

## 2,3,4,5-Tetrahalogeno-1-(2,3-di-n-propylcyclopropenylidene)cyclopentadiene

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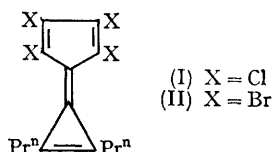
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SEVERAL derivatives of 1-cyclopropenylidene-cyclopentadiene† have been described in the literature,<sup>1</sup> and we have reported recently the synthesis and some properties of 2,3,4,5-tetrachloro-1-(2,3-diphenylcyclopropenylidene)cyclopentadiene.<sup>2</sup>

We now describe the synthesis of the compounds (I: X = Cl; II: X = Br), the simplest derivatives of this system yet described,<sup>3</sup> and the experimental derivation of the dipole moment of the 1-cyclopropenylidene-cyclopentadiene skeleton in a rational manner.



Condensation of di-n-propylcyclopropenone<sup>4</sup> with 1,2,3,4-tetrachloro- or 1,2,3,4-tetrabromo-cyclopentadiene in methanol, afforded colourless leaflets of (I) (from benzene, melting with decomposition at 180°, 25·7% yield) or colourless leaflets of (II) (from benzene, darkens without melting at about 140°, 31·4% yield), respectively.

These structures were established by i.r. spectra [in KBr, (I): 1865, 1544; (II): 1860, 1528 cm.<sup>-1</sup>], u.v. spectra [in acetonitrile, (I): 314 mμ, log ε, 4·56; (II): 318 mμ, log ε, 4·60, and in cyclohexane, (I): 316·5 mμ, log ε, 4·42; (II): 320 mμ, log ε,

4·70] and n.m.r. spectra in 95% sulphuric acid [(I): triplet at 5·32, sextet at 4·44, triplet at 3·14 and singlet at 0·96 p.p.m.; (II): triplet at 5·31, sextet at 4·45, triplet at 3·11, and singlet at 0·85 p.p.m. all upfield from external benzene reference. Relative areas of signals in both (I) and (II) are 6:4:4:1].

The observed dipole moment of (I) (7·56 ± 0·03 D, in benzene at 25°C) clearly demonstrates the contribution of a dipolar structure in the ground-state of 1-cyclopropenylidene-cyclopentadiene. If we use the value of 1·53 D for the effect of four chlorine atoms,<sup>2b</sup> the estimated dipole moment of the skeleton should be 5·63 D because the additional moment caused by the two propyl groups can be regarded as being about 0·4 D. This value (5·63 D) is in good agreement with the value of 5·69 D<sup>5</sup> derived for 1-cyclopropenylidene-cyclopentadiene by the LCAO-MO method using the bond alternation technique, and is larger than the theoretical dipole moment of sesquifulvalene (5·05 D).<sup>6</sup> This means that the electron-releasing power of a cyclopropenylidene group is appreciably greater than that of a cycloheptatrienylidene group.

Compounds (I) and (II) reacted reversibly with tetracyanoethylene in chloroform to give an unstable π-complex which showed charge-transfer bands at 656 ± 1 mμ and 660 ± 5 mμ, respectively.

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† The use of the trivial names "calicene" and "triapentafulvalene" for this system is questionable—Ed.

<sup>1</sup> W. M. Jones and R. S. Pyron, *J. Amer. Chem. Soc.*, 1965, **87**, 1608; A. S. Kende and P. T. Izzo, *ibid.*, p. 1609; H. Prinzbach, D. Seip, and U. Fisher, *Angew. Chem.*, 1965, **77**, 258; H. Prinzbach and U. Fisher, *ibid.*, p. 621; A. S. Kende and P. T. Izzo, *J. Amer. Chem. Soc.*, 1965, **87**, 4162; E. D. Bergmann and I. Agranat, *Chem. Comm.*, 1965, 512.

<sup>2</sup> (a) M. Ueno, I. Murata, and Y. Kitahara, *Tetrahedron Letters*, 1965, 2967; (b) I. Murata, M. Ueno, Y. Kitahara, and H. Watanabe, to be published; (c) E. D. Bergmann and I. Agranat also obtained this compound by an identical method. We are grateful to Professor Bergmann for informing us of his results prior to publication; E. D. Bergmann and I. Agranat, *Tetrahedron*, in the press.

<sup>3</sup> Cf. "Highlights from Current Literature," compiled by A. R. Katritzky *et al.*, *Chem. and Ind.*, 1965, 1642.

<sup>4</sup> R. Breslow, L. T. Altman, A. Krebs, E. Mohacsi, I. Murata, R. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, 1965, **87**, 1326.

<sup>5</sup> T. Nakajima, private communication.

<sup>6</sup> T. Nakajima and S. Katagiri, *Mol. Phys.*, 1963, **7**, 149.