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LAYERED COMPOUNDS. VIII1). PARACYCLOPHANE CONTAINING 1,2,3,4,5-HEXAPENTAENE GROUP

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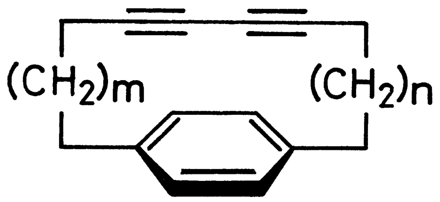
Paracyclophanes containing 1,2,3,4,5-hexapentaene group (IIb and IXc) and alicyclic hexapentaene (IIa) have been synthesized and it is concluded on the basis of their electronic spectra that there was appreciable transannular interaction between benzene nucleus and hexapentaene group in IIb.

In the previous papers2) of this series, we have reported a remarkable transannular interaction between benzene nucleus and diacetylenic group in some [m.n]paracyclophadiynes (I) where both groups are separated by methylene bridges from each other. In this communication we wish to report the synthesis and properties of a few cyclic 1,2,3,4,5-hexapentaene derivatives in order to examine the interaction between benzene nucleus and cumulenic group. There have been many investigations on acyclic hexapentaenes, i.e. tetraaryl3) and tetraalkyl4) derivatives, but no study concerning cyclic one so far except annulene system5) containing formal hexapentaene unit. We have synthesized two paracyclophahexapentaene derivatives, 4,4,11,11-tetramethyl-5,10-di-t-butyl-5,6,7,8,9-[14]paracyclophapentaene (IIb) and 3,3,10,10,21,21,28,28-octamethyl-4,9,22,27-tetra-t-butyl-



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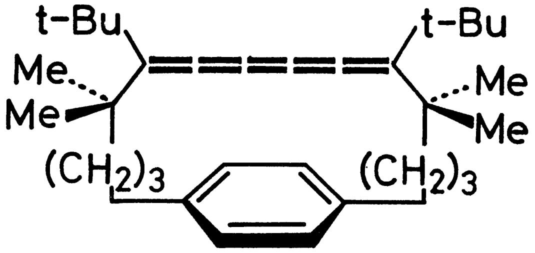
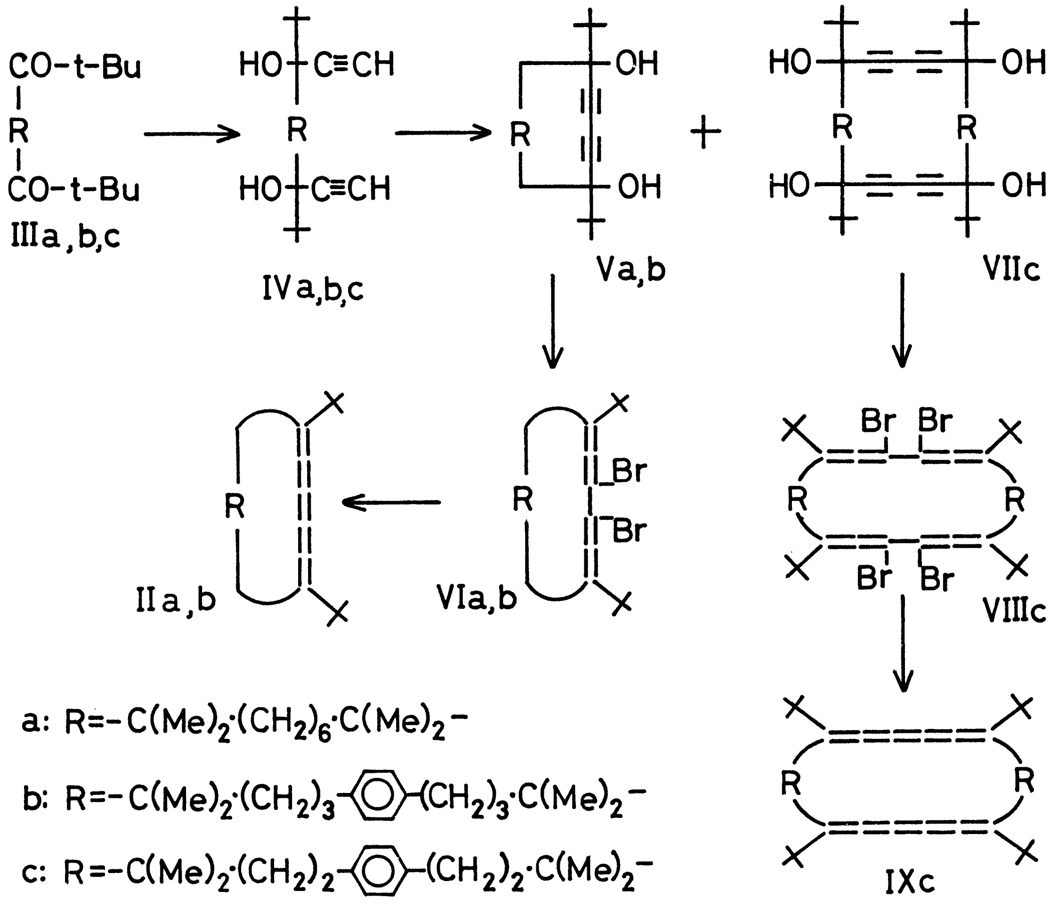


IIb

4,5,6,7,8,22,23,24,25,26-[12.12]paracyclophadecaene (IXc), and an alicyclic reference hexapentaene, cyclotetradeca-1,2,3,4,5-pentaene (IIa), as first examples of cyclic non-conjugated cumulenes.



Bisethynylcarbinols IV were prepared by the ethynylation of diketones III with ethynyl magnesium bromide in good yields: IVa [colorless oil (78% yield); νmax 3490 and 3310 cm^{-1}; NMR (CCl_4) 2.34 (s, 2H) and 1.8~1.1 ppm (1.75(s), 1.3(m), 1.18(s), and 1.10(s), 44H)], IVb [colorless oil (67%); νmax 3560 and 3305 cm^{-1}; NMR (CCl_4) 7.00 (s, 4H), 2.5 (m, 4H), 2.33 (s, 2H), 1.8~1.5 (m, 10H), and 1.15 and 1.09 ppm (d, 30H)], and IVc [colorless crystalline conglomerate (80%); mp 63~65°C; νmax 3520 and 3300 cm^{-1}; NMR (CCl_4) 6.97 (s, 4H), 2.8~2.4 (m, 4H), 2.37 (s, 2H), 2.1~1.6 (m, 6H), and 1.20 ppm (s, 30H)]. Intramolecular oxidative coupling of IV with cupric acetate in pyridine gave cyclic diacetylene glycol V, 32% yield of Va and 13% of Vb. The glycols Va and Vb were separated by column chromatography on silica gel into two isomers (A and B), respectively, probably a meso and a racemic isomers (Table 1). On the other hand, the oxidative reaction of IVc afforded a cyclic dimolecular product VIIc[6)] [colorless fine crystals (34% yield); mp 240~241°C;

Mol wt, Found 865 (Osmometry), Calcd for VIIc 872; ν_{max} 3580, 3480, and 2130 cm^{-1}; NMR ($CDCl_3$) 7.07 (s, 8H), 2.8~2.4 (m, 8H), 2.1~1.7 (m, 12H), and 1.21 ppm (s, 60H)] in place of V depending upon presumable steric strain.

Table 1. Yields and Physical Properties of V, VI, and VIII.

Compound	Yield, %	mp, °C	Mol wt	λmax ($\varepsilon \times 10^{-4}$)[e]
Va-A[6,a]	20	202 dec.[b]	388[c]	
Va-B[6]	12	142~143	388[c]	
Vb-A[6,a]	7.6	160.7~161	464[c]	
Vb-B[6]	5.5	175.5~176	464[c]	
VIa-A[6]	45	132~134	514[c]	231 (3.87)
VIa-B[6]	--	134~135	---	231 (4.17)
VIb[6]	62	145~146	590[c]	232 (45.3)
VIIIc	63	204~205	1092[d]	222, 231

a) early eluted isomer on chromatography, b) in sealed tube, c) mass spectroscopy, d) osmometry in CH_2Cl_2, e) in cyclohexane

Bromination of Va-A and Va-B was performed with phosphorus tribromide in benzene at 50°C to give diallene dibromides, VIa-A and VIa-B, respectively (Table 1). The dibromide VIa-A was debrominated by treatment with active zinc powder in ether at room temperature for 3 days, followed by column chromatography on neutral alumina, to afford pale greenish yellow crystals of a cyclic hexapentaene IIa in 70% yield, mp 146~147°C[7] [MS (m/e) 354 (M^+), 297 (M—Bu-t), and 240 (M—2Bu-t); NMR (CCl_4) 1.45~1.2 ppm; UV Fig. 1], whereas debromination product of VIa-B obtained under the same condition exhibited no spectral evidence characteristic of 1,2,3,4,5-hexapentaene. However, both dibromides, which were sharply indistinguishable by spectroscopic methods, gave the identical and desired hexapentaene IIa by debromination with methyl magnesium iodide. These facts indicate that both dibromides are isomeric with each other and that both debromination reactions possibly proceed by different mechanisms. The synthesis of paracyclophahexapentaene IIb was carried out in a manner similar to the case of IIa to give a greenish yellow oil [IIb; MS (m/e) 430 (M^+), 373 (M—Bu-t), and 316 (M—2Bu-t); NMR (CCl_4) 6.90 (s, 4H), 2.7~2.4 (m, 4H), 1.4 (m, 8H), and 1.25 and 1.27 ppm (d, 30H); UV Fig. 1].

A tetraallene tetrabromide VIIIc obtained by bromination of VIIc was debrominated by the

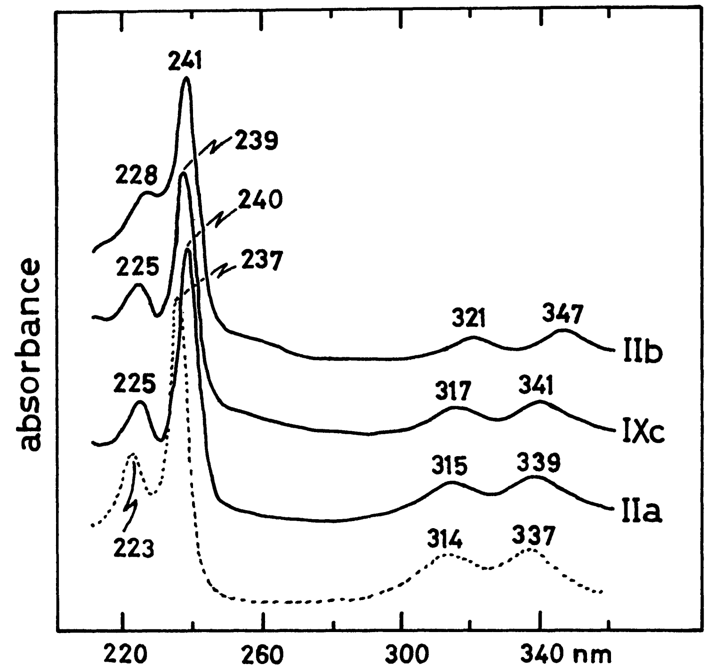


Fig. 1. Electronic Spectra of cyclic hexapentaenes (——) and tetra-t-butyl hexapentaene (····) in ether.

Grignard method to give 37% yield of unstable greenish yellow crystals which were presumed to be a cyclic bis(hexapentaene) compound IXc judging from negative Beilstein's test and the electronic spectral behavior (Fig. 1).

The electronic spectrum of IIa is very similar to that of open chain analog, tetra-t-butyl hexapentaene[4c], in respects of wavelengths of maxima and curve shape. On the other hand, the longest wavelength band of IIb appears at longer wavelength by 8 nm than that of IIa. It can be seen from Stuart-Briegleb's molecular model that both cyclic hexapentaenes, IIa and IIb, are strainless and in similar steric environment around the hexapentaene group with each other. Consequently, it is concluded that the red shift in the spectrum of IIb may be caused by the transannular π-electronic interaction between benzene nucleus and 1,2,3,4,5-hexapentaene group.

References

1) T. Otsubo, Z. Tozuka, S. Mizogami, Y. Sakata, and S. Misumi, Tetrahedron Lett., 1972 in press.

2) T. Matsuoka, Y. Sakata, and S. Misumi, ibid., 1970, 2549; T. Matsuoka, T. Negi, T. Otsubo, Y. Sakata, and S. Misumi, Bull. Chem. Soc. Jap., 45, 1825 (1972); T. Matsuoka, T. Negi, and S. Misumi, Synth. Commun., 2, 87 (1972).

3) For reviews on cumulenes; P. Cadiot, W. Chodkiewicz, and J. Rauss-Godineau, Bull. Soc. Chim. Fr., 1961, 2176; H. Fischer, "The Chemistry of Alkenes", ed. by S. Patai, Interscience Publishers, New York, N. Y. (1964), p. 1025.

4) a) F. Bohlmann and K. Kieslich, Chem. Ber., 87, 1363 (1954); b) L. Skattebøl, Tetrahedron, 21, 1357 (1965); Tetrahedron Lett., 1965, 2175; c) H. D. Hartzler, J. Amer. Chem. Soc., 88, 3155 (1966).

5) J. Ojima, T. Katakami, G. Nakaminami, and M. Nakagawa, Tetrahedron Lett., 1968, 1115; K. Fukui, T. Okamoto, and M. Nakagawa, ibid., 1971, 3121; T. Katakami, S. Tomita, K. Fukui, and M. Nakagawa, Chemistry Lett., 1972, 225.

6) Satisfactory elemental analysis data have been obtained for all new compounds.

7) After the melting point has been reached the resulting yellow oil immediately solidified to form colorless crystals of mp 280~282°C. This product was determined to be a dimer by UV and MS spectra.

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