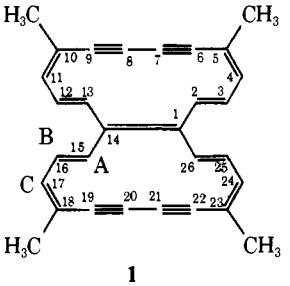
The Synthesis of Derivatives of [14]Annuleno[14]annulene, [14]Annuleno[16]annulene, and [14]Annuleno[18]annulene, Bicyclic Compounds Consisting of Two Ortho Fused Macrocyclic Conjugated π Systems[1†]

Terry M. Cresp and Franz Sondheimer*

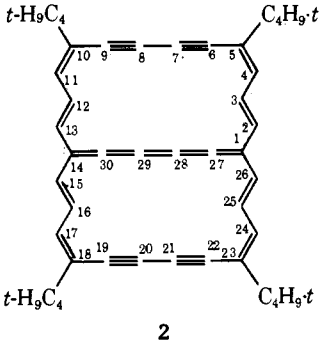
Contribution from the Department of Chemistry, University College, London WC1H OAJ, England. *Received July 6, 1976*

Abstract: A new and improved synthesis of the dimethylbisdehydro[14]annuleno[*c*]furan **6** (7,12-dimethyl-8,9,10,11-tetradehydrocyclotetradeca[*c*]furan) is described. This substance has been converted to the tetramethyltetrakisdehydro[14]annuleno[14]annulene **1** (5,10,18,23-tetramethylbicyclo[12.12.0]hexacosa-1(14),2,4,10,12,15,17,23,25-nonaene-6,8,19,21-tetrayne), the tetramethyltetrakisdehydro[14]annuleno[16]annulene **3** (7,12,20,25-tetramethylbicyclo[14.12.0]octacosa-1(16),2,4,6,12,14,17,19,25,27-decaene-8,10,21,23-tetrayne), and the tetramethyltetrakisdehydro[14]annuleno[18]annulene **4** (7,12,22,27-tetramethylbicyclo[16.12.0]triaconta-1(18),2,4,6,12,14,16,19,21,27,29-undecaene-8,10,23,25-tetrayne). These vinylogs of naphthalene are the first examples of bicyclic compounds consisting of two ortho fused macrocyclic conjugated π systems. The effect that each ring exerts on the other is examined, mainly by ^{1}H NMR spectrometry, and comparisons with suitable model substances are made.

Macrocyclic conjugated polyenes (annulenes) have now been thoroughly investigated.[2] Bicyclic systems made up of two fused conjugated polyene rings (annulenoannulenes) in which one ring is benzenoid have also received considerable attention.[3] Examples are benzocyclobutadiene,[4] naphthalene,[5] benzocyclooctatetraene,[6] a monodehydrobenzo[12]annulene,[7] and a bisdehydrobenzo[14]annulene.[8] By contrast, annulenoannulenes in which both rings are macrocyclic have been unknown until recently. The first examples, the [14]annuleno[14]annulene **1**[9] and the [18]annuleno[18]annulene **2**,[10]



1

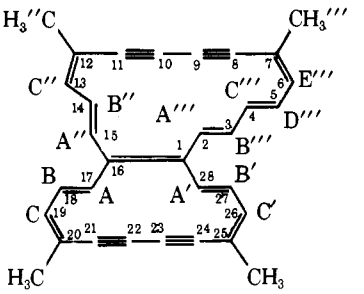


2

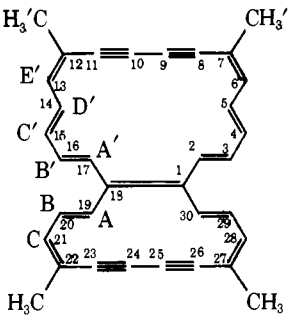
in which both the fused rings are identical and $(4n + 2)$-membered, were only reported last year.

We have now extended our work, and report the synthesis of the [14]annuleno[16]annulene **3** and the [14]annuleno-[18]annulene **4**. Compound **3** is an example of the fusion of a $(4n + 2)$- and a $(4n)$-membered ring, and **4** of the fusion of two different $(4n + 2)$-membered rings. Details of the synthesis of the [14]annuleno[14]annulene **1** are also given.

Nomenclature. We propose that a bicyclic system made up of two ortho fused [*m*]- and [*n*]annulenes be named a [*m*]annuleno[*n*]annulene ($m \leq n$) The numbering is as shown in formulas **1, 3,** and **4** and the number of acetylenes is indicated by the prefix monodehydro-, bisdehydro-, trisdehydro-, tetrakisdehydro-, etc.[11] Compound **1** is therefore named 5,10,18,23-tetramethyl-6,8,19,21-tetrakisdehydro[14]annuleno[14]annulene,[12a] **3** is named 7,12,20,25-tetramethyl-8,10,21,23-tetrakisdehydro[14]annuleno[16]annulene,[12b] and **4** is named 7,12,22,27-tetramethyl-8,10,23,25-tetrakisdehydro[14]annuleno[18]annulene.[12c] We suggest that the annulenoannulene **2,** in which the two dehydro[18]annulene rings are not ortho fused, be named 5,10,18,23-tetra-*tert*-butyl-6,8,19,21,27,29-hexakisdehydro[12.12.4][18]annuleno[18]-annulene. This incorporates the "bicyclo" nomenclature, as proposed by Nakagawa et al.[10]

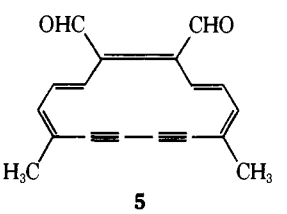


3

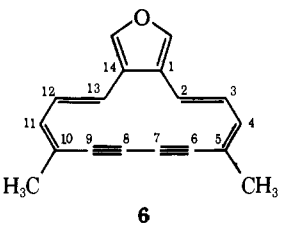


4

Syntheses. A suitable intermediate for the synthesis of **1, 3,** and **4** appeared to be the dialdehyde **5**. We considered it possible that this substance might be obtainable from the known dimethylbisdehydro[14]annuleno[*c*]furan **6**.[13] Unfortunately,



5



6

† Dedicated to Professor R. B. Woodward on the anniversary of his 60th birthday.

the previously described synthesis of **6**[13] proceeded only in poor yield and required relatively high dilution conditions for the oxidative coupling. An improved route to **6** was therefore developed, based on the synthesis of related bisdehydrobenzoannulenes, carried out in these laboratories.[14]

Reduction of the commercially available diethyl furan-3,4-dicarboxylate (**7**) with lithium aluminum hydride gave the diol **8**[15] in ~75% yield. This diol has been oxidized to furan-3,4-dicarboxaldehyde (**9**) in ~40% yield by a two-step procedure (manganese dioxide followed by lead tetraacetate),[15] but we have found this conversion to be carried out most conveniently (also in ~40% yield) in one step by means of pyridinium chlorochromate.[16] The dialdehyde **9** was then converted to the bis-trans vinylog **12** in 60% yield by Wittig reaction with 1,3-dioxolan-2-ylmethyltriphenylphosphonium bromide (**10**)[17] and lithium methoxide, followed by hydrolysis of the resulting bisacetal **11** (stereoisomeric mixture) with dilute hydrochloric acid and isomerization with iodine.

Grignard reaction of the dialdehyde **12** with the magnesium derivative of 3-bromo-1-butyne[18] gave the diol **13**, which was oxidatively coupled either under "Glaser" conditions (oxygen, cuprous chloride, ammonium chloride, and concentrated hydrochloric acid in aqueous ethanol and benzene)[19,20] or under "Eglinton" conditions (cupric acetate monodehydrate in pyridine).[19] The macrocyclic diol **14** obtained by either method was then converted to the dimethanesulfonate **15** by means of methanesulfonyl chloride and triethylamine.[21] Compounds **13**, **14**, and **15** were stereoisomeric mixtures, separation of which proved to be unnecessary. Finally, treatment of **15** with 1,5-diazabicyclo[4.3.0]non-5-ene gave the yellow dimethylbisdehydro[14]annuleno[*c*]furan **6** in ~35% overall yield (based on the dialdehyde **12**), irrespective of the method used for the coupling of **13** to **14**. The advantage of the presently described route to **6** over that previously reported[13] is that the disubstituted double bonds are introduced stereospecifically in the required trans configuration and that the oxidative coupling of acetylenic diols of type **13** proceeds satisfactorily without the need for high dilution conditions. As already discussed,[13] we believe **6** to be conformationally mobile on the NMR time scale, and no particular conformation is implied in the formula.

The next objective was the conversion of **6** to the dialdehyde **5** through suitable modification of the furan ring. Various methods which had been used for the transformation of furan to malealdehyde were investigated.[22] After a considerable number of unsuccessful experiments, it was found that oxidation of **6** with lead tetraacetate in acetic acid[22b,23] readily gave the diacetoxydihydrofuran **16**. Substance **16** was decomposed by aqueous mineral acid,[22b] but was smoothly hydrolyzed with oxalic acid in aqueous tetrahydrofuran. The spectral properties of the product showed it to be the hemiacetal **17**[24] instead of the dialdehyde **5**. Attempted hydrolysis of the diacetate **16** with potassium hydroxide in aqueous methanol led to the dimethyl acetal **18** as the only product isolated. The acetal **18** was obtained in much better yield (72%) by treatment of **16** with sodium methoxide in absolute methanol. Substance **18** could also be obtained directly from the furan **6**, but only in very poor yield (3%) by low temperature photooxygenation in dichloromethane and methanol in the presence of Rose Bengal, followed by reduction with triphenylphosphine.[22c] The ^{1}H NMR spectra of the dihydrofurans **16**, **17**, and **18** showed them to be ~1:1 mixtures of the cis and trans stereoisomers,[22b,23] but these were not separated.

The dialdehyde **5** could not be isolated by attempted dehydration of the hemiacetal **17** (e.g., through heating with benzene in a Dean and Stark apparatus). Substance **17** also proved to be base sensitive, and an attempted Wittig reaction with the phosphonium salt **10**[17] in the presence of lithium methoxide was unsuccessful. On the other hand, treatment of **17** with an excess of carbethoxymethylenetriphenylphosphorane[25] in boiling benzene smoothly gave the stable diester **19**, the newly formed double bonds having almost entirely the required trans stereochemistry (see Experimental Section). The overall yield of **19** based on **6** was 55%. Our objective, involving the use of the furan **6** as a "protected" form of the dialdehyde **5**, which could then be transformed further, has therefore been realized.

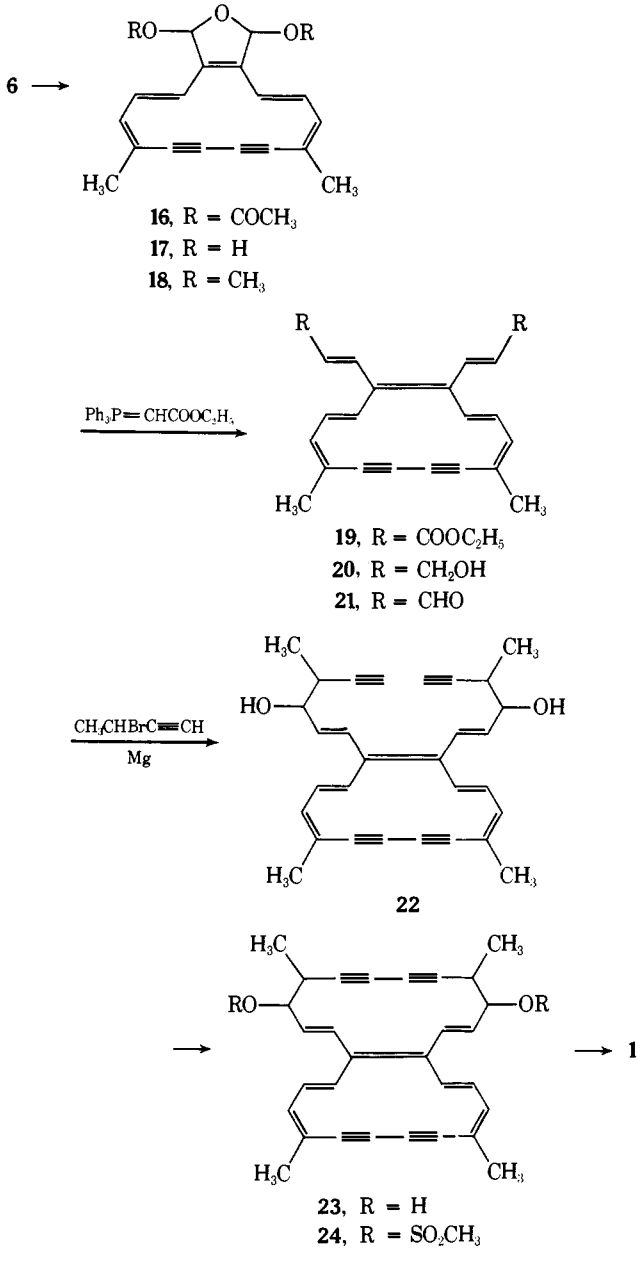
The remaining steps required for the synthesis of the [14]annuleno[14]annulene **1** proceeded in the expected manner. Thus, reduction of the diester **19** with diisobutylaluminum hydride and oxidation of the resulting diol **20** with manganese dioxide led to the dialdehyde **21** in 74% yield (based on **19**). Grignard reaction of **21** with the magnesium derivative of 3-bromo-1-butyne,[18] as previously, then gave the diol **22** as a steroisomeric mixture. The oxidative coupling of this substance could not be effected under "Glaser" conditions, presumably for solubility reasons. "Eglinton" type coupling of **22** under several different conditions was investigated, the best results being obtained by means of cupric acetate monohydrate in dimethylformamide at 65 °C. The crude diol **23** obtained in this manner was converted to the corresponding dimethanesulfonate **24** with methanesulfonyl chloride and triethylamine.[21] Finally, treatment with 1,5-diazabicyclo[4.3.0]non-5-ene furnished the required [14]annuleno[14]annulene **1** in ~5% yield (based on **21**) as dark red-brown prisms, which decomposed above 200 °C without melting on attempted melting point determination. The substance was relatively stable, both in the solid state and in ether solution.

We now turn our attention to the synthesis of the [14]annuleno[16]annulene **3**. Wittig reaction of the dialdehyde **21** with 1 molar equiv of carbethoxymethylenetriphenylphosphorane[25] in dichloromethane at room temperature yielded 56% of the aldehydo ester **25**, as well as 9% of the diester **31**

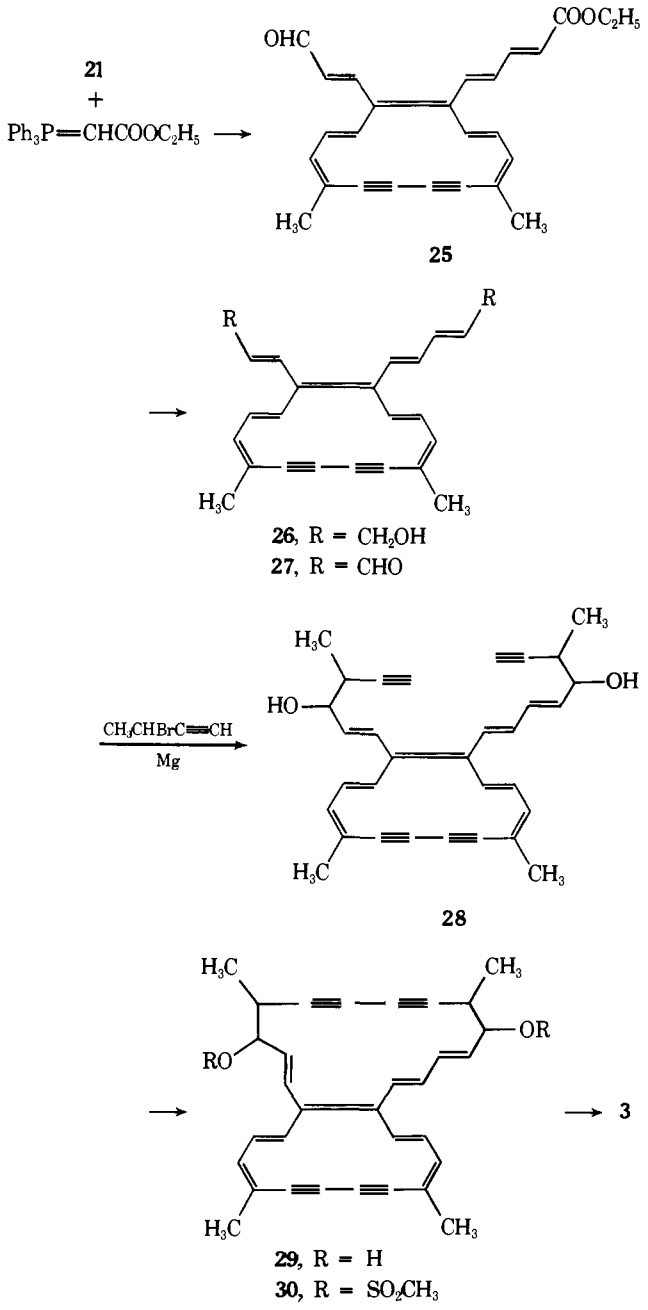
Table I. Electronic Absorption Spectra of the Annulenoannulenes **1**, **3**, and **4**, Determined in Ether; Maxima or Shoulders (sh) in nm (ε Values in Parentheses)

[14][14], **1**:	258 (14 400), 278 sh (16 800), 292 (21 100), **387 (45 400)**, 552 sh (1050), 607 sh (580)
[14][16], **3**:	258 sh (17 600), 286 (28 100), 350 sh (49 100), **380 (61 000)**, 405 sh (44 300)[a]
[14][18], **4**:	275 (30 300), 299 (35 900), **395 (80 200)**, 446 sh (25 700), 589 sh (2200)

[a] With absorption to ~630 nm.



(see below). Reduction of **25** with diisobutylaluminum hydride and oxidation of the resulting diol **26** with manganese dioxide gave 73% (based on **25**) of the dialdehyde **27**. This substance was then transformed to the [14]annuleno[16]annulene **3** in ~3% overall yield via the diols **28** and **29**, and the dimethanesulfonate **30**, essentially as described for the conversion of **21** to **1** (the oxidative coupling of **28** to **29** was best carried out with anhydrous cupric acetate in pyridine–ether at 55–60 °C). Substance **3** formed relatively stable deep purple prisms which decomposed above 170 °C without melting on attempted melting point determination.



The [14]annuleno[18]annulene **4** could be obtained from the above-mentioned diester **31**, which was synthesized most conveniently, in ~70% yield, by the Wittig reaction of the dialdehyde **21** with an excess of carbethoxymethylenetriphenylphosphorane.[25] Reduction of **31** with diisobutylaluminum hydride to the diol **32**, followed by oxidation with manganese dioxide, led to the dialdehyde **33** in 82% yield (based on **31**). The four-step sequence **33** → **34** → **35** → **36** → **4** was then carried out in 20% overall yield essentially in the same way as the conversion of **27** to **3**. The [14]annuleno[18]annulene **4** formed fairly stable deep brown-violet prisms which decomposed above 260 °C without melting on attempted melting point determination.

Electronic Spectra. The electronic absorption spectra of the tetramethyltetrakisdehydroannulenoannulenes **1**, **3**, and **4** proved to be complex, and the maxima and shoulders are given in Table I. It is noteworthy that the main maximum of the 26π system **1** (387 nm) resembles those of the known dehydro[26]-annulenes (monodehydro, 386 nm; trisdehydro, 383 nm). The main maximum of the 28π system **3** (380 nm) resembles that of the only known dehydro[28]annulene (bisdehydro, 373 nm),

Table II. Some ^{1}H NMR Parameters of Dimethylbisdehydro[14]annulenes in $CDCl_3$ at 100 or 220 MHz (τ Values; Internal Standard Me_4Si)

Compd	H^A, $H^{A'}$	H^B, $H^{B'}$	H^C, $H^{C'}$	CH_3, CH_3'
Model, **37a**[a]	12.12	1.22	1.79	7.02
[14][18], **4**	8.22	1.77	2.28	7.28
[14][16], **3**	8.58, 8.68	2.17, 2.37	2.46, 2.50	7.33
[14][14], **1**	6.18	2.13	2.69	7.52
[14][6], **38**	5.01	2.56	2.92	7.64
Δ (**1** − **38**)	+1.17	−0.43	−0.23	−0.12

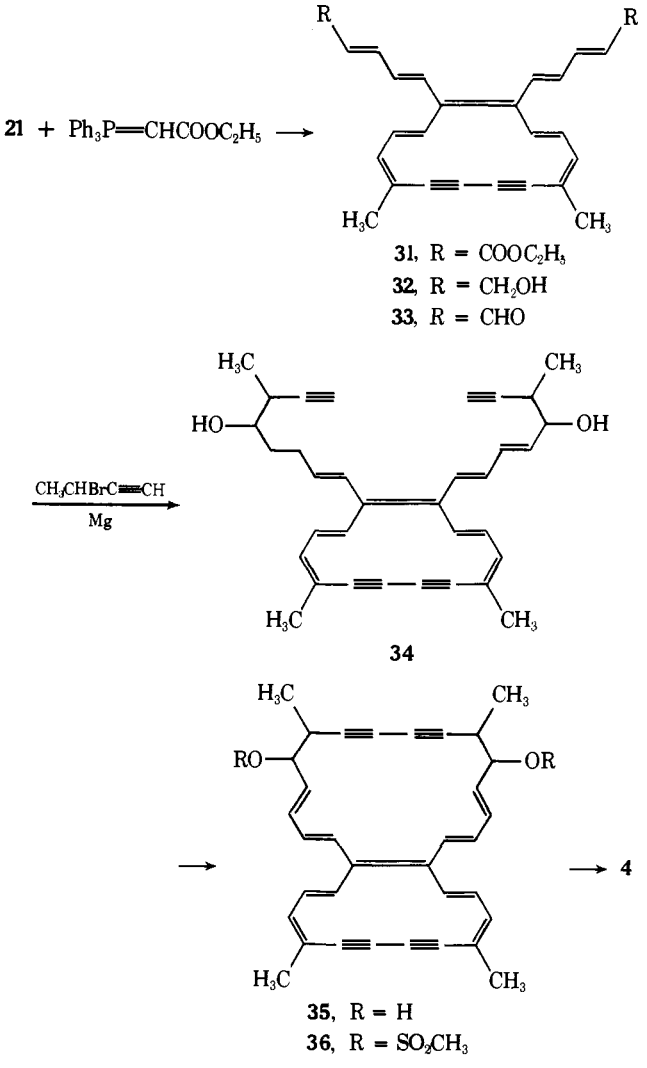
[a] At −60 °C.

Table III. Some ^{1}H NMR Parameters of Dimethylbisdehydro[16]annulenes in $CDCl_3$ at 100 or 220 MHz (τ Values; Internal Standard Me_4Si)

Compd	$H^{A''}$	$H^{B''}$	$H^{C''}$	$H^{A'''}$	$H^{B'''}$	$H^{C'''}$	$H^{D'''}$	$H^{E'''}$	CH_3'', CH_3'''
[14][16], **3**	2.99	−0.04	3.72	0.54	3.42	0.13	4.25	4.01	8.26, 8.32
[6][16], **39**	3.89	0.55	3.93	1.10	3.80	0.58	4.27	4.06	8.30
Δ (**3** − **39**)	−0.90	−0.59	−0.21	−0.56	−0.38	−0.45	−0.02	−0.05	−0.04, +0.02

Table IV. Some ^{1}H NMR Parameters of Dimethylbisdehydro[18]annulenes in $CDCl_3$ at 100 or 220 MHz (τ Values; Internal Standard Me_4Si)

Compd	$H^{A'}$	$H^{B'}$	$H^{C'}$	$H^{D'}$	$H^{E'}$	CH_3'
Model, **42**	10.38	1.98	1.48	11.06	1.30	6.94
[14][18], **4**	4.40	2.79	3.69	4.27	2.93	7.68
[6][18], **40**	4.77	2.76	3.15	5.06	2.83	7.72
Δ (**4** − **40**)	−0.37	+0.03	+0.54	−0.79	+0.10	−0.04



and the main maximum of the 30π system **4** (395 nm) resembles those of the known dehydro[30]annulenes (trisdehydro, 397 nm; pentakisdehydro, 389 nm).[26] It is evident that in the annulenoannulenes the same alternation in the wavelengths of the main electronic absorption maxima of $(4n + 2)$ and $4n$ systems occurs, as has already been observed for the monocyclic annulenes.[26]

^{1}H NMR Spectra. The ^{1}H NMR spectra of the tetramethyltetrakisdehydroannulenoannulenes **1**, **3**, and **4** are given in Figures 1, 2, and 3, as well as in Tables II, III, and IV. The low solubility of compounds **3** and **4** in organic solvents necessitated the use of Fourier transform techniques, and this is responsible for the water and solvent impurity peaks in the spectra of these compounds.

The assignments of the resonances to the individual protons of the [14]annuleno[14]annulene **1** follow explicitly from the multiplicities and coupling constants. In contrast, the spectrum of the unsymmetrical [14]annuleno[16]annulene **3** was complex. The assignments of the resonances in **3** are also based on the multiplicities and coupling constants, and the assumption that protons in a similar environment resonate at similar field. The same considerations apply to the interpretation of the spectrum of the [14]annuleno[18]annulene **4**, with the exception that the $H^{C'}$ protons resonate at higher field than expected due to rotation about the $H^{C'}$, $H^{D'}$ double bonds (see below). The analyses of the spectra of **1**, **3**, and **4** are fully in accord with the following consideration of ring currents.

The effect on the ^{1}H NMR spectrum of the dimethylbisdehydro[14]annulene system produced by fusion of [18]-, [16]-, [14]-, and [6]annulenes is given in Table II. As shown previously,[27] the "model" bisdehydro[14]annulene **37** is strongly diatropic, the inner protons absorbing at very high field, and the outer protons at low field (at −60 °C). The best ring current probe is provided by the H^C, $H^{C'}$ and CH_3, CH_3' resonances, since these protons are furthest from the point of fusion, and must be conformationally fixed. These bands show that the diatropicity of the 14-membered ring falls off as the size of the fused annulene is decreased (**37a** > **4** > **3** > **1** > **38**),

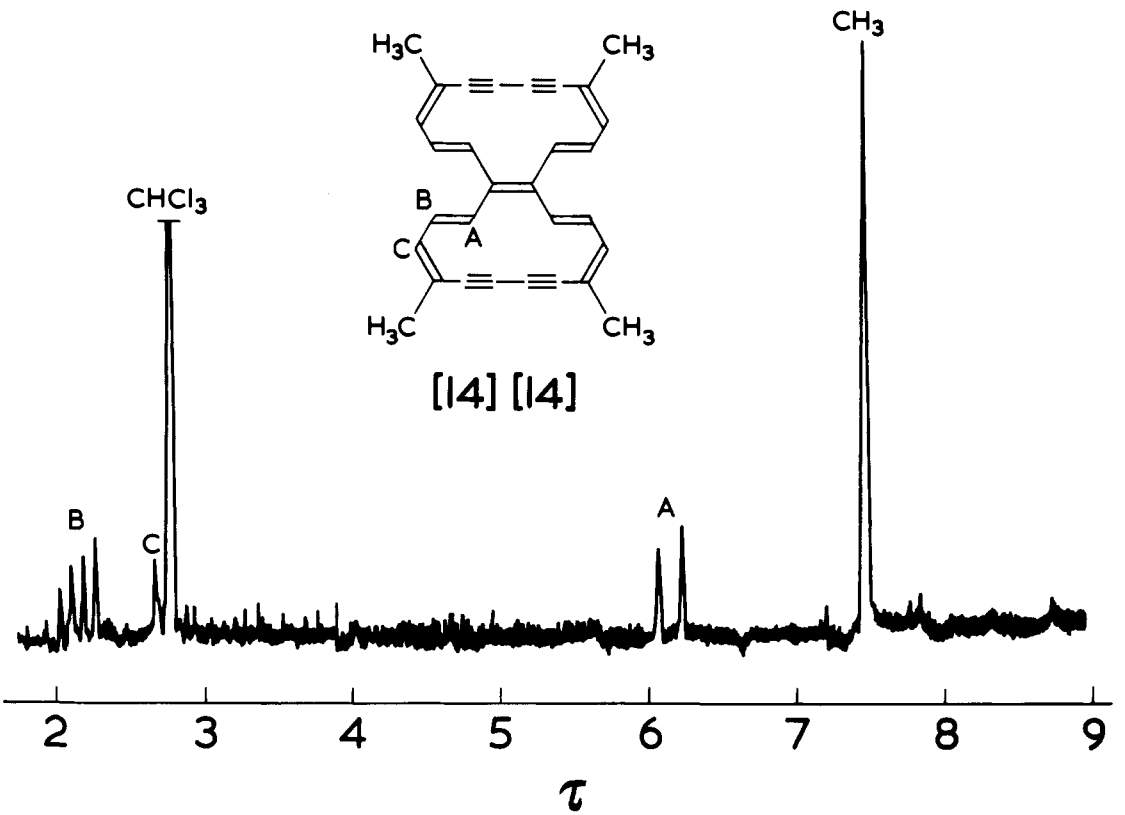
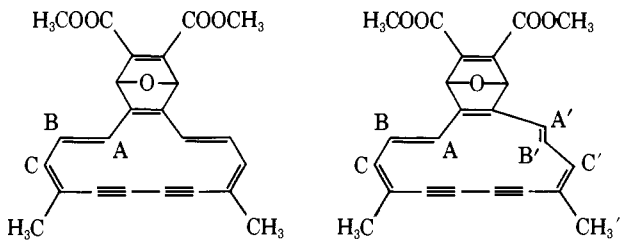
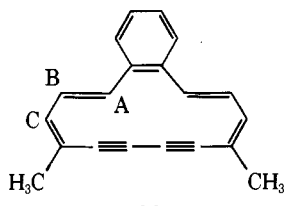


Figure 1. ^{1}H NMR spectrum of the tetramethyltetrakisdehydro[14]annuleno[14]annulene **1** in $CDCl_3$ at 100 MHz (τ values, internal standard Me_4Si).



37a

37b

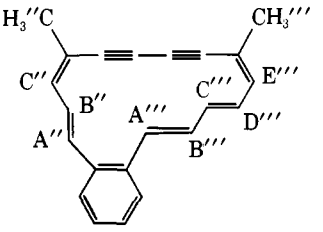


38

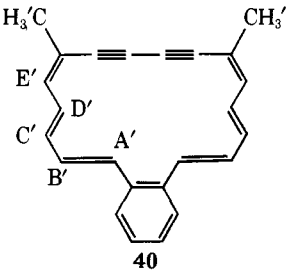
irrespective of whether this annulene is $(4n + 2)$ or $4n$ membered. This order of diatropicity is confirmed by the H^A, $H^{A'}$ and H^B, $H^{B'}$ resonances, except for the [14]annuleno[16] annulene **3**, in which these bands are at higher field than would be expected from the H^C, $H^{C'}$ and CH_3, CH_3' resonances. We believe that this effect is due to shielding by the 16-membered ring of the adjacent protons. Presumably, there is a corresponding deshielding contribution to the diatropicity of the 14-membered ring in compounds **4, 1,** and **38** which contain fused $[4n + 2]$annulenes. It is of interest that the diamagnetic ring current of the 14-membered ring predominates over the deshielding effect of the other ring in **4, 1,** and **38.** In naphthalene ([6]annuleno[6]annulene) one cannot separate these two effects, since all the protons resonate at lower field than in benzene.

It has been shown that the ^{1}H NMR spectrum of the "model" bisdehydro[14]annulene **37** is temperature dependent, and that it exists as a mixture of **37a** and **37b** in a ratio of ~3:7.[27] The spectra of the related compounds **16** and **18** were also temperature dependent. By contrast, the spectra of the fused bisdehydro[14]annulenes **1, 3, 4,** and **38,** as well as those of the monocyclic compounds **19, 20,** and **21,** were essentially temperature independent in the range −60 to 100 °C. That these substances exist in the indicated conformations is supported by the similarity of the H^B, $H^{B'}$ to the H^C, $H^{C'}$ resonances, the high field H^A, $H^{A'}$ resonances, and the s-cis $J_{B,C}$ values of 7.5–9 Hz (the s-trans $J_{B'C'}$ value in **37b**[27] and related compounds is 12 Hz).

The dimethylbisdehydrobenzo[16]annulene **39** and dimethylbisdehydrobenzo[18]annulene **40** have recently been



39



40

prepared.[14] The ^{1}H NMR resonances of the 16-membered ring protons in the [14][16] system **3** and the [6][16] system **39** are given in Table III. The [16]annulene rings in these compounds are clearly paratropic, the inner protons absorbing at low field and the outer protons at high field. However, fusion of the $(4n + 2)$-membered rings has decreased the paratropicity of the bisdehydro[16]annulene ring, as shown by comparison with the inner $H^{A'''}$ resonance (τ −3.05) of the 1,3-bisdehydro-[16]annulene **41** (no particular conformation implied),[28] the closest available model. The chemical shifts of the other protons in **41** cannot be compared directly with the corresponding ones in **3** and **39,** since **41** is conformationally mobile on the

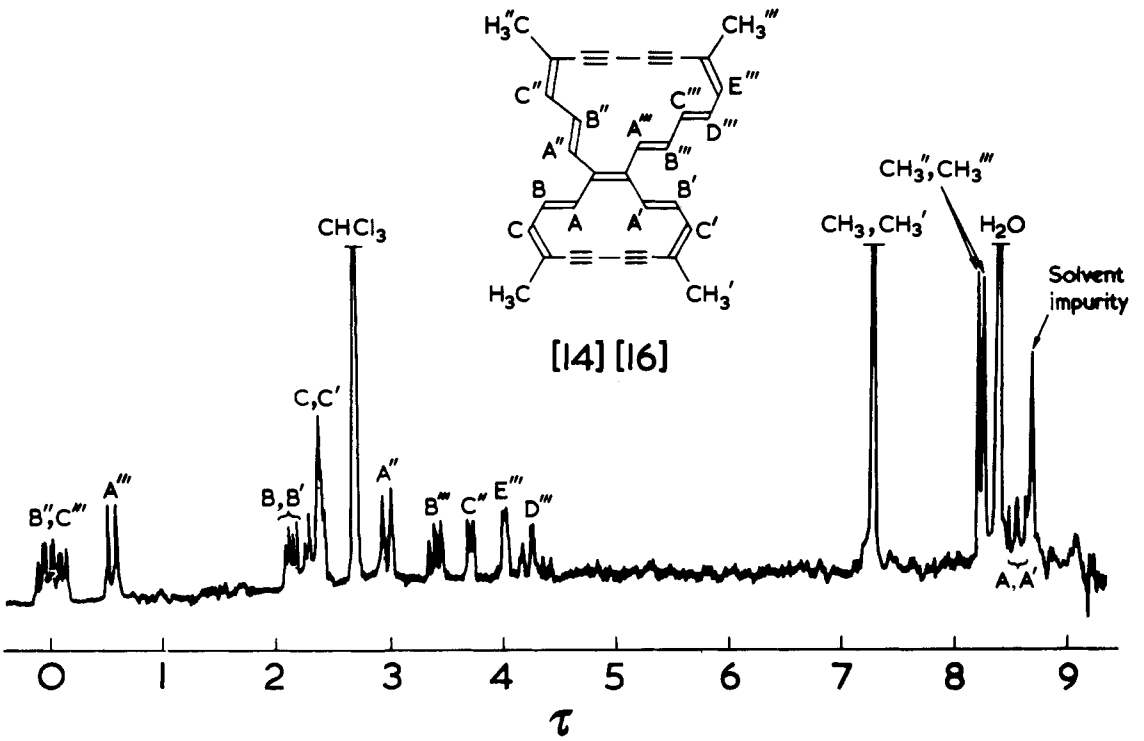
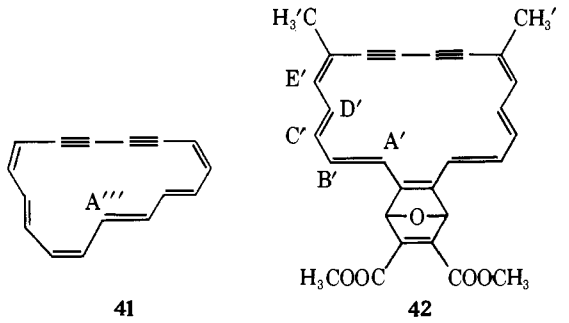


Figure 2. ^{1}H NMR spectrum of the tetramethyltetrakisdehydro[14]annuleno[16]annulene **3** in $CDCl_3$ at 220 MHz (τ values, internal standard Me_4Si; FT, 1500 pulses).



41 **42**

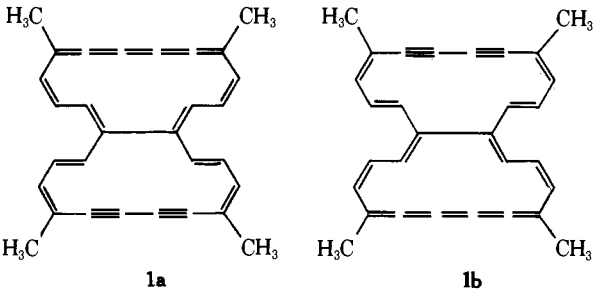
NMR time scale.[28] By contrast, the fused bisdehydro[16] annulenes **3** and **39** were found to be conformationally fixed in the indicated conformations, as evidenced by the temperature independence of the NMR spectra (−60 to 30 °C) and the observed chemical shifts.

The ^{1}H NMR resonances of the 18-membered ring protons in the [14][18] system **4**, the [6][18] system **40**, and the "model" **42**[1] are given in Table IV. The high-field inner proton resonances and the low-field outer proton resonances show the 18-membered ring in these compounds to be diatropic, although this effect is clearly greatly reduced by fusion of the 14- and 6-membered rings. The spectra of **42**, **4**, and **40** were found to be temperature independent in the range −60 to 30 °C, and the chemical shifts and coupling constants of **42** and **40** show them to exist in the indicated conformations. On the other hand, the C',D' double bonds of **4** appear to be conformationally mobile, as indicated by the fact that the $H^{C'}$ chemical shift is similar to that of $H^{D'}$, but dissimilar to that of $H^{E'}$.

The change produced in the chemical shifts of the various 16-membered ring protons on passing from the [14][16] system **3** to the [6][16] system **39** are given in Table III [Δ (**3**–**39**)]. It is apparent that the inner and outer olefinic proton resonances have all moved to lower field. This effect, which must be due to the deshielding of the $(4n + 2)$-membered rings, decreases with the distance of the protons from these rings. The effect is negligible for the furthest removed protons ($H^{D'''}$, $H^{E'''}$, CH_3'', CH_3'''), showing the paratropic ring current of the 16-membered rings in **3** and **39** to be essentially the same. It is evident from the negative values of Δ (**3**–**39**) that the deshielding produced by the 14-membered ring is greater than that produced by the 6-membered ring.

In the 18-membered ring series, fusion of a 14π or a 6π system also causes a similar effect on the ring current of the macrocycle [see Δ (**4**–**40**) in Table IV; the $H^{C'}$,$H^{D'}$ resonances cannot be taken into account due to the conformational mobility of the $H^{C'}$,$H^{D'}$ double bond in **4**]. The deshielding produced by the 14-membered ring again appears to be greater than that produced by the 6-membered ring, although this effect is much less marked than in the annelated 16-membered ring series.

On the other hand, in the 14-membered ring series, passing from the [14][6] system **38** to the [14][14] system **1** [Δ (**1**–**38**) in Table II] causes the inner protons to move to higher field and the outer ones to lower field. This indicates that in this case the diamagnetic ring current of the 14-membered ring in **1** is greater than that in **38**. This may be due to the fact that, unlike in **3** and **4**, the symmetrical [14]annuleno[14]annulene **1** possesses two equivalent Kekulé structures (**1a**, **1b**).



1a **1b**

Experimental Section

General Procedures. Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Infrared spectra were measured on a Unicam SP 200 spectrophotometer or on a Perkin-Elmer 177 grating spectrophotometer (s = strong, m = medium, w

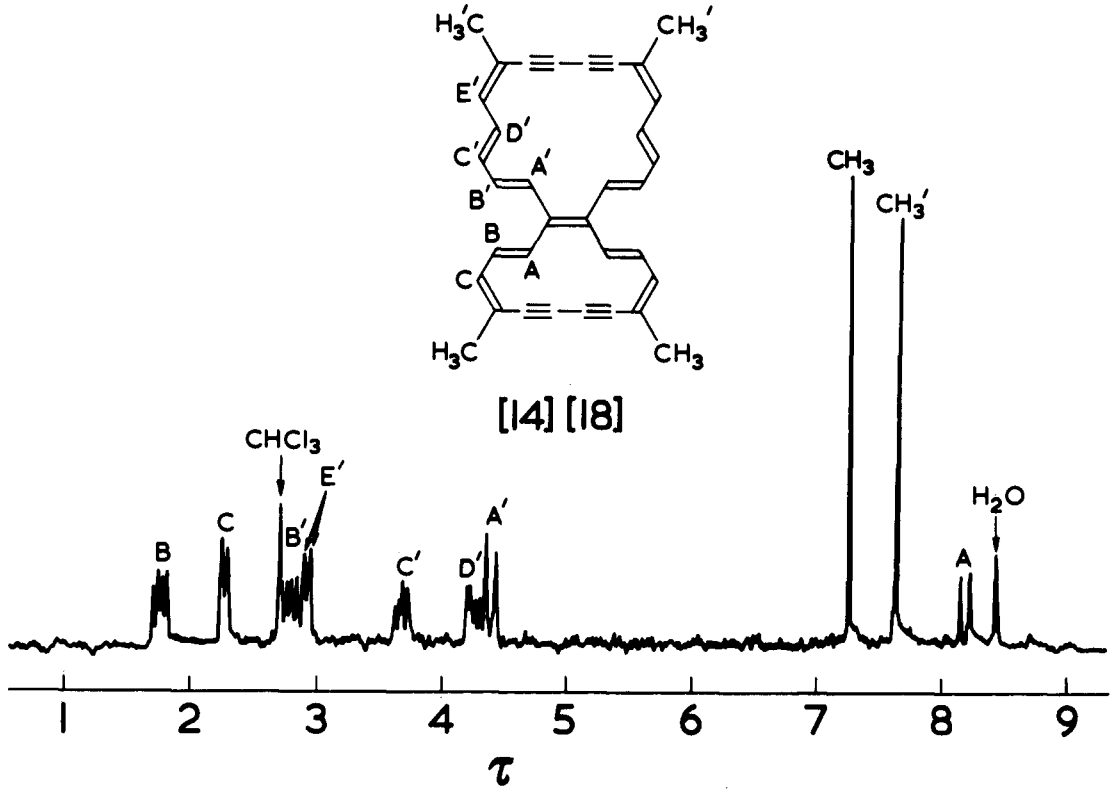


Figure 3. ^{1}H NMR spectrum of the tetramethyltetrakisdehydro[14]annuleno[18]annulene **4** in $CDCl_3$ at 220 MHz (τ values, internal standard Me_4Si; FT, 92 pulses).

= weak); only significant maxima are reported. Electronic spectra were determined on a Unicam SP 800 or a Unicam SP 1800 spectrophotometer (sh = shoulder). ^{1}H NMR spectra were recorded as $CDCl_3$ solutions on a Varian T-60 (60 MHz), a Varian HA-100 (100 MHz), or a Perkin-Elmer R34 (220 MHz) spectrometer, tetramethylsilane being used as an internal standard. Assignments were clarified by the use of decoupling experiments where necessary. Mass spectra were determined on an AEI MS-12 or (for accurate mass measurements) on an AEI MS-902 spectrometer, both operating at 70 eV. Alumina for column chromatography refers to Woelm activity III and silica to Woelm activity II. Compounds were preadsorbed from ether or dichloromethane solution onto the adsorbant before column chromatography on the same adsorbant. Thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 F_{254} precoated aluminum plates. Benzene, dimethylformamide (DMF), and 1,5-diazabicyclo[5.4.0]non-5-ene (DBN) were stored over 4 Å molecular sieves for a prolonged period before use. Petrol (light petroleum, bp 40–60 °C) was distilled from P_4O_{10} before use. Tetrahydrofuran (THF) was refluxed over $LiAlH_4$ and distilled under argon before use. Reactions were carried out under prepurified nitrogen, and organic extracts were washed with saturated aqueous NaCl and dried over magnesium sulfate before solvent removal.

Furan-3,4-dicarboxaldehyde (9). A solution of the diol **8**[15] (10.0 g, 0.08 mol) in dichloromethane (50 ml) was added over 10 min to a stirred, ice-cooled suspension of pyridinium chlorochromate (67.0 g, 0.31 mol)[16] in dichloromethane (400 ml). After a further 15 min, the ice bath was removed, and the mixture was stirred for a further 7 h and then diluted with ether (500 ml). The black residue remaining after decantation was washed with ether (2 × 100 ml) and the combined organic extracts were filtered through a short column of Florisil. The eluent was concentrated and the residue crystallized from cyclohexane to give the dialdehyde **9** (4.0 g, 41%) as needles, identical with that previously described.[15] Essentially the same yield was obtained when commercial (Aldrich) pyridinium chlorochromate was used. The use of pyridinium chlorochromate buffered with sodium acetate[16] failed to improve the yield.

***trans,trans*-3,3'-(3,4-Furandiyl)bis-2-propenal (12).** Lithium methoxide [from lithium (0.278 g, 40 mg-atoms)] in absolute methanol (37 ml) was added dropwise over 2.5 h to a stirred solution of the dicarboxaldehyde **9** (1.24 g, 10 mmol) and 1,3-dioxolan-2-ylmethyltriphenylphosphonium bromide[17] (**10**, 17.16 g, 40 mmol) in DMF (150 ml) at 80 °C (bath). After a further 0.5 h the reaction mixture was cooled and poured into water (500 ml). The resultant mixture was extracted exhaustively with ether and the combined extracts washed with water. The yellow semisolid (9.0 g) remaining after solvent removal was chromatographed on a column of Woelm basic alumina (activity IV, 12 × 5 cm) with ether as eluent. Early fractions, which contained no triphenylphosphine oxide by ^{1}H NMR examination, were concentrated and dissolved in ethanol (40 ml). To this solution hydrochloric acid (0.5 N, 70 ml) was added and the mixture stirred for 10–15 min until precipitation of the solid appeared complete. The precipitate was separated by filtration, washed well with water, and dried in vacuo. The resultant solid, which contained (^{1}H NMR examination) a mixture of **12** and the corresponding cis,trans isomer, was isomerized by allowing it to stand for 24 h in dichloromethane containing a crystal of iodine. Crystallization of the isomerized mixture from dichloromethane–ether afforded the dialdehyde **12** (1.05 g, 60%) as needles: mp 158–160 °C; MS *m/e* 176.047 (M^+, calcd 176.047), 175 ($M^+ - H$), 159 ($M^+ - OH$), 148 ($M^+ - CO$), 147 ($M^+ - CHO$); UV (Et_2O) 249 (ϵ 19 200), 282 nm (24 900); IR (Nujol) 1670 s (C=O), 975 cm^{-1} m (trans HC=CH); ^{1}H NMR (60 MHz) τ 0.30 (d, $J_{CHO,1}$ = 7 Hz, CHO), 2.14 (s, furan H), 2.50 (d, $J_{2,1}$ = 16 Hz, H-2), 3.47 (dd, $J_{1,CHO}$ = 7, $J_{1,2}$ = 16 Hz, H-1).

Anal. Calcd for $C_{10}H_8O_3$: C, 68.18, H, 4.58. Found: C, 68.03; H, 4.52.

3,4-Bis[1-(3-hydroxy-4-methyl-1-hexen-5-ynyl)]furan (13). A small portion of a solution of 3-bromo-1-butyne[29] (2.01 g, 0.015 mol) in dry ether (5 ml) was added to a stirred mixture of magnesium (0.46 g, 0.019 g-atom) and mercuric chloride (15 mg) in dry ether (20 ml). When the ether had become cloudy (ca. 5 min) the mixture was cooled in an ice bath and the remainder of the bromide solution added over 2 min. After 2 h the mixture was cooled to −30 °C and a solution of the dialdehyde **12** (0.50 g, 2.8 mmol) in THF (20 ml) added in a thin stream. The resultant mixture was allowed to warm to 0 °C over 15 min, saturated aqueous NH_4Cl (20 ml) was added, and the mixture was extracted with ether. Concentration of the organic solution afforded the stereoisomeric diol **13** (together with some THF which could not be removed under reduced pressure) as a yellow gum (1.21 g). A small sample was purified by chromatography on a short column of silicic acid with chloroform as eluent. Early fractions afforded the

stereoisomeric diol **13** as a pale yellow gum: MS *m/e* 284.141 (M^+, calcd 284.141); IR (film) 3390 m (OH), 3280 s (C≡CH), 2100 w (C≡C), 970 cm^{-1} s (trans HC=CH); ^1H NMR (60 MHz) τ 2.57 (s, furan H), 3.47 (d, $J_{1,2}$ = 16 Hz, H-1), 3.87 and 4.15 (each dd, $J_{2,1}$ = 16, $J_{2,3}$ = 6 Hz, H-2), 5.85 (m, H-3), 7.30 (m, H-4), 7.65 (s (b), OH), 7.84 (m, H-6), 8.79 (dd, $J_{CH_3,4}$ = 7, $J_{CH_3,6}$ = 2 Hz, CH_3).

7,12- Dimethyl-6,13- dihydroxy-6,7,12,13- tetrahydro-8,9,10,11-tetradehydrocyclotetradeca[*c*]furan (14). A. By Glaser Coupling. A solution of the crude diol **13** (1.21 g) in ethanol (130 ml) was added to a stirred mixture of cuprous chloride (15 g), ammonium chloride (24 g), and concentrated hydrochloric acid (1 ml) in water (90 ml) at 60 °C (bath). After 5 min a benzene-ethanol mixture (4:1, 75 ml) was added and a stream of oxygen bubbled through the mixture. The volume was maintained by the occasional addition of benzene-ethanol (5:1). After 2 h the mixture was cooled in an ice bath and sufficient 1 N hydrochloric acid was added to dissolve the salts. The separated aqueous layer was extracted with ether and the combined organic layers washed with water. The residue after concentration of the organic extract afforded the cyclic diol **14** (together with a little benzene which could not be removed under reduced pressure) as a yellow gum (1.01 g). A small sample was purified by chromatography on a short column of silicic acid with 5% methanol-chloroform as eluent. Early fractions gave the stereoisomeric diol **14** as a cream froth: no satisfactory MS could be obtained; IR (KBr) 3380 s (OH), 2240 w (C≡C), 965 s cm^{-1} (trans HC=CH); ^1H NMR (60 MHz) τ 2.60 (s, furan H), 3.54 (d, $J_{4,5}$ = $J_{15,14}$ = 16 Hz, H-4, H-15), 3.9-4.4 (m, H-5, H-14), 5.5-6.1 (m, H-6, H-13), 7.1-7.5 (m, H-7, H-12), 7.87 (s (b), OH), 8.77 (d (b), $J_{CH_3,7}$ = $J_{CH_3,12}$ = 7 Hz, CH_3).

B. By Eglinton Coupling. A solution of the crude diol **13** (0.77 g, from 0.42 g of the dicarboxaldehyde **12**) in pyridine (20 ml) was added dropwise over 1 h to a stirred mixture of cupric acetate monohydrate (15 g) in pyridine (180 ml) at 60-65 °C (bath). After a further 1 h the mixture was cooled and diluted with benzene (50 ml). The salts were separated by filtration and washed well with benzene. The combined filtrate and washings were concentrated and the residue taken up in benzene (150 ml). The solution was washed with 1 N hydrochloric acid and then water. Solvent removal afforded the cyclic diol **14** (together with a little benzene which could not be removed under reduced pressure) as a yellow gum (0.66 g). It was identical with that obtained by Glaser coupling.

5,10-Dimethyl-6,8-bisdehydro[14]annuleno[*c*]furan (6). Methanesulfonyl chloride (0.82 g, 7.2 mmol) was added to a stirred, ice-cooled solution of the crude cyclic diol **14** (1.01 g, 3.6 mmol), obtained from the above mentioned Glaser coupling, in THF (25 ml). Triethylamine (0.72 g, 7.1 mmol) was then added and the mixture was stirred for 1.5 h. The salts were removed by filtration and the filtrate stirred under ice cooling while a solution of DBN (3.0 g, 0.024 mol) in THF (10 ml) was added over 15 min. After addition was complete, the reaction mixture was stirred at ambient temperature for 3 h, poured onto water (100 ml), and extracted with ether, and the combined extracts were washed with water. The residue after solvent removal was chromatographed on a column of alumina (10 × 4 cm) with petrol as eluent. Early fractions afforded the annulene **6** as yellow needles (0.24 g, 35% from the dialdehyde **12**). It formed yellow needles, mp 123-125 °C dec, from petrol: MS *m/e* 246.101 (M^+, calcd 246.105); UV (Et_2O) 260 sh (ϵ 17 100), 275 sh (25 400), 303 (41 500), 395 nm (4500); ^1H NMR (100 MHz) τ 2.18 (s, furan H), 3.28 (d (b), $J_{4,3}$ = $J_{11,12}$ = 10 Hz, H-4, H-11), 3.48 (d, $J_{2,3}$ = $J_{13,12}$ = 16 Hz, H-2, H-13), 3.69 (dd, $J_{3,2}$ = $J_{12,13}$ = 16, $J_{3,4}$ = $J_{12,11}$ = 10 Hz, H-3, H-12), 7.94 (s (b), CH_3).

Anal. Calcd for $C_{18}H_{14}O$: C, 87.78; H, 5.73. Found: C, 87.87, H, 5.73.

When the same reaction was performed on the crude cyclic diol **14** obtained from the above mentioned Eglinton coupling of **13**, a similar yield of **6** was obtained. The annulene **6** was air and light sensitive, but could be stored in a nitrogen flushed sealed tube at −20 °C for several months without appreciable decomposition.

2′,5′-Diacetoxy-2′,5′-dihydro-5,10-dimethyl-6,8-bisdehydro[14]-annuleno[*c*]furan (16). Lead tetraacetate (4.0 g, 7.9 mmol) was added portionwise over 10 min to a stirred mixture of the annuleno[*c*]furan **6** (0.60 g, 2.4 mmol) in acetic acid (50 ml). After 0.5 h the resultant red solution was poured onto ice and water (150 ml), and extracted with ether. The extract was washed with water and saturated aqueous $NaHCO_3$. Concentration of the solvent left the crude diacetate **16** as a red, frothy gum (1.19 g). A small sample was chromatographed on alumina, with dichloromethane as eluent (considerable hydrolysis and decomposition occurred on the column) to afford the stereoisomeric diacetates **16** as an orange gum: MS *m/e* 364.132 (M^+, calcd 364.131), 305 (M^+ − OAc), 304 (M^+ − AcOH), 262 (M^+ − OAc − Ac); UV (Et_2O) 307 sh (ϵ 62 500), 319 (91 500), 371 (9800), 393 (9300), 458 sh (300), 504 sh (300), 552 nm sh (200); IR ($CHCl_3$) 2085 w (C≡C), 1750 s (C=O), 962 cm^{-1} m (trans HC=CH); ^1H NMR (100 MHz) τ 1.94, 2.17 (each 2 H, s, H-2′, H-5′), 2.09 (4 H, d, $J_{4,3}$ = $J_{11,12}$ = 8 Hz, H-4, H-11), 3.7-4.3 (4 H, m, H-3, H-12), 7.22 (12 H, s, CH_3), 7.83 (12 H, s, $COCH_3$), 7.7-8.1 (4 H, m, H-2, H-13).

2′,5′-Dihydroxy-2′,5′-dihydro-5,10-dimethyl-6,8-bisdehydro[14]-annuleno[*c*]furan (17). The above mentioned crude diacetoxyannulene **16** (1.19 g) was dissolved in THF (60 ml) and added to a solution of oxalic acid dihydrate (4.0 g) in water (60 ml). The resultant red solution was stirred for 12 h, poured onto water (250 ml), and extracted with ether. The extracts were washed with saturated aqueous $NaHCO_3$. Solvent removal afforded the hemiacetal **17** as an orange solid (0.8 g): essentially one spot by TLC examination; MS *m/e* 262 (M^+ − H_2O); IR (KBr) 3420 s (OH), 2100 cm^{-1} w (C≡C); ^1H NMR (60 Mhz, $(CD_3)_2SO$) τ 2.23 (d, $J_{4,3}$ = $J_{11,12}$ = 8 Hz, H-4, H-11), 3.4-4.0 (m, H-3, H-12, OH exchangeable with D_2O), 6.93 (s, CH_3), 8.53 (d, $J_{2,3}$ = $J_{13,12}$ = 16 Hz, H-2, H-13).

5,14-Dimethyl-9,10-bis[2′(1′-ethoxycarbonyl-1′-ethenyl)]-1,3-bisdehydro[14]annulene (19). The above mentioned hemiacetal **17** (0.8 g, 2.9 mmol) was stirred under reflux with carbethoxymethylenetriphenylphosphorane[25] (8.0 g, 23 mmol) in dry benzene (150 ml) for 16 h. The solution was then cooled, concentrated to ca. 30 ml and preadsorbed onto silica gel. Early fractions from chromatography on a column of silica gel (10 × 4 cm), with 15% ethyl acetate-petrol as eluent, afforded the diester **19** as a red solid (0.54 g, 55% yield from **6**). It formed deep orange needles: mp 141-142 °C from dichloromethane-petrol; MS *m/e* 402.184 (M^+, calcd 402.183); UV (Et_2O) 343 (ϵ 62 500), 405 sh (14 800), 418 nm (15 600); IR (KBr) 2150 w (C≡C), 1705 s (C=O), 1625 m (C=C), 965 m and 990 cm^{-1} m (trans HC=CH); ^1H NMR (100 MHz) τ 1.75 (d, $J_{2',1'}$ = 16 Hz, H-2′), 2.07 (dd, $J_{7,8}$ = $J_{12,11}$ = 16, $J_{7,6}$ = $J_{12,13}$ = 8 Hz, H-7, H-12), 2.31 (d (b), $J_{6,7}$ = $J_{13,12}$ = 8 Hz, H-6, H-13), 3.62 (d, $J_{1',2'}$ = 16 Hz, H-1′), 5.65 (q, $CO_2CH_2CH_3$), 7.29 (s (b), CH_3), 8.59 (t, $CO_2CH_2CH_3$), 8.83 (d, $J_{8,7}$ = $J_{11,12}$ = 16 Hz, H-8, H-11).

Anal. Calcd for $C_{26}H_{26}O_4$: C, 77.59; H, 6.51. Found: C, 77.52; H, 6.55.

The mother liquors from the crystallization of a number of preparations of **19** were reduced with diisobutylaluminum hydride and then oxidized with activated manganese dioxide in the manner described below. This gave in addition to the trans,trans dialdehyde **21** a small amount of the corresponding cis,trans dialdehyde: ^1H NMR (60 MHz, inter alia) τ 0.18 (d, J = 8 Hz, CHO), 0.48 (d, J = 8 Hz, CHO), 7.23 (s (b), CH_3). Treatment of a THF solution of this cis,trans isomer of **21** with hydrochloric acid (1 N, 2 h, ambient temperature) effected isomerization to the trans,trans isomer **21.**

2′,5′-Dimethoxy-2′,5′-dihydro-5,10-dimethyl-6,8-bisdehydro-[14]annuleno[*c*]furan (18). A. By Base Treatment of the Diacetoxy[14]-annulene 16. The diacetate **16** (76 mg, 0.2 mmol) in absolute methanol (5 ml) was added to an ice-cooled, stirred solution of sodium methoxide [from sodium (0.2 g, 0.9 mg-atom)] in absolute methanol (20 ml). After 1 h the solution was poured onto water and extracted with ether. The extracts were washed with dilute aqueous oxalic acid and then water. Solvent removal left the stereoisomeric dimethoxyannulene **18** as an orange solid (45 mg, 72%). It formed orange prisms: mp 118-126 °C from dichloromethane-petrol; MS *m/e* 308.141 (M^+, calcd 308.141); UV (Et_2O) 296 sh (ϵ 32 800), 313 sh (58 900), 319 (82 000), 364 (9400), 375 (9200), 392 (8700), tailing to 570 nm; IR (KBr) 2100 w (C≡C), 970 cm^{-1} m (trans HC=CH); ^1H NMR (100 MHz, 95 °C) τ 2.18 (4 H, d (b), $J_{4,3}$ = $J_{11,12}$ = 8 Hz, H-4, H-11), 3.18 and 3.50 (each 2 H, s, H-2′, H-5′), 3.66 and 3.70 (each 2 H, dd, $J_{3,2}$ = $J_{12,13}$ = 16, $J_{3,4}$ = $J_{12,11}$ = 8 Hz, H-3, H-12), 6.48 and 6.62 (each 6 H, s, OCH_3), 7.30 (12 H, s (b), CH_3), 7.70 (4 H, d, $J_{2,3}$ = $J_{13,12}$ = 16 Hz, H-2, H-13); ^1H NMR (100 MHz, −110 °C, CD_2Cl_2) τ 1.7-2.4 (8 H, m, H-3, H-4, H-11, H-12), 2.92 and 3.44 (each 2 H, s, H-2′, H-5′), 6.50 and 6.66 (each 6 H, s, OCH_3), 7.12 (12 H, s (b), CH_3), 9.64 and 9.82 (each 2 H, d, $J_{2,3}$ = $J_{13,12}$ = 16 Hz, H-2, H-13). The same dimethoxyannulene **18** could be obtained in low yield (ca. 10%) by treatment of the diacetate **16** with aqueous methanolic potassium hydroxide (1 M, 1 h, ambient temperature).

B. By Low-Temperature Photooxygenation of the Furoannulene 6. A slow stream of oxygen was passed over the surface of a stirred so-

lution of the furoannulene **6** (0.18 g, 0.71 mmol) in dichloromethane (100 ml) and absolute methanol (10 ml) containing Rose Bengal (ca. 2 mg) at −70 °C for 0.5 h while being irradiated by a 500-W lamp. The lamp was then removed and the oxygen replaced by a nitrogen stream. A solution of triphenylphosphine (0.5 g, 1.9 mmol) in dichloromethane (5 ml) was added and the temperature of the resultant solution allowed to rise to 20 °C over 2 h. After a further 15 h at ambient temperature the solution was concentrated. Chromatography on a column of silica gel (6 × 4 cm) with 0–5% ethyl acetate–petrol as eluent gave, after a forerun containing unidentified compounds, the dimethoxyannulene **18** (6.4 mg, 3%) identical with that described above.

5,14-Dimethyl-9,10-bis[3′-(1′-hydroxy-2′-propenyl)]-1,3-bisdehydro[14]annulene (20). A solution of diisobutylaluminum hydride (0.6 g, 4.2 mmol) in dry benzene (6 ml) was added dropwise over 10 min to a stirred solution of the trans,trans diester **19** (0.26 g, 0.64 mmol) in dry benzene (20 ml), the solution being maintained just above its freezing point with an ice bath. After a further 15 min, methanol (2 ml) was cautiously added and the resultant mixture stirred for 15 min before being poured onto ice-cold hydrochloric acid (1 N, 100 ml). The mixture was extracted with ether, and the extracts were washed with 1 N ice-cold hydrochloric acid and then with water. The residue after solvent removal gave the diol **20** as a red solid (0.20 g, 97%), homogeneous by TLC examination. A small sample formed red needles, mp >180 °C dec, from dichloromethane: MS *m/e* 318.162 (M^+, calcd 318.162), 300 ($M^+ - H_2O$), 287 ($M^+ - CH_2OH$), 269 ($M^+ - CH_2OH—OH$); UV (Et_2O) 336 (ε 56 400), 384 sh (9900), 396 sh (10 700), 413 (13 400), 476 (4900), 520 (500), 569 nm (400); IR (KBr) 3290 s (OH), 2090 w (C≡C), 965 cm^{-1} m (trans HC=CH); ^1H NMR (100 Mhz, THF-d_8) τ 1.88 (dd, $J_{7,8} = J_{12,11} = 15$, $J_{7,6} = J_{12,13} = 8$ Hz, H-7, H-12), 2.22 (d (b), $J_{6,7} = J_{13,12} = 8$ Hz, H-6, H-13), 2.84 (d, $J_{3',2'} = 16$ Hz, H-3′), 3.70 (dt, $J_{2',3'} = 16$, $J_{2',1'} = 5$ Hz, H-2′), 5.64 (d (b), $J_{1',2'} = 5$ Hz, H-1′), 6.92 (s (b), OH), 7.28 (s (b), CH_3), 9.24 (d, $J_{8,7} = J_{11,12} = 16$ Hz, H-8, H-11).

5,14-Dimethyl-9,10-bis[2′-(1′-formyl-1′-ethenyl)]-1,3-bisdehydro[14]annulene (21). The above-mentioned diol **20** (0.20 g, 0.63 mmol) in dichloromethane (50 ml) was stirred with activated manganese dioxide[30] (0.91 g). After 20 min, a further quantity of activated manganese dioxide (0.43 g) was added. The mixture was stirred for a further 40 min; it was then filtered through a pad of Celite and the manganese dioxide washed well with dichloromethane. Solvent removal left the dialdehyde **21** as an orange solid (147 mg, 74%), homogeneous by TLC examination. It formed orange needles, mp >120 °C dec, from dichloromethane–petrol: MS *m/e* 314.131 (M^+, calcd 314.131), 299 ($M^+ - CH_3$), 285 ($M^+ - CHO$); UV (Et_2O) 263 (ε 10 000), 347 (51 900), 420 (15 900), tailing to 600 nm; IR (KBr) 1696 m, 1688 s, 1680 s, 1660 m (C=O), 1608 m (C=C), 978 cm^{-1} m (trans HC=CH); ^1H NMR (100 MHz) τ 0.08 (d, $J_{CHO,1'} = 8$ Hz, CHO), 1.90 (d, $J_{2',1'} = 16$ Hz, H-2′), 2.1–2.3 (m, H-6, H-7, H-12, H-13), 3.28 (dd, $J_{1',2'} = 16$, $J_{1',CHO} = 8$ Hz, H-1′), 7.26 (s (b), CH_3), 8.56 (d, $J_{8,7} = J_{11,12} = 15$ Hz, H-8, H-11).

5,10,18,23-Tetramethyl-6,8,19,21-tetrakisdehydro[14]annuleno-[14]annulene (1). A small portion of a solution of 3-bromo-1-butyne[29] (0.25 g, 1.9 mmol) in dry ether (5 ml) was added to a stirred mixture of magnesium (46 mg, 1.9 mg-atoms) and mercuric chloride (2 mg) in dry ether (5 ml). After the ethereal solution had become cloudy (ca. 5 min) the reaction mixture was cooled in an ice bath and the remainder of the bromide solution was added over 2 min. The mixture was stirred with ice-bath cooling for 2 h and cooled to −30 °C and a solution of the dialdehyde **21** (94 mg, 0.30 mmol) in THF (8 ml) was then added in a thin stream. The temperature of the mixture was allowed to rise to 0 °C over 15 min. Saturated aqueous NH_4Cl was added and the mixture was extracted with ether. Solvent removal left a stereoisomeric mixture of 5,14-dimethyl-9,10-bis[6′-(3′-methyl-4′-hydroxyhex-5′-en-1′-ynyl)]-1,3-bisdehydro[14]annulene (**22**) (together with a little THF which could not be removed under reduced pressure) as a red gum (155 mg): IR (film) 3450 s (OH), 3320 s (C≡CH), 2130 w (C≡C), 968 cm^{-1} m (trans HC=CH), ^1H NMR (60 MHz) τ 2.07 (dd, $J_{7,8} = J_{12,11} = 15$, $J_{7,6} = J_{12,13} = 8$ Hz, H-7, H-12), 2.40 (d, $J_{6,7} = J_{13,12} = 8$ Hz, H-6, H-13), 2.87 (d, $J_{6',5'} = 16$ Hz, H-6′), 3.6–4.1 (m, H-5′), 5.5–5.8 (m, H-4′), 7.08 (m, H-3′), 7.30 (s (b), CH_3-5, CH_3-14), 7.76 (m, H-1′), 8.67 (d, $J = 7$ Hz, CH_3-3′), 9.34 (d, $J_{8,7} = J_{11,12} = 15$ Hz, H-8, H-11).

A solution of the diol **22** (155 mg) in DMF (30 ml) was added dropwise over 45 min to a stirred solution of cupric acetate monohydrate (7.5 g) in DMF (100 ml) at 65 °C (bath). After a further 3.5 h the solution was cooled, poured onto water (300 ml), and extracted exhaustively with ether. The combined ethereal extracts were washed with water. The red gum (142 mg) left after solvent removal was dissolved in THF (20 ml). A solution of methanesulfonyl chloride (90 mg, 0.79 mmol) in THF (3 ml) was added at 0 °C with stirring, followed by the addition of a solution of triethylamine (108 mg, 1.1 mmol) in THF (3 ml). After 30 min the mixture was filtered under N_2 and the filtrate stirred at 0 °C. A solution of DBN (1.5 g, 0.011 mol) in THF (5 ml) was then added over 10 min. The solution was stirred at ambient temperature for 3 h, poured onto water, and extracted with ether and the extracts washed with water. The residue after solvent removal was applied as a benzene solution to a column of silica gel (6 × 4 cm), which was eluted with benzene. The fast moving colored band on evaporation afforded a dark solid which was triturated with ether to leave the bisannulene **1** as a dark red-brown solid (5.4 mg, 5% based on **21**). It formed small deep red-brown prisms, mp >200 °C dec, from chloroform: MS *m/e* 384.187 (M^+, calcd 384.188); UV, see Table I; IR (KBr) 2130 w (C≡C), 970 cm^{-1} m (trans HC=CH); ^1H NMR (100 MHz, see Figure 1) τ 2.13 (dd, $J_{3,2} = J_{12,13} = J_{16,15} = J_{25,26} = 16$, $J_{3,4} = J_{12,11} = J_{16,17} = J_{25,24} = 8$ Hz, H-3, H-12, H-16, H-25), 2.69 (d (b), $J_{4,3} = J_{11,12} = J_{17,16} = J_{24,25} = 8$ Hz, H-4, H-11, H-17, H-24), 6.18 (d, $J_{2,3} = J_{13,12} = J_{15,16} = J_{26,25} = 16$ Hz, H-2, H-13, H-15, H-26), 7.52 (s (b), CH_3).

5,14-Dimethyl-9[4′-(1′-ethoxycarbonyl-1′,3′-butadienyl)]-10-[2″-(1″-formyl-1″-ethenyl)]-1,3-bisdehydro[14]annulene (25) and 5,14-Dimethyl-9,10-bis[4′-(1′-ethoxycarbonyl-1′,3′-butadienyl)]-1,3-bisdehydro[14]annulene (31) from 21. A solution of the dialdehyde **21** (0.19 g, 0.61 mmol) and carbethoxymethylenetriphenylphosphorane[25] (0.21 g, 0.61 mmol) in dichloromethane (50 ml) was stirred for 12 h, concentrated to ~5 ml, and then applied to a column of silica gel (6 × 4 cm). The column was eluted with dichloromethane and fractions of 25 ml were collected. Fractions 11–13 afforded the pure monoester **25** as a red solid (98 mg). Mixed fractions were combined and chromatographed on four preparative layer plates (each 20 × 20 × 0.1 cm) of Kieselgel 60 PF_{254} developed with dichloromethane. The top band afforded the diester **31** as a red solid (25 mg, 9%). The second band afforded the monoester **25** (34 mg, total 132 mg, 56%) and the bottom band yielded the starting dialdehyde **21** (10 mg, 5%).

A sample of the monoester **25** formed small, brick-red prisms, mp >200 °C dec, from dichloromethane–petrol: MS *m/e* 384 (M^+), 356 ($M^+ - CO$); UV (Et_2O) 352 (ε 57 800), 420 (22 000), 522 (400), 576 nm (200); IR (KBr) 2100 w (C≡C), 1702 s and 1678 s (C=O), 1622 m and 1610 w (C=C), 998 cm^{-1} m (trans HC=CH); ^1H NMR (100 MHz) τ 0.18 (d, $J_{CHO,1''} = 8$ Hz, CHO), 2.08 (d, $J_{2'',1''} = 16$ Hz, H-2″), 2.21, 2.23 (each dd, $J_{7,8} = J_{12,11} = 16$, $J_{7,6} = J_{12,13} = 8$ Hz, H-7, H-12), 2.39 (d (b), $J_{6,7} = J_{13,12} = 8$ Hz, H-6, H-13), 2.43 (dd, $J_{2',1'} = 16$, $J_{2',3'} = 12$ Hz, H-2′), 2.65 (d, $J_{4',3'} = 16$ Hz, H-4′), 3.28 (dd, $J_{1'',CHO} = 8$, $J_{1'',2''} = 16$ Hz, H-1″), 3.37 (dd, $J_{3',2'} = 12$, $J_{3',4'} = 16$ Hz, H-3′), 3.96 (d, $J_{1',2'} = 16$ Hz, H-1′), 5.71 (q, $CO_2CH_2CH_3$), 7.31 (s (b), CH_3), 8.64 (t, $co_2CH_2CH_3$), 8.72 (d, $J_{8,7} = J_{11,12} = 16$ Hz, H-8, H-11).

Anal. Calcd for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29. Found: C, 81.38; H, 6.52.

The diester **31** could be isolated in ~70% yield by reaction of the dicarboxaldehyde **21** with an excess of carbethoxymethylenetriphenylphosphorane (ambient temperature, 15 h) in dichloromethane, followed by column chromatography (silica gel; dichloromethane as eluent). It formed red prisms, mp 164–166 °C, from dichloromethane-petrol: MS *m/e* 454 (M^+), 439 ($M^+ - CH_3$), 409 ($M^+ - OEt$); UV (Et_2O) 357 (ε 67 700), 426 (26 900), 526 (600), 582 nm (300); IR (KBr) 2105 w (C≡C), 1705 s (C=O), 1620 s (C=C), 998 m, 965 cm^{-1} w (trans HC=CH); ^1H NMR (100 MHz) τ 2.14 (dd, $J_{7,8} = J_{12,11} = 16$, $J_{7,6} = J_{12,13} = 8$ Hz, H-7, H-12), 2.34 (d (b), $J_{6,7} = J_{13,12} = 8$ Hz, H-6, H-13), 2.40 (dd, $J_{2',1'} = 15$, $J_{2',3'} = 11$ Hz, H-2′), 2.58 (d, $J_{4',3'} = 15$ Hz, H-4′), 3.20 (dd, $J_{3',4'} = 15$, $J_{3',2'} = 11$ Hz, H-3′), 3.96 (d, $J_{1',2'} = 15$ Hz, H-1′), 5.73 (q, $CO_2CH_2CH_3$), 7.30 (s (b), CH_3), 8.64 (t, $CO_2CH_2CH_3$), 8.72 (d, $J_{8,7} = J_{11,12} = 16$ Hz, H-8, H-11).

Anal. Calcd for $C_{30}H_{30}O_4$: C, 79.27; H, 6.65. Found: C, 78.88; H, 6.64.

5,14-Dimethyl-9-[4′-(1′-formyl-1′,3′-butadienyl)]-10-[2″-(1″-formyl-1″-ethenyl)]-1,3-bisdehydro[14]annulene (27). A solution of diisobutylaluminum hydride (0.2 g, 1.4 mmol) in dry benzene (1 ml) was added dropwise over 10 min to a stirred solution of the monoester **25** (62 mg, 0.16 mmol) in dry benzene (10 ml). After 30 min, the solution was cooled in an ice bath, and methanol (3 ml) was added

cautiously. The resultant mixture was then poured onto 1 N hydrochloric acid and extracted with ether. The extracts were washed successively with 1 N hydrochloric acid, water, and saturated aqueous $NaHCO_3$. The red solid crude diol **26** (56 mg) left after solvent removal was stirred in dichloromethane with activated manganese dioxide[30] (0.1 g). After 20 min a further quantity of activated manganese dioxide (0.3 g) was added and the mixture stirred for a further 30 min. The manganese dioxide was separated by filtration and washed well with dichloromethane. Solvent removal left the dialdehyde **27** as an orange solid (40 mg, 73% based on **25**), pure by TLC examination. A sample formed small, orange prisms, mp >170 °C dec, from dichloromethane-petrol: MS *m/e* 340.146 (M^+, calcd 340.146); UV (Et_2O) 354 (ε 51 000), 416 nm (19 700); IR (KBr) 2125 w (C≡C), 1665 s (C=O), 1600 m (C=C), 995 w and 962 cm^{-1} w (trans HC=CH); ^1H NMR (100 MHz) τ 0.16 (d, $J_{CHO,1''}$ = 8 Hz, 1''-CHO), 0.20 (d, $K_{CHO,1'}$ = 8 Hz, 1'-CHO), 2.03 (d, $J_{2'',1''}$ = 16 Hz, H-2''), 2.05-2.77 (m, H-6, H-7, H-12, H-13, H-4'), 2.31 (dd, $J_{2',1'}$ = 16, $J_{2',3'}$ = 10 Hz, H-2'), 3.19 (dd, $J_{3',4'}$ = 16, $J_{3',2'}$ = 10 Hz, H-3'), 3.31 (dd, $J_{1'',2''}$ = 16, $J_{1'',CHO}$ = 8 Hz, H-1''), 3.71 (dd, $J_{1',2'}$ = 16, $J_{1',CHO}$ = 8 Hz, H-1'), 7.28 (s (b), CH_3), 8.64 (d, $J_{8,7}$ = $J_{11,12}$ = 16 Hz, H-8, H-11).

7,12,20,25-Tetramethyl-8,10,21,23-tetrakisdehydro[14]annuleno[16]annulene (3). The dialdehyde **27** (60 mg, 0.18 mmol) was treated with the product from the reaction of 3-bromo-1-butyne (0.24 g, 1.8 mmol), magnesium (42 mg, 1.8 mg-atoms), and mercuric chloride (8 mg), exactly as described above for the preparation of **22.** This gave the crude stereoisomeric diol **28** as a red gum (85 mg).

A solution of the crude diol **28** (85 mg) in pyridine (20 ml) was added dropwise over 2 h to a stirred solution of anhydrous cupric acetate[31] (1.5 g) in pyridine-ether (4:1, 100 ml) at 55-60 °C. After a further 30 min at this temperature, the mixture was concentrated, and the residue was diluted with water and extracted with ether. The organic extracts were washed successively with 1 N hydrochloric acid, saturated aqueous $NaHCO_3$, and water. Solvent removal led to the crude bicyclic diol **29** (85 mg) as a red solid.

The crude diol **29** (85 mg) was allowed to react with methanesulfonyl chloride (54 mg, 0.47 mmol) and triethylamine (61 mg, 0.60 mmol), followed by treatment of the resulting dimethanesulfonate **30** with DBN (0.28 g, 2.2 mmol), exactly as described above for the preparation of **1.** A solution of the product in the minimum amount of dichloromethane was applied to a column of silica gel (6 × 4 cm). The colored band eluted with 10% dichloromethane-petrol afforded a residue which on trituration with a little ether yielded the [14]annuleno[16]annulene **3** as a purple solid (2.4 mg, 3% based on **27**), homogeneous by TLC examination. Crystallization from chloroform-petrol gave deep purple prisms: mp >180 °C dec; MS *m/e* 410.205 (M^+, calcd 410.203); UV, see Table I; ^1H NMR (220 MHz, FT, 1500 pulses, see Figure 2) τ −0.04 (dd, $J_{14,15}$ = 16, $J_{14,13}$ = 10 Hz, H-14), 0.13 (dd, $J_{4,5}$ = 15, $J_{4,3}$ = 11 Hz, H-4), 0.54 (d, $J_{2,3}$ = 16 Hz, H-2), 2.17 and 2.37 (each dd, $J_{18,17}$ = $J_{27,28}$ = 16, $J_{18,19}$ = $J_{27,26}$ = 9 Hz, H-18, H-27), 2.46 and 2.50 (each d, $J_{19,18}$ = $J_{26,27}$ = 9 Hz, H-19, H-26), 2.99 (d, $J_{15,14}$ = 16 Hz, H-15), 3.42 (dd, $J_{3,2}$ = 16, $J_{3,4}$ = 11 Hz, H-3), 3.72 (d, $J_{13,14}$ = 10 Hz, H-13), 4.01 (d, $J_{6,5}$ = 6 Hz, H-6), 4.25 (dd, $J_{5,4}$ = 15, $J_{5,6}$ = 6 Hz, H-5), 7.33 (s, CH_3-20, CH_3-25), 8.26 and 8.32 (each s, CH_3-7, CH_3-12). 8.58 and 8.68 (each d, $J_{17,18}$ = $J_{28,27}$ = 16 Hz, H-17, H-28).

5,14-Dimethyl-9,10-bis[4'-(1'-formyl-1',3'-butadienyl)]-1,3-bisdehydro[14]annulene (33). A solution of the diester **31** (111 mg, 0.24 mmol) in dry benzene (10 ml) was reduced with diisobutylaluminum hydride (0.13 g, 0.98 mmol), and the resulting crude diol **32** was then oxidized with activated manganese dioxide (800 mg), exactly as described above for the synthesis of the dialdehyde **27.** This sequence afforded the dialdehyde **33** as an orange solid (73 mg, 82% based on **31**), homogeneous by TLC examination. A sample formed copper-colored needles, mp >110 °C dec, from dichloromethane-petrol: MS *m/e* 366.163 (M^+, calcd 366.162); UV (Et_2O) 241 (ε 29 800), 265 (21 000), 282 sh (24 300), 362 (57 500), 424 nm (26 300); IR (KBr) 2110 w (C≡C), 1675 s (C=O), 1613 m (C=C), 989 w and 978 w (trans HC=CH); ^1H NMR (100 MHz) τ 0.29 (d, $J_{CHO,1'}$ = 8 Hz, CHO), 2.15 (dd, $J_{7,8}$ = $J_{12,11}$ = 15, $J_{7,6}$ = $J_{12,13}$ = 8 Hz, H-7, H-12), 2.34 (d (b), $J_{6,7}$ = $J_{13,12}$ = 8 Hz, H-6, H-13), 2.47 (d, $J_{4',3'}$ = 16 Hz, H-4'), 2.59 (dd, $J_{2',1'}$ = 15, $J_{2',3'}$ = 11 Hz, H-2'), 3.06 (dd, $J_{3',4'}$ = 16, $J_{3',2'}$ = 11 Hz, H-3'), 3.69 (dd, $J_{1',2'}$ = 15, $J_{1',CHO}$ = 8 Hz, H-1'), 7.30 (s (b), CH_3), 9.62 (d, $J_{8,7}$ = $J_{11,12}$ = 15 Hz, H-8, H-11).

7,12,22,27-Tetramethyl-8,10,23,25-tetrakisdehydro[14]annuleno[18]annulene (4). The dialdehyde **33** (44 mg, 0.12 mmol) was treated with the product from the reaction of 3-bromo-1-butyne (0.24 g, 1.8 mmol), magnesium (42 mg, 1.8 mg-atoms), and mercuric chloride (10 mg), exactly as described above for the preparation of **22.** This gave the crude stereoisomeric diol **34** (60 mg) as a red oil, homogeneous by TLC examination.

A solution of the crude diol **34** (60 mg) in pyridine (20 ml) was added dropwise over 3 h to a stirred solution of anhydrous cupric acetate[31] (1.0 g) in pyridine-ether (8:3, 110 ml) at 50 °C. After a further 30 min at this temperature, the mixture was concentrated, and the product was isolated exactly as described above for the synthesis of **29.** This procedure gave the crude bicyclic diol **35** (62 mg) as a red solid.

The crude diol **35** (62 mg) was allowed to react with methanesulfonyl chloride (56 mg, 0.49 mmol) and triethylamine (48 mg, 0.48 mmol), followed by treatment of the resulting dimethanesulfonate **36** with DBN (0.20 g, 1.6 mmol), exactly as described above for the preparation of **1.** A solution of the product in the minimum amount of dichloromethane was applied to a column of silica gel (5 × 4 cm). The colored band eluted with 10% dichloromethane-petrol on evaporation and crystallization from chloroform-petrol gave the [14]annuleno[18]annulene **4** (10.3 mg, 20% based on **33**) as deep brown-violet prisms: mp >260 °C dec; MS *m/e* 436.212 (M^+, calcd 436.213); UV, see Table I; ^1H NMR (220 MHz, FT, 92 pulses, see Figure 3) τ 1.77 (dd, $J_{20,19}$ = $J_{29,30}$ = 16, $J_{20,21}$ = $J_{29,28}$ = 8 Hz, H-20, H-29), 2.28 (d, $J_{21,20}$ = $J_{28,29}$ = 8 Hz, H-21, H-28), 2.79 (dd, $J_{3,2}$ = $J_{16,17}$ = 16, $J_{3,4}$ = $J_{16,15}$ = 9 Hz, H-3, H-16), 2.93 (d, $J_{6,5}$ = $J_{13,14}$ = 9 Hz, H-6, H-13), 3.69 (dd, $J_{4,5}$ = $J_{15,14}$ = 16 Hz, $J_{4,3}$ = $J_{15,16}$ = 9 Hz, H-4, H-15), 4.27 (dd, $J_{5,4}$ = $J_{14,15}$ = 16, $J_{5,6}$ = $J_{14,13}$ = 9 Hz, H-5, H-14), 4.40 (d, $J_{2,3}$ = $J_{17,16}$ = 16 Hz, H-2, H-17), 7.28 (s, CH_3-22, CH_3-27), 7.68 (s, CH_3-7, CH_3-12), 8.22 (d, $J_{19,20}$ = $J_{30,29}$ = 16 Hz, H-19, H-30).

Acknowledgments. Financial support from the Science Research Council and the Royal Society is gratefully acknowledged. We also thank Perkin-Elmer Ltd., Beaconsfield, Bucks, for kindly determining the 220-MHz ^1H NMR spectra.

References and Notes

(1) Unsaturated Macrocyclic Compounds. 118. For part 117 see R. H. Wightman, T. M. Cresp, and F. Sondheimer, *J. Am. Chem. Soc.*, **98**, 6052 (1976).
(2) For a review, see F. Sondheimer, *Acc. Chem. Res.*, **5**, 81 (1972).
(3) The bicyclo[6.2.0]decapentaene system, made up of fused four- and eight-membered conjugated rings, has also been investigated; see G. Schröder and H. Röttele, *Angew. Chem.*, **80**, 665 (1968).
(4) See O. L. Chapman, C. C. Chang, and N. R. Rosenquist, *J. Am. Chem. Soc.*, **98**, 261 (1976), and references cited therein.
(5) See W. T. Brande, *J. Sci. Arts*, **8**, 287 (1819); A. Garden, *Ann. Philos.*, **15**, 74 (1820); J. Kidd, *Philos. Trans. R. Soc. London*, **111**, 209 (1821); *Ann. Philos.*, **3**, 143 (1822); M. Faraday, *Philos. Trans. R. Soc. London*, **141**, II, 140 (1826).
(6) See G. Wittig, H. Eggers, and P. Duffner, *Justus Liebigs Ann. Chem.*, **619**, 10 (1959); J. A. Elix and M. V. Sargent, *J. Am. Chem. Soc.*, **91**, 4734 (1969).
(7) R. H. Wightman and F. Sondheimer, *Tetrahedron Lett.*, 4179 (1975).
(8) R. T. Weavers and F. Sondheimer, *Angew. Chem.*, **86**, 167 (1974) A benzo[14]annulene has now been prepared: U. E. Meissner, A. Gensler, and H. A. Staab, *Angew. Chem.*, **88**, 374 (1976).
(9) T. M. Cresp and F. Sondheimer, *J. Am. Chem. Soc.*, **97**, 4412 (1975).
(10) T. Kashitani, S. Akiyama, M. Iyoda, and M. Nakagawa, *J. Am. Chem. Soc.*, **97**, 4424 (1975).
(11) See P. J. Garratt and K. Grohmann in Houben-Weyl, "Methoden der Organischen Chemie", Vol. 5, Part 1d, Georg Thieme Verlag, Stuttgart, 1972, pp 543-544.
(12) IUPAC nomenclature: (a) 5,10,18,23-tetramethylbicyclo[12.12.0]hexacosa-1(14),2,4,10,12,15,17,23,25-nonaene-6,8,19,21-tetrayne; (b) 7,-12,20,25 - tetramethylbicyclo[14.12.0]octacosa - 1(16),2,4,6,12,14,17,-19,25,27-decaene-8,10,21,23-tetrayne; (c) 7,12,22,27-tetramethylbicyclo[16.12.0]triaconta - 1(18),2,4,6,12,14,16,19,21,27,29 - undecaene-8,10,23,25-tetrayne.
(13) P. J. Beeby, R. T. Weavers, and F. Sondheimer, *Angew. Chem.*, **86**, 163 (1974).
(14) N. Darby, T. M. Cresp, and F. Sondheimer, *J. Org. Chem.*, in press.
(15) See M. J. Cook and E. J. Forbes, *Tetrahedron*, **24**, 4501 (1968).
(16) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 2647 (1975).
(17) T. M. Cresp, M. V. Sargent, and P. Vogel, *J. Chem. Soc., Perkin Trans. 1*, 37 (1974).
(18) M. Gaudemar, *Ann. Chim. (Paris)*, **1**, 161 (1956); G. Prévost, M. Gaudemar, L. M. Miginiac, F. Bardone-Gaudemar, and M. Andrac, *Bull. Soc. Chim. Fr.*, 679 (1959).
(19) See G. Eglinton and W. McCrae, *Adv. Org. Chem.*, **4**, 225 (1963).
(20) R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.*, **87**, 5720 (1965).
(21) See R. L. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).

(22) Inter alia, see (a) N. Clauson-Kaas and J. Fakstorp, *Acta Chem. Scand.*, **1**, 210 (1947); (b) N. Elming, *Adv. Org. Chem.*, **2**, 67 (1960); (c) E. Koch and G. O. Schenk, *Chem. Ber.*, **99**, 1984 (1966).
(23) N. Elming and N. Clauson-Kaas, *Acta Chem. Scand.*, **6**, 535 (1952); N. Elming, *ibid.*, **6**, 578 (1952).
(24) This type of hemiacetal structure has ample precedent in the literature; e.g., 1,2,4,5-benzenetetracarboxaldehyde exists as the bishemiacetal, from which the tetraaldehyde can be obtained by heating: M. Kerfanto and N. Soyer, *C. R. Acad. Sci., Ser. C*, **264**, 1072 (1967).
(25) O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957).
(26) See P. J. Garratt and K. Grohmann in Houben-Weyl, "Methoden der Organischen Chemie", Vol. V, Part 1d, Georg Thieme Verlag, Stuttgart, 1972, pp 533–535.
(27) R. T. Weavers and F. Sondheimer, *Angew. Chem.*, **86**, 165 (1974).
(28) I. C. Calder, Y. Gaoni, P. J. Garratt, and F. Sondheimer, *J. Am. Chem. Soc.*, **90**, 4954 (1968).
(29) F. Sondheimer and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **85**, 52 (1963).
(30) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).
(31) E. Spath, *Sitzungsber. Akad. Wiss. Wien*, **120**, 1117 (1911).

Solvolysis of Deuterium-Labeled β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonates. Multiple Cation Automerizations in Tight Ion Pairs[1]

Robert S. Bly,* Ruta K. Bly,* John B. Hamilton, and Satya P. Jindal

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received August 21, 1975*

Abstract: The brosylates of α,α-$^2H_2$-, β,β-$^2H_2$-, and α,α,β,β-$^2H_4$-β-(*syn*-7-norbornenyl)ethanol have been prepared and solvolyzed at 25 °C in buffered acetic acid, in buffered formic acid, and in buffered 90% acetone–water. The deuterated *exo*-2-brendyl and *exo*-4-brexyl derivatives produced in each case after a single hydrogen or deuterium shift have been converted to deuterated brendan-2-one and brexan-4-one mixtures and the position of the deuterium labels in each ketone determined mass spectrometrically. Comparison of the deuterium content of the brexan-4-one both before and after base-catalyzed exchange with protium permits analysis of the fractions of solvolysis product derived from each recognizably discrete rearranged cation. From these results it is clear that some hydrogen or deuterium migration occurs from each methylenic carbon of the starting brosylate and that 10–19% of those migrations are preceded by at least one Wagner–Meerwein automerization. A similar analysis of the products from the formolysis of internally returned $^2H_2$-*exo*-2-brendyl brosylate, isolated originally from the acetolysis of α,α-$^2H_2$-β-(*syn*-7-norbornenyl)ethyl brosylate, confirms that the hydrogen or deuterium shift that converts an initial 2-brexyl cation into a product-producing, rearranged cation is irreversible under solvolysis conditions and implies that all carbon and/or hydrogen or deuterium shifts occur within the initially formed ion pair. It is suggested that the observed effect of the different solvents on the product distribution is due in part to ion pairing which affects the rate of transformations that change the net charge separation in the initial intermediate. The possible structure of the 2-brexyl cation is considered, and it is demonstrated by means of equivalent kinetic models that a choice between the classical (C_2) and nonclassical (C_s) structures cannot be made on the basis of our deuterium scrambling analysis since it does not discriminate between 8,8- and 9,9-dideuterated brexyl derivatives.

The acetolysis of β-(*syn*-7-norbornenyl)ethyl *p*-bromobenzenesulfonate (**1**-OBs) is accelerated by π-electron participation[2] and yields, in addition to some deltacyclane (**2**), a 1.1 to 1.0 mixture of *exo*-2-brendyl and *exo*-4-brexyl acetates, **3**- and **4**-OAc, respectively.[2,3] No 2-brexyl acetate (**5**-OAc) can be detected. The acetolysis is accompanied by extensive ion pair return to *exo*-2-brendyl brosylate (**3**-OBs) and probably to the kinetically undetectable[2,4] *exo*-4-brexyl isomer (**4**-OBs) as well. The less reactive[4] 2-brexyl brosylate (**5**-OBs) has not been detected. When solvolyzed separately both **3**- and **4**-OBs produce mixtures of **2**, **3**-OAc, and **4**-OAc which are similar to the ultimate acetolysis mixture from **1**-OBs.[2,4]

The most concise interpretation clearly consistent with these data is that of an initially formed 2-brexyl ion pair, R^+OBs^-, being converted by a hydrogen shift directly to the product-forming intermediate, a rearranged cation or ion pair[5] (Scheme I).

The actual situation, however, may be much more complex for studies utilizing only nonlabeled starting material leave important questions unanswered. Is the initial 2-brexyl cation, R^+, charge delocalized? Does this potentially 20-fold degenerate cation[7] undergo one or more Wagner–Meerwein automerizations prior to hydrogen migration? What is the provenance of the migrating hydrogen? Is the hydrogen migration reversible? And finally, how important is ion pairing in the overall solvolytic process?

The use of specifically labeled starting material would permit these aspects of the solvolysis to be investigated. By analogy with its unlabeled counterpart, a β-(*syn*-7-norbornenyl)ethyl brosylate (**1**-OBs) having a *gem*-dideuterio label at C-α, C-β, C-5, or C-6 will generate one or more of the four possible classical (C_2) or nonclassical (C_s) 2-brexyl cations shown in Schemes II and III, respectively. The shift of one or the other of two symmetrically situated hydrogens and/or deuteriums will convert each of these "initial" cations into one or two of the four isotopically diastereomeric "rearranged" (4-brexyl) cations depited in Scheme IV.[9] Nucleophilic solvent attack on each of these "rearranged" cations will produce a single pair of specifically deuterated *exo*-2-brendyl ($^2H_2$-**3**-OS) and *exo*-4-brexyl ($^2H_2$-**4**-OS) isomers; cf. Scheme IV. The analogous possibilities in the case of a vicinal, bis-gem-dideuterated starting material are outlined in Schemes V–VII.

Obviously a knowledge of the product mixtures resulting from the solvolyses of α,α-$^2H_2$-, β,β-$^2H_2$-, and α,α,β,β-$^2H_4$-β-(*syn*-7-norbornenyl)ethyl brosylates would permit us to answer some of the questions which we had previously been unable to consider. In this paper we report the preparation,