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THE AXIAL-EQUATORIAL ISOMER OF 1,2-DIMETHYL [2.2] METACYCLOPHANE

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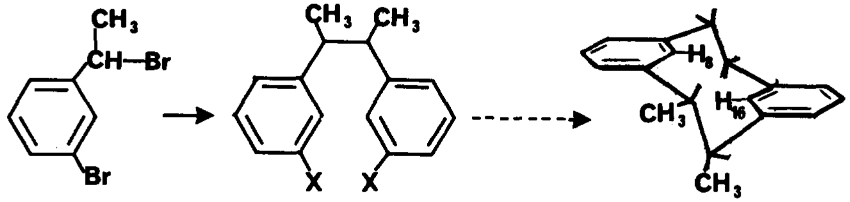
We wish to report the synthesis of the title compound (III), which is the first reported [2.2] metacyclophane with substituents on the side chain[3] and, by virtue of its conformation is also the first [2.2] metacyclophane in which H_8 and H_{16} are magnetically non-equivalent.



D,L-
I

meso
II

III

The required meso-2,3-bis(3-bromophnyl)butane (II, X = -Br) was obtained by coupling D,L-1-(3-bromophenyl)-bromoethane (I) with iron powder in refluxing dioxane[4] affording meso-butane II (X = -Br) in 21% yield[5].

The corresponding meso-bis(bromomethyl) compound (II, X = $-CH_2Br$) was obtained by a series of reactions previously employed for the synthesis of [2.2] metacyclophanes[6]. The final ring closure, employing a modification[7] of the sodium tetraphenylethylene Wurtz reaction[8], afforded metacyclophane III, mp 66.5-68°, in 74% yield (0.18% overall yield from acetophenone in ten steps).

The structure of III was established by combustion analysis (*Anal*. Calcd for

$C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.23 91.53; H, 8.77, 8.47), mass spectrum (parent peak m/e 236, m/e-15 at 221), infrared spectrum, which is very similar to that of [2.2] metacyclophane in the 5-6μ region[9], and ultraviolet spectrum (cyclohexane): λ_{max} 211 mμ (41,100) and 271 (504)[10].

The nmr spectrum[11] of metacyclophane III is most striking and provides conclusive evidence for the gross structure and conformation of the compound. Six features warrant attention. (1) The methylene protons on the unsubstituted bridge (6.93 and 7.92 τ, J = 8 cps) occur only about 0.05τ downfield from the absorption of these protons in [2.2] metacyclophane. (2) The two methyl groups show different chemical shifts (8.52 and 9.15τ) and the higher field absorption is attributed to the axial methyl group[12]. Further, it is interesting to note that J_{CH_3} (a)-H(e) = J_{CH_3}(e)-H(a) = 7 cps. (3) The chemical shifts for H_8 (5.78τ) and H_{16} (5.50τ) are different, although H_8 shows the same chemical shift as [2.2] metacyclophane (5.78τ)[13]. This is compatible with the structural assignment in which there is some distortion of the molecule due to the $CH_{3(a)}$-H_{16} interaction, but there should be little or no effect of $CH_{3(e)}$ on -H_8. Both H_8 and H_{16} are slightly split (*ca*. 0.5 cps) probably by the meta aromatic protons. (4) The chemical shifts of the remaining aromatic protons are unchanged from those in [2.2] metacyclophane. (5) A double resonance experiment clearly established that the axial methine proton at 7.48τ is coupled to the equatorial methyl group at 8.52τ. (6) It is clear from the 100 Mc nmr spectrum that the methine protons are, as expected, octets.

Further work will be directed toward the synthesis of the diaxial and diequatorial isomers and an elucidation of their exact geometries as well as the chemical reactions of these unusual molecules.

REFERENCES

1. We are grateful for funds from ACS-PRF Grant #3385-B, which made possible this investigation. This paper represents part of the work submitted by R.W.B to the Division of Natural Sciences of New College in partial fulfillment of the requirements for the B. A. degree, June 1968.
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