000)			380	(3600)	352	(5510)

acidic conditions.

Thus, we could prepare only 3-ethyl-2-alkanones **9b** and **11b**. For ketones such as **9c—d** and **11c—d**, attempts were tried in vain to make them condense with aldehyde **7** or **10** to get their corresponding acyclic ketones. Starting with ketones **9b** and **11b**, syntheses of α-ethyl-substituted [13]annulenones **3—6** were carried out according to the previously reported procedure,[1,2] outlined in Scheme 2.

Ketone **9b** was condensed with (*Z*)-3-methyl-2-penten-4-ynal **7**[4] in the presence of ethanolic sodium ethoxide in ether to give the acyclic ketone **12** in 77% yield. Oxidative coupling of **12** with anhydrous copper(II) acetate in pyridine and ether at 50 °C[6] afforded annulenone **3** in 32% yield. Condensation of **9b** with *o*-ethynylbenzaldehyde **10**,[5] allowed to proceed similarly to that of **9b** with **7**, gave the acyclic ketone **13** in 47% yield. Oxidation of **13**, as with **12**, gave the monobenzannulenone **4** in 44% yield. Similarly, condensation of ketone **11b** with **7** gave ketone **14** in 28% yield, which was oxidized to give another monobenzannulenone **5** in 37% yield. Reaction of **11b** and **10** afforded ketone **15** in 47% yield. Oxidation of **15** gave dibenzannulenone **6** in 46% yield. The structures of these new compounds were established on the basis of their spectral properties and results of elemental analysis.

Treatment of annulenones **3—6** with trifluoroacetic acid or trifluoroacetic acid-*d* gave their corresponding protonated or deuteronated carbonyl species **3′—6′**, respectively; **3′—5′** were dark red and **6′** was yellow. Quenching of **3′—6′** with aqueous sodium hydrogencarbonate resulted in regeneration of **3—6**, respectively.

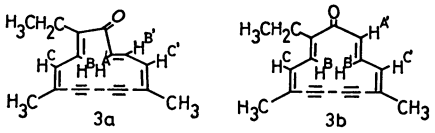
Properties. Electronic absorption maxima (in ether) of annulenones **3—6** are given in Table 1. As expected, the spectra are similar to one another, the medium bands exhibiting an appreciable bathochromic shift with increasing number of fused benzene rings, as observed for some benzo-annelated annulenes.[6] In contrast, the longest wavelength bands of these annulenones exhibit absorption shift toward longer wavelengths in the sequence of **3>4≃5>6**, demonstrating the sequence for the degree of extended conjugation of π-electron systems in the bisdehydro-[13]annulenone ring. Electronic absorption maxima of annulenones **3—6** in trifluoroacetic acid are given in Table 2, and it is evident that protonation with this acid causes a bathochromic shift of their main maxima.

Table 2. Electronic absorption maxima of bisdehydro-[13]annulenones in trifluoroacetic acid λ_{max}/nm(Relative extinction coefficient)[a)]

3	4	5	6
250 sh (0.60)	277 sh (0.91)	273 sh (0.81)	285 sh (0.83)
268 sh (0.89)	292 (1.00)	287 (1.00)	299 (1.00)
281 (1.00)	354 sh (0.17)	342 sh (0.16)	352 sh (0.12)
345 sh (0.12)	420 sh (0.08)	415 (0.12)	413 sh (0.04)

a) All the spectra showed tailing to ≈700 nm.

^{1}H NMR chemical shifts of the protons of annulenones **3**—**6** and those of their corresponding acyclic ketones at 90 MHz are listed in Table 3, together with data for the deuteronated species **3′**—**6′**, obtained through dissolution in trifluoroacetic acid-*d*. Individual assignments were made on the basis of multiplicity, coupling constants (see Experimental), and data of closely related compounds.[1,2)] Variable-temperature ^{1}H NMR spectra of **3**—**6** were taken at 100 MHz over the range −60 to 60 °C, chemical shifts being summarized in Table 4. As indicated in Fig. 1, the spectra of ethyldimethyl-6,8-bisdehydro-[13]annulenone **3** are temperature-dependent. At 35 °C (and above), the $H^{A'}$, $H^{B'}$, and $H^{C'}$ bands of **3** are unresolved multiplets. On cooling, the bands become resolved, and the expected first-order pattern is observed at −30 °C. Further cooling results in increased separation of the $H^{A'}$ and the $H^{B'}$ bands. These observations are similar to those for the spectra of the corresponding α-methyl derivative **2**[1)] and indicate that the ethyldimethylbisdehydro[13]annulenone **3** exists as conformer **3a** and not **3b**. A marked



difference observed in variable-temperature ^{1}H NMR spectra between **2** and **3** is that a spectrum of complete first-order pattern for the structure of **3a** is attained at −30 °C, whereas for the structure of **2a** it is attained at −60 °C. This result reveals that the introduction of the extra ethyl group into **1** to give **3** is more effective than that of the extra methyl group into **1** to give **2**, causing a conformational change on the other *trans* double bond in this bisdehydro[13]-annulenone ring system. On the other hand, the spectra of annulenones **4**—**6** were found essentially temperature-independent (Table 4), revealing that the conformations indicated for **4**—**6** will remain unchanged over the range −60 to 60 °C; similar temperature independence has been obtained for their corresponding α-methyl derivatives.[2)]

If we judge the tropicity of these annulenones from differences in chemical shift among various protons for the cyclic ketone (annulenone) and its corresponding acyclic model (upfield shift for the outer protons and downfield shift for the inner) (Table 3), annulenone **3** is taken to be a paratropic molecule, while **4**—**6** to be atropic ones. It has been observed that the paratropicity of the α-unsubstituted bisdehydro-[13]annulenone series decreases with increasing number of fused benzene rings.[7)] However, an examination of the data shown in Table 3 reveals that α-ethyl-substituted series (**3**—**6**) does not show such a trend.

Table 3. ^{1}H NMR chemical shifts of **3**—**6**, **12**—**15** (in $CDCl_3$), and **3′**—**6′** (in CF_3COOD) at 90 MHz, determined at 35 °C (τ Value; Internal standard, Me_4Si)

Compd	$H^{A'}$	H^{B}	$H^{B'}$	H^{C}	$H^{C'}$	ArH	$-CH_2CH_3$	$-CH_2CH_3$	CH_3
12	3.13	2.52	2.23	3.27	3.49		7.49	8.98	7.92, 7.97
3[a)]	2.10	0.38	2.50	3.37	3.73		7.69	9.00	8.17
3′	b)	−0.37	b)	3.45	3.79		7.65	8.95	8.20
Δ(**3**−**12**)	−1.03	−2.14	+0.27	+0.10	+0.24		+0.20	+0.02	+0.20—+0.25
Δ(**3′**−**12**)		−2.89		+0.18	+0.30		+0.16	−0.03	+0.23—+0.28
13	(2.25———2.75)		1.88	3.23		2.25—2.75	7.43	8.92	7.93
4	2.50	0.95	2.12	3.24		2.6—2.8	7.57	8.94	8.10
4′	2.18	0.18	1.93	3.25		2.6—2.9	7.54	8.90	8.10
Δ(**4**−**13**)			+0.24	+0.01			+0.14	+0.02	+0.17
Δ(**4′**−**13**)			+0.05	+0.02			+0.11	−0.02	+0.17
14	3.13	2.30	2.17		3.45	2.4—2.8	7.42	8.92	7.93
5	2.87	2.17	1.98		3.40	2.5—2.8	7.52	9.02	8.10
5′	3.12	2.28	1.31		3.25	2.5—2.7	7.47	8.97	8.00
Δ(**5**−**14**)	−0.26	−0.13	−0.19		−0.05		+0.10	+0.10	+0.17
Δ(**5′**−**14**)	−0.01	−0.02	−0.86		−0.20		+0.05	+0.05	+0.07
15	(2.4—2.8)	2.18	1.78			2.4—2.8	7.38	8.87	
6	2.18	1.86	1.97			2.5—2.8	7.40	8.90	
6′	1.98	1.66	1.72			2.4—2.8	7.35	8.89	
Δ(**6**−**15**)		−0.32	+0.19				+0.02	+0.03	
Δ(**6′**−**15**)		−0.52	−0.06				−0.03	+0.02	

a) At −25 °C. b) The $H^{A'}$ and $H^{B'}$ chemical shifts of **3′** appeared as a multiplet at τ 1.67—2.13, due to conformational mobility.

Table 4. ^{1}H NMR data for compounds **3**—**6** (in $CDCl_3$) at 100 MHz (τ Value; Internal standard, Me_4Si)

Compd	T/°C	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	ArH	$-C\underline{H}_2CH_3$	CH_3	$-CH_2C\underline{H}_3$
3	+60	2.32	0.65	2.52	3.48	3.82		7.69	8.22, 8.24	9.00
	+22	2.31	0.58	2.53	3.47	3.82		7.70	8.22	9.01
	−30	2.18	0.48	2.56	3.43	3.81		7.70	8.19	9.01
	−60	2.09	0.42	2.63	3.41	3.80		7.70	8.18	9.01
4	+60	2.55	1.05	2.18	3.29		2.7—2.9	7.59	8.15	8.96
	+22	2.54	1.01	2.16	3.28		2.7—2.8	7.60	8.14	8.97
	−30	2.53	0.93	2.14	3.27		2.7—2.8	7.61	8.12	8.97
	−60	2.52	0.90	2.14	3.25		2.7—2.8	7.61	8.11	8.97
5	+60	2.89	2.24	2.09		3.48	2.7—2.9	7.55	8.12	9.02
	+22	2.94	2.22	2.02		3.45	2.7—2.8	7.54	8.11	9.02
	−30	3.10	2.24	1.84		3.41	2.7—2.8	7.51	8.09	9.03
	−60	3.22	2.26	1.73		3.38	2.7—2.8	7.50	8.07	9.04
6	+60	2.07	1.98	2.23			2.5—2.8	7.43		8.93
	+22	2.04	1.93	2.21			2.5—2.8	7.42		8.93
	−30	2.03	1.88	2.19			2.5—2.8	7.40		8.92
	−60	2.03	1.87	2.18			2.5—2.7	7.38		8.91

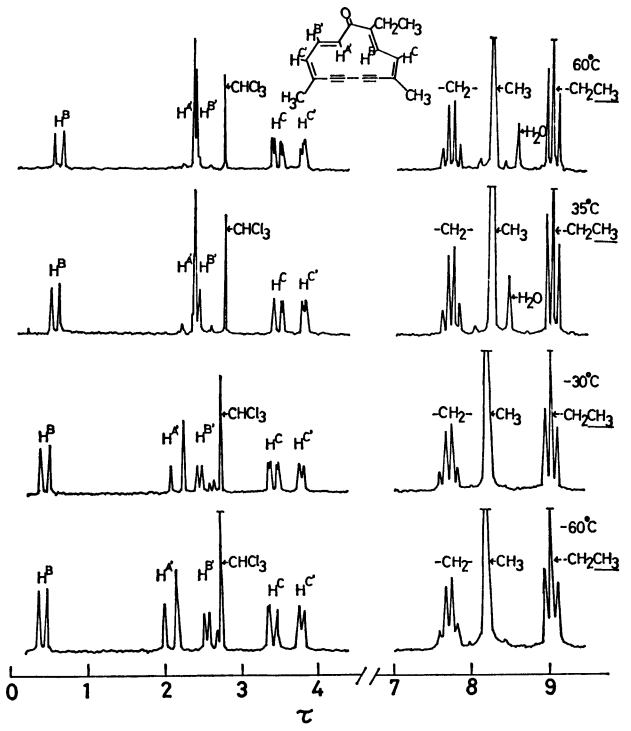


Fig. 1. The ^{1}H NMR FT spectra of **3** in $CDCl_3$ at 100 MHz (Internal standard, TMS).

Because it has been pointed out that annelation of an aromatic ring with an antiaromatic system exerts rather a minor effect on the paratropicity of the $4n\pi$ electron system,[8] and that the patatropicity of $4n$ moiety in the annelated [$4n$]annulene is quite sensitive to even a minor change in conformation,[9] the above-mentioned trend observed in the series of α-ethyl-substituted bisdehydro[13]annulenone (**3**—**6**) should be ascribed to small change in the conformation of the [13]annulenone ring due to ethyl substitution at α-position and benzo-annelation, although the local anisotropic effect of the diacetylene unit can not be excluded.

In conclusion, the results obtained from this study indicate that the change of α-substituent from methyl to ethyl group causes both paratropic nature and conformational stability to decrease in the bisdehydro-[13]annulenone ring system.

Experimental

Deoxygenated ether was used to minimize oxidation of the compounds used for aldol condensation, and was freed from peroxide by passage through a short column of basic alumina (Woelm Act. I) followed by flushing with nitrogen immediately before use. Melting points were uncorrected. Mass spectra were recorded by the direct insertion technique with a JEOL JMS-200 spectrometer operating at 75 eV. IR spectra were taken on a Hitachi EPI-S2 spectrophotometer; only those absorptions characteristic of the carbonyl group are given in cm^{-1} for compounds **9** and **11**. UV spectra were measured on a Hitachi 124 instrument in ethanol solution, unless otherwise specified, and recorded in nm. ε-Values are given in parentheses, shoulders being denoted by sh. ^{1}H NMR spectra were recorded on a Varian EM-390 (90 MHz) or a JEOL FX-100 (100 MHz) spectrometer, and the data taken with a Varian EM-390 instrument are specified in this section by τ-value in $CDCl_3$ solution, TMS being used as an internal standard, unless otherwise stated. The coupling constants (J) are given in Hz. Alumina (Act. II—III) was used for column chromatography.

*3-Ethyl-6-methyl-3,5-octadien-7-yn-2-one (**9b**).* A solution of aldehyde **7**[4] (3.00 g, 32 mmol) in acetic acid (16 ml) was added dropwise during 2 h to a stirred solution of 2-pentanone **8b** (10.0 g, 16 mmol) and concentrated sulfuric acid (2.8 ml) in acetic acid (110 ml) at ambient temperature. The solution was stirred for a further 4.5 h, and then was cautiously poured into saturated aqueous potassium carbonate (200 ml). The mixture was diluted with water, and extracted with benzene. The extracts were washed with saturated aqueous sodium chloride solution, and dried over sodium sulfate. The residue obtained after removal of the solvent was chromatographed on alumina (80 g) with 5% ether in hexane. The early fractions gave ketone **9b** (2.08 g, 40%) as a light yellow oil; MS, *m/e*, 162 (M^+, 70%) and 119 (100); mol wt 162.2; IR (neat) 1660 cm^{-1}; UV_{max} 304 nm (51600); NMR τ=2.47 (d, 11, 1H, H^B), 3.27 (d, 11, 1H, H^C), 6.33 (s, 1H, $-C\equiv CH$), 7.57 (q, 8, 2H, $-C\underline{H}_2CH_3$), 7.60 (s, 3H, CH_3), 7.90 (s, 3H, CH_3), and 9.02 (t, 8, 3H, $-CH_2C\underline{H}_3$).

Found: C, 79.86; H, 8.40%. Calcd for $C_{11}H_{14}O$: C,

81.44; H, 8.70%. Attempts to improve the elemental analysis failed.

*2,8-Dimethyl-5,7-decadien-9-yn-4-one (**9c**)*: Yield 12% (acidic conditions) and 23% (basic conditions); light yellow oil; MS, *m/e*, 176 (M^+, 13%) and 119 (100); mol wt 176.2; IR (neat) 1680 and 1660 cm^{-1}; UV_{max} 305 nm (33500); NMR τ=2.40 (dd, 15.5, 11, 1H, H^B), 3.56 (d, 11, 1H, H^C), 3.80 (d, 15.5, 1H, H^A), 6.43 (s, 1H, $-C\equiv CH$), 7.53 (d, 7, 2H, $-C\underline{H}_2CH-$), 7.76 (m, 1H, $-CH_2C\underline{H}-$), 7.95 (s, 3H, CH_3), and 9.03 (d, 7, 6H, $-CH(C\underline{H}_3)_2$). Found: C, 81.94; H, 8.95%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

*2,2,8-Trimethyl-5,7-decadien-9-yn-4-one (**9d**)*: Yield 18% (acidic conditions) and 25% (basic conditions); light yellow oil; MS, *m/e*, 190 (M^+, 16%) and 134 (100); mol wt 190.2; IR (neat) 1675, 1660, and 1650 cm^{-1}; UV_{max} 304 nm (39700); NMR τ=2.42 (dd, 16, 12, 1H, H^B), 3.55 (d, 12, 1H, H^C), 3.80 (d, 16, 1H, H^A), 6.42 (s, 1H, $-C\equiv CH$), 7.52 (s, 2H, $-C\underline{H}_2-$), 7.95 (s, 3H, CH_3), and 8.95 (s, 9H, $-C(C\underline{H}_3)_3$). Found: C, 79.78; H, 9.15%. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54%. Attempts to improve the elemental analysis faield.

Ketones **9c** and **9d** were prepared by reaction of **8c** and **8d** with **7**, respectively, in a manner similar to that described above for the preparation of **9b**. Compounds **9c** and **9d** were also prepared by the reaction, under basic conditions, described below for the preparation of **9e**, and the yields under both acidic and basic conditions are given below.

*8-Methyl-5,7-decadien-9-yn-4-one (**9e**)*. A solution of 2.6% aqueous sodium hydroxide (7.0 ml) was added to an ice-cooled stirred solution of aldehyde **7** (1.0 g, 11 mmol) and **8b** (2.8 g, 33 mmol) in ethanol (6 ml). The solution was stirred for a further 2 h at 3 °C, and aqueous sulfuric acid (2 M, 10 ml) was then added. The solution was diluted with water and extracted with benzene. The extracts were washed with aqueous sodium hydrogencarbonate and sodium chloride solution, and dried over sodium sulfate. The residue obtained after removal of the solvent was chromatographed on alumina (70 g). The fractions eluted with 5% ether in hexane afforded ketone **9e** (425 mg, 35%) as a light yellow oil: MS, *m/e*, 162 (M^+, 17%) and 129 (100); mol wt 162.2; IR (neat) 1685 and 1660 cm^{-1}; UV_{max} 301 nm (27000); NMR τ=2.37 (dd, 16, 11, 1H, H^B), 3.54 (d, 11, 1H, H^C), 3.79 (d, 16, 1H, H^A), 6.37 (s, 1H, $-C\equiv CH$), 7.42 (t, 8, 2H, $-C\underline{H}_2CH_2-$), 7.97 (s, 3H, CH_3), 8.34 (m, 8, 2H, $-CH_2C\underline{H}_2-$), and 9.05 (t, 8, 3H, $-CH_2C\underline{H}_3$). Found: C, 81.24; H, 8.44%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

Reactions of **8b**—**d** with aldehyde **10**[5] were carried out similarly to those with aldehyde **7** under both acidic and basic conditions.

*3-Ethyl-4-(o-ethynylphenyl)-3-buten-2-one (**11b**)*. Yield 29%; yellow oil; MS, *m/e*, 198 (M^+, 23%) and 155 (100); mol wt 198.2; IR (neat) 1665 cm^{-1}; UV_{max} 227 sh (25100), 239 (31700), and 281 nm (19600); NMR τ=2.17 (s, 1H, H^B), 2.33—2.80 (m, 4H, ArH), 6.52 (s, 1H, $-C\equiv CH$), 7.52 (s, 3H, CH_3), 7.53 (q, 7, 2H, $-C\underline{H}_2CH_3$), and 8.90 (t, 7, 3H, $-CH_2C\underline{H}_3$). Found: C, 84.71; H, 7.15%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

*6-(o-Ethynylphenyl)-2-methyl-5-hexen-4-one (**11c**)*. Yield 17% (acidic conditions) and 67% (basic conditions); yellow oil MS, *m/e*, 212 (M^+, 15%) and 155 (100); mol wt 212.2; IR (neat) 1680, 1670, and 1660 cm^{-1}; UV_{max} 228 (31900), 242 (40900), 247 sh (39700), and 293 nm (37100): NMR τ= 1.92 (d, 16, 1H, H^B), 2.29—2.70 (m, 4H, ArH), 3.23 (d, 16, 1H, H^A), 6.45 (s, 1H, $-C\equiv CH$), 7.44 (d, 7, 2H, $-C\underline{H}_2-$), 7.52—7.99 (m, 1H, $-CH<$), and 9.02 (d, 7, 6H, $-CH-(C\underline{H}_3)_2$). Found: C, 84.68; H, 7.35%. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60%.

*2,2-Dimethyl-6-(o-ethynylphenyl)-5-hexen-4-one (**11d**)*. Yield 34% (acidic conditions) and 71% (basic conditions); yellow oil; MS, *m/e*, 226 (M^+, 6%) and 155 (100); mol wt 226.3; IR (neat) 1680 and 1650 cm^{-1}; UV_{max} 229 (22400), 243 (27900), 248 (27400), and 294 nm (26100); NMR τ=1.88 (d, 16, 1H, H^B), 2.23—2.68 (m, 4H, ArH), 3.18 (d, 16, 1H, H^A), 6.50 (s, 1H, $-C\equiv CH$), 7.40 (s, 2H, $-C\underline{H}_2-$), and 8.90 (d, 9H, $-C(C\underline{H}_3)_3$). Found: C, 84.84; H, 7.95%. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02%.

*6-(o-Ethynylphenyl)-5-hexen-4-one (**11e**)*. Yield 37%; light yellow cubes from hexane–benzene; mp 64—65.5 °C; MS, *m/e*, 198 (M^+, 14%) and 155 (100); mol wt 198.2; IR (KBr disk) 1675 cm^{-1}; UV_{max} 228 (14200), 242 (19800), 247 sh (19000), and 292 nm (18100); NMR τ=1.90 (d, 16, 1H, H^B), 2.35—2.80 (m, 4H, ArH), 3.22 (d, 16, 1H, H^A), 6.49 (s, 1H, $-C\equiv CH$), 7.33 (t, 7, 2H, $-C\underline{H}_2CH_2-$), 8.28 (m, 7, 2H, $-CH_2C\underline{H}_2-$), and 9.01 (t, 7, 3H, CH_3). Found: C, 84.99; H, 7.00%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

*5-(o-Ethynylphenyl)-4-penten-3-one (**11f**)*. Yield 38%; light yellow oil; MS, *m/e*, 184 (M^+, 14%) and 155 (100); mol wt 184.2; IR (neat) 1685 and 1665 cm^{-1}; UV_{max} 229 (16300), 243 (22400), 249 (21500), 261 (8340), and 290 nm (18500); NMR τ=1.89 (d, 16, 1H, H^B), 2.2—2.7 (m, 4H, ArH), 3.20 (d, 16, 1H, H^A), 6.43 (s, 1H, $-C\equiv CH$), 7.25 (q, 8, 2H, $-C\underline{H}_2-$), and 8.80 (t, 8, 3H, CH_3). Found: C, 83.60; H, 6.39%. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57%. Attempts to improve the elemental analysis failed.

*6-Ethyl-3,11-dimethyl-3,5,8,10-tridecatetraene-1,12-diyn-7-one **12**.* To a mixture of aldehyde **7**[4] (1.30 g, 14 mmol) and ketone **9b** (562 mg, 3.4 mmol) in deoxygenated ether (20 ml) was added a 20% methanolic potassium hydroxide solution (1.7 ml) with stirring at 0 °C. The mixture was then stirred for 6 h at the same temperature. Neutralization with acetic acid (4.6 ml) followed by pouring into water (200 ml) and extraction with benzene gave an organic extract which was worked up as usual. The residue obtained by evaporation of the solvent was chromatographed on alumina (100 g). The initial fractions gave the unchanged ketone **9b** (164 mg). The following fractions eluted with hexane–ether (4:1) afforded ketone **12** (626 mg, 77%) as a solid. Recrystallization from hexane–benzene afforded yellow needles; mp 74.5—75 °C, MS, *m/e*, 238 (M^+, 10%) and 165 (100); mol wt 238.3; IR (KBr disk) 3250 ($-C\equiv CH$), 2100 ($-C\equiv C-$), 1645 (C=O), 1605, 1590, 1580 (C=C), and 980 cm^{-1} (*trans* C=C); UV_{max} (ether) 251 (19200), 256 (19300), 269 sh (17200), 293 (15300), 324 sh (27500), 336 (29800), and 354 nm sh (20900); NMR τ=2.23 (dd, 15, 11, 1H, $H^{B'}$), 2.52 (d, 11, 1H, H^B), 3.13 (d, 15, 1H, $H^{A'}$), 3.27 (d, 11, 1H, H^C or $H^{C'}$), 3.49 (d, 11, 1H, H^C or $H^{C'}$), 6.46 (s, 1H, $-C\equiv CH$), 6.52 (s, 1H, $-C\equiv CH$), 7.49 (q, 8, 2H, $-C\underline{H}_2CH_3$), 7.92 (s, 3H, CH_3), 7.97 (s, 3H, CH_3), and 8.98 (t, 8, 3H, $-CH_2C\underline{H}_3$). Found: C, 85.39; H, 7.63%. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

*2-Ethyl-5,10-dimethyl-6,8-bisdehydro[13]annulenone (**3**)*. A solution of ketone **12** (825 mg, 3.5 mmol) in pyridine (48 ml) and dry ether (18 ml) was added dropwise during 3.5 h to a stirred solution of anhydrous copper(II) acetate (4.40 g) in pyridine (100 ml) and dry ether (35 ml) at 49—53 °C (bath). The solution was stirred at the same temperature for a further 1.5 h and then cooled. After addition of benzene (200 ml), the mixture was filtered through a Hyflo Super-Cel. The precipitates were washed with benzene (100 ml × 3) and the filtrate was poured into water. The organic layer was separated and the aqueous layer was extracted with benzene. The combined organic extracts were washed successively with 7% hydrochloric acid,

aqueous sodium hydrogencarbonate, and water, and dried over sodium sulfate. The dark red liquid obtained after removal of the solvent was chromatographed on alumina (80 g). The fractions eluted with hexane–ether (9:1) afforded annulenone **3** (257 mg, 32%), which formed red plates from hexane; mp 49—50 °C, MS, *m/e*, 236 (M^+, 28%) and 178 (100); mol wt 236.3; IR (KBr disk) 2150 (–C≡C–), 1650 (C=O), 1620 (C=C), and 985 cm^{-1} (*trans* C=C); UV, see Tables 1 and 2; NMR (−25 °C) τ=0.38 (d, 10, 1H, H^B), 2.10 (d, 16, 1H, $H^{A'}$), 2.50 (dd, 16, 6, 1H, $H^{B'}$), 3.37 (d, 10, 1H, H^C), 3.73 (d, 6, 1H, $H^{C'}$), 7.69 (q, 8, 2H, $-C\underline{H}_2CH_3$), 8.17 (s, 6H, CH_3), and 9.00 (t, 8, 3H, $-CH_2C\underline{H}_3$), and see Figure 1; NMR (CF_3COOD) τ=−0.37 (d, 10.5, 1H, H^B), 1.67—2.13 (m, 2H, $H^{A'}$ and $H^{B'}$), 3.45 (dd, 10.5, 1.5, H^C), 3.79 (dd, 6, 1.5, 1H, $H^{C'}$), 7.65 (q, 8, 2H, $-C\underline{H}_2CH_3$), 8.20 (broad s, 6H, CH_3), and 8.95 (t, 8, 3H, $-CH_2C\underline{H}_3$). Found: C, 86.30; H, 6.76%. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83%.

*4-Ethyl-1-(o-ethynylphenyl)-7-methyl-1,4,6-nonatrien-8-yn-3-one (**13**).* A solution of *o*-ethynylbenzaldehyde **10**[5] (1.40 g, 10.6 mmol) in deoxygenated ether (20 ml) was added dropwise during 30 min with ice-bath cooling to a stirred solution of ketone **9b** (1.20 g, 7.3 mmol) in deoxygenated ether (35 ml) containing ethanolic sodium ethoxide (2.1 ml) [from sodium (760 mg) and absolute ethanol (50 ml)]. After stirring for a further 6 h at the same temperature, the reaction was quenched by addition of aqueous oxalic acid. The mixture was poured into water (100 ml) and extracted with benzene. After working up as usual, the red liquid obtained was chromatographed on alumina (100 g). The early fractions gave the recovered aldehyde **10** (285 mg). The following fractions eluted with hexane–ether (17:3) gave ketone **13** (1.18 g, 47%) as a solid. Recrystallization from hexane–benzene afforded light yellow needles: mp 114—115 °C; MS, *m/e*, 274 (M^+, 15%) and 245 (100); mol wt 274.3; IR (KBr disk) 3250 (–C≡CH), 2150 (–C≡C–), 1645 (C=O), 1590 (C=C), 990, and 980 cm^{-1} (*trans* C=C); UV_{max} (ether) 230 (21600), 252 (22100), 259 sh (20600), 309 sh (17200), 327 (19700), and 352 nm sh (13600); NMR τ=1.88 (d, 16, 1H, $H^{B'}$), 2.25—2.75 (m, 6H, $H^{A'}$, H^B, and ArH), 3.23 (d, 11, 1H, H^C), 6.42 (s, 1H, –C≡CH), 6.51 (s, 1H, –C≡CH), 7.43 (q, 8, 2H, $-C\underline{H}_2CH_3$), 7.93 (s, 3H, CH_3), and 8.92 (t, 8, $-CH_2C\underline{H}_3$). Found: C, 87.38; H, 6.45%. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61%.

*13-Ethyl-10-methyl-4,5-benzo-6,8-bisdehydro[13]annulenone (**4**).* A solution of ketone **13** (1.1 g, 4 mmol) in pyridine–dry ether (3:1, 84 ml) was added dropwise during 3 h to a stirred solution of anhydrous copper(II) acetate (5.0 g) in pyridine–dry ether (3:1, 180 ml) at 45—50 °C (bath). The solution was stirred for a further 30 min at the same temperature and then cooled. After working up as in the preparation of **3**, the red liquid obtained was chromatographed on alumina (100 g). The fractions eluted with hexane–ether (17:3) gave monobenzannulenone **4** (481 mg, 44%). Recrystallization from hexane–benzene afforded yellow needles; mp 119—120 °C; MS, *m/e*, 272 (M^+, 20%) and 229 (100); mol wt 272.3; IR (KBr disk) 2150 (–C≡C–), 1650 (C=O), 1600 (C=C), and 980 cm^{-1} (*trans* C=C); UV, see Tables 1 and 2, NMR τ=0.95 (d, 11, 1H, H^B), 2.12 (d, 16.5 1H, $H^{B'}$), 2.50 (d, 16.5, 1H, $H^{A'}$), 2.6—2.8 (m, 4H, ArH), 3.24 (dd, 11, 1, 1H, H^C), 7.57 (q, 8, 2H, $-C\underline{H}_2CH_3$), 8.10 (d, 1, 3H, CH_3), and 8.94 (t, 8, 3H, $-CH_2C\underline{H}_3$); NMR (CF_3COOD) τ=0.18 (d, 11, 1H, H^B), 1.93 (d, 16.5, 1H, $H^{B'}$), 2.18 (d, 16.5, 1H, $H^{A'}$), 2.6—2.9 (m, 4H, ArH), 3.25 (d, 11, 1H, H^C), 7.54 (q, 8, 2H, $-C\underline{H}_2CH_3$), 8.10 (s, 3H, CH_3), and 8.90 (t, 8, 3H, $-CH_2C\underline{H}_3$). Found: C, 88.40; H, 5.67%. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92%.

*2-Ethyl-1-(o-ethynylphenyl)-7-methyl-1,4,6-nonatrien-8-yn-3-one (**14**).* Potassium hydroxide–ethanol (5.0 ml; 10% W/V) was added to a solution of ketone **11b** (2.40 g, 12.1 mmol) in dry tetrahydrofuran (35 ml), and a solution of aldehyde **7** (2.3 g, 24 mmol) in dry tetrahydrofuran (17 ml) was then added dropwise during 40 min with stirring at 9—10 °C. After stirring for a further 3 h at the same temperature, the reaction was quenched by addition of acetic acid (7 ml). The resulting solution was poured into water (150 ml) and extracted with benzene. The usual working up afforded a red liquid which was chromatographed on alumina (120 g). The early fractions gave the recovered ketone **11b** (586 mg). The following fractions, eluted with hexane–ether (9:1), gave ketone **14** (885 mg, 28%) as a partly crystallized liquid. Crystallization from hexane–benzene afforded yellow cubes: mp 90—92 °C; MS, *m/e*, 274 (M^+, 5%) and 217 (100); mol wt 274.3; IR (KBr disk) 3300, 3250 (–C≡CH), 2100 (–C≡C–), 1650 (C=O), 1595 (C=C), and 980 cm^{-1} (*trans* C=C); UV_{max} (ether) 226 (21000), 244 (18000), and 315 nm (22200); NMR τ=2.17 (dd, 15, 11, 1H, $H^{B'}$), 2.30 (s, 1H, H^B), *ca.* 2.4—2.8 (m, 4H, ArH), 3.13 (d, 15, 1H, $H^{A'}$), 3.45 (d, 11, 1H, $H^{C'}$) 6.50 (s, 1H, –C≡CH), 6.60 (s, 1H, –C≡CH), 7.42 (q, 8, 2H, $-C\underline{H}_2CH_3$), 7.93 (s, 3H, CH_3), and 8.92 (t, 8, 3H, $-CH_2C\underline{H}_3$). Found: C, 87.59; H, 6.40%. Calcd for $C_{20}H_{18}O$: 87.56; H, 6.61%.

*2-Ethyl-10-methyl-4,5-benzo-6,8-bisdehydro[13]annulenone (**5**).* A solution of ketone **14** (737 mg, 2.7 mmol) in pyridine–dry ether (3:1, 56 ml) was added dropwise during 2.5 h to a stirred solution of anhydrous copper(II) acetate (3.4 g) in pyridine–dry ether (3:1, 120 ml) at 45—50 °C (bath). The solution was stirred at the same temperature for a further 45 min and then cooled. After working up as in the preparation of **3**, the red liquid obtained was chromatographed on alumina (100 g). The fractions eluted with hexane–ether (9:1), gave benzannulenone **5** (269 mg, 37%). Recrystallization from hexane–benzene afforded yellow cubes: mp 101—102 °C; MS, *m/e*, 272 (M^+, 100%); mol wt 272.3; IR (KBr disk) 2150 (–C≡C–), 1625 (C=O), 1595 (C=C), and 970 cm^{-1} (*trans* C=C); UV, see Tables 1 and 2; NMR τ=1.98 (dd, 16, 9, 1H, $H^{B'}$), 2.17 (s, 1H, H^B), 2.5—2.8 (m, 4H, ArH), 2.87 (d, 16, 1H, $H^{A'}$), 3.40 (d, 9, 1H, $H^{C'}$), 7.52 (q, 8, 2H, $-C\underline{H}_2CH_3$), 8.10 (s, 3H, CH_3), 9.02 (t, 8, 3H, $-CH_2C\underline{H}_3$); NMR (CF_3COOD) τ=1.31 (dd, 16, 11, 1H, $H^{B'}$), 2.28 (s, 1H, H^B), 2.5—2.7 (m, 4H, ArH), 3.12 (d, 16, 1H, $H^{A'}$), 3.25 (d, 11, 1H, $H^{C'}$), 7.47 (q, 8, 2H, $-C\underline{H}_2CH_3$), 8.00 (s, 3H, CH_3), and 8.97 (t, 8, 3H, $-CH_2C\underline{H}_3$). Found: C, 88.44; H, 5.76%. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92%.

*2-Ethyl-1,5-bis(o-ethynylphenyl)-1,4-pentadien-3-one (**15**).* A solution of *o*-ethynylbenzaldehyde **10** (2.0 g, 15 mmol) in deoxygenated ether (17 ml) was added dropwise during 30 min with ice-bath cooling to a stirred solution of ketone **11b** (0.86 g, 4 mmol) in deoxygenated ether (43 ml) containing ethanolic sodium ethoxide (24 ml) [from sodium (0.38 g) and absolute ethanol (50 ml)]. After stirring for a further 8 h at the same temperature, the reaction was quenched by addition of aqueous oxalic acid. The mixture was poured into water (100 ml) and extracted with benzene. After usual working up, the semi-solid obtained was chromatographed on alumina (120 g). The early fractions gave the recovered aldehyde **10** (434 mg). The following fractions eluted with hexane–ether (4:1) gave ketone **15** (626 mg, 47%). Recrystallization from hexane–benzene afforded light yellow needles: mp 117—118 °C; MS, *m/e*, 310 (M^+, 13%) and 155 (100); mol wt 310.3; IR (KBr disk) 3250 (–C≡CH), 2150 (–C≡C–), 1655 (C=O), 1600 (C=C), and 980 cm^{-1} (*trans* C=C); UV_{max} (ether) 225

(28800), 245 (25200), 254 sh (20600), and 302 nm (16700); NMR τ=1.78 (d, 16, 1H, $H^{B'}$), 2.18 (s, 1H, H^{B}), *ca.* 2.4—2.8 (m, 9H, $H^{A'}$ and ArH), 6.54 (s, 1H, $-C\equiv CH$), 6.62 (s, 1H, $-C\equiv CH$), 7.38 (q, 8, 2H, $-C\underline{H}_2CH_3$), and 8.87 (t, 8, 3H, $-CH_2C\underline{H}_3$). Found: C, 89.18; H, 5.67%. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85%.

2-Ethyl-4,5:10,11-dibenzo-6,8-bisdehydro[13]annulenone (6). A solution of ketone **15** (0.52 g, 1.7 mmol) in pyridine–dry ether (3:1, 36 ml) was added dropwise during 3.5 h to a stirred solution of anhydrous copper(II) acetate (2.2 g) in pyridine–dry ether (3:1, 80 ml) at 45—50 °C. The solution was stirred for a further 30 min at the same temperature and then cooled. After working up as in the preparation of **3**, the brown solid obtained was chromatographed on alumina (90 g). The fractions eluted with hexane–ether (3:2) gave dibenzannulenone **6** (241 mg, 46%). Recrystallization from hexane–benzene afforded yellow needles: mp 154 °C (dec); MS, *m/e*, 308 (M^+, 100%); mol wt 308.3; IR (KBr disk) 2200 ($-C\equiv C-$), 1660 (C=O), 1610 (C=C), 995 and 985 cm^{-1} (*trans* C=C); UV, see Tables 1 and 2; NMR τ=1.86 (s, 1H, H^{B}), 1.97 (d, 16, 1H, $H^{B'}$), 2.18 (d, 16, 1H, $H^{A'}$), *ca.* 2.5—2.8 (m, 8H, ArH), 7.40 (q, 8, 2H, $-C\underline{H}_2CH_3$), and 8.90 (t, 8, 3H, $-CH_2C\underline{H}_3$); NMR (CF_3COOD) τ=1.66 (s, 1H, H^{B}), 1.72 (d, 16, 1H, $H^{B'}$), 1.98 (d, 16, 1H, $H^{A'}$), *ca.* 2.4—2.8 (m, 8H, ArH), 7.35 (q, 8, 2H, $-C\underline{H}_2CH_3$), and 8.89 (t, 8, $-CH_2C\underline{H}_3$). Found: C, 89.31; H, 5.00. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23%.

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