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THE SYNTHESIS OF 8,13-DIMETHYL-2,9,11-TRISDEHYDRO[16]ANNULENE-1,4-DIONE. THE PROTONATION OF A [4*n*]ANNULENEDIONE TO A STRONGLY DIATROPIC DICATION [1]

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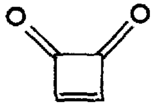
Several macrocyclic vinylogues of *p*-benzoquinone ("[6]annulene-1,4-dione") containing (4*n*+2)-membered rings have recently been synthesized (*n* = 3 [2]; *n* = 4 [3,4]).[5] On the other hand, in the [4*n*]annulenedione series, the only members known until now were cyclobutenedione (1) [6] and derivatives [7] (*n* = 1), as well as 2,5,7-cyclooctatriene-1,4-dione (2) (*n* = 2).[8] We now describe a remarkably simple synthesis of 8,13-dimethyl-2,9,11-trisdehydro[16]annulene-1,4-dione (3),[9] the first macrocyclic [4*n*]annulenedione derivative (*n* = 4). This substance proved to be appreciably diatropic ("aromatic"), indicating the contribution of canonical forms such as 3a. More importantly, treatment of the dione 3 with D_2SO_4 has been found to give rise to the strongly diatropic dication 8, a type of transformation which has not hitherto been observed in this series of diketones.



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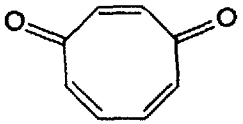

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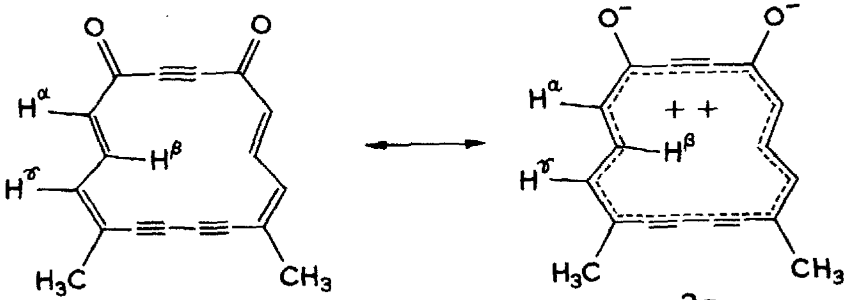

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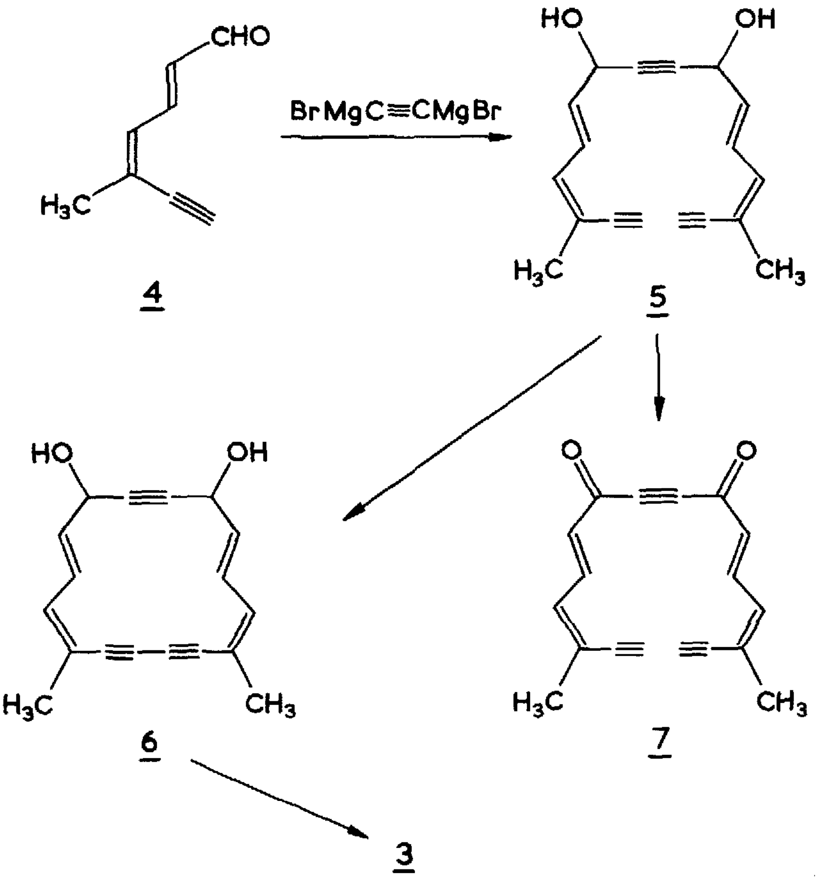
3a

Addition of acetylenedimagnesium bromide to 5-methyl-2,4-heptadien-6-yn-1-al (**4**) [4] in benzene at room temp gave a stereoisomeric mixture of the rather unstable diol **5** as a viscous oil [10] in quantitative yield. This diol was oxidatively coupled with oxygen, cuprous chloride, ammonium chloride, and conc hydrochloric acid in aqueous ethanol and benzene at 40° for 75 min. Chromatography of the product on silica gel yielded *ca* 50% of a stereoisomeric mixture of the solid cyclic diol **6**.[10] Finally, oxidation of **6** with manganese dioxide in dichloromethane at room temp for 30 min, followed by chromatography on silicic acid, gave in *ca* 30% yield the relatively stable [16]annulenedione **3** as bright yellow needles, which decomposed above 100° on attempted melting point determination;[11] *m/e* 260 (M^+); λ_{max} ($CHCl_3$) 266 (ε 23,900), 277sh (21,000), 312 (25,000), *ca* 343sh (14,500), 398 (12,500), *ca* 422sh nm (10,500); ν_{max} ($CHCl_3$) 1625(s) (C=O) cm^{-1}.



The acyclic diketone **7**, required as a model, was obtained in *ca* 40% yield as a very unstable pale yellow solid[10] by oxidation of the acyclic diol **5** with manganese dioxide in dichloromethane at room temp for 1 hr.

The ^1H nmr spectral parameters of the trisdehydro[16]annulenedione **3** are given in Table I. By comparison with the spectrum of the acyclic analogue **7** [**3** ($CDCl_3$) - **7** ($CDCl_3$)], it is evident that **3** is significantly diatropic, the outer proton resonances having moved to lower field and the inner ones to higher field. The diatropicity of **3** was increased appreciably by solution in CF_3COOD [**3** (CF_3COOD) - **3** ($CDCl_3$)]. Solution of **3** in D_2SO_4 produced a highly diatropic species [**3** (D_2SO_4) -

3 ($CDCl_3$)], presumably due to the formation of the dication 8.[12] This was confirmed by the electronic spectrum of the dark violet solution, which showed λ_{max} (H_2SO_4) 391 (ϵ 71,200), 404 (49,400), 578 nm (13,800).[13]

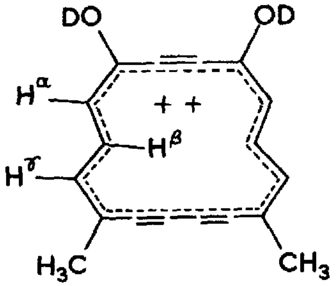


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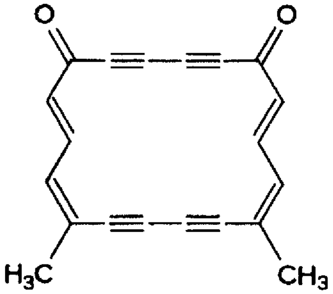
Table I. ^{1}H Nmr Parameters of the Diketones 3 and 7 (τ Values, Internal Standard TMS, J Valu in Hz in Parentheses)

Compd	H^α	H^β	H^γ	CH_3
7 ($CDCl_3$) [a]	3.70d (16)	2.03dd (11.5, 16)	3.49d (11.5)	7.92s
3 ($CDCl_3$) [b]	3.41d (14.5)	2.91dd (11, 14.5)	3.02d (11)	7.84s
3 (CF_3COOD) [b]	3.01d (15.5)	3.21dd (11.5, 15.5)	2.68d (11.5)	7.68s
3 (D_2SO_4) [a]	0.93d (14)	8.96dd (13, 14)	0.52d (13)	6.65s
3 ($CDCl_3$) - 7 ($CDCl_3$)	-0.29	+0.88	-0.47	-0.08
3 (CF_3COOD) - 3 ($CDCl_3$)	-0.40	+0.30	-0.34	-0.16
3 (D_2SO_4) - 3 ($CDCl_3$)	-2.48	+6.05	-2.50	-1.19

[a] Determined at 100 MHz; [b] Determined at 300 MHz (FT) since the 100 MHz spectrum was not first-order.

The electrochemical reduction of the [16]annulene-1,4-dione 3 first to the radical anion and then to the dianion, using the technique of second harmonic a.c. polarography[14] at a dropping mercury electrode, was kindly carried out by Professor R. Breslow and Dr. R. Goodin. It was found that 3 was ca 0.5 eV less easily reduced to the dianion than the corresponding [18]annulene-1,6-dione 9.[4,15] While this difference might reflect that reduction of 3 leads to an antiaromatic 16π-dianion, while reduction of 9 leads to an aromatic 18π-dianion, it may simply be due to the different separation of the carbonyl groups in 3 and 9. Thus, dibenzoylacetylene is ca 0.4 eV less easily reduced than is dibenzoyldiacetylene.[15]



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9. IUPAC name: 8,13-dimethyl-5,7,13,15-cyclohexadecatetraene-2,9,11-triyne-1,4-dione.
10. Mass, ^{1}H nmr, and electronic spectra compatible with the assigned structures were obtained for all new compounds.
11. *Anal*: Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 82.91; H, 4.62.
12. By comparison, the outer protons in the ^{1}H nmr spectra of [16]annulene dication resonate at *ca* τ -0.7; and the inner protons at τ 12.58 - 14.48 (J.F.M. Oth, D.M. Smith, U. Prange and G. Schröder, *Angew. Chem.*, 85, 352 (1973)). The effect of the two positive charges, if they were evenly distributed throughout the 16-membered ring and neglecting ring current effects, would be to shift all of the olefinic proton resonances downfield by *ca* 1.25 ppm.
13. The ε values are based on the assumption of complete conversion of 3 to 8, and are minimum ones since the values decreased on standing.
14. See D.E. Smith in "Electroanalytical Chemistry", A.J. Bard, Ed., Marcel Dekker, New York, N.Y., Vol 1, 1966, p.1.
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