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APPLICATION OF THE STEVENS REARRANGEMENT-ELIMINATION PROCEDURE FOR THE SYNTHESIS OF [2.2]METAPARACYCLOPHANE-1,9-DIENE.(1)

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In an accompanying communication,(2) we describe a procedure for replacing a sulfide linkage with a carbon-carbon double bond. To test the generality of this method we have investigated its use for the synthesis of [2.2]-metaparacyclophane-1,9-dienes, a class of compounds having some theoretical interest.(3)

The reaction of p-xylylene dibromide with m-xylylene dimercaptan in a basic solution of aqueous ethanol gave 2,11-dithia[3.3]metaparacyclophane (1) as white crystals, m.p. 158.5-159.5°, in 30% yield. The properties of 1 are in agreement with those reported earlier by Vögtle using an alternate route.(4) The reaction of 1 with dimethoxycarbonium fluoroborate(5) proceeded smoothly in essentially quantitative yield to give the disulfonium salt 2 as white crystals, m.p. 210° dec.[a] The Stevens rearrangement of 2 using sodium hydride in dimethyl sulfoxide gave 3 as a colorless oil in 67% yield.

Even though 3 was a mixture of stereoisomers, its nmr spectrum clearly showed the typical [2.2]metaparacyclophane pattern(6) with the internal proton at the 8-position appearing as a broad singlet at τ 4.70. Treatment of 3 with dimethoxycarbonium fluoroborate then gave 4 in 87% yield as white crystals, decomposing above 236°. No attempt was made to separate the mixture of isomers represented by 4 but, instead, it was treated with n-butyllithium at -78°.

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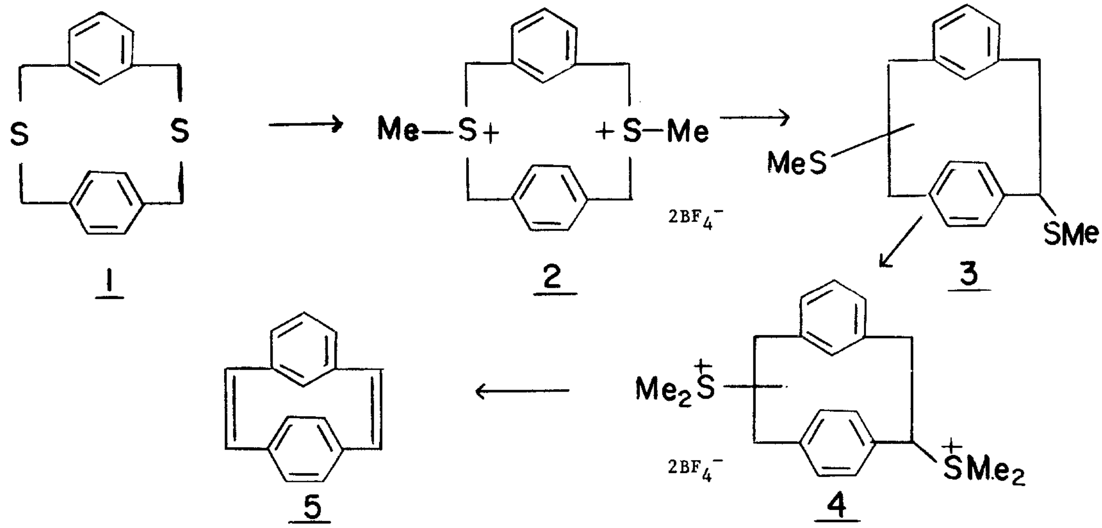
[a] For the new compounds being reported satisfactory analyses and mass spectra, where appropriate, have been obtained.

This gave the desired [2.2]metaparacyclophane-1,9-diene (5) in 50% yield. The properties of this product were identical in all respects to those reported earlier for 5.(3)



Although an x-ray crystallographic analysis shows the aromatic rings of 5 to be inclined at an angle of 41° from perpendicular,(7) the nmr spectrum of 5 in solution shows the four para-bridged aromatic protons as a singlet at τ 3.19.(8) The convenience of the present method of synthesis of 5 should allow a closer examination of its geometry in solution as well as the question of electronic transmission effects between rings in the case of appropriate derivatives of 5.

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