pseudo-INDOR spectra of **6** were obtained by using a 10° observation pulse and a recovery time of 30 s. Eight FID's were acquired with the decoupler set exactly on a given resonance; eight FID's with the decoupler off-resonance were then substracted. This procedure was repeated until an adequate signal-to-noise ratio was achieved.

The natural-abundance ^{13}C spectrum of **3** was obtained in the PFT mode at 100.61 MHz on the same instrument by using quadrature detection. A total of 7200 transients were acquired with a sweep width of 1240 Hz and 16k complex data points, thus leading to a digital resolution of 0.15 Hz in the frequency domain. To improve the shape of the absorption spectrum zero filling up to 32K data points was performed before transforming the FID.

The computations were performed on a Telefunken TR 440 computer in the Rechenzentrum der Universität Würzburg by using the programs LAOCOON III[29] and LAME.[30] The root-mean-square values were as follows: **3**, 0.036; **4**, 0.019; *cis*-**5**, 0.042; *trans*-**5**; 0.045; **6**, 0.010, **7**, 0.038.

Acknowledgment. We thank Dr. Binger, Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim (Ruhr), for samples of the methylenecyclopropanes investigated in this study. Financial support was provided by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. **3**, 6142-73-0; **4**, 18631-84-0; *cis*-**5**, 4866-55-1; *trans*-**5**, 5070-00-8; **6**, 4372-94-5; **7**, 34462-28-7.

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(31) **Note Added in Proof**: For 2,2-dimethylmethylenecyclopropane (**6**), the relation $|^4J_{cisoid}| < |^4J_{transoid}|$ has now been established by Nuclear Overhauser difference spectroscopy.

(32) **Note Added in Proof**: The analysis of the carbon-13 satellite spectrum of the ring methylene group of methylenecyclopropane in [$^2H_6$]benzene by W. Herrig has led to essentially the same results: $\delta_{1,2} = 5.44$, $\delta_{3-6} = 1.03$; $^2J_{1,2} = 1.6 \pm 0.8$, $^2J_{3,4} = -9.7 \pm 0.5$, $^3J_{3,5} = 9.93 \pm 0.02$, $^3J_{3,6} = 5.77 \pm 0.02$, $^4J = -1.74 \pm 0.02, -2.49 \pm 0.02$ (Herrig, W., Diploma Thesis, University of Cologne, 1972). We thank Professor Günther, University of Siegen, West Germany, for bringing these data to our attention.

Syntheses of 2-Carbomethoxy-5,10-dimethyl-6,8-bisdehydro[13]annulenone, a Potential Precursor of Macrocyclic Azulene Analogues, and (*Z*)- and (*E*)-14-Carbethoxy-2-carbomethoxy-5,10-dimethyl-6,8-bisdehydro[13]fulvenes[1]

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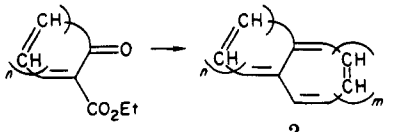
Received September 13, 1982

The synthesis of 2-carbomethoxy-5,10-dimethyl-6,8-bisdehydro[13]annulenone (**15**), a potential precursor of macrocyclic azulene analogues, and its elaboration into (*E*)- (**19**) and (*Z*)-14-carbethoxy-2-carbomethoxy-5,10-dimethyl-6,8-bisdehydro[13]fulvene (**20**) is reported. The ^1H NMR spectrum of **15** is interpreted to indicate that in the average conformation the C-12,13 double bond is not coplanar with the ring, and a reappraisal of the conformation of 2,5,10-trimethyl-6,8-bisdehydro[13]annulenone (**16b**) is made. The [13]fulvenes **19** and **20** show little or no paratropicity and serve as model systems for the estimation of paratropicity in **15** and related systems.

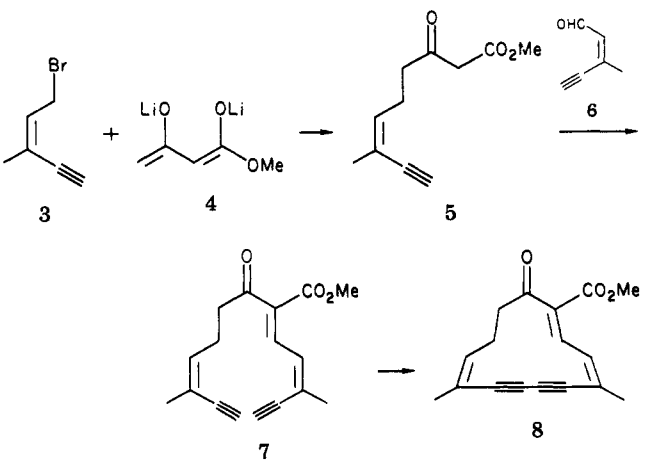
The first synthesis of macrocyclic analogues of naphthalene in which both rings are larger than benzene were reported in 1975.[2,3] These successes focussed attention on the possibility of preparing macrocyclic analogues of azulene[4] and octalene,[5] and we devised an approach to the azulene-type systems which involved the annelation of a 2-substituted [4*n* + 1]annulenone. It was envisaged that the combined functionality supplied by the ketone group and the 2-substituent would allow the fabrication of the second ring, and a β-keto ester was chosen as the target compound, allowing the transformation **1** → **2**.[6] We now



1 2

report the synthesis of 2-carbomethoxy-5,10-dimethyl-6,8-bisdehydro[13]annulenone (**15**), a 2-substituted [4*n* + 1]annulenone and a potential precursor of azulene type systems, and describe some of its chemistry.

Scheme I



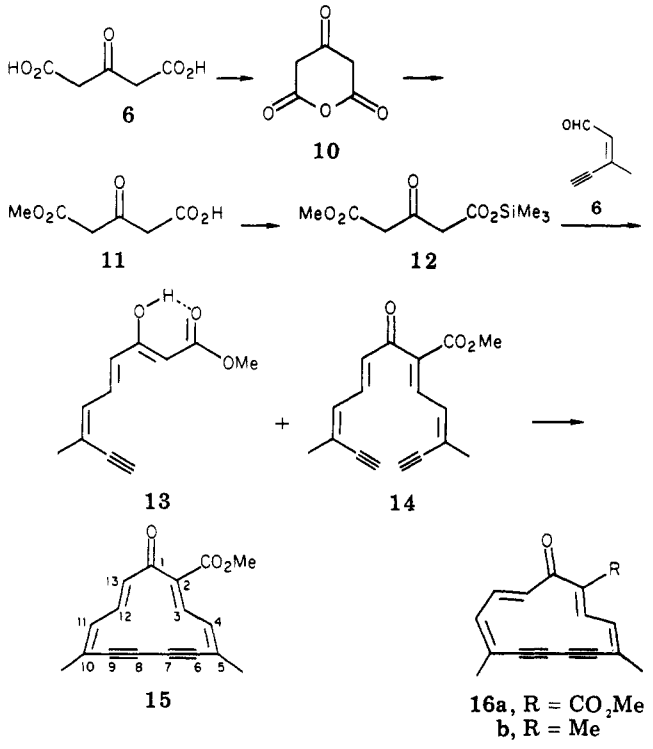
Our initial approach was based on our recently reported synthesis of 5,10-dimethyl-6,8-bisdehydro[13]annulenone,[7]

† Deceased, February 11, 1981.

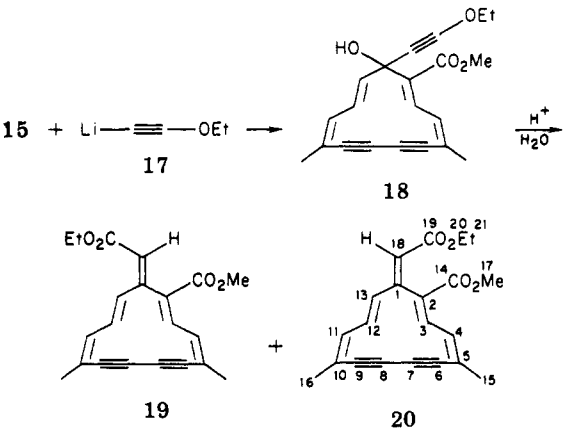
(1) Unsaturated Macrocyclic Compounds. 131. For part 129, see: Taylor, R. J. K.; Sondheimer, F. *J. Org. Chem.* **1981**, *46*, 4594. For part 130, see: Cresp, T. M.; Sondheimer, F. *Tetrahedron Lett.* **1982**, *23*, 1731.

0022-3263/83/1948-2379$01.50/0

Scheme II



Scheme III



but this route rapidly proved abortive. We next turned our attention to a synthetic sequence based on the preparation of the 12,13-dihydro derivative **8**, which was expected to be readily transformed into the desired fully unsaturated system **15**. The route to **8** is outlined in Scheme I.

Dilithiated methyl acetoacetate **4**[8] was alkylated with the bromide **3**, prepared by the method of Isler,[9] the alkylation occurring exclusively in the γ-position to give **5** in 44% yield. Compound **5** showed the expected resonance signals in the ^1H and ^{13}C NMR spectra. Knoevenagel reaction of **5** with the aldehyde **6** in the presence of piperidine gave the desired product **7** in 92% yield as a mixture of *E,Z* isomers. No attempt was made to separate this mixture, which was treated under the conditions required for oxidative acetylene coupling, the Glaser (O_2, Cu_2Cl_2, NH_4Cl) being found preferable to the Eglinton ($Cu(OAc)_2$, pyridine) conditions in this case. Compound **8** was isolated, after chromatography, in ca. 20% yield as yellow needles, and the assigned structure is supported by the spectral properties (Tables I and II) and the mode of synthesis.

All attempts to convert **8** into the fully unsaturated system **15** failed; either starting material was recovered or no material that we could characterize was isolated. With this failure to effect dehydrogenation of **8** an alternative route to **15** was investigated. This is outlined in Scheme II.

Acetonedicarboxylic acid (**9**) was converted into its monomethyl ester **11** via the anhydride **10**.[10] The monomethyl ester **11** was then esterified with Me_3SiCl in the presence of pyridine to give the mixed diester **12**. Treatment of **12** with 2 equiv of the aldehyde **6** under the Knoevenagel conditions gave a mixture (1:8) of **13** and **14**. Compound **13** was separated from **14** by chromatography, and the ^1H and ^{13}C NMR spectra indicated that **14** was a mixture of isomers. This mixture was then treated under the Eglinton conditions for the oxidative coupling of acetylenes, when a complex mixture of products was obtained. Chromatography on silica gel provided the desired **15** as a red, crystalline solid in ca. 10% yield. The mass spectral and analytical data are in accord with the assigned molecular formula, and the electronic and infrared spectra are similar to those of 5,10-dimethyl-6,8-bisdehydro[13]-annulenone and its 2-methyl derivative.[7] The ^1H NMR (Table I) and ^{13}C NMR spectra (Table II) are also in accord with the assigned structure. The ^1H NMR spectrum is similar to that of 2,5,10-trimethyl-6,8-bisdehydro[13]-annulenone (**16b**) at −60 °C *except* that in the spectrum of **15** the H-12 proton is at lower field than that of the H-13 proton whereas in **16b** the chemical shift of the H-13 is to lower field. An interpretation of this difference can be found in the Discussion.

The low yield obtained in the oxidation coupling reaction severely hampered attempts to elaborate **15** into a bicylic azulene analogue. However, we explored the conversion of the carbonyl function into a side chain replete with further functionality. Compound **15** was treated with lithium ethoxyacetylide (**17**) to give the crude acetylenic alcohol **18** (Scheme III). No attempt was made to purify this material which was treated with dilute sulfuric acid to give, after chromatography, the fulvene analogues **19** and **20** in the ratio 2:1.

The gross structures assigned to **19** and **20** are supported by the ^1H and ^{13}C NMR spectra (Tables I and II). Compounds **19** and **20** differ only in the arrangement of the groups around the exocyclic double bond. The assignment of the *Z* configuration to **20** and the *E* configuration to **19** is based on the interpretation of the ^1H NMR spectra as described in the Discussion.

Discussion

The ^1H NMR spectra of **15**, **19**, and **20** illuminate the conclusions that had previously been made on the conformation of the [13]annulenones.[7] In the spectrum of the ester **15**, the proton H-3 is at a chemical shift similar to that of the H-3 proton in 5,10-dimethyl-6,8-bisdehydro-[13]annulenone (**21**), whereas the H-12 proton, although

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(4) See: Heilbronner, E. in "Non-benzenoid Aromatic Compounds"; Ginsburg, D., Ed.; Interscience: New York, 1959.
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(6) This system could also act as a precursor to fused $(4n + 2)(4n + 2)$-π-electron bicycles.
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Table I. ^{1}H NMR Spectral Data of 5,10-Dimethyl-6,8-bisdehydro[13]annulenone (21), 8, 15, 16b, and 20[a]

	chemical shift										
compd	H-3	H-4	H-11	H-12	H-13	H-15(3H)	H-16(3H)	H-17(3H)	H-18	H-20(2H)	H-21(3H)	ref
21	9.39 (dd, J = 16.5, 9.5)	6.29 (d, J = 9.5)	6.29	9.39	6.10[b] (d, J = 16.5)							7
8	7.07 (d, J = 11.3)	7.17 (dq, J = 11.3, 1.3)	6.39 (tq, J = 7.8, 1.3)									
15	9.20 (dd, J = 10.2, 0.8)	7.08 (dq, J = 10.2, 1.6)	6.43 (ddd, J = 7.6, 1.7, 1.17)	8.12 (ddd, J = 16.2, 7.7, 1.0)	7.19 (J = 15.8)	1.86 (dd, J = 1.17, 0.7)	1.83 (br s)	3.80 (s)				
16b	9.55 (d, J = 11)	6.54 (d, J = 11)	6.18 (m)	7.49[c] (dd, J = 16, 6)	7.90[c] (d, J = 16)							7
19	7.26 (dd, J = 8.2, 1.2)	7.45 (dq, J = 8.2, 1.6)	6.52 (dt, J = 9.4, 1.2)	7.66 (dd, J = 15.9, 9.6)	6.12 (d, J = 16.2)	1.89 (m, J = 1.4)	1.83 (br s)	3.68 (s)	6.14 (s)	4.14 (q, J = 7.1)	1.26 (t, J = 7.1)	
20	7.50 (ddd, J = 8.2, 1.2)	6.83 (dq, J = 8.4, 1.6)	6.58 (d, J = 9.4)	7.78 (dd, J = 16.9, 9.9)	7.46 (d, J = 16.2)	1.80 (t, J = 1.4)	1.75 (br s)	3.70 (s)	5.71 (s)	4.12 (q, J = 7.2)	1.19 (t, J = 7.2)	

[a] Spectra were recorded in $CDCl_3$ at 200 MHz and 27 °C except where stated otherwise, chemical shifts are reported in δ units from $(CH_3)_4Si$ as internal standard, and J values are in hertz. For numbering see structure 20 in text. [b] Identical shift for H-2. [c] At −60 °C.

Table II. ^{13}C NMR Spectral Data of 8, 15, 19, and 20[a,b]

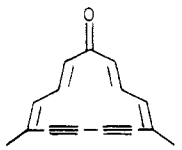
	chemical shift																			
compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16	C-17	C-18	C-19	C-20	C-21
8	196.8	120.3	145.0	137.2	133.4*	78.05	90.6	95.3	98.5	134.8*	142.0	28.6	39.2	165.9	20.5*	20.0*	52.1				
15	191.6	125.3	145.0	137.5	130.7*	82.9	89.1	96.3	98.3	132.0*	139.6	140.7	127.6	165.3	21.1*	20.35*	52.1				
19	150.9	123.1	141.5	134.5	125.6*	85.6	86.35	97.9	99.7	129.5*	139.2	139.4	123.2	165.8*	20.2*	20.0*	51.7	123.2	165.9*	60.4	14.25
20	149.9	121.4	143.0	136.6	125.8*					131.7*	137.6	138.7	123.7	166.0	20.3*	19.6*	52.2	123.7	166.0	60.3	14.25

[a] Spectra were recorded in $CDCl_3$ and are reported in parts per million from $(CH_3)_4Si$ as an internal standard. [b] Spectral assignments which could be interchanged are indicated by an asterisk.

Table III. ^{1}H NMR Chemical Shift Differences (δ) of the Ring Protons in Compounds 21, 15, and 16b[a]

	shift difference				
compds	H-3	H-4	H-11	H-12	H-13
21 − 15	0.19	−0.79	−0.14	1.27	−1.09
21 − 16b	−0.16	−0.25	0.11	1.90	−1.80
15 − 16b	−0.35	0.54	0.25	0.63	−0.71

[a] A positive number indicates that the proton in the first compound is at *lower* field.



21

at lower field than the H-11,13 protons, is at higher field than the H-12 proton in **21**.[7] In 2,5,10-trimethyl-6,8-bisdehydro[13]annulenone (**16b**), the chemical shift of the H-13 proton was at *lower* field than that of H-12 in the low-temperature, slow-equilibrating spectrum. This was interpreted to indicate that the 2-methyl derivative was in the conformation represented by **16b** with the C-11,12 bond in the *s*-cis orientation.[7] As can be seen from Table I and as is illustrated in Table III, the ester **15** has chemical shifts of the H-12 and H-13 protons intermediate between those of **16b** and **21**. The smaller, less consistent shift differences of the remaining ring protons certainly reflect the introduction of the ester group at C-2. This is most clearly shown in the case of the H-4 proton which is shifted to lower field in **15**, as expected for a proton in a cis-1,6 arrangement to a carbonyl group. The value of the coupling constant across the C-11,12 single bond (ca. 7.5 Hz) is again intermediate between the values observed for **16b** (6 Hz) and **21** (9.5 Hz) but is closer to the former.

Both the chemical shift value and the magnitude of the *s*-11,12 coupling constant suggest that the *average* C-12,13 double bond position in **15** is *not* coplanar with the remainder of the ring. If the conformation in which the C-12,13 double bond is *perpendicular* to the ring plane is taken as the reference, then the average conformation of **15** would appear to have H-13 inclined toward the inside and H-12 inclined toward the outside of the ring. The magnitude of the effects observed in **15** now suggest that, in all probability, the C12,13 double bond in **16b** is also not coplanar with the ring, but, in this case, the average conformation has H-13 inclined inward and H-12 outward from the perpendicular reference structure.

The similar chemical shift of the H-3 proton in all three compounds suggests that each has a similar paratropic contribution despite the different average orientations of the C-12,13 double bond. This is not at variance with the general experience gained with the annulenes which suggests that diatropic and paratropic effects on the ^{1}H NMR spectrum are little disturbed by deviations from planarity in these macrocyclic systems.[11]

The assignment of the *E* stereochemistry to **19** and the *Z* stereochemistry to **20** is based on the chemical shift differences of the H-18 and H-4 protons. In **19**, the signal for H-18 is at lower field than the signal for this proton in **20**, and this is consistent with deshielding by the ester group at C-2. The signal for H-4 is also at lower field in **19** than in **20**, and this we attribute to the steric crowding of the two ester groups in **20**, forcing the C-2 ester group out of the ring plane. The high-field signal of H-13 in **19** is something of an anomaly, but this may indicate that H-13 and the C-18 carbonyl group are not in the same plane and that H-13 is, in fact, shielded by this group.[12]

The ^{1}H NMR chemical shifts of the ring protons in both **19** and **20** suggest that these molecules are much less paratropic than the [13]annulenones. The general effect of such a decrease in paratropicity would be for the outer protons to shift to lower and the inner protons to higher field, and these changes are, in the main, observed when the spectra of **19** and **20** are compared with that of **15**. The chemical shift difference between H-3 and H-4 in **19** and **20** is small, and, from the magnitude of the minor coupling constants, in **19** it appears to be *reversed*, with H-4 at lower field. The small upfield shift (δ 0.25) of the H-4 proton in **20** compared to that in **15**, a shift contrary to this paratropic argument, can also be explained by the out-of-plane position of the C-2 ester group as suggested previously.

The ^{13}C NMR spectral data of **8**, **15**, **19**, and **20** are presented in Table II. The assignments for compound **15** are based on the partially coupled spectrum which allows identification of the carbon signal with its attached hydrogen.[13] The assignments to the resonance signals in **19** and **20** are based on analogy with the signals in **8** and **15**, taking into account the difference in structure. The ^{13}C NMR spectra do not give any indication of a difference in paratropicity or stereochemistry between these substances, a not unexpected finding in accord with previous ^{13}C NMR spectral findings in the annulenes.

Experimental Section

^{1}H NMR spectra were obtained on either a Varian T-60 or XL-200 spectrometer in $CDCl_3$ as the solvent and are reported in δ units with Me_4Si as an internal standard. ^{13}C NMR spectra were recorded on a Varian CFT-20 or XL-200 spectrometer in $CDCl_3$ as the solvent and are reported in δ units with Me_4Si as an internal standard. Mass spectra were obtained on a VG-7000 G spectrometer. IR spectra were recorded on a Unicam SP-200 spectrometer, and only strong and medium bands are reported. Electronic spectra were recorded on a Cary-14 spectrophotometer. Melting points were taken on a Kofler hot-stage melting point apparatus and are uncorrected. Unless stated otherwise, reactions were worked up by addition of water and extraction with ether, the ethereal extract being washed with water and dried. Pyridine was distilled from KOH and stored over 4A molecular sieves. Solvents were dried by standard methods.

Methyl 7-Methyl-3-oxonon-6-en-8-ynoate (5). *n*-BuLi (18.5 mL, 1.78 M in hexane, 33 mmol) was added dropwise under N_2 to a stirred solution of diisopropylamine (3.43 g, 34 mmol) in dry THF (75 mL) at 0 °C. After 20 min, methyl acetoacetate (1.91 g, 16.5 mmol) dissolved in dry THF (10 mL) was added over 5 min and the resulting yellow solution stirred for a further 20 min. 5-Bromo-3-methylpent-3-en-1-yne (**3**; 2.62 g, 16.5 mmol) in THF (10 mL) was then added dropwise over 10 min and the temperature of the mixture then allowed to rise to 8 °C over 45 min. The reaction mixture was then quenched by the addition of dilute HCl (16 mL, 3.0 M) in ether (30 mL) and worked up to give a pale brown oil (2.64 g). Chromatography on silica gel, eluting with pentane–ether (5:1), gave **5**: 1.42 g (44%); mass spectrum, *m/e* (relative intensity) 194.0942 (calcd for $C_{11}H_{14}O_3$ 194.0942), 194 (M^+), 162 ($M^+ - 32$), 135 ($M^+ - 59$), 120 ($M^+ - 74$), 91 ($M^+ - 103$, 100); ^{1}H NMR 5.70 (t, 1 H, J = 7 Hz), 3.73 (s, 3 H), 3.43 (s, 2 H), 3.10 (s, 1 H), 2.60 (br s, 4 H), 1.83 (br s), 3 H); ^{13}C NMR 201.7, 167.4, 136.8, 118.4, 82.3, 81.2, 52.1, 48.7, 41.9, 24.3, 22.6; UV (Et_2O) λ_{max} 225 nm (ϵ 6900), 250 (1200).

Knoevenagel Reaction of 5 with 3-Methylpent-2-en-4-yn-1-al (6). Piperidinium acetate (50 mg) was added to a stirred solution of **5** (1.94 g, 10 mmol) and the aldehyde **6** (0.94, 10 mmol) in dry ether (35 mL) at −10 °C. The temperature was then allowed to slowly rise to 10 °C over 90 min, by which time all of the starting materials had been consumed. Ether (100 mL) was added and the mixture worked up to give **7**, as a mixture of isomers: 2.60 g (96%); ^{1}H NMR 7.62 (overlapping d, 1 H, $J \approx 12$ Hz), 6.73 (2 overlapping d, 1 H), $J \approx 2$ Hz), 5.75 (m, 1 H), 3.83 (2 overlapping s, 3 H), 3.60 (d, $J \approx 2$ Hz), 3.07 (s, 1 H), 2.33–2.79 (m, 4 H), 2.10 (s, 3 H), 1.87 (s, 3 H); UV (Et_2O) λ_{max} 235 nm, 304. Compound **7** was used without further purification.

(11) See: Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573. Sondheimer, F. *Acc. Chem. Res.* **1972**, *5*, 81.

(12) See: Jackman, L. M.; Sternhell, S. "Application of NMR Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Oxford, 1969; p 91.

(13) We thank Mr. C. J. Cooksey for assistance with these experiments.

2-Carbomethoxy-11,12-dihydro-5,10-dimethyl-6,8-bisdehydro[13]annulenone (8). The isomeric mixture of **7** (2.30 g, 8.5 mmol) was dissolved in methanol (20 mL) and the solution added to a mixture of Cu_2Cl_2 (27.0 g) and NH_4Cl (45.0 g) in water (150 mL). Oxygen was bubbled vigorously through the mixture for 4 h, while methanol (ca. 20 mL) was added periodically to compensate for losses in the oxygen stream. The mixture was then cooled to 0 °C, acidified with dilute HCl (2 M), and extracted with a mixture (1:1) of ether–benzene (4 × 50 mL). The combined extracts were worked up to give a yellow viscous oil (2.20 g) which was chromatographed on silica gel, eluting with pentane–EtOAc, to give **8** (0.60 g), crystallized from pentane/EtOAc as yellow needles: 0.210 g (9.2%, based on total amount of **7**); mp 107–108 °C; mass spectrum, *m/e* 268.1097 ($C_{17}H_{16}O_3$ requires 268.1099); ^1H NMR, see Table I; ^{13}C NMR, see Table II; IR 2162 (w), 2100 (w), 1735, 1645, 1595, 985 cm^{-1}; UV (Et_2O) λ_{max} 262 nm (ϵ 2700), 275 (3000), 358 (1050). Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.12; H, 5.97. Found: C, 75.77; H, 6.26.

Methyl Trimethylsilyl Acetonedicarboxylate (12). Acetonedicarboxylic acid (14.6 g, 100 mmol) was added in small portions over 10 min to cooled (ice bath), vigorously stirred acetic anhydride (30 mL), and the stirring was continued for a further 40–60 min during which time the anhydride **10** separated as a colorless solid. The solid was removed by filtration, washed with benzene (20 mL) and ether (2 mL), and dried to give **10** (11.04 g, 85%). Absolute methanol (80 mL) was added to **10** (20.0 g, 156 mmol) and the mixture swirled for ca. 5 min during which time the reaction mixture became slightly warm. The mixture was then stirred at room temperature for 90 min and the excess methanol removed under reduced pressure to give the monomethyl ester **11** (23.90 g, 149 mmol) as a light brown oil. This material was dissolved in ether (180 mL) containing pyridine (11.85 g, 150 mmol), aand the solution was cooled to −15 °C and stirred. Me_3SiCl (16.30 g, 150 mmol) in dry ether (40 mL) was then added dropwise over 20 min. After the addition the mixture was allowed to warm to room temperature and was stirred for 18 h. Pentane (100 mL) was added, and the precipitated solid was removed by filtration and washed with ether (4 × 50 mL). The combined filtrates were reduced in volume under reduced pressure, and the residue was distilled under vacuo to give **12**: 17.5 g (48%), bp 94–95 °C (0.25 Hgmm); colorless liquid; ^1H NMR 3.70 (s, 4 H), 3.55 (br s, 3 H), 0.25 (s, 9 H). Anal. Calcd for $C_9H_{16}O_5Si$: C, 46.55; H, 6.89. Found: C, 46.43; H, 6.53.

Methyl 7-Methyl-3-oxonona-4,6-dien-8-yne-1-carboxylate (13) and 6-Carbomethoxy-3,11-dimethyltrideca-3,5,8,10-tetraene-1,12-diyn-7-one (14). The silyl ester **12** (6.96 g, 30 mmol) and **6** (5.64 g, 64 mmol) were dissolved in a mixture of benzene–ether (1:1, 20 cm^3), and the solution was stirred and cooled to −20 °C. Piperidinium acetate (280 mg) was added and the mixture allowed to warm to room temperature with stirring. Stirring was continued for 18 h, and the mixture was then washed with water (4 × 25 mL) and saturated NaCl solution (1 × 25 mL) and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue chromatographed on silica gel, eluting with pentane–EtOAc (4:1), to give **13**: 380 mg (6.6%); crystallized from pentane; orange crystals; mp 66–68 °C; mass spectrum, *m/e* (relative intensity) 192.0781 ($C_{11}H_{12}O_3$ requires 192.0786); 192 (M^+, 66), 177 ($M^+ - 15$, 14), 161 ($M^+ - 31$, 11), 160 ($M^+ - 32$, 26), 145 ($M^+ - 47$, 15), 133 ($M^+ - 59$, 40), 132 ($M^+ - 60$, 47), 131 ($M^+ - 61$, 17), 119 ($M^+ - 73$, 100); ^1H NMR, 11.9 (d, 1 H), 7.48 (dd, 1 H, J = 15, 11 Hz), 6.37 (m, 1 H, J = 11 Hz); 5.95 (m, 1 H, J = 15 Hz), 5.09 (s, 1 H), 3.72 (s, 3 H), 3.49 (s, 1 H), 2.05 (br s, 3 H); UV (Et_2O) λ_{max} 223 nm (sh, ϵ 4500), 231 (4800), 320 (29 000). Further elution gave **14**: 3.23 g (26.4%); yellow oil; mass spectrum (relative intensity) *m/e* 268.1100 ($C_{17}H_{16}O_3$ requires 268.1100); 269 ($M^+ + 1$, 7.5), 268 (M^+, 44), 253 ($M^+ - 15$, 46), 237 ($M^+ - 31$, 11), 221 ($M^+ - 47$, 13), 210 ($M^1 - 58$, 16), 209 ($M^+ - 59$, 87), 208 ($M^+ - 60$, 16), 207 ($M^+ - 61$, 11), 194 ($M^+ - 74$, 12), 193 ($M^+ - 75$, 15), 181 ($M^+ - 87$, 31), 180 ($M^+ - 88$, 17), 179 ($M^+ - 89$, 26), 177 ($M^+ - 90$, 11), 167 ($M^+ - 101$, 13), 166 ($M^+ - 102$, 49), 165 ($M^+ - 103$, 100); UV (Et_2O) λ_{max} 213 nm, 288 (sh), 314.

2-Carbomethoxy-5,10-dimethyl-6,8-bisdehydro[13]-annulenone (15). The crude product **14** (3.23 g, 12 mmol), obtained in the previously described reaction, was dissolved in ether (30 mL) and added dropwise over 90 min to a mixture of anhydrous copper(II) acetate (6.50 g, 35 mmol) in pyridine (180 mL) and ether (540 mL), at 45–50 °C. The temperature was maintained for a further 90 min, the mixture cooled, and the solvent removed under vacuo below 35 °C. The residue was extracted with ether, the extracts were filtered, and the filtrate was reduced in volume under reduced pressure. The residue was chromatographed on silica gel, eluting with pentane–ethyl acetate (4:1), to give **15** as a red oil which was crystallized from ether/pentane as red crystals: 270 mg (8.1%); mp 118–119 °C; mass spectrum, *m/e* (relative intensity) 266.0943 ($C_{17}H_{14}O_3$ requires 266.0942), 266 (M^+, 10), 251 ($M^+ - 15$, 14), 238 ($M^+ - 28$, 15), 235 ($M^+ - 31$, 13); 234 ($M^+ - 32$, 29), 223 ($M^+ - 43$, 33), 207 ($M^+ - 59$, 37), 206 ($M^+ - 60$, 27), 205 ($M^+ - 61$, 16), 195 ($M^+ - 71$, 28), 180 ($M^+ - 86$, 10), 179 ($M^+ - 87$, 27), 178 ($M^+ - 88$, 100); ^1H NMR, see Table I: ^{13}C NMR, see Table II; IR 2160 (w), 2105 (w), 1715, 1668, 1625 cm^{-1}; UV (Et_2O) λ_{max} 246 nm (sh, ϵ 10 700), 260 (sh, 19 000), 277 (29 200), 390 (1200). Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.69; H, 5.26. Found: C, 76.48; H, 5.32.

Addition of Lithium Ethoxyacetylide to 15. Synthesis of (*Z*)- (20) and (*E*)- (19) 14-Carbethoxy-2-carbomethoxy-5,10-dimethyl-6,8-bisdehydro[13]fulvenes. *n*-BuLi (0.58 mL, 1.7 M solution in hexane, 1.01 mmol) was added dropwise over 10 min to a stirred solution of ethoxyacetylene (0.04 mL, 40% solution in hexane, 1.34 mmol) in dry THF (10 mL) at −78 °C under N_2. Stirring was continued for a further 30 min, and then a solution of **15** (90 mg, 0.337 mmol) in THF (7 mL) was added and the mixture allowed to warm to room temperature over 2.5 h. A saturated solution of NH_4Cl (10 mL) containing aqueous NH_3 (5 drops) was added, and the ether layer was separated and washed with water (2 × 10 mL) and then brine (15 mL). The combined aqueous layers were washed with ether (2 × 15 mL), and the ethereal extracts were combined and concentrated under reduced pressure to give a brown oil (210 mg), presumably impure **18**. The oil was dissolved in a mixture of ethanol (8 mL) and ether (30 mL), aqueous H_2SO_4 (10% 20 mL) was added, and the mixture was stirred at room temperature for 2 h. The dark red ether layer was separated and washed with water (2 × 20 mL), and the combined aqueous layers were saturated with NH_4Cl and extracted with ether (2 × 25 mL). The combined ethereal extracts were dried (Na_2SO_4), and the solvent was removed under reduced pressure to give a pale brown oil (270 mg). Short-path chromatography on silica gel (20 g), eluting with 30:70 ether/petroleum ether, gave, after removal of the solvent, separate fractions containing **19** and **20**. Recrystallization of each separate fraction from ether/pentane gave the following.

19: 30 mg (22.5%); red-orange rhomboids; mp 84–85 °C dec; mass spectrum, *m/e* (relative intensity) 336.1436 ($C_{21}H_{20}O_4$ required 336.1362), 337 ($M^+ + 1$, 6), 336 (M^+, 38), 304 ($M^+ - 32$, 24), 278 ($M^+ - 58$, 17), 277 ($M^+ - 59$, 100), 267 ($M^+ - 69$, 16), 262 ($M^+ - 74$, 11), 258 ($M^+ - 78$, 13), 249 ($M^+ - 87$, 10), 248 ($M^+ - 88$, 22), 247 ($M^+ - 89$, 15), 232 ($M^+ - 104$, 22), 231 ($M^+ - 105$, 76), 230 ($M^+ - 106$, 30), 219 ($M^+ - 117$, 15), 207 ($M^+ - 129$, 25), 205 ($M^+ - 131$, 19), 204 ($M^+ - 132$, 25), 203 ($M^+ - 133$, 53), 202 ($M^+ - 134$, 86), 201 ($M^+ - 135$, 13); ^1H NMR, see Table I; ^{13}C NMR, see Table II; UV (cyclohexane) λ_{max} 270 nm (sh, ϵ 11 800), 305 (27 400), 365 (sh, 5890), 430 (sh, 1340).

20: 60 mg (53%); red-orange rhomboids; mp 110–112 °C dec; mass spectrum, *m/e* (relative intensity) 336.1290 ($C_{21}H_{20}O_4$ requires 336.1362), 337 ($M^+ + 1$, 10), 336 (M^+, 50), 304 ($M^+ - 32$, 25), 278 ($M^+ - 58$, 20), 277 ($M^+ - 59$, 100), 262 ($M^+ - 74$, 13), 258 ($M^+ - 78$, 14), 249 ($M^+ - 87$, 12), 248 ($M^+ - 88$, 19), 247 ($M^+ - 89$, 185), 232 ($M^+ - 104$, 23), 231 ($M^+ - 105$, 75), 230 ($M^+ - 106$, 32), 219 ($M^+ - 117$, 15), 205 ($M^+ - 131$, 17), 204 ($M^+ - 132$, 24), 203 ($M^+ - 133$, 51), 202 ($M^+ - 134$, 79), 201 ($M^+ - 135$, 14), 200 ($M^+ - 136$, 10); ^1H NMR, see Table I; ^{13}C NMR, see Table II; UV (cyclohexane) λ_{max} 270 nm (sh, ϵ 10 500), 302 (sh, 31 400), 309 (34 000), 420 (sh, 1900).

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