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THE SYNTHESIS OF 1,1'-(1,2-ETHENEDIYLIDENE)BIS(5,10-DIMETHYLCYCLOTRIDECA-2,4,10,12-TETRAENE-6,8-DIYNE), A MACROCYCLIC FULVALENE CONTAINING A CUMULENE LINKAGE [1]

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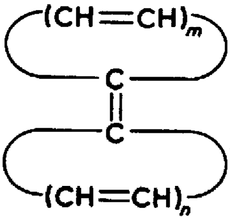
Although bicyclic fulvalenes of type 1 are well known, the only homologues containing an allene (type 2) or cumulene (type 3) linkage between the two rings to be prepared until now all contain additional fused benzene rings.[2] We now report the synthesis of the title compound (6), the first example of a non-annelated fulvalene derivative of type 3, which proved to be a surprisingly stable substance.



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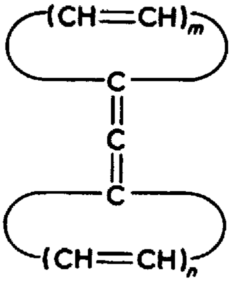

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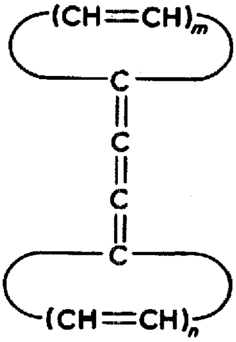

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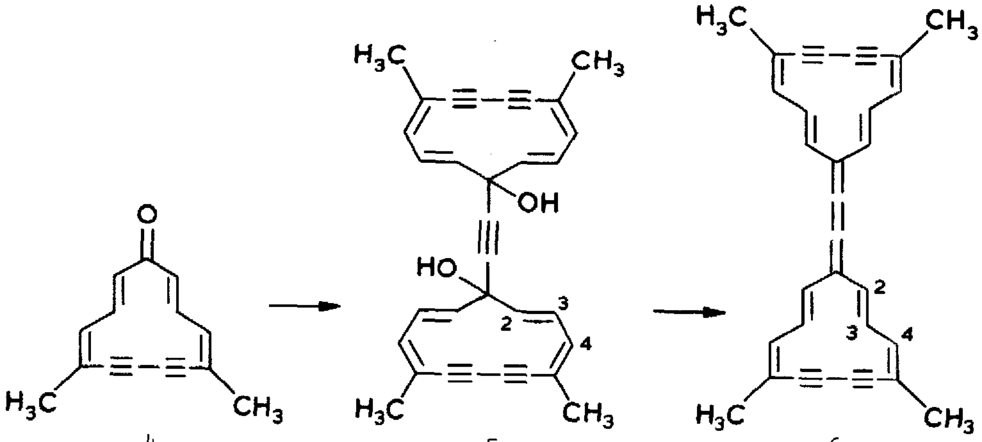
Grignard reaction of 5,10-dimethyl-6,8-bisdehydro[13]annulenone 4 [3,4] with an excess of acetylenedimagnesium bromide (prepared in benzene, followed by decantation) in tetrahydrofuran at room temp for 2.5 hr gave 45% of the diol 5 [6a] as a colourless powder, which decomposed above 170° on attempted mp determination;[7a] m/e 442; λ_{max} ($CHCl_3$) 263 (ε 27,800), 329 nm (9300); ν_{max} (KBr) 2175w (C≡C), 1180m, 1100m (C-OH), 968m, 955s (trans C=C) cm^{-1}; ^{1}H-nmr (THF-d_8, 100Mz) τ 3.26 (m, $J_{4,3}$ = 4Hz, $J_{4,2}$ = 1.5Hz, H^4), 3.70 (two m, $J_{3,2}$ = 15Hz, $J_{3,4}$ = 4Hz, H^3), 5.60 (dd, $J_{2,3}$ = 15Hz, $J_{2,4}$ = 1.5Hz, H^2), 8.04 (finely split s, CH_3). The indicated conformation of 5 follows from the ^{1}H-nmr chemical shifts and J values, which are similar to those of the alcohol[4] obtained by the reduction of the keto group of 4.

Reduction of the diol 5 with $SnCl_2 \cdot 2H_2O$ and HCl gas in ether[8] at 0° for 2 hr led to the cumulene 6[6b] in 65% yield as sparingly soluble dark blue-green prisms showing a metallic lustre (violet in $CHCl_3$ solution), which decomposed above 130° on attempted mp determination;[7b]



m/e 408; λ_{max} (CHCl$_3$) 284 (ε 30,100), 566nm (83,500); ν_{max} (KBr) 2130m (C≡C), 960m (*trans* C=C) cm^{-1}; ^{1}H-nmr [CS$_2$, CD$_2$Cl$_2$ (2:1); 90MHz, FT, 1000 scans] τ 2.11 (dd, $J_{3,2}$ = 16 Hz, $J_{3,4}$ = 11 Hz, H^3), 3.53 (d, $J_{4,3}$ = 11Hz, H^4), 3.73 (d, $J_{2,3}$ = 16Hz, H^2), 8.15 (s, CH$_3$). That *6* possesses the same conformation as *4* [3,4] follows from the ^{1}H-nmr chemical shifts and *J* values. As expected, the ^{1}H-nmr spectrum of *6* gives no indication of any appreciable ring current.

The cumulene *6* could be kept in the solid state for several days with no apparent decomposition, and CHCl$_3$ solutions showed no appreciable change (electronic spectrum) after 1 month at room temp without protection from light or air.

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6. Isolated by chromatography on (a) Al$_2$O$_3$ (Woelm, act. III); (b) silica gel (Woelm, act. III).
7. *Anal.* (a) Calcd. for C$_{32}$H$_{26}$O$_2$: C, 86.88; H, 5.88. Found: C, 86.51; H, 5.94; (b) Calcd. for C$_{32}$H$_{24}$: C, 94.12; H, 5.88. Found: C, 93.91; H, 5.97.
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