## PREPARATION OF (-)-(M)-[2.2]PARACYCLOPHANO-HEXAHELICENE FROM (-)-(M)-1,4-DIMETHYLHEXAHELICENE AND ABSOLUTE CONFIGURATION OF 4-SUBSTITUTED [2.2]PARACYCLOPHANES

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Photo-cyclization of a cis-trans mixture of the l,2-diarylethylene precursor l gave l,4-dimethylhexahelicene (2) whose levorotatory enantiomer with (M)-helicity was converted into (-)-(M)-[2.2]paracyclophano-hexahelicene (7), mp 236-237°C,  $[\alpha](abs)_{577}$ -5520°l) confirming the (R)-configuration previously assigned to (-)-[2.2]paracyclophanecarbaldehyde (8).

In 1972, Martin et al.<sup>2)</sup> reported preparation of (-)-[2.2] paracyclophanohexahelicene (7) from (-)-(R)-[2.2] paracyclophanecarbaldehyde (8) whose unique stereochemistry should force the final product 7 to have (M)-helicity; comparison of ORD cuve of (-)-7 with that of (-)-hexahelicene (3) enabled them to assign (M)helicity to (-)-3. Since the (M)-helicity of (-)-3 had been well established by various methods,<sup>3)</sup> Martin's work can rather be regarded as a most reliable chemical correlation to assign (R)-configuration<sup>4)</sup> to the (-)-aldehyde 8. Unfortunately, however, their specimen of (-)-7, apparently impure, was poorly characterized seemingly because of its reported instability.

Our recent experimental study<sup>5)</sup> which has revised the absolute configurations of the closely related 4-substituted [2.2]metacyclophanes prompted us to prepare this doubly layered hexabelicene 7 in optically active modification from 1,4dimethylhexabelicene (2) with known configuration.

A ca. 1:1 cis-trans mixture of the 1,2-diarylethylene precursor  $1^{6}$  prepared by the Wittig reaction between 2,5-dimethylbenzaldehyde and 2-benzo[c]phenanthrylmethyltriphenylphosphonium bromide, was dissolved in benzene containing a small amount of iodine and was irradiated with a medium pressure mercury lamp for 4 hr. Column chromatography (Al<sub>2</sub>O<sub>3</sub>) of the product furnished 1,4-dimethylhexahelicene (2) (64% yield), mp 252-253°C, characterized by its two CH<sub>3</sub> nmr signals at § 0.45 and 2.42 corresponding to the inner and outer methyl groups respectively.

Optical resolution of 2 was accomplished by column chromatography over chiral poly(triphenylmethyl methacrylate)<sup>7</sup>; elution with hexane afforded a specimen of (-)-2, mp 241-243°C,  $[\alpha]_{577}$  -432° whose ca. 12% optical purity<sup>8</sup>) was estimated from the reported  $[\alpha]_{578}$  -3756°<sup>9</sup>) for (-)-hexahelicene (3) (Figure 1).

Photochemical NBS bromination in  $CCl_4$  with benzoyl peroxide converted (-)-2 into the crude bromide 4 which was directly transformed to the ammonium salt 5,  $[\alpha]_D$  -465°. Starting from a 2:1 mol equivalent mixture of p-methylbenzyltrimethyl-ammonium bromide (6) and (-)-5, the Cram's method afforded a complex mixture of

doubly layered cyclophanes whose column chromatography (SiO<sub>2</sub>) followed by preparative TLC (SiO2) gave a 4% yield of (-)-7, which was recrystallized from ethyl acetate to yield yellow prisms, mp 236-237°C,  $[\alpha]_{577}$  -662°.<sup>8)</sup>

Comparison of the CD spectrum of (-)-7 (Figure 1) with that of (-)-(M)-hexahelicene (3) led us to conclude that (-)-7 possesses the same (M)-helicity, and this coupled with Martin's experiment should provide a convincing evidence to support the (R)-configuration of (-)-[2.2]paracyclophanecarbaldehyde (8).



Figure 1.8) CD spectra of (-)-1,4-dimethylhexahelicene (2) (---), (-)-double layered hexahelicene (7) (-----), and (+)-hexahelicene (----) in hexane.

References and Notes

- All optical rotations reported in this communication refer to the CHCl<sub>3</sub> solution at 27°C.
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