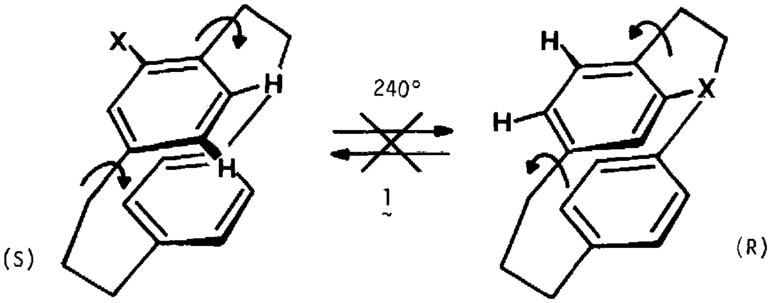
Tetrahedron Letters No. 50, pp 4559-4562. 1976. Pergamon Press. Printed in Great Britain.

5,6-DEHYDRO[3.3]PARACYCLOPHANE:
BRIDGED BENZOBARRELENE FORMATION BY INTRAMOLECULAR TRAPPING OF A NOVEL ARYNE

Daniel T. Longone[1a] and J. A. Gladysz[1b]
Department of Chemistry, University of California, Los Angeles
Los Angeles, California 90024[1c]
and
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104

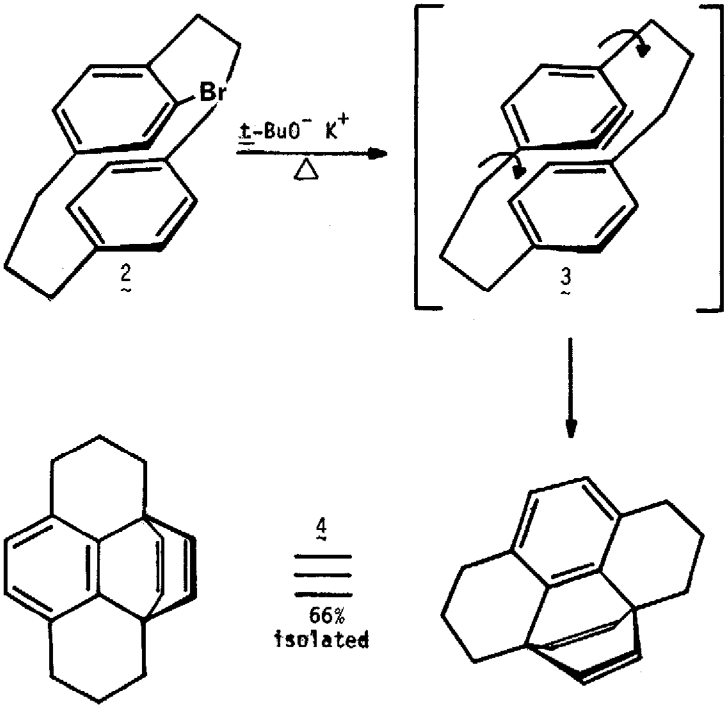
(Received in USA 1 September 1976; received in UK for publication 25 October 1976)

The steric inhibition of benzenoid ring rotation in the [m.n]paracyclophanes has been extensively studied.[2] Thermal racemization of chiral 4-carbomethoxy[2.2]paracyclophane occurs at 200° ($\Delta G^\ddagger$ ca. 38 kcal/mol) and proceeds via homolytic bridge cleavage at the benzylic position.[3] No evidence of ring rotation by any pathway has ever been observed in the [3.3]paracyclophanes; optically active 5-carboxy[3.3]paracyclophane (**1**, X = COOH) was recovered without racemization or decomposition after 72 hr in refluxing tridecane (240°).[4] Carboxy[4.3]paracyclophane, however, undergoes ring rotation at 160° ($\Delta G^\ddagger$ ca. 33.5 kcal/mol),[3] and [4.4]paracyclophane derivatives have resisted resolution to date.[5] Hence the accumulation of four methylene groups in each bridge permits facile attainment ($\Delta G^\ddagger$ < 20 kcal/mol) of a transition state in which the two benzene rings are mutually perpendicular.



In this communication, we report a reaction which 1) requires the intermediacy of an unencumbered 5,6-dehydro[3.3]paracyclophane (**3**), 2) demonstrates the perpendicular arrangement of benzene rings required for ring rotation in the [3.3]paracyclophane series is energetically accessible upon removal of the two offending vicinal hydrogens and superposition of a transannular attraction with an energy minimum at that position on the reaction coordinate, and 3) provides a synthetic entry into a novel bridged benzobarrelene system (4). The experimental details are as follows:

To 108 mg (0.343 mmol) of 5-bromo[3.3]paracyclophane (2)[6] in 8 ml *t*-butylbenzene was added 824 mg (20 equiv) *t*-BuO$^-$ K$^+$. The reaction mixture was refluxed in an oil bath at 180° (conditions previously used for the generation of arynes[7,8]) and monitored gas chromatographically. Clean, quantitative conversion to a single product was observed, which was isolated by solvent removal and preparative thin layer chromatography (52.5 mg, 66%). Slow chloroform-ethanol recrystallization afforded white platelets, m.p. 130.5-132, chromatographically distinct from an authentic sample of *sym*-hexahydropyrene (m.p. 132)[9] and analyzing for $(CH)_n$ (calc: C 92.26, H 7.74; found: C 92.11, H 7.82).



The structural assignment 4 is based upon extensive spectral characterization. The mass spectrum displays a molecular ion (base peak) at m/e 234 ($C_{18}H_{18}$, overall loss of HBr from 2) and other significant fragments at 235 (18%), 233 (12), 206 (21), 205 (20), 191 (16), 179 (8), 178 (13), and 165 (17). The proton magnetic resonance spectrum in $CDCl_3$ reveals two aliphatic multiplets (δ 1.95, 4H; 2.55, 8H; TMS internal standard) and a single sharp absorption at δ 6.61

(6H) which is split into two singlets (6.50, 4H, vinylic; 6.55, 2H, aryl) when the spectrum is recorded in C_6D_6. This is consistent only with the highly symmetric structure **4**, and the relevant chemical shifts are comparable to those reported by Zimmerman for benzobarrelene[10] and anthrabarrelene.[11] The uv spectrum resembles that of benzobarrelene[10] [λ_{max}, cyclohexane, 283 nm (ε 260), 271 (520), 262 (sh, 730), 218 (38,000), 213 (sh, 36,000)], and the ir spectrum features the expected absorptions ($CHCl_3$, cm^{-1}): 3042 w, 3008 m, shp, 2978 s, 2958 m, 1482 m, 1448 w, 1447 w, 1441 m, 1431 w, 1396 w, 1336 w, 1335 w, 1328 w, 1257 w, 1184 w, 1093 w, br, 1012 w, br, 955 w, shp, 897 w, shp, 857 w, 838 w, 708 s, 584 m.

Previous work by one of us[8] and by Cram[12] demonstrated that 4,5-dehydro[2.2]paracyclophane can be obtained from 4-bromo[2.2]paracyclophane and *t*-BuO^- K^+. The bridge length in this aryne is apparently not long enough to allow formation of an intramolecular adduct analogous to **4**, but external trapping (*e.g.*, anthracene) is possible.[8] Transannular Diels-Alder adducts can be obtained photochemically from [2.2]paracyclophane derivatives.[13] Such species have received consideration as intermediates in the photochemical racemization of (-)-4-methyl[2.2]paracyclophane and related compounds.[14]

There is a complete lack of products arising from *t*-BuO^- K^+ addition to **3**, despite the twentyfold excess of base employed. This is in sharp contrast to similarly generated 4,5-dehydro[2.2]-paracyclophane,[8,12] where such products dominate. Therefore the barrier to ring rotation must be substantially diminished by the addition of an extra methylene group to each bridge. While **3** is the smallest-bridged paracyclophane in which a perpendicular ring orientation can be thermally achieved, the question of whether the aryne ring can rotate through 180° without reaction awaits a more sophisticated chemical test.

Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We warmly thank Professor Cram for the sample of **2** used in these experiments.

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