Synthesis of Cyclotetradeca-3,4,5,10,11,12-hexaene-1,8-dione, a Monocyclic Dicumulenedione

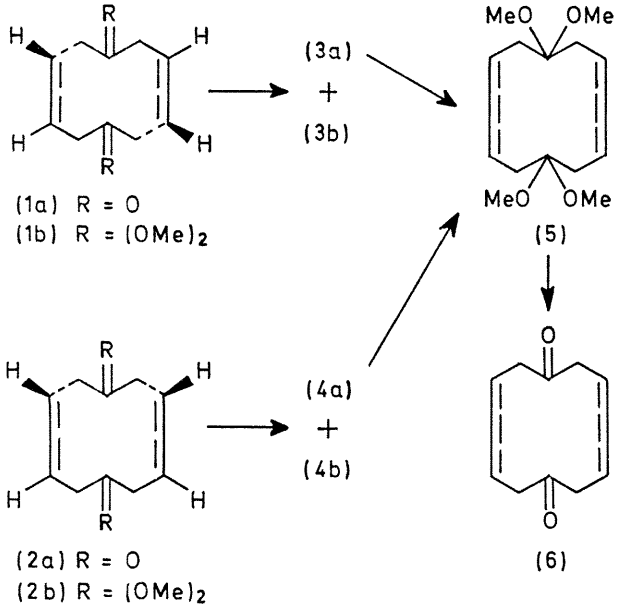
By P. J. GARRATT,* K. C. NICOLAOU, and F. SONDHEIMER

(*Department of Chemistry, University College London*, 20, *Gordon Street, London* WC1H OAJ)

Summary The synthesis of cyclotetradeca-3,4,5,10,11,12-hexaene-1,8-dione is described.

CUMULENES are rather unstable systems,[1] and there are only a few examples of cyclic cumulenes.[2,3] Our recent finding[4] that the diastereomeric cyclic diallenediones (**1a**) and (**2a**) are relatively stable systems led us to extend our synthesis to the corresponding cyclic dicumulenediones. We now report the synthesis of cyclotetradeca-3,4,5,10,11,-12-hexaene-1,8-dione (**6**), and its characterisation as a crystalline compound. This is the first known cyclic cumulene containing a functional group.

Treatment of the racemic diallene diacetal (**1b**) (m.p. 116—117°)† with an excess of bromoform and potassium t-butoxide[5] gave a mixture of two bis(dibromocarbene) adducts, (**3a**) (45%; m.p. 117—118°) and (**3b**) (18%; m.p. 95—97°).‡ The spectral properties (n.m.r.; absence of 1960 cm^{-1} allene band in i.r.) clearly indicated that dibromocarbene addition had occurred to each allene group, but the orientation and stereochemistry of these additions is not known. A similar reaction of the *meso*-diallene (**2b**) (m.p. 86—88°)† gave two further bis(dibromocarbene) adducts, (**4a**) (50%; m.p. 79—80°) and (**4b**) (15%; m.p. 77—78°).



Again, addition to each allene group had occurred, as shown by the spectral data.

Reaction of either of the major isomers (**3a**) or (**4a**) with MeLi in ether at -10°[6] gave a solution of the rather unstable dicumulene diacetal (**5**).§ The n.m.r. spectrum (CCl_4; 10°) showed signals at τ 4·85 (m, 4H, vinylic), 6·82 (s, 12H, OMe) and 7·52 (m, 8H, allylic); λ_{max} (n-hexane) 224 (ϵ 10,300), 243 (15,900), and 290 (sh) nm (1350).¶ The n.m.r. spectrum is temperature dependent (-30 to $+30^{\circ}$), but irreversible changes in the spectrum begin to occur above 20°. Catalytic hydrogenation with concomitant hydrolysis (Pd–C; EtOAc) gave cyclotetradecane-1,8-dione (m.p. 148—149°, lit.,[7] 147—148°), identified by its spectral properties.

Hydrolysis of the diacetal (**5**) with conc. H_2SO_4 in ether at 0° for 1 min gave the crystalline dione (**6**) (decomp. *ca.* 130°) in 75% yield from either (**3a**) or (**4a**). The n.m.r. spectrum ($CDCl_3$) showed bands at τ 4·40 (t, 4H, *J* 6 Hz, vinylic) and 6·60 (d, 8H, *J* 6 Hz, allylic); the i.r. spectrum (KBr) exhibited a band at 1701 cm^{-1} (C=O) with no appreciable cumulene absorption in the 2000 cm^{-1} region; λ_{max} (EtOH) 223 (ϵ 15,000), 244 (26,000), and 290(sh) nm (4250), indicating the presence of the cumulene chromophore.[1,2] Catalytic hydrogenation of (**6**) (Pd–C; EtOAc) again gave cyclotetradecane-1,8-dione (m.p. 146—148°).

The dicumulene (**6**) is relatively stable in solution and in the crystalline state, although in the latter condition the crystals develop an insoluble coating. In the formation of (**5**) from either (**3a**), (**4a**), or a mixture of all the bis(dibromocarbene) adducts, no evidence could be detected for the presence of any other compound. The n.m.r. spectrum of (**5**) shows only one type of methoxy-group, and that of (**6**) shows only one type of vinylic and one type of allylic proton. These data show that both of the cumulene groups have the same stereochemistry. Strainless models of both the di-*cis*- and di-*trans*-stereomers of (**5**) and (**6**) can be built, and it is hoped to distinguish between these possibilities by an *X*-ray crystallographic analysis of (**6**).

We thank the S.R.C. for an award (to K.C.N.).

(*Received, June* 14*th*, 1971; *Com.* 971.)

---

† The identity of the racemic and *meso*-diallenes has now been resolved, and will be reported elsewhere.

‡ Satisfactory analytical and m.s. data were obtained for all new crystalline compounds.

§ Reaction of the mixture (**3a**), (**3b**), (**4a**), and (**4b**) with MeLi also gave (**5**).

¶ The extinction coefficients are minimal values, which are based on complete conversion of the bis(dibromocarbene) adducts.

[1] See H. Fischer in 'The Chemistry of the Alkanes,' ed. S. Patai, Interscience, New York, 1964, Ch. **13**.

[2] W. R. Moore and T. M. Ozretich, *Tetrahedron Letters*, 1967, 3205.

[3] W. Jasiobedski, *Roczniki Chem.*, 1967, **41**, 1265, (*Chem. Abs.*, 1968, **68**, 29,344e).

[4] P. J. Garratt, K. C. Nicolaou, and F. Sondheimer, *Chem. Comm.*, 1970, 1219; J. Ojima, T., Katakami, G. Nakaminami, and M. Nakagawa, *Tetrahedron Letters*, 1968, 1115.

[5] See W. von Doering and A. K. Hoffman, *J. Amer. Chem. Soc.*, 1954, **76**, 6161.

[6] See L. Skatteböl, *Tetrahedron Letters*, 1965, 2175; W. J. Ball, S. R. Landor, and N. Punja, *J. Chem. Soc.* (*C*), 1967, 194.

[7] A. T. Blomquist and R. D. Spencer, *J. Amer. Chem. Soc.*, 1948, **70**, 30; F. Sondheimer and Y. Gaoni, *J. Amer. Chem. Soc.*, 1959, **81**, 6301.