

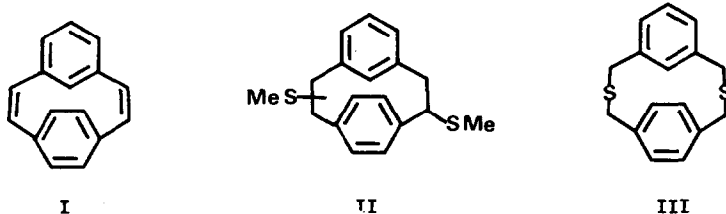
STEVENS REARRANGEMENTS IN A NAPHTHALENE CYCLOPHANE<sup>1</sup>

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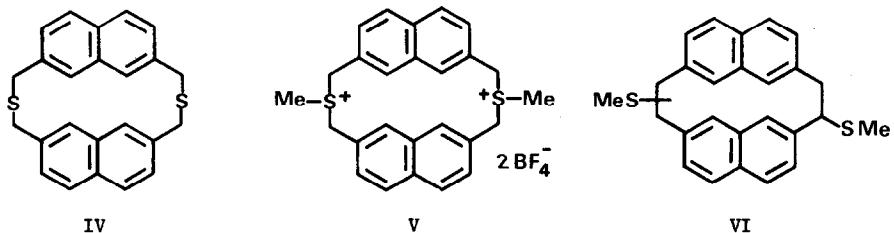
Boekelheide<sup>2-5</sup> has successfully utilized a four-step reaction sequence to prepare sterically strained cyclophanes incorporating unsaturated bridging groups. For example, [2.2]metaparacyclophane-1,9-diene (I) was synthesized<sup>3</sup> by an elimination reaction of a di-sulphonium salt derived from II, in turn prepared by a Stevens rearrangement of the bis-methylsulphonium salt of the bishioether III.



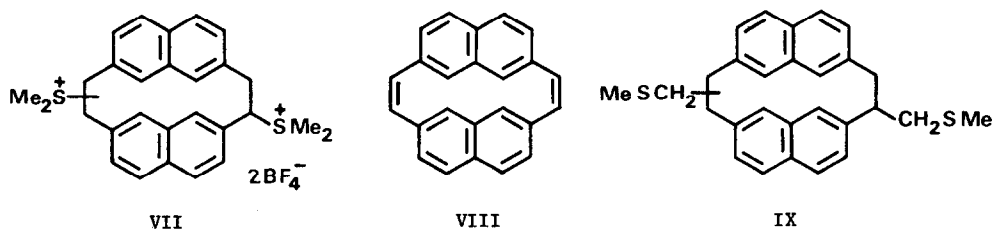
We wish to report an unexpected Stevens rearrangement in a naphthalenophane.

2,13-Dithia-[3.3](2,7)naphthalenophane (IV), m.p., 240-244°, (lit.,<sup>6</sup> 245-247°) was synthesized from 2,7-bis(bromomethyl)naphthalene and sodium sulphide. Compound IV was methylated with dimethoxycarbonium tetrafluoroborate in methylene chloride to produce in quantitative yield, the sulphonium salt V, m.p., > 300°. The Stevens rearrangement of the salt V was effected with sodium hydride in tetrahydrofuran. The bis(methylthio)[2.2](2,7)-naphthalenophane (VI), m.p., 190-195°, was isolated as white crystals in 90% yield. The determination of the configuration of the methylthio groups will be published elsewhere. The n.m.r. and mass spectra confirmed the gross structure of the rearranged product. Desulphurization of the product with Raney nickel in ethanol produced [2.2](2,7)naphthalenophane in 90% yield, m.p., 234-236° (lit.,<sup>7</sup> 237-238°). The cyclophane VI reacted with dimethoxycarbonium

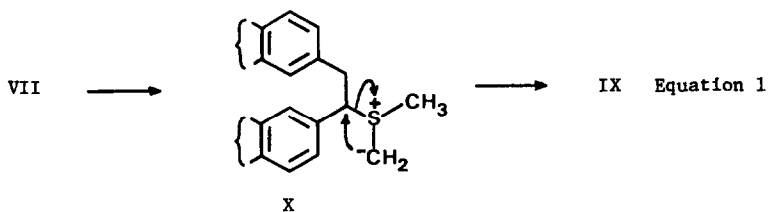
tetrafluoroborate to form the disulphonium salt VII, m.p.,  $> 360^\circ$ , in 75% yield. This compound was then treated with either sodium hydride in tetrahydrofuran or potassium 2,6-di-*t*-butylphenoxide in tetrahydrofuran in an attempt to generate the elimination product, [2.2](2,7)-naphthalenophane-1,11-diene (VIII).



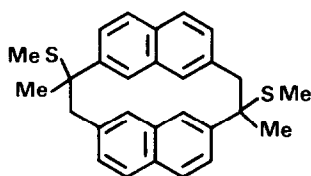
On work-up of the reaction mixture, a single major compound was isolated, m.p.,  $211-213^\circ$ , in 53% yield. Its n.m.r. spectrum showed peaks at  $\delta$ , 1.93 (singlet, 3H; S-CH<sub>3</sub>) and  $\delta$ , 3.81 (doublet, 2H; J, 7Hz; -CH<sub>2</sub>-S). The mass spectrum of the product showed a parent molecular ion at  $\underline{m/e}$ , 428. Both spectra were consistent with a bis(methylthiomethylene)naphthalenophane (IX) formed by a second Stevens rearrangement. The product is probably a mixture of stereoisomers. None of the desired elimination product VIII was isolated or detected. Further evidence for the structure of the cyclophane IX was obtained by desulphurization with Raney nickel to give a corresponding dimethylnaphthalenophane.



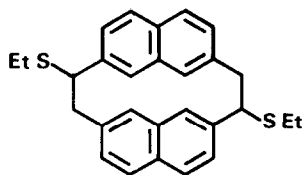
It is apparent that in the reaction between the sulphonium salt VII and either of the bases used, a 1,2-elimination reaction did not occur to form the diene VIII. Instead, a Stevens



rearrangement took place involving a [1,2]sigmatropic shift of the benzylic moiety from the S atom to the methyl C atom, as shown in Equation 1. Carbanion formation at either of the benzylic positions and subsequent reaction under the basic conditions used is apparently not favoured and instead, the ylide X is generated and rearranges to give the observed product. Compounds XI and XII which may be derived from the two other possible Stevens rearrangement pathways from the sulphonium salt VII were not detected. There are also two other competing reaction modes open to such sulphonium ylides; direct nucleophilic displacement and the Sommelet-Hauser rearrangement.<sup>8</sup> Products from neither of these latter two processes were observed.



XI



XII

There is considerable evidence<sup>9</sup> at hand to suggest that 1,2-eliminations of 'onium' salts to form alkenes may proceed via either a syn- or anti-mechanism. The failure of the sulphonium salt VII to eliminate under the basic conditions, irrespective of the stereochemistry of the leaving groups, may be rationalized in terms of the steric strain associated with the introduction of a double bond into the naphthalenophane. Consequently, a competing pathway of lower energy, namely the Stevens rearrangement, must be the preferred route.

The results obtained in this work contrast with those reported by Boekelheide,<sup>2-5</sup> in which unsaturated bridging groups were successfully introduced into cyclophanes by elimination reactions of sulphonium salts. It is apparent that the prime factors which determine the reaction pathway of choice taken by a sulphonium ylide have yet to be fully elucidated.

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