pentane–ether yielded a cyclic trimeric dichloro compound (25 mg) as fairly stable pale yellow prisms, which decomposed at ~225–230° on attempted melting point determination: infrared spectrum (KBr), bands at 2185 (w), 2120 (w) (RC≡CR′), and 1555 cm^{-1} (w) (C=C); λ_{max} (ether) 248 (ϵ 9550), 298 sh (47,500), 303 (56,000), 317 (94,300), 337 sh (10,300), 344 (9500), 361 (7200), 372 (6850), 389 (5700), 415 sh (800), and 440 nm (485); nmr spectrum ($CDCl_3$), 2 H multiplet at τ 6.80–7.00, 6 H multiplet at 7.00–7.25, and 4 H multiplet at 7.30–7.55 (allylic methylene), and 12 H multiplet at 8.00–8.35 (nonallylic methylene); mass spectrum, molecular ion peaks at *m/e* 458 (10.5%), 456 (65%), and 454 (100%) (calcd for $C_{30}H_{24}Cl_2$: *m/e* 458–454).

Further elution with pentane–ether (49:1) gave a mixture of two isomeric linear trimeric dichloro compounds, which were separated by rechromatography on alumina (Woelm, activity IV). The first isomer to be eluted (50 mg, 3.1%) crystallized from ether–pentane as rather unstable yellow crystals, which showed a blue fluorescence in solution, and became black at ~120–130° on attempted melting point determination: infrared spectrum (KBr), bands at 3305 (m), 3285 (m) (≡CH), 2185 (w) (RC≡CR′), and 2085 cm^{-1} (w) (RC≡CH); λ_{max} (ether) 271 (ϵ 17,900), 300 (32,600), 315 (25,900), 330 (24,200), and 385 sh nm (815); mass spectrum, molecular ion peaks at *m/e* 460 (26.5%), 458 (77.5%), and 456 (100%) (calcd for $C_{30}H_{26}Cl_2$: *m/e* 460–456). The second isomer to be eluted (120 mg, 7.5%) crystallized from ether–pentane as yellow needles, which also showed a blue fluorescence in solution, and became black at ~150–160° on attempted melting point determination: infrared spectrum (KBr), bands at 3300 (m), 3280 (m) (≡CH), 2185 (w) (RC≡CR′), and 2085 cm^{-1} (w) (RC≡CH); λ_{max} (ether) 242 sh (ϵ 23,500), 271 (18,700), 290 sh (25,400), 300 (33,700), 325 sh (21,850), and 335 nm (23,300); mass spectrum, molecular ion peaks at *m/e* 460 (25.5%), 458 (77.5%), and 456 (100%) (calcd for $C_{30}H_{26}Cl_2$: *m/e* 460–456).

Acknowledgments. G. M. P. is indebted to the Science Research Council for the award of a Research Studentship (1965–1967) and to New Hall, Cambridge, for the award of a Junior Research Fellowship (1967–1968).

The Synthesis and Reactions of 4,5:10,11-Bis(tetramethylene)-4,10-cyclotridecadiene-2,6,8,12-tetrayn-1-one, a Derivative of [13]Annulenone[1]

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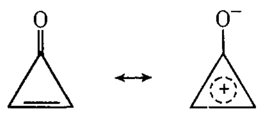
Contribution from the University Chemical Laboratory, Cambridge, England. *Received August 10, 1970*

Abstract: 1,2-Diethynylcyclohexene (**12**) has been converted to 1,5-di(2′-ethynylcyclohexenyl)-1,4-pentadiyn-3-ol (**13**) by reaction of the mono-Grignard derivative with ethyl formate. Oxidative coupling of **13** gave the corresponding cyclic "monomer" **14**, which was oxidized to 4,5:10,11-bis(tetramethylene)-4,10-cyclotridecadiene-2,6,8,12-tetrayn-1-one (**15**). Alternatively, **13** was oxidized to the corresponding ketone **17**, which was coupled to give **15**. The ketone **15** is a tetraalkylated tetradehydro[13]annulenone, and is the first derivative of a macrocyclic annulenone (fully unsaturated monocarbocyclic ketone) to be reported. Some evidence for the nonaromatic nature of **15** could be obtained from the nmr spectrum, which gave an indication of a paramagnetic ring current. Some reactions of **15** have been investigated. Of most interest is its condensation with cyclopentadiene to give 1-cyclopentadienylidene-4,5,10,11-bis(tetramethylene)-4,10-cyclotridecadiene-2,6,8,12-tetrayne (**33**), a derivative of pentatridecafulvalene (**32**).

Fully conjugated monocarbocyclic ketones are an interesting class of compounds, for which we have proposed the generic name "annulenones."[3] Related ketones in which one or more of the ethylenic bonds have been replaced by an acetylenic linkage are named dehydroannulenones. If the carbonyl group is polarized in the usual way, an annulenone or dehydroannulenone containing a ($4n + 3$)-membered ring should represent a ($4n + 2$) π-electron system and be aromatic. Well-known examples are cyclopropenone (**1**) ($n = 0$)[4] and tropone (**2**) ($n = 1$).[5,6] Conversely,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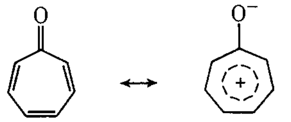
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such compounds containing a ($4n + 1$)-membered ring should represent a $4n$ π-electron system and be nonaromatic.[7] An example is cyclopentadienone (**3**) ($n = 1$),[8] which is unstable and readily undergoes self-condensation. Moreover, the relatively high-field positions of the ring-proton resonances in the nmr spectrum of 2,4-di-*tert*-butylcyclopentadienone (**4**)[9] may

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[1] Unsaturated Macrocyclic Compounds. LXXIV. [For part LXXIII, see G. M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.*, **93**, 1970 (1971).] Taken from the Ph.D. Dissertation of G. M. Pilling, Cambridge University, Aug 1968.

[2] Author to whom inquiries should be addressed at the Chemistry Department, University College, London, W.C.1, England.

[3] G. M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 5610 (1968).

[4] See R. Breslow, G. Ryan, and J. T. Groves, *ibid.*, **92**, 988 (1970), and references cited there.

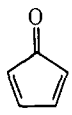
[5] *Inter al.*, see A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 279; L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1963, p 383; D. Lloyd, "Carbocyclic Non-benzenoid Aromatic Compounds," Elsevier, Amsterdam, 1966, Chapter VI; G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, London, 1969, p 85.

[6] The aromatic nature of tropone has been questioned recently: D. Bertelli and T. G. Andrews, *J. Amer. Chem. Soc.*, **91**, 5280 (1969); D. Bertelli, T. G. Andrews, and P. O. Crews, *ibid.*, **91**, 5286 (1969).

[7] See F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, *Chem. Soc., Spec. Publ.*, No. **21**, 75 (1967).

[8] For a review, see M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965).

[9] E. W. Garbisch and R. F. Sprecher, *J. Amer. Chem. Soc.*, **88**, 3433 3434 (1966); **91**, 6785 (1969).



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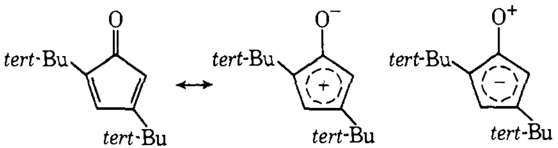

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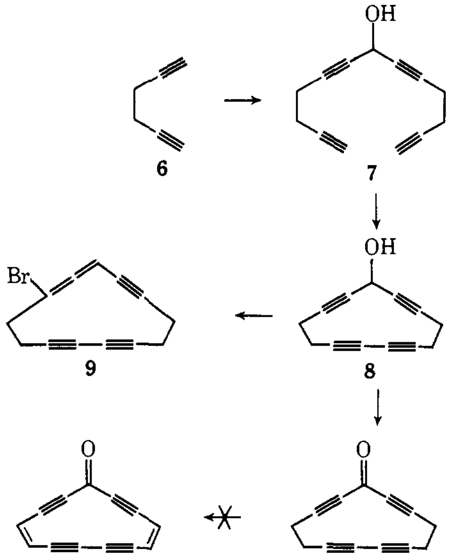
be indicative of a paramagnetic ring current due to its nonaromatic character,[10] although they were ascribed to contributions from **5**.[9]

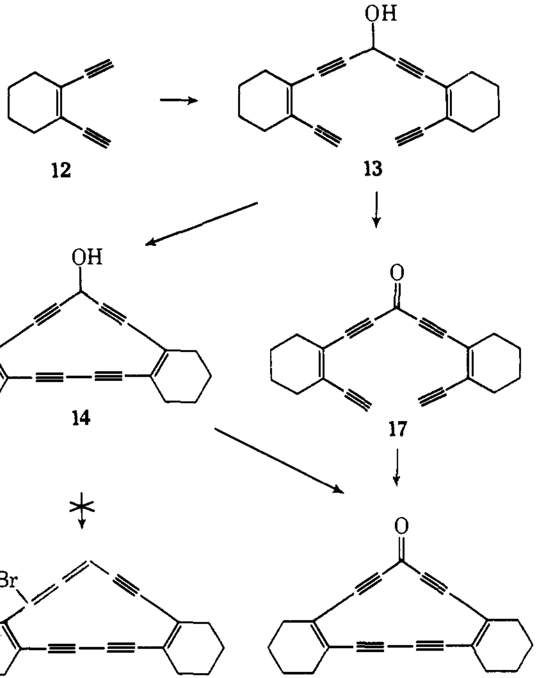
No annulenone, or derivative of an annulenone containing a ring larger than the seven-membered one was known when we started our work in this field. It appeared of interest to synthesize and study the properties of higher members, both in the theoretically aromatic [4*n* + 3]annulenone and in the theoretically nonaromatic [4*n* + 1]annulenone series, and work toward this end was initiated some years ago in our laboratory. In this paper we describe the synthesis of the tetraalkylated tetradehydro[13]annulenone **15** [4,5:10,11-bis(tetramethylene)-4,10-cyclotridecadiene-2,6,8,12-tetrayn-1-one][11] the first macrocyclic annulenone derivative to be reported.[12] This is a derivative of [13]annulenone (*e.g.*, **19**), and was expected to be nonaromatic. Some reactions of **15** have been studied, and it has been converted to 1-cyclopentadienylidene-4,5:10,11-bis(tetramethylene)-4,10-cyclotridecadiene-2,-6,8,12-tetrayne (**33**), a derivative of pentatridecafulvalene (*e.g.*, **32**).[15]

Synthesis of the Tetradehydro[13]annulenone 15. The conversion of 1,5-hexadiyne (**6**) to the 13-membered ring cyclic alcohol **8** by reaction of the mono-Grignard derivative with ethyl formate to give **7**, and subsequent oxidative coupling, has been described previously by our group.[16] Reaction of **8** with phosphorus tribromide gave the unstable bromoallene **9**,[16] while oxidation with manganese dioxide led to the unstable and explosive ketone **10**.[17] Unfortunately all attempts to introduce two double bonds into **10** in order to obtain the tetradehydro[13]annulenone **11** were unsuccessful,[17] as were attempts to rearrange **10** to a bisdehydro[13]annulenone.[17]

Since it was not found possible to introduce the missing double bonds as the last step in the projected tetradehydro[13]annulenone synthesis, it was decided to commence with a 1,5-hexadiyne which was already conjugated. A suitable starting material appeared to be 1,2-diethynylcyclohexene (**12**), two syntheses of which have been described in the preceding paper.[1]

Treatment of **12** with 1 mol equiv of ethylmagnesium bromide, followed by 0.5 mol equiv of ethyl formate, gave the alcohol **13** in 27% yield as an unstable colorless oil. The electronic spectrum of **13** [λ_{max} (EtOH) 257 sh nm (ϵ 23,200), 264 (24,800), and 277 (23,100)] was similar to that of **12** [λ_{max} (EtOH) 249 sh nm (ϵ 10,200), 256 (12,400), 260 sh (11,100), and 269 (9700)],[1] the bathochromic shift of $\sim$8 nm being due to the additional alkyl substitution. In the nmr spectrum of **13** (CCl_4), the methine proton appeared as a 1 H broadened singlet at τ 4.74, and the acetylenic protons as a 2 H singlet at τ 6.96.





The oxidative coupling of **13** with oxygen, cuprous chloride, and ammonium chloride in aqueous ethanol and benzene under the conditions used for the coupling of **7**[16] was studied. It was found that the oxidation of **13** proceeded more slowly than that of **7**, and all the starting material was consumed only when double the usual amount of cuprous chloride was used, and the reaction time was extended to 2 hr. These conditions resulted in $\sim$40%[18] of the 13-membered ring alcohol

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[10] See J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966); F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch. A*, **22**, 103 (1967); H. C. Longuet-Higgins, *Chem. Soc., Spec. Publ.*, No. 21, 109 (1967).

[11] For a preliminary communication, see ref 3.

[12] Three bridged [11]annulenones[13] and three dehydro[17]annulenones[14] have now been prepared.

[13] E. Vogel, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **12**, 215 (1968); W. Grimme, J. Reisdorff, W. Junemann, and E. Vogel, *J. Amer. Chem. Soc.*, **92**, 6335 (1970).

[14] G. W. Brown and F. Sondheimer, *ibid.*, **91**, 760 (1969); J. Griffiths and F. Sondheimer, *ibid.*, **91**, 7518 (1969); G. W. Brown, J. Griffiths, G. V. Meehan, and F. Sondheimer, unpublished experiments.

[15] For a preliminary communication, see G. M. Pilling and F. Sondheimer, *J. Amer Chem. Soc.*, **90**, 5611 (1968).

[16] C. C. Leznoff and F. Sondheimer, *ibid.*, **90**, 731 (1968).

[17] R. M. McQuilkin and F. Sondheimer, unpublished experiments.

[18] The yield is approximate and is based on the electronic spectrum, since solutions of **14** could not be taken to dryness without considerable decomposition.

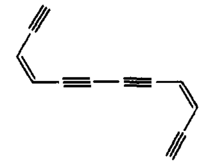
14, as well as $\sim$1% of the desired ketone **15** (presumably derived by oxidation of **14** under the reaction conditions). Four chlorine-containing substances were also obtained, but were not investigated further. The cyclic alcohol **14** was purified by chromatography on silicic acid, and proved to be a very unstable yellow oil. The structure was confirmed by high-resolution mass spectrometry, and by the absence of terminal acetylene bands in the infrared and nmr spectra. In the nmr spectrum of **14** (CCl_4), the methine proton appeared as a 1 H broadened singlet at τ 5.12, which represents an upfield shift of $\sim\tau$ 0.4 compared with the corresponding proton in **13**.

The cyclic alcohol **14** is an example of a rare type of system, a macrocyclic compound containing an extended, but not completely conjugated chromophore. The electronic spectra of such "homoannulenes" are of interest,[19] and the spectrum of **14** is presented in Table I and Figure 1. Compared with the linear model substance **18**[17] (see Table I and Figure 1), each of the three highest wavelength bands of **14** are bathochromically shifted by 41 (±3) nm [or 340 (±20) cm^{-1}] and greatly decreased in intensity. The bathochromic shift may be explained by the presence of the six extra alkyl substituents in **14** compared with **18**. The lowered intensity is presumably a reflection of the much smaller distance between the ends of the chromophore in **14** compared with **18**.[19,20]

Table I. Electronic Spectra of Cyclic and Linear Dienetetraynes, in Ether[a]

14[b]	**23**	**18**[b]
258 (24,800)	259 (24,500)	250 (18,200)
278 sh (8,000)	350 sh (3,700)	260 sh (17,500)
348 sh (3,900)	367 (5,600)	269 (18,500)
365 (5,200)	393 (5,200)	274 sh (17,700)
391 (4,300)		279.5 (16,800)
		284 (17,900)
		302.5 (15,800)
		310 sh (12,100)
		323.5 (22,000)
		347 (21,200)

[a] λ_{max} in nanometers; sh = shoulder; ϵ values in parentheses. [b] The ϵ values represent minimum ones, due to the instability of the substance.



18

Attempts were made to convert the cyclic alcohol **14** to the potentially "Moebius" bromoallene **16** by means of phosphorus tribromide in tetrahydrofuran, following the method used for the transformation of the related cyclic alcohol **8** to the corresponding bromoallene **9**.[16] This reaction when applied to **14** resulted in a less polar product (tlc analysis), which proved to be too unstable to isolate or examine spectroscopically, and it could not be determined whether in fact **16** had been formed.

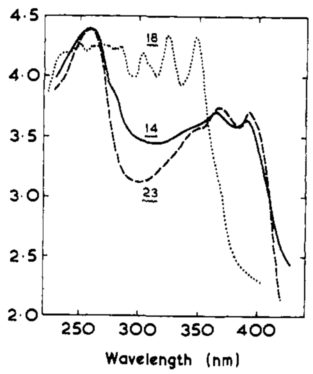


Figure 1. Electronic spectra (in ether) of the cyclic dienetetraynes **14** (solid line) and **23** (dashed line), and of the linear dienetetrayne **18** (dotted line).

On the other hand, the oxidation of the cyclic alcohol **14** to the corresponding ketone **15** could be brought about readily by a variety of reagents. The best yield of **15** (>90%) was obtained when the oxidation of **14** was effected with manganese dioxide[25] in ether at room temperature, but chromium trioxide in acetic acid,[26] Jones reagent,[27] or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[28] could also be used. The ketone **15** was also formed in low yield when ether solutions of **14** were exposed to air at 0° for several days.

An alternative route to **15** involved firstly oxidation of the alcohol **13** with manganese dioxide[25] in ether, whereby the unstable ketone **17** was formed as pale yellow crystals in 85% yield. The ketone **17** was also obtained in poor yield by allowing ether solutions of **13** to stand in air at 0° for several days. Oxidative coupling of **17**, essentially under the conditions used with **13**, then led to the cyclic ketone **15** in 8% yield.

The tetradehydro[13]annulenone **15** was obtained as red crystals. Although the solid gradually decomposed on being allowed to stand in light and air at room temperature ($\sim$50% decomposition after 24 hr), the substance was considerably more stable than the cyclic precursor **14**, and a satisfactory elemental analysis could be obtained. Further proof of structure of **15** was provided by spectral means. The mass spectrum (70 eV) showed the expected molecular ion at *m/e* 284 (100%) with very few fragmentation peaks. The infrared spectrum (CCl_4) exhibited bands at 2190 (s) (acetylene), 1626 (s) (carbonyl), and 1555 cm^{-1} (w) (ethylene). The electronic spectrum (Table II and Figure 2) showed main maxima below 280 nm, like that of the corresponding alcohol **14**, but subsidiary maxima and shoulders up to 535 nm were also apparent. The nmr spectrum (see Figure 3) consisted of an 8 H

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(19) See J. Dale and A. J. Hubert, *J. Chem. Soc.*, 5475 (1963).

(20) A similar effect is shown by 1,3,5-cycloheptatriene [λ_{max} 263 nm (ϵ 4400)][21] and 1,3,5-cyclooctatriene [λ_{max} 265 nm (ϵ 3700)],[22] compared with the linear model 2,4,6-octatriene [all-trans isomer: main λ_{max} 264 nm (ϵ 42,000);[23] trans,trans,cis isomer: main λ_{max} 267 nm (ϵ 41,600)[24]].

(21) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, 75, 297 (1953).

(22) A. C. Cope and C. G. Overberger, *ibid.*, 70, 1433 (1948).

(23) P. Nayler and M. C. Whiting, *J. Chem. Soc.*, 3037 (1955).

(24) K. Alder and H. von Brachel, *Justus Liebigs Ann. Chem.*, **608**, 195 (1957).

(25) See R. M. Evans, *Quart. Rev., Chem. Soc.*, **13**, 61 (1959).

(26) See T. Böhm-Gössl, W. Hunsmann, L. Rohrschneider, W. M. Schneider, and W. Ziegenbein, *Chem. Ber.*, **96**, 2504 (1963).

(27) See K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(28) See D. Burn, V. Petrov, and G. O. Weston, *Tetrahedron Lett.*, **No. 9**, 14 (1960).

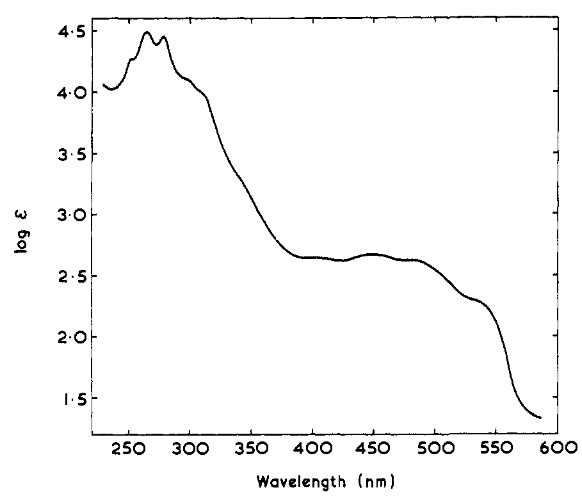


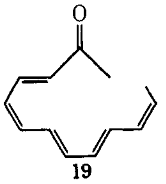
Figure 2. Electronic spectrum (in ether) of the tetradehydro[13]-annulenone **15**.

multiplet at τ 7.85–8.20 (allylic methylene protons) and an 8 H multiplet at τ 8.30–8.60 (nonallylic methylene protons).

Table II. Electronic Spectra of the Tetradehydro[13]annulenone **15** and the Fulvalene **33**, in Ether[a]

15	33
252 (18,600)	250 (18,700)
264 (30,800)	260 (17,900)
279 (28,100)	273 (14,700)
295 sh (13,000)	290 (15,100)
308 sh (10,700)	299 (14,900)
400 sh (450)	383 (36,100)
450 (470)	401 (43,500)
475 sh (425)	
535 sh (190)	

[a] λ_{max} in nanometers; sh = shoulder; ϵ values in parentheses.



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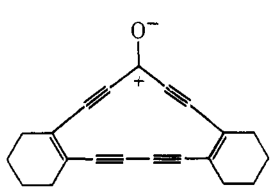

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Substance **15** is a derivative of [13]annulenone (*e.g.*, **19**), containing a $(4n + 1)$-membered ring. If there is appreciable contribution from the polarized structure **20**, the system will contain $4n$ out-of-plane π electrons ($n = 3$). It should therefore be nonaromatic, and sustain a paramagnetic ring current in an applied magnetic field.[7,10] Unfortunately, no clear-cut evidence regarding this point could be obtained from the nmr spectrum, since **15** contains no protons bound directly to the macrocyclic ring. However, it is probably significant that the allylic methylene proton resonances in the nmr spectrum of **15** (τ 7.85–8.20) occur at rather high field. By comparison, the corresponding protons in the spectra of **14** and the subsequently described **23** (which contain the 13-membered ring but not the carbonyl group) resonate at τ 7.65–8.00, and in the spectrum of **17** (which contains the carbonyl group but not the 13-membered ring) at τ 7.55–7.90 (see Figure 3). The upfield shift of τ 0.2–0.3 of these protons in **15** is presumably due to a paramagnetic ring current, although the shift is too small to be considered conclusive evidence.[29] A similar upfield shift of the allylic methylene protons has already been observed in the nmr spectrum of the $4n$ π-electron system **21**, presumably due to the existence of a paramagnetic

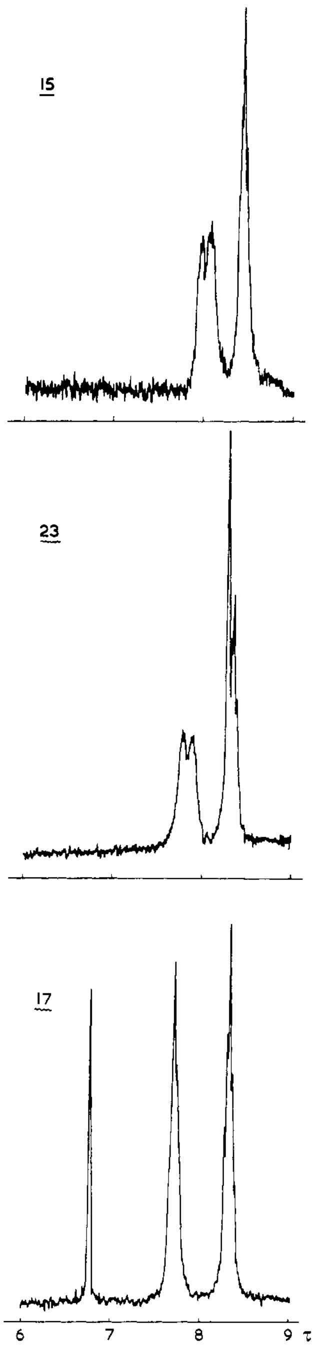
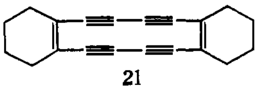


Figure 3. Nmr spectra (100 MHz, in CCl_4) of the tetradehydro[13]-annulenone **15** (top curve), the tertiary alcohol **23** after shaking with D_2O (middle curve), and the ketone **17** (bottom curve).



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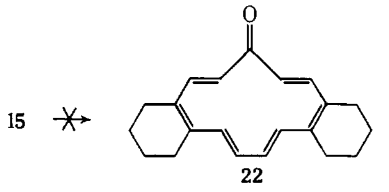
[29] Definite evidence for a paramagnetic ring current in the related dehydro[17]annulenones has now been obtained (see ref 14).

ring current, the shift in this case amounting to τ 0.5–0.6 (see preceding paper[1]).

The low infrared carbonyl frequency of **15** (1626 cm^{-1} in CCl_4) is ascribed to the presence of the flanking acetylenic bonds, rather than to enhanced polarization of the carbonyl group, since the open-chain analog **17** and other α,α'-diacetylenic ketones[30] show similar carbonyl absorptions (1623–1639 cm^{-1}). It will be of interest to study the molecular geometry of **15**, and an X-ray crystallographic study is now in progress.[31]

The attempted partial hydrogenation of the tetradehydro[13]annulenone **15** to the corresponding [13]-annulenone (*e.g.*, **22**) was investigated, using a Lindlar lead-poisoned palladium/calcium carbonate catalyst,[32] or a 10% palladium/charcoal catalyst. However, no detectable amount of the [13]annulenone could be obtained from any experiment, despite the fact that related hydrogenations of dehydroannulenes to the corresponding annulenes under these conditions have been carried out successfully.[33] This lack of success may be due to the fact that the [13]annulenone (*e.g.*, **22**) should not be aromatic, and, if formed, might well undergo self-condensation in the same way as the lower homolog cyclopentadienone (**3**).[8] The presence of the acetylenic bonds in the tetradehydro[13]annulenone **15** would prevent similar self-condensation, and this substance may well owe its existence to the presence of these acetylenic bonds.



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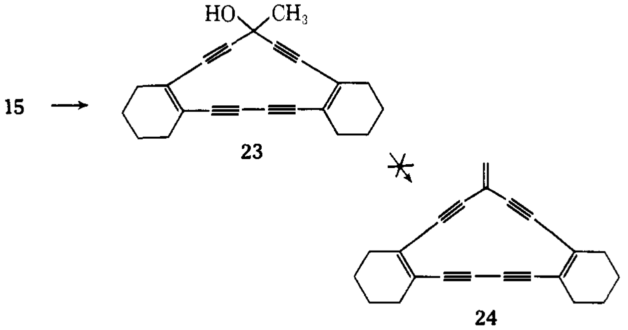
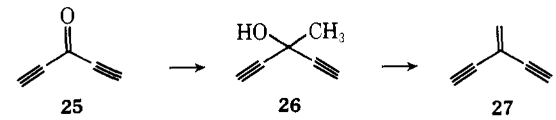
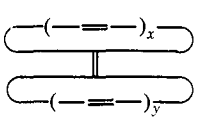
The carbonyl group of the cyclic ketone **15** was found to react normally. Thus, **15** could be readily converted to a 2,4-dinitrophenylhydrazone under the usual conditions. Treatment of **15** with an excess of methylmagnesium iodide led to 55% of the tertiary alcohol **23**, which proved to be considerably more stable than the secondary alcohol **14**. As expected, the electronic spectrum of **23** (see Table I and Figure 1) was very similar to that of **14**. In the nmr spectrum of **23**, the methyl protons appeared as a singlet at τ 8.29, and the allylic methylene protons had shifted downfield to τ 7.65–8.00, as in **14** (see Figure 3).





Attempts to prepare the macrocyclic fulvene **24** by dehydration of **23** (with metaphosphoric acid, phosphorus oxychloride, and pyridine, etc.) were unsuccessful. Equally unavailing were attempts to obtain **24** by the Wittig reaction between **15** and methylenetriphenylphosphorane under a variety of conditions. By comparison, 3-methylene-1,4-pentadiyne **27** has been prepared from 1,4-pentadiyn-3-one (**25**) by conversion to the tertiary alcohol **26** and subsequent dehydration with metaphosphoric acid, but **27** could not be obtained directly from **25** by Wittig reaction with methylenetriphenylphosphorane.[26]

Synthesis of the Tetradehydropentatridecafulvalene 33. Bicyclic polyenes containing a cyclic cross-conjugated π-electron system (fulvalenes, type **28**) have been investigated extensively in recent years, both theoretically and experimentally.[34] These substances may be divided into two different groups. One group, in which one ring is ($4n + 1$) membered and the other is ($4n + 3$) membered, is potentially aromatic since polarization of the central double bond will make both rings ($4n + 2$) π-electron systems; a typical example is pentaheptafulvalene (**29**). The other group, in which both rings are ($4n + 1$) membered, or both are ($4n + 3$) membered, is not potentially aromatic since polarization of the central double bond will make one ring a ($4n + 2$) π-electron system, but the other a $4n$ system; a typical example is pentafulvalene (**30**). The only known macrocyclic compounds of type **28** are derivatives of pentaundecafulvalene (*e.g.*, **31**)[35] belonging to the first group. Condensation of the tetradehydro[13]annulenone **15** with cyclopentadiene appeared to offer a route to the tetradehydropentatridecafulvalene (**33**). This is a derivative of pentatridecafulvalene (**32**), belonging to the second group; both rings are ($4n + 1$) membered, and it is a higher homolog of pentafulvalene (**30**).



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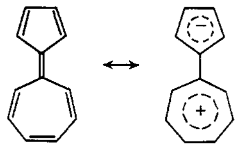

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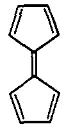

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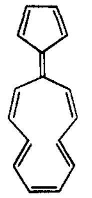

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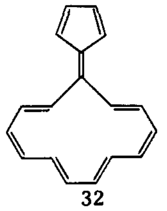

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In practice, reaction of **15** with cyclopentadiene in the presence of sodium methoxide in methanol[36] indeed led to the fulvalene **33** [1-cyclopentadienylidene-4,5:10,-

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[30] See F. Wille and R. Strasser, *Chem. Ber.*, **94**, 1606 (1961); M. Fontaine, J. Chauvelier, and P. Barchewitz, *Bull. Soc. Chim. Fr.*, 2145 (1962).

[31] R. Mason, private communication.

[32] H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952); H. Lindlar and R. Dubois, *Org. Syn.*, **46**, 89 (1966).

[33] See F. Sondheimer, *Proc. Roy. Soc., Ser. A*, **297**, 173 (1967).

[34] For a review, see E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968).

[35] H. Prinzbach and L. Knothe, *Angew. Chem.*, **79**, 620 (1967); **80**, 698 (1968); H. Prinzbach, L. Knothe, and A. Diffenbacher, *Tetrahedron Lett.*, 2093 (1969).

[36] *Inter al.*, see E. P. Kohler and J. Kable, *J. Amer. Chem. Soc.*, **56**, 2756 (1934); **57**, 917 (1935).

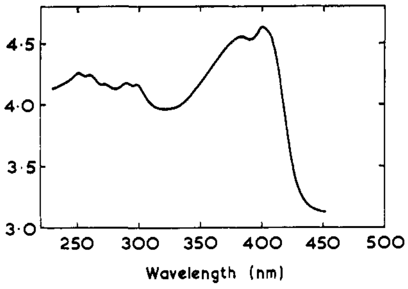
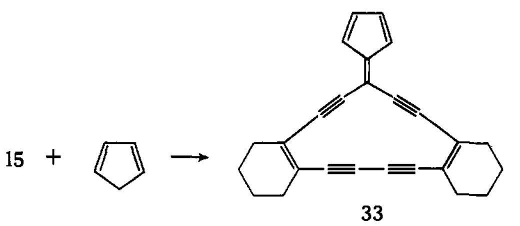


Figure 4. Electronic spectrum (in ether) of the fulvalene **33**.

11-bis(tetramethylene)-4,10-cyclotridecadiene-2,6,8,12-tetrayne] as brick-red needles in 61% yield. The structure of **33** was established by high-resolution mass spectrometry and the elemental analysis, as well as by other spectral means.



The infrared spectrum of **33** (chloroform) exhibited bands at 2190 (m), 2160 (w) (acetylene), and 1570 (m) cm^{-1} (ethylene). In the electronic spectrum (Table II and Figure 4) the main maxima occurred at 383 and 401 nm. The nmr spectrum of **33** (Figure 5) consisted of a 4 H singlet at τ 3.61 (cyclopentadiene protons),[37] an 8 H multiplet at 7.55–8.00 (allylic methylene protons), and an 8 H multiplet at 8.20–8.50 (nonallylic methylene protons).

Most of the pentafulvalenes which have been isolated and characterized previously (*e.g.*, the derivatives of the macrocyclic member **31**[35]) contain a substituted cyclopentadiene ring, since those containing an unsubstituted cyclopentadiene ring are usually very unstable. Rather surprisingly, the fulvalene **33**, which contains an unsubstituted cyclopentadiene, proved to be relatively stable. Thus, **33** was considerably more stable than the precursor **15**, although it also gradually decomposed on being allowed to stand in light and air at room temperature (half-life ~ 7 days).

It was not possible to extract the fulvalene **33** from organic solvents by shaking with 85% phosphoric acid[38] or sodium hydroxide solution. It also could not be protonated with trifluoroacetic acid or 70% perchloric acid in ethanol, unlike some derivatives of the potentially aromatic tripentafulvalene,[39] pentaheptafulvalene (**29**),[40] and pentaundecafulvalene (*e.g.*, **31**).[35]

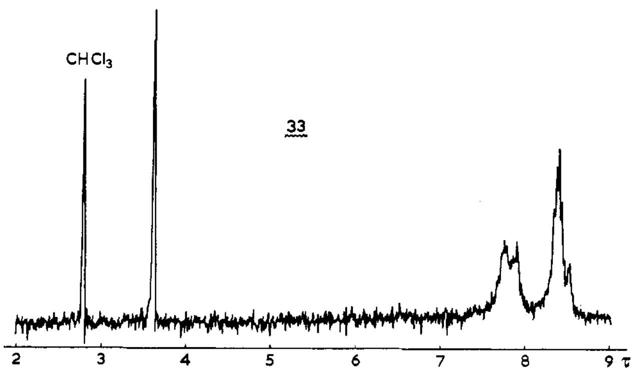


Figure 5. Nmr spectrum (100 MHz, in CDCl$_3$) of the fulvalene **33**.

In the nmr spectrum of **33**, the positions of the allylic methylene and cyclopentadiene[37,41] proton bands are quite normal. This indicates the central double band not to be greatly polarized, in agreement with expectation. Moreover, the fact that passing from the annulenone **15** to the fulvalene **33** results in a small downfield shift of the allylic methylene proton resonance (τ 0.2–0.3), giving a completely normal value for **33**, provides additional evidence that the slightly high-field position of these protons in the nmr spectrum of **15** is indeed due to the existence of a paramagnetic ring current.

Experimental Section[42]

1,5-Di(2′-ethynylcyclohexenyl)-1,4-pentadiyn-3-ol (13). A solution of ethylmagnesium bromide [prepared from ethyl bromide (7.2 g, 0.066 mol) and magnesium turnings (1.6 g, 0.066 g-atom)] in dry tetrahydrofuran (65 ml) was added under nitrogen during 15 min to a stirred solution of 1,2-diethynylcyclohexene (**12**, 8.55 g, 0.066 mol)[1] in tetrahydrofuran (130 ml). The mixture was stirred for 2 hr, and a solution of ethyl formate (2.44 g, 0.033 mol) in tetrahydrofuran (65 ml) was then added during 30 min. The mixture was stirred for a further 20 hr, and the complex was then decomposed by addition of saturated ammonium chloride solution. Ether was added, and the ether layer was washed successively with dilute hydrochloric acid and saturated sodium chloride solution. The dried ether extract was evaporated, and the residue was chromatographed on silicic acid–Supercel (800 g). Pentane–ether (99:1) eluted unchanged **12** (1.52 g, 18%). Pentane–ether (4:1) then eluted 1,5-di(2′-ethynylcyclohexenyl)-1,4-pentadiyn-3-ol (**13**, 2.54 g, 27%) as a colorless unstable oil, homogenous on tlc: infrared spectrum (CCl$_4$), bands at 3600 (m), 3505 (w) (OH), 3310 (s) ($\equiv$CH), 2215 (w) (RC$\equiv$CR′), and 2090 cm^{-1} (w) (RC$\equiv$CH); electronic spectrum, see Discussion; nmr spectrum (CCl$_4$), 1 H broadened singlet at τ 4.74 (methine), 2 H singlet at 6.96 (acetylenic), 9 H multiplet at 7.60–8.10 (allylic methylene and hydroxyl; reduced to 8 H on shaking with D$_2$O), and 8 H multiplet at 8.20–8.60 (nonallylic methylene); mass spectrum, molecular ion peak at *m/e* 288.151 (6.5%) (calcd for $^{12}C_{21}{}^{1}H_{20}{}^{16}O$: 288.151), with fragmentation peaks at *m/e* 287 (M − 1, 11%), 271 (M − 17, 5.5%), 259 (M − 29, 52%), 243 (M − 45, 25%), and 231 (M − 57, 100%). The substance rapidly became dark on standing in air and light at room temperature. Ether solutions at 0° in the dark slowly decomposed to give mainly insoluble polymeric material, as well as small amounts of the ketone **17**. The last-mentioned compound formed pale-yellow crystals (after chromatography on silicic acid–Supercel and crystallization from pentane), identified with **17** obtained by oxidation of **13** with manganese dioxide (see below).

Oxidative Coupling of 13 to the Cyclic Alcohol 14 and the Cyclic Ketone 15. A solution of **13** (1 g) in ethanol (25 ml) was added to a mixture of cuprous chloride (40 g), ammonium chloride (64 g), and water (170 ml), containing concentrated hydrochloric acid (0.4 ml). The stirred mixture was placed in a water bath at 60°,

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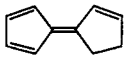
(37) The cyclopentadiene protons in the nmr spectra of other fulvene derivatives have been shown to appear as a singlet. For instance, in dihydropentafulvalene (i) these protons appear as a singlet at τ 3.73 (K. V. Sherer, *J. Amer. Chem. Soc.*, **85**, 1550 (1963)).



i

(38) *Inter al.*, see J. Mayer and F. Sondheimer, *ibid.*, **88**, 602 (1966).

(39) See H. Prinzbach and U. Fischer, *Helv. Chim. Acta*, **50**, 1669 (1967).

(40) See H. Prinzbach, D. Seip, L. Knothe, and W. Faisst, *Justus Liebigs Ann. Chem.*, **698**, 34 (1966).

(41) See G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960); T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

(42) For general procedures, see preceding paper.[1]

and after 5 min more ethanol (25 ml) and benzene (100 ml) were added. A vigorous stream of oxygen was then bubbled for 2 hr into the well-stirred mixture at 60°, the volume being maintained by periodic addition of benzene. The cooled mixture was extracted with ether, and the organic layer was washed successively with dilute hydrochloric acid and water. The extract was dried, evaporated under reduced pressure on a rotatory evaporator (bath temperature $\sim$20°), and the brown residue was immediately chromatographed on silicic acid–Supercel (400 g).

Pentane–ether (19:1) eluted small amounts of five compounds. The third in order of elution proved to be the cyclic ketone **15** (10 mg, 1%); it formed bright red prisms from pentane, and was identified with the ketone obtained by oxidation of **14** with manganese dioxide (see below). The other four compounds each contained at least one chlorine atom (mass spectral examination), and were not investigated further.

Pentane–ether (4:1) then eluted the cyclic alcohol **14** [4,5:10,11-bis(tetramethylene)-4,10-cyclotridecadiene-2,6,8,12-tetrayn-1-ol] ($\sim$400 mg, 40%)[18] as a very unstable pale yellow oil, homogeneous on tlc: infrared spectrum (CCl_4), bands at 3600 (w) (OH), 2220 (w), and 2185 cm^{-1} (w) ($RC\equiv CR'$); electronic spectrum, see Figure 1 and Table I; nmr spectrum (CCl_4), 1 H broadened singlet at τ 5.12 (methine), 9 H multiplet at 7.65–8.00 (allylic methylene and hydroxyl; reduced to 8 H on shaking with D_2O), and 8 H multiplet at 8.20–8.50 (nonallylic methylene); mass spectrum, molecular ion peak at *m/e* 286.135 (100%) (calcd for $^{12}C_{21}{}^{1}H_{18}{}^{16}O$: 286.136), with a fragmentation peak at *m/e* 284 (M − 2, 27%). Neat **14** rapidly decomposed at room temperature. Solutions in carbon tetrachloride were also very unstable and rapidly darkened. Substance **14** was usually stored in ether solution at 0° in the dark, but these solutions also gradually decomposed, giving rise to insoluble polymeric material as well as small amounts of the ketone **15**.

Reaction of 14 with Phosphorus Tribromide. Phosphorus tribromide (0.1 ml) was added to a solution of **14** (40 mg) in dry tetrahydrofuran (5 ml) at ~ -80° (Dry Ice–acetone bath). The bath was removed, and the solution was allowed to stand at room temperature for 30 min (deep red solution). Ether was then added and the solution was washed with water and dried. Tlc examination showed the presence of much material at the origin, no starting material, and one relatively nonpolar compound ($R_f \sim 0.75$, pentane); λ_{max} (Et_2O; crude reaction product) 231 sh (relative optical density 0.71), 264 (1.00), 350 sh (0.23), and 400 sh nm (0.18). Decomposition of the nonpolar compound occurred on attempted chromatography on silicic acid–Supercel or neutral alumina (Woelm, activity V) columns, as well as on a preparative tlc plate (Kieselgel G). It also decomposed on evaporation of the ether solution, or in the presence of carbon tetrachloride or chloroform.

Oxidation of 14 to the Tetradehydro[13]annulenone 15. A. With Manganese Dioxide.[25] A solution of **14** ($\sim$400 mg)[18] in ether (100 ml) was added to a vigorously stirred suspension of manganese dioxide (4.0 g; prepared by the method of Attenburrow, *et al.*[43]) in ether (200 ml). The flask was stoppered, and stirring was continued at room temperature for 1 hr. The mixture was filtered through Supercel, and the residue was washed well with ether. The orange-red filtrate was evaporated under reduced pressure on a rotatory evaporator (bath temperature $\sim$20°). Crystallization from pentane at −70° then gave the tetradehydro[13]annulenone **15** (372 mg, $\sim$94%) as unstable bright red prisms, which decomposed at 90–95° on attempted melting point determination: homogeneous on tlc; infrared spectrum (CCl_4), see Discussion; (KBr), bands at 2185 (s), 2160 (s) ($RC\equiv CR'$), 1615 (s) (C=O), and 1550 cm^{-1} (m) (C=C); electronic spectrum, see Table II and Figure 2; nmr spectrum (CCl_4), see Discussion and Figure 3; mass spectrum, see Discussion.

Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.48; H, 5.80.

Substance **15** was soluble in ether, carbon tetrachloride, or chloroform, and moderately soluble in pentane or ethanol. The crystals became brown on standing in light and air ($\sim$50% decomposition after 24 hr at room temperature or 2 weeks at 0°, determined from the electronic spectrum); they could be kept for short periods at −70° with little deterioration, but **15** was conveniently stored in ether solution at 0° in the dark.

B. With Jones Reagent.[27] A solution of **14** ($\sim$30 mg)[18] in acetone (20 ml) was cooled in ice–water, and titrated with Jones reagent [$\sim$1 ml; solution prepared by dissolving anhydrous chromium trioxide (13.4 g) in concentrated sulfuric acid (11.5 ml) and diluting to 50 ml with water]. Water was added, and the mixture was poured into ether. The organic extract was washed successively with saturated sodium bicarbonate solution and water, and was then dried and evaporated as previously. Chromatography on silicic acid–Supercel (100 g), elution with pentane–ether (19:1), and crystallization from pentane at −70°, gave **15** (16 mg, $\sim$54%) as bright red prisms, identified with the sample obtained by method A.

C. With 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone. A solution of **14** ($\sim$20 mg)[18] in ether (20 ml) was added to a stirred solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[28] (50 mg) in ether (10 ml). The color immediately became orange-red, and the mixture was stirred for 5 min. The crude reaction product obtained by evaporation was chromatographed on silicic acid–Supercel (100 g). Elution with pentane–ether (19:1) and crystallization from pentane at −70° yielded **15** (5 mg, $\sim$25%) as bright red prisms, identified with the sample obtained by method A.

1,5-Di(2′-ethynylcyclohexenyl)-1,4-pentadiyn-3-one (17). A solution of **13** (100 mg) in ether (20 ml) was added to a vigorously stirred suspension of manganese dioxide (1.0 g; prepared by the method of Attenburrow, *et al.*[43]) in ether (40 ml). The flask was stoppered, and stirring was continued at room temperature for 1 hr. The mixture was filtered through Supercel, and the residue was washed well with ether. The filtrate was evaporated under reduced pressure on a rotatory evaporator (bath temperature $\sim$20°). Crystallization from ether–pentane yielded the ketone **17** (85 mg, 86%) as unstable pale yellow prisms, which decomposed at 80–85° on attempted melting point determination: homogeneous on tlc; infrared spectrum (CCl_4), bands at 3318 (s) ($\equiv$CH), 2210 (s), 2200 (s) ($RC\equiv CR'$), 1626 (s) (C=O), and 1582 cm^{-1} (m) (C=C); λ_{max} (Et_2O) 245 (ϵ 18,400), 322 (15,800), 331 (16,000), and 350 sh nm (11,800); nmr spectrum (CCl_4, see Figure 3), 2 H singlet at τ 6.78 (acetylenic), 8 H multiplet at 7.55–7.90 (allylic methylene), and 8 H multiplet at 8.20–8.50 (nonallylic methylene); mass spectrum, peaks at *m/e* 286 (M, 24.5%), 258 (M − 28, 23.5%), 257 (M − 29, 28%), 241 (M − 45, 35%), 229 (M − 57, 98.5%), 215 (M − 71, 100%), and 202 (M − 84, 93%).

Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.19; H, 6.20.

The ketone **17** was very sensitive to heat and traces of acids, and partial decomposition occurred on a silicic acid–Supercel column. The crystalline substance became brown on standing in light and air at room temperature ($\sim$50% decomposition after 24 hr). Solutions in carbon tetrachloride decomposed very rapidly. Solutions in ether were more stable, although some polymer had formed after 7 days at 0°.

Oxidative Coupling of 17 to the Tetradehydro[13]annulenone 15. The coupling of **17** (40 mg) was carried out as described above for the coupling of **13**, using cuprous chloride (40 g), ammonium chloride (64 g), water (170 ml), concentrated hydrochloric acid (0.4 ml), ethanol (two 25-ml portions), and benzene (100 ml). The reaction was terminated after 75 min, and the product was then isolated as previously. The brown residue was chromatographed on silicic acid–Supercel (150 g). Elution with pentane–ether (19:1) and crystallization from pentane at −70° gave **15** (3 mg, 8%) as bright red crystals, identified by comparison with a sample obtained by oxidation of **14**. Further elution with pentane–ether (19:1) led to unchanged **17** (9 mg, 23%).

2,4-Dinitrophenylhydrazone of 15. Substance **15** (15 mg) was dissolved in the minimum amount of ethanol ($\sim$20 ml) with very gentle warming. A reagent (0.5 ml), prepared from 2,4-dinitrophenylhydrazine (500 mg), ethanol (25 ml), and concentrated sulfuric acid (1 ml) was added; the solution was warmed gently for $\sim$2 min, and then cooled in ice (red precipitate). The mixture was allowed to stand in ice for 30 min, and the solid was collected. Crystallization from ethyl acetate–ethanol gave the 2,4-dinitrophenylhydrazone of **15** as long red needles, which blackened without melting at $\sim$210°: λ_{max} (Et_2O) 253 sh (ϵ 25,300), 263 (26,800), 337 sh (7450), 402 (31,000), and 441 nm (34,800); λ_{max} ($CHCl_3$) 255 sh (ϵ 26,400), 265 (27,500), 412 (30,900), and 450 nm (35,200).

Anal. Calcd for $C_{27}H_{20}O_4N_4$: C, 69.82; H, 4.34; N, 12.06. Found: C, 70.01; H, 4.45; N, 11.67.

1-Methyl-4,5:10,11-bis(tetramethylene)-4,10-cyclotridecadiene-2,6,8,12-tetrayn-1-ol (23). A solution of **15** (200 mg, 0.7 mmol) in dry ether (80 ml) was added during 10 min to a stirred solution of methylmagnesium iodide [from magnesium (96 mg, 4 mg-atoms) and methyl iodide (565 mg, 4 mmol)] in ether (40 ml), cooled in an ice–water bath. The mixture was then stirred at room tem-

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(43) 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).

perature for 5 hr, and the reaction was quenched by addition of saturated ammonium chloride solution. The ether layer was washed successively with water and saturated sodium chloride solution, and was then dried and evaporated. The residue was chromatographed on silicic acid–Supercel (250 g). Elution with pentane–ether (4:1) and crystallization from pentane at −70° yielded the tertiary alcohol **23** (115 mg, 55%) as a cream colored solid, which decomposed at 70–80° on attempted melting point determination: homogeneous on tlc; infrared spectrum (CCl_4), bands at 3595 (m) (OH), 2215 (w), 2185 (w) ($RC\equiv CR'$), and 1560 cm^{-1} (w) ($C{=}C$); electronic spectrum, see Table I and Figure 1; nmr spectrum (CCl_4, see Figure 3), broad singlet at τ 7.85 (hydroxyl) superimposed on multiplet at 7.65–8.00 (allylic methylene) (total 9 H, reduced to 8 H on shaking with D_2O), and singlet at 8.29 (methyl) superimposed on multiplet at 8.20–8.45 (nonallylic methylene) (total 11 H); mass spectrum, molecular ion peak at *m/e* 300.148 (100%) (calcd for ${}^{12}C_{22}{}^{1}H_{20}{}^{16}O$: 300.151), with a fragmentation peak at *m/e* 285 (M − 15, 12.5%). The solid compound was comparatively stable at room temperature; a sample had only slightly decomposed after standing for 1 week in air and light (determined by the electronic spectrum).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.89; H, 6.83.

1-Cyclopentadienylidene-4,5:10,11-bis(tetramethylene)-4,10-cyclotridecadiene-2,6,8,12-tetrayne (33). Freshly distilled cyclopentadiene (0.4 ml) was added to an ice-cooled solution of sodium methoxide [from sodium (50 mg)] in methanol (20 ml) under nitrogen, and the solution was stirred at 0° for 10 min. The ketone **15** (50 mg) in ether (10 ml) was then added, when a deep red-purple color was formed. The reaction was quenched by the addition of water, and the mixture was extracted with ether. The ether layer was washed successively with water and saturated sodium chloride solution. The extract was dried and evaporated under reduced pressure on a rotatory evaporator (bath temperature ~20°), and the deep red solid residue was chromatographed on silicic acid–Supercel (200 g). Elution with pentane–ether (49:1) and crystallization from ether led to the fulvalene **33** (36 mg, 61%) as brick-red needles, which decomposed at 135–140° on attempted melting point determination: homogeneous on tlc; infrared spectrum ($CHCl_3$), see Discussion; (KBr), bands at 2185 (m), 2155 (w) ($RC\equiv CR'$), and 1567 cm^{-1} (m) ($C{=}C$); electronic spectrum, see Table II and Figure 4; nmr spectrum ($CDCl_3$), see Discussion and Figure 5; mass spectrum, molecular ion peak at *m/e* 332.155 (100%) (calcd for ${}^{12}C_{26}{}^{1}H_{20}$: 332.156), very little fragmentation.

Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 94.05; H, 6.27.

The fulvalene **33** was moderately soluble in benzene, ether, carbon tetrachloride, or chloroform, and essentially insoluble in pentane or ethanol. The solid gradually decomposed on standing in air and light at room temperature (~50% decomposition after 7 days, determined by the electronic spectrum).

Acknowledgments. G. M. P. is indebted to the Science Research Council for the award of a Research Studentship (1965–1967) and to New Hall, Cambridge, for the award of a Junior Research Fellowship (1967–1968).

The Chemistry of 1,4 Diradicals. I. Intermediates in the Norrish Type II Photocleavage

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Abstract: The photoreactions of methyl *erythro*- and *threo*-3,4-dimethyl-6-ketoheptanoate have been studied. Both *cis*- and *trans*-3-methyl-3-pentenoic acid methyl esters are products of the photocleavage. Reactions of the ketone excited singlet state are shown to be highly stereospecific while those of the triplet component of the reaction show little selectivity.

Difunctional intermediates have been used to rationalize transformations of organic compounds since the earliest studies of reaction mechanisms. 1,4 diradicals have been a commonly invoked member of this class. In recent years, these species and their analogs extended by vinyl conjugation, although never directly observed, have been strongly implicated in the pyrolysis of cyclobutanes[1] and cyclobutanols,[2] the triplet-sensitized cycloaddition reactions of conjugated dienes,[3] and the cycloaddition reactions of highly halogenated olefins,[4] to mention a few.

In a recent elegant contribution, Bartlett and Porter[5] were able to generate these species by decomposition of six-membered ring azo compounds. They found large differences in the stereospecificity of the cyclobutane-forming fraction of this reaction depending on the spin state (singlet or triplet) of the azo precursor to the diradical. This work, coupled with the earlier work of Bartlett,[4] and the more recent work of Turro[6] and Yang[7] leads one to conclude that singlet and triplet states are easily distinguished in the 1,4 diradical system.

The simplicity and convenience of the Norrish type II photocleavage prompted us to explore this reaction as an alternate route to the 1,4 diradical system. In addition, the availability of a range of substrates allows the stereospecificity of the ring closure, cleavage, and internal disproportionation steps to be examined. With these aims in mind we have prepared both *erythro*- and *threo*-3,4-dimethyl-6-ketoheptanoic acid methyl esters and wish to describe the photochemistry of these molecules below.

Synthesis and Results

I (erythro) and II (threo) were prepared from the Diels–Alder adducts between purified maleic anhydride,

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