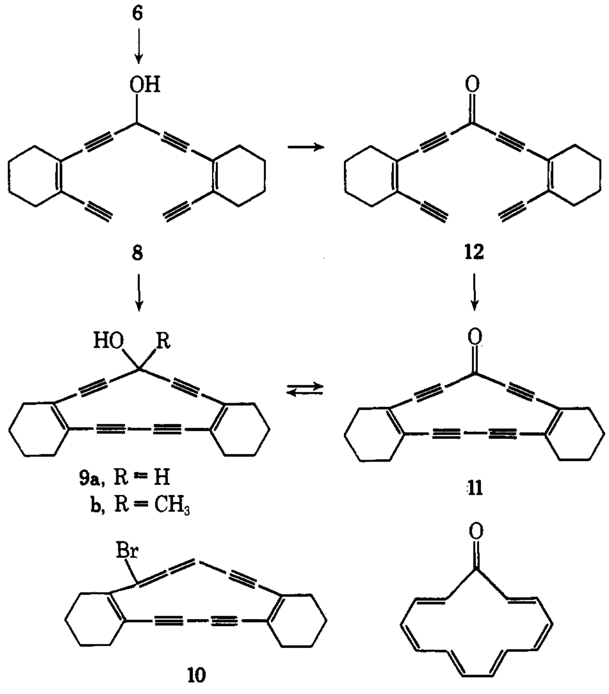
product was formed (tlc analysis), it proved to be too unstable for spectral examination.

The cyclic alcohol **9a** could be oxidized to the ketone **11** with a variety of reagents, the best yield (over 90%) being obtained with manganese dioxide in ether at room temperature. Alternatively, **8** was oxidized first with manganese dioxide in ether to the ketone **12** (85% yield), pale yellow prisms which decomposed at 80–85° on attempted melting point determination; λ_{max}^{ether} 245 mμ (ε 18,400), 322 (15,800), 331 (16,000), and 350 sh (11,800); $\nu_{max}^{CCl_4}$ (cm^{-1}) 3318 s (HC≡), 2210 s, 2200 s (C≡C), 1626 s (C=O), and 1582 m (C=C); nmr spectrum, two-proton singlet at τ 6.78 (acetylenic protons), eight-proton multiplet at 7.55–7.90 (allylic protons), and eight-proton multiplet at 8.20–8.50 (methylene protons). Coupling of **12** as previously then gave **11** in 8% yield.



Substance **11** formed red prisms which decomposed at 90–95° on attempted melting point determination; λ_{max}^{ether} 252 mμ (ε 18,600), 264 (30,800), 279 (28,100), 295 sh (13,000), 308 sh (10,700), 400 sh (450), 450 (470), 475 sh (425), and 535 sh (190); $\nu_{max}^{CCl_4}$ (cm^{-1}) 2190 s (C≡C), 1626 s (C=O), and 1555 w (C=C); nmr spectrum, eight-proton multiplet at τ 7.85–8.20 (allylic protons) and eight-proton multiplet at 8.30–8.60 (methylene protons); mass spectrum, molecular ion at *m/e* 284 (100%). *Anal.* Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.48; H, 5.80. The compound was considerably more stable than the cyclic precursor **9a**, although the crystals gradually decomposed on being allowed to stand in light and air (*ca.* 50% decomposition after 24 hr). The ketone **11** could be converted to a 2,4-dinitrophenylhydrazone [red needles; main λ_{max}^{ether} 441 mμ (ε 34,800)], and on reaction with an excess of methylmagnesium iodide in ether at room temperature gave 55% of the tertiary alcohol **9b** [cream solid; λ_{max}^{ether} 259 mμ (ε 24,450), 350 sh (3740), 367 (5600), and 393 (5170)]. Attempted partial hydrogenation of the tetradehydro[13]annulenone **11** in benzene over a Lindlar or a 10% palladium–calcium carbonate catalyst did not lead to any detectable amounts of the corresponding [13]annulenone.

Substance **11** is a [4*n* + 1]annulenone derivative and is therefore not expected to be aromatic. Although no definite evidence regarding this point has yet been obtained, the fact that the allylic protons in the nmr spectrum of **11** show an upfield shift of τ 0.2–0.3 compared with those of other 1,2-diethynylcyclohexenes (*e.g.*, **6** and **12**) may be of significance.[13] The low infrared carbonyl frequency of **11** (1626 cm^{-1}) is presumably due to the presence of the flanking acetylenic bonds, since the open-chain analog **12** and other α,α′-diacetylenic ketones[14] show similar carbonyl absorptions (1623–1639 cm^{-1}).

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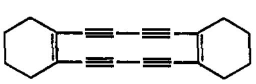
[13] A similar upfield shift of the allylic protons has been observed in the nmr spectrum of the 4*n* system i (G. M. Pilling and F. Sondheimer, unpublished).



i

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

[15] Recipient of a Science Research Council Research Studentship (1965–1967) and a New Hall Research Fellowship (1967–1968).

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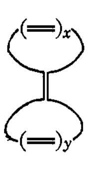
The Synthesis of 1-Cyclopentadienylidene-4,5:10,11-bis(tetramethylene)-4,10-cyclotridecadiene-2,6,8,12-tetrayne, a Derivative of Pentatridecafulvalene[1]

Sir:

Bicyclic polyenes containing a cyclic cross-conjugated π-electron system (type **1**) have been studied extensively in recent years, both theoretically and experimentally.[2] These substances may be divided into a potentially aromatic group in which both rings can form (4*n* + 2) π-electron systems through polarization of the centra double bond [triapentafulvalene (**1**, $x = 1$; $y = 2$) pentaheptafulvalene (**1**, $x = 2$; $y = 3$)], and a second group in which this is not possible [pentafulvalene (**1**, $x = y = 2$), heptafulvalene (**1**, $x = y = 3$)]. The only known macrocyclic compound of type **1** is a derivative of pentaundecafulvalene (**1**, $x = 2$; $y = 5$),[3] belonging to the first group. We now describe the synthesis of 1-cyclopentadienylidene-4,5:10,11-bis(tetramethylene)-4,10-cyclotridecadiene-2,6,8,12-tetrayne (**4**); this is a derivative of pentatridecafulvalene (*e.g.*, **2**),



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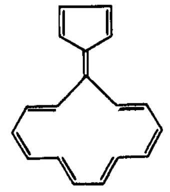

2

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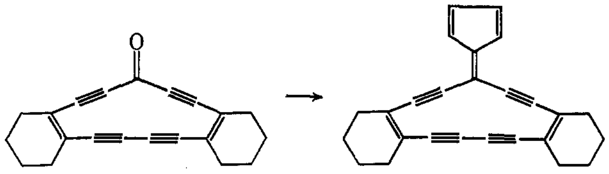
[1] Unsaturated Macrocyclic Compounds. LXIII. For part LXII, see G. M. Pilling and F. Sondheimer, *J. Am. Chem. Soc.*, **90**, 5610 (1968).

[2] See E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968).

[3] H. Prinzbach and L. Knothe, *Angew. Chem.*, **79**, 620 (1967).

belonging to the second group. Compound **2**, like pentafulvalene (**1**, $x = y = 2$), is made up of two ($4n + 1$)-membered rings.

Substance **4** was obtained simply by the reaction of the ketone **3**[1] with cyclopentadiene in the presence of sodium methoxide.[4] Cyclopentadiene (0.4 ml) was added to an ice-cooled solution of sodium methoxide (from 50 mg of sodium) in methanol (20 ml) under nitrogen, and the ketone **3** (50 mg) in ether (10 ml) was added after stirring for 10 min. An immediate deep red-purple color was formed, and the reaction was quenched by the addition of water. Isolation with ether and chromatography on silicic acid gave **4** in 61% yield as brick-red needles from ether, which decomposed at 135–140° on attempted melting point determination; $\lambda_{\max}^{\text{ether}}$ 250 mμ (ϵ 18,700), 260 (17,900), 273 (14,700), 290 (15,100), 299 (14,900), 383 (36,100), and 401 (43,500); $\nu_{\max}^{\text{KBr}}$ (cm^{-1}) 2185 m, 2155 w (C≡C), and 1567 m (C=C); nmr spectrum ($CDCl_3$, 100 Mcps), four-proton singlet at τ 3.61 (cyclopentadiene protons),[5] eight-proton multiplet at 7.55–8.00 (allylic protons), and eight-proton multiplet at 8.20–8.50 (methylene protons); mass spectrum (70 eV, direct inlet), molecular ion at m/e 332.155 (100%) (calcd 332.156), very little fragmentation. *Anal.* Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 94.05; H, 6.03.

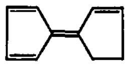


3 **4**

Compound **4** was more stable than the precursor **3**, but it also gradually decomposed on being allowed to stand in light and air (*ca.* 50% decomposition after 7 days). It was not protonated with trifluoroacetic acid or 70% perchloric acid in ethanol, unlike derivatives of triapentafulvalene[6a] and pentaheptafulvalene.[6b] The normal positions of the allylic[1] and cyclopentadiene[5,7] proton bands in the nmr spectrum of **4** indicate the central double bond not to be greatly polarized, in agreement with expectation.

(4) Among others, see E. P. Kohler and J. Kable, *J. Am. Chem. Soc.*, **56**, 2756 (1934); 57, 917 (1935).

(5) The cyclopentadiene protons in the nmr spectra of other fulvene derivatives have been shown to appear as a singlet. For example, the cyclopentadiene protons in dihydropentafulvalene (i) appear as a singlet at τ 3.73 (K. V. Scherer, *ibid.*, **85**, 1550 (1963)).



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(6) See (a) H. Prinzbach and U. Fischer, *Helv. Chim. Acta*, **50**, 1669 (1967); (b) H. Prinzbach, D. Seip, L. Knothe, and W. Faisst, *Ann.*, **698**, 34 (1966).

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

(8) Recipient of a Science Research Council Research Studentship (1965–1967) and a New Hall Research Fellowship (1967–1968).

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Photochemistry without Light and the Stereochemistry of the Type A Dienone Rearrangement. Organic Photochemistry. XXXVI[1]

Sir:

One of the most intriguing of photochemical rearrangements is the type A transformation[2] of 2,5-cyclohexadienones (*e.g.*, **2**). Of particular interest is the stereochemistry of the process. Thus, *a priori*, the zwitterion **4** postulated[3] to be a photochemical reaction intermediate can rearrange by either of two types of stereochemistry (see Chart I). The pivot mechanism is one in which bond 5,6 remains essentially intact with pivoting about this bond and with the orbital at C-6 detaching itself from C-1, then bonding to C-4. The "slither" mechanism can be pictured as involving two 1,2 shifts with C-6 migrating from C-5 to C-4 and then from C-1 to C-5.

The problem is simplified if one begins with zwitterion **4** rather than with its dienone precursor. This we have done, and we now report a stereospecific stereochemical course for the rearrangement of the zwitterion. 6-*exo*-Phenyl-6-*p*-bromophenylbicyclo[3.1.0]hex-2-ene (**6a**), mp 105–106°, and 6-*endo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]hex-2-ene (**6b**), bp 105° (0.005 mm), were synthesized[4] from cyclopentadiene and phenyl-*p*-bromophenyldiazomethane. The *exo*-olefin **6a** on hydroboration gave 6-*exo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]-hexan-2-ol (**7a**), mp 143–144°, and 6-*exo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]hexan-3-ol (**8a**), mp 185–186°. Oxidation of **7a** gave 6-*exo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]hexan-2-one (**9a**), mp 130–131°, and oxidation of the *exo*-3-alcohol **8a** gave 6-*exo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]hexan-3-one(**10a**), mp 110–111°. This synthesis rigorously related the configurations of the *exo*-2-one **9a** and the *exo*-3-one **10a**.[5] Similarly, hydroboration of the 6-*endo*-phenyl olefin **6b** and oxidation of the resulting alcohols gave the *endo*-2-one **9b**, mp 124–125°, and *endo*-3-one **10b**, mp 109–110°, whose configurations must then be the same and *endo*,[5] having been derived from the single *endo*-olefin **6b**. Bromination of the enol acetates, mp 170–171° and 104–105, of each of the *exo*- and *endo*-3-ones gave 2-bromo-6-*exo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]hexan-3-one (**11a**), mp 147–148°, and 2-bromo-6-*endo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]-hexan-3-one (**11b**), mp 113–114°, respectively.

Previously we reported[6] that treatment of 2-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one with potassium *t*-butoxide in *t*-butyl alcohol at 40° gave 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. The reaction was postulated as proceeding *via* zwitterion **4** ($R_1 = R_2 =$

(1) For paper XXXV of the series, see H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Am. Chem. Soc.*, in press.

(2) The type A dienone transformation is typified by the rearrangement of 4,4-diphenylcyclohexadienone to 6,6-diphenylbicyclo[3.1.0]-hex-3-en-2-one.[3]

(3) (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4484 (1961); (b) *ibid.*, **84**, 4527 (1962); (c) H. E. Zimmerman and J. S. Swenton, *ibid.*, **86**, 947 (1964); (d) *ibid.*, **89**, 906 (1967); (e) H. E. Zimmerman, 17th National Organic Chemistry Symposium, Bloomington, Ind., June 1961, Abstracts, p 31.

(4) Synthetic details will be given in our full paper. All compounds were completely characterized and gave satisfactory analyses.

(5) The *exo vs. endo* assignments are based on nmr arguments which are not absolute. However, the stereochemical course is independent of this and relies only on knowing that **9a** and **10a** have the one configuration while **9b** and **10b** have the other configuration.

(6) H. E. Zimmerman, D. Döpp, and P. S. Huyffer, *J. Am. Chem. Soc.*, **88**, 5352 (1966).