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A SIMPLE ROUTE TO THE 7H-CYCLOPENTA[a]PENTALENE SYSTEM: PREPARATION OF THE 1,2,3,4,5,6-HEXACHLORO-DERIVATIVE.

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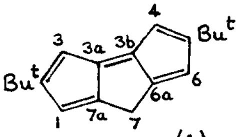
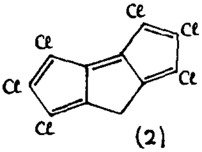
Summary. Reaction of octachlorofulvene (3) with diazomethane leads to the formation of the tricyclic tetraene (4), which on dechlorination with tin(II) chloride gives 1,2,3,4,5,6-hexachloro-7H-cyclopenta[a]pentalene[1] (2).

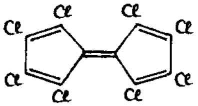
Very recently, Hafner and Thiele[2] described the synthesis of 2,5-di-t-butyl-7H-cyclopenta[a]pentalene (1) and its conversion into the corresponding anion. Here we report a simple preparation of the hexachloro-derivative (2) from the known[3-5] octachlorofulvalene (3), a dark blue compound [λ_{max} (iso-octane) 386, 590 nm (ε 35800, 505)[4]] which forms a deep green solution in benzene. When an excess of ethereal diazomethane is added to this solution at room-temperature, the green colour is rapidly discharged, and crystallisation of the crude product from ether then yields a colourless compound $C_{11}H_2Cl_8$, m.p. 151-152°C, which can be assigned structure (4) on the basis of the spectral evidence. In particular, the ^{13}C NMR spectrum (22.5MHz; $CDCl_3$) shows resonances at 144.7, 133.3, 131.3, 129.8 ($>C=$), 75.9 ($\underset{-}{>}C-Cl$), and 24.1 ppm ($>CH_2$), and UV absorption maxima (cyclohexane) are observed at 271 and 323 nm (ε 2100 and 1560). The latter evidence enables the possible alternative structure (5), in which there is a conjugated tetraene system, to be rejected.



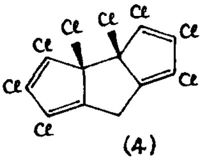
(1)



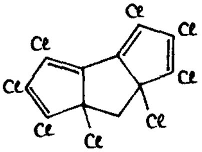
(2)



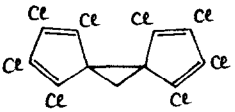
(3)



(4)



(5)

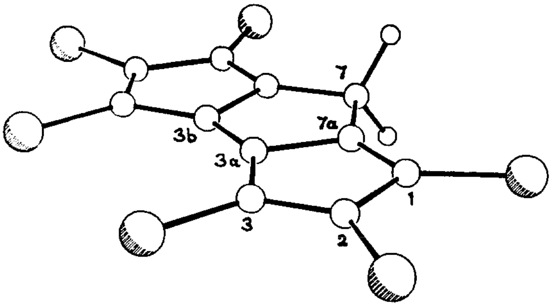


(6)

It would seem reasonable to assume that the dispiro-undecatetraene (6) is an intermediate in the above reaction, its conversion into the observed product (4) proceeding by a symmetry-allowed thermal [5,5] sigmatropic rearrangement (suprafacial-suprafacial). This would lead to cis-stereochemistry for the chlorine atoms at positions 3a and 3b, likely in any case from considerations of strain.

Treatment of (4) with tin(II) chloride in refluxing acetone results in the rapid separation of black needles[6] of the tricyclic pentaene (2), m.p. 179.5 - 180°C (from benzene-acetone); δ_c [50.1MHz; C_6D_6 + $Cr(acac)_3$] 145.45, 142.4, 139.8, 121.0, 113.3 ($>C=$) and 23.8 ppm ($>CH_2$); λ_{max} (cyclohexane) 311, 325, 341, and 358 nm (ε 9 400, 25 400, 55 600, and 71 000).

An X-ray crystal structure determination of octachlorofulvalene (3) has shown that there is an angle of 37° between the planes of the two five-membered rings.[7] In contrast, calculations using the semi-empirical MNDO method[8,9] indicate that the methylene-bridged derivative (2) is planar, with C_{2v} symmetry (see Figure).



C-C bond lengths	(Å)
1-2	1.489
2-3	1.378
3-3a	1.467
3a-3b	1.354
3a-7a	1.519
1-7a	1.362
7-7a	1.510

Figure

Calculated structure of (2) (optimized geometry)

An investigation of the chemistry of this tricyclic 10π system is in progress.

Acknowledgements

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References and Footnotes

1. Alternative name: 3,4,5,9,10,11-hexachlorotricyclo[$6.3.0.0^{2,6}$]undeca-1,3,5,8,10-pentaene.
2. K. Hafner and G.F. Thiele, Tetrahedron Letters 25, 1445 (1984).
3. V. Mark, Tetrahedron Letters 333 (1961).
4. V. Mark, Org. Synth. 46, 93 (1966).
5. R.M. Smith and R. West, J.Org.Chem. 35, 2681 (1970).
6. Light transmitted through a thin crystal appeared yellow; a deep purple-red solution was formed in benzene.
7. H.L. Ammon, G.L. Wheeler, and I. Agranat, Tetrahedron 29, 2695 (1973).
8. M.J.S. Dewar and W. Thiel, J.Am.Chem.Soc., 99, 4899, 4907 (1977).
9. Calculations were performed on a VAX-11/750 computer, using the MOPAC general molecular orbital package.

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