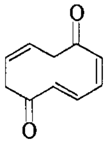
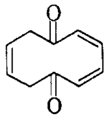
Cyclodeca-2,4,8-triene-1,6-dione, a Diketo Tautomer of 1,6-Dihydroxy[10]annulene[1]

Sir:

We report the synthesis of cyclodeca-2,4,8-triene-1,6-dione (the *cis,trans,cis* isomer **1a** or the all-*cis* isomer **1b**). This is a diketo tautomer of 1,6-dihydroxy[10]annulene ("[10]annulene-hydroquinone") (*e.g.*, **2**), and the possibility existed that it might be convertible to this conjugated ten-π-electron system.[2,3] In practice, substance **1** could not be transformed to **2**, or derivatives of **2**, under a variety of conditions. This is in contrast to cyclohex-2-ene-1,4-dione (**3**), which is readily isomerized to hydroquinone (**4**) with dilute acid.[4]


1a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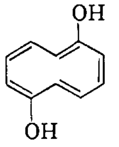
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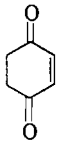
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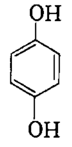
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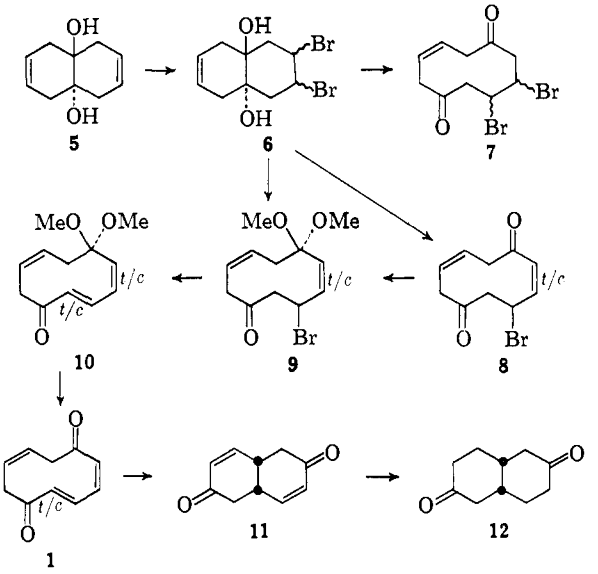
Bromination of 1,4,5,8,9,10-hexahydronaphthalene-*trans*-9,10-diol (**5**)[5] with 1 equiv of bromine in chloroform at 0° gave 60% of the dibromide **6** (mp 114–116°),[7] apparently as one pure stereoisomer. In contrast to the corresponding tetrabromide[6c,8] the 1,2-diol group in **5** was cleaved readily with lead tetraacetate (1.6 equiv) and trichloroacetic acid (3.0 equiv) in methanol.[6b] The product depended on the reaction conditions. When the cleavage was carried out at 0° for 5 hr (followed by stirring at 25° for 5 hr), the main product was the expected *cis*-8,9-dibromocyclodec-3-ene-1,6-dione (**7**). This compound, obtained in 55% yield, formed crystals which decomposed at *ca.* 90° on attempted melting point determination;[7] $\nu_{\max}^{\text{Nujol}}$ 1700 (s), 1640 (w), 976 (m), and 966 (m) cm^{-1}; nmr spectrum (100 Mcps, CDCl$_3$), 2-H multiplet at τ 3.9–4.3 (olefinic protons), 2-H multiplet at 5.0–5.4 (α-bromo protons), and 8-H multiplet at 6.3–7.2 (methylene protons).

When the lead tetraacetate oxidation of **6** was performed at 25° for 24 hr, the principal product was 4-bromocyclodeca-2,8-diene-1,6-dione (*trans,cis or cis,cis*) (**8**), formed by cleavage and monodehydrobromination. Substance **8**, isolated in 40% yield, was a crystalline solid, mp 85–87°;[7] $\lambda_{\max}^{\text{EtOH}}$ 221 mμ (ϵ 7500) and 300 (250); $\nu_{\max}^{\text{KBr}}$ 1715 (s), 1690 (s), 1645 (m), 985 (m), 965 (w), and 950 (m) cm^{-1}; nmr spectrum (100 Mcps, CDCl$_3$), 1-H multiplet at τ 3.2–3.6 and 3-H multiplet at 3.9–4.7 (olefinic protons), 1-H multiplet at 5.3–5.7 (α-bromo proton), and 6-H multiplet at 6.1–7.3 (methylene protons).



Lead tetraacetate cleavage of **6** at reflux for 2 hr gave 1,1-dimethoxy-4-bromocyclodeca-2,8-dien-6-one (*trans,-cis or cis,cis*) (**9**) as the main product (35% yield); crystals, mp 90–92°;[7] $\lambda_{\max}^{\text{EtOH}}$ 295 mμ (ϵ 125); $\nu_{\max}^{\text{Nujol}}$ 1710 (s), 1658 (w), 990 (m), 979 (w), and 948 (w) cm^{-1}; nmr spectrum (100 Mcps, CDCl$_3$), 4-H multiplet at τ 3.8–4.8 (olefinic protons), 1-H multiplet at 5.3–5.7 (α-bromo proton), 6-H multiplet at 6.2–7.6 (methylene protons), and 6-H singlet at 6.78 (methyl protons).

Dehydrobromination of the β-bromo ketone **9** was effected with excess 1,5-diazabicyclo[4.3.0]non-5-ene[9] in dimethyl sulfoxide at room temperature for 10 min, or more conveniently by absorption in ether on a column of alkaline alumina for 24 hr.[10] The resulting 1,1-dimethoxycyclodeca-2,4,8-trien-6-one (*trans,cis,cis*, *cis,-trans,cis*, or all-*cis*) (**10**), was obtained in 65 and 80% yield. respectively, as crystals, mp 68–70°;[7] $\lambda_{\max}^{\text{EtOH}}$ 257 mμ (ϵ 4900) and 327 (250); $\nu_{\max}^{\text{Nujol}}$ 1668 (s), 1653 (s), 1598 (w), 986 (m), 954 (s), and 946 (m) cm^{-1}; nmr spectrum (100 Mcps, CCl$_4$), 6-H multiplet at τ 3.2–4.8 (olefinic protons), 4-H multiplet at 6.6–7.8 (methylene protons), and 6-H singlet at 6.88 (methyl protons). The dimethoxy trienone **10** was also formed (in 20% yield) from the bromo dienedione **8** by treatment with *p*-toluenesulfonic acid in boiling methanol for 5 min, followed by dehydrobromination on alkaline alumina.

Finally, the ketal protecting group in **10** was removed by reaction with *p*-toluenesulfonic acid in aqueous acetone at room temperature for 20 hr, or by shaking a solution in methylene chloride with 2 *N* hydrochloric acid for 4 hr.[11] The resulting trienedione **1**, isolated in *ca.* 30% yield by either method, formed crystals, mp 80–81°;[7] $\lambda_{\max}^{\text{EtOH}}$ 257 mμ (ϵ 5300) and *ca.* 325 sh (330); $\nu_{\max}^{\text{Nujol}}$ 1690 (s), 1653 (s), 1642 (s), 1617 (m), 1593 (m), 990 (w), 960 (s), and 942 (m) cm^{-1}; nmr spectrum (100

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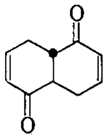
[1] Unsaturated Macrocyclic Compounds. LVI. For part LV, see C. C. Leznoff and F. Sondheimer, *J. Am. Chem. Soc.*, in press.

[2] For references to [10]annulene, see E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967).

[3] A previous attempt to synthesize **2** *via* enolization of *trans*-1,4,5,8,9,10-hexahydronaphthalene-1,5-dione (i) was not successful (W. S. Johnson, J. D. Bass, and K. L. Williamson, *Tetrahedron*, **19**, 861 (1963)).


i

[4] E. W. Garbisch, *J. Am. Chem. Soc.*, **87**, 4971 (1965).

[5] Obtained from naphthalene in *ca.* 70% by a three-step sequence.[6]

[6] (a) W. Hückel and H. Schlee, *Chem. Ber.*, **88**, 346 (1955); (b) C. A. Grob and P. W. Schiess, *Helv. Chim. Acta*, **43**, 1546 (1960); (c) A. Shani and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 6310 (1967).

[7] Satisfactory elemental analyses were obtained for all new compounds.

[8] A. Shani, Ph.D. Thesis, Weizmann Institute of Science, Rehovoth, Israel, 1965.

[9] H. Oediger, H. J. Kabbe, F. Möller, and K. Eiter, *Chem. Ber.*, **99**, 2012 (1966).

[10] Similar base treatment of the unprotected β-bromo ketone **8** did not lead to the trienedione **1** directly.

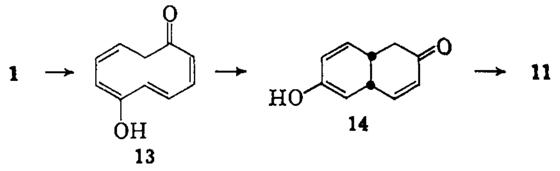
[11] See M. M. Janot, X. Lusinchi, and R. Goutarel, *Bull. Soc. Chim. France*, 2109 (1961).

Mcps, CCl_4), 6-H multiplet at τ 3.0–4.6 (olefinic protons) and 4-H multiplet at 6.5–7.0 (methylene protons). The monocyclic nature of **1** was confirmed by catalytic hydrogenation in ethyl acetate over palladium–charcoal. This reaction smoothly led to cyclodecane-1,6-dione (mp 96–98°), identified by direct comparison with an authentic sample (mp 95–97°).[12]

So far, it has not been possible to convert the two keto groups of **1** to the corresponding bis(enol acetate) (1,6-diacetoxy[10]annulene) or bis(vinyl chloride) (1,6-dichloro[10]annulene).[13] Addition of dilute aqueous potassium hydroxide to **1** resulted in the instantaneous formation of a bright red solution (principal λ_{max}^{EtOH} 374 mμ), acidification of which did not regenerate the starting material.

Substance **1** was unaffected by dilute mineral acids or *p*-toluenesulfonic acid at room temperature. However, reaction of **1** with *p*-toluenesulfonic acid in boiling acetone for 30 min yielded *ca.* 25% *cis*-1,2,5,6,9,10-hexahydronaphthalene-2,6-dione (**11**) as crystals, mp 149–151°;[7] λ_{max}^{EtOH} 220 mμ (ϵ 16,500); ν_{max}^{Nujol} 1674 (s) and 1617 (w) cm^{-1}; nmr spectrum (60 Mcps, $CDCl_3$), 2-H double doublet (J = 10 and 4 cps) at τ 3.09 (β-olefinic protons), 2-H doublet (J = 10 cps) at 3.84 (α-olefinic protons), and 6-H multiplet at 6.4–7.7 (methylene and methine protons). The structure and stereochemistry of **11** was established by catalytic hydrogenation in ethanol over palladium–charcoal. The resulting *cis*-decahydronaphthalene-2,6-dione (**12**) (mp 72–73°) proved to be identical with an authentic sample (mp 72–74°).[14]

It is tempting to speculate that the conversion of **1** to **11** involves 1,6-dihydroxy[10]annulene (*e.g.*, **2**) as an intermediate, formed by enolization of both keto groups. However, we believe that most probably only one keto group in **1** is enolized to give **13**, which then undergoes valence tautomerism to **14**, a monoenol of **11**.



The structure of **1** follows unequivocally from the above-described data, but the stereochemistry has not yet been elucidated. The reasonable assumption has been made that the isolated Δ^8-double bond retains the *cis* stereochemistry. The remaining two conjugated double bonds cannot be accommodated in the ten-membered ring if they were both *trans*, and the compound therefore possesses either the *cis,trans,cis* configuration **1a** or the all-*cis* configuration **1b**. The infrared spectra of **1** and of its ten-membered ring precursors all exhibit medium or strong bands in the 990–940-cm^{-1} region; however, this cannot be considered as definite evidence for the presence of a *trans* double bond,[15] since certain oxygenated derivatives of *cis*-cyclodecene (*e.g.*, **7**) and of cyclodeca-1,6-diene (*cis,cis*)[16] also show medium or strong bands in this region. An X-ray crystallographic analysis of **1** is now being carried out by Mrs. O. Kennard, *et al.*, in order to elucidate the stereochemistry.

Acknowledgments. We are indebted to P. J. Garratt (Cambridge) for valuable discussions. Thanks are also due to Professor Dr. O. Bayer and Dr. H. Oediger (Leverkusen) for a generous gift of 1,5-diazabicyclo-[4.3.0]non-5-ene and to Dr. R. L. Clarke (Rensselaer) for kindly providing a sample of *cis*-decahydronaphthalene-2,6-diol.

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(12) *Inter. al.*, W. Hückel, R. Danneel, A. Schwartz, and A. Gercke, *Ann.*, **474**, 121 (1929).

(13) For the synthesis of the corresponding 2,7-dihydro compound, see K. Grohmann and F. Sondheimer, *Tetrahedron Letters*, 3121 (1967).

(14) R. L. Clarke and C. M. Martini, *J. Am. Chem. Soc.*, **81**, 5716 (1959).

(15) See L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

(16) K. Grohmann, P. J. Mulligan, and F. Sondheimer, unpublished observations.

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Mono-*trans*-1,2:3,4:7,8-tribenz[10]annulene[1]

Sir:

We report the synthesis of mono-*trans*-1,2:3,4:7,8-tribenz[10]annulene (**3**). This is the first annelated derivative of the ($4n$ + 2) π-electron system, [10]annulene,[2] for which a Kekulé structure incorporating the cyclodecapentaene system can be written.

Wittig reaction of 2,2′-bis(triphenylphosphoniomethyl)biphenyl dibromide (**1a**)[5] and *o*-phthalaldehyde (**2a**) with lithium methoxide in ether and methanol at room temperature under nitrogen gave a mixture of substances, separated by chromatography on silica gel. The products derived by ring formation proved to be **3** (15% yield) and 9,10-dihydro-1,2:3,4-dibenzanthracene (**6**) (1.5% yield, see below). The same tribenz[10]annulene **3** was also obtained by the Wittig reaction of biphenyl-2,2′-dicarboxaldehyde (**1b**)[6] and *o*-xylylenebis(triphenylphosphonium bromide) (**2b**)[7] with lithium methoxide, although the yield was only 1.5%.

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(1) Unsaturated Macrocyclic Compounds. LVII. For part LVI, see P. J. Mulligan and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 7118 (1967).

(2) Other annelated [10]annulenes have been prepared ([2.2]metacyclophane-1,9-diene derivatives: V. Boekelheide, *et al.*, *ibid.*, **87**, 130 (1965); **89**, 1695, 1704, 1709 (1967); 1,2,3:6,7,8-di(1′,8′-naphth)-[10]annulene: R. H. Mitchell and F. Sondheimer, *ibid.*, in press). 1,6-Bridged [10]annulenes have been synthesized by E. Vogel, *et al.* (*Angew. Chem.*, **76**, 145, 785 (1964); **78**, 754 (1966); *Tetrahedron Letters*, 3613, 3625 (1965)), and by our own group (F. Sondheimer and A. Shani, *J. Am. Chem. Soc.*, **86**, 3168 (1964); A. Shani and F. Sondheimer, *ibid.*, **89**, 6310 (1967)). Very recently, evidence has been obtained that all-*cis*- or 1,5-di-*trans*-[10]annulene is formed as a very unstable substance in the photolysis of *trans*-9,10-dihydronaphthalene at −190°,[3] while mono-*trans*-[10]annulene has been postulated as an unstable intermediate in the conversion of bicyclo[6.2.0]deca-2,4,6,9-tetraene to *trans*-9,10-dihydronaphthalene.[4]

(3) E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967).

(4) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *ibid.*, **89**, 4804 (1967).

(5) D. M. Hall and B. Prakobsantisukh, *J. Chem. Soc.*, 6311 (1965); H. J. Bestmann, H. Häberlein, H. Wagner, and O. Kratzer, *Chem. Ber.*, **99**, 2848 (1966); E. D. Bergmann, P. Bracha, I. Agranat, and M. A. Kraus, *J. Chem. Soc., Sect. C*, 328 (1967).

(6) P. S. Bailey and R. E. Erickson, *Org. Syn.*, **41**, 41 (1961).

(7) C. E. Griffin, K. R. Martin, and B. E. Douglas, *J. Org. Chem.*, **27**, 1627 (1962); C. E. Griffin and J. A. Peters, *ibid.*, **28**, 1715 (1963).