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THE TRANSFORMATION OF A SULFIDE LINKAGE TO A CARBON-CARBON DOUBLE BOND IN HIGHLY STRAINED MOLECULES. A CONVENIENT SYNTHESIS OF 15,16-DIMETHYLDIHYDROPYRENE.(1)

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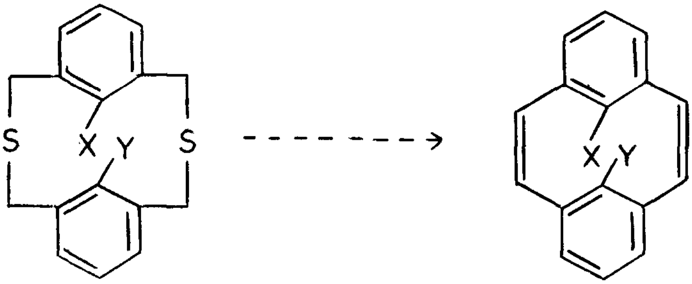
The publication of Gault, Price and Sutherland on the conformational mobility of [2.2]-2,6-pyridinophane(2) has stimulated similar studies with a number of other metacyclophanes. Of particular interest are the extensive studies of Vögtle(3) on the temperature dependence of the nmr spectra of a series of 2,11-Dithia[3.3]metacyclophanes containing groups X and Y with varying steric requirements at the 9 and 18 positions as shown by structure 1. Independently, and somewhat inadvertently,(4) we became interested in structures such as 1 as possible precursors for the synthesis of [2.2]metacyclophane-1,9-dienes such as 2. Quite obviously what was needed was a method for transforming sulfide linkages into carbon-carbon double bonds and so converting 1 into the 15,16-dihydropyrene valence tautomer 2. We now report a highly useful method for accomplishing this conversion.



1 2

Although the Ramberg-Bäcklund rearrangement is a well known method for extruding sulfur with concomitant formation of a carbon-carbon double bond, as both Corey(5) and Paquette(6) have recently shown in definitive papers on the synthesis of $\Delta^{1,5}$-bicyclo[3.3.0]octene, we felt that an alternate approach might be both more efficient and more successful for highly-strained molecules such as 2. The concept of this alternate approach was to employ a Stevens rearrangement of the sulfonium salt 6 to give a rearranged sulfide 7, which by a normal elimination process would yield the olefin 2. For the Stevens rearrangement to be successful requires that it occur in an intramolecular, frontside fashion, since this is the only path allowed by the rigid, step-wise geometry of the [3.3]metacyclophanes. Although there is a paucity of mechanistic studies of the Stevens rearrangement of sulfonium salts, extensive studies(7-9) on the Stevens rearrangements of ammonium salts have shown that reaction to involve an intramolecular, frontside displacement, exactly as required in the present case.

When 2,6-bis(bromomethyl)toluene (3) was treated with sodium sulfide in boiling ethanol under similar conditions to those described by Vögtle,(3) there formed two isomeric products, 4 and 5. After purification by chromatography over silica gel, 4 was isolated in 14% yield as white crystals, m.p. 250-255°; whereas 5 was obtained in 2% yield as white crystals, m.p. 238-240°.[a] With internal groups as large as methyl, the barrier to conformational flipping is sufficiently large that the cis and trans conformers can be isolated and show no evidence for interconversion at normal reaction temperatures. The assignments of structure are based on nmr data. Thus, the protons of the internal methyl groups show an upfield shift due to the ring current of the opposite aromatic ring and appear at τ 8.70, whereas the internal methyl protons of 5 are normal and appear at τ 7.46. Similarly, the aromatic protons

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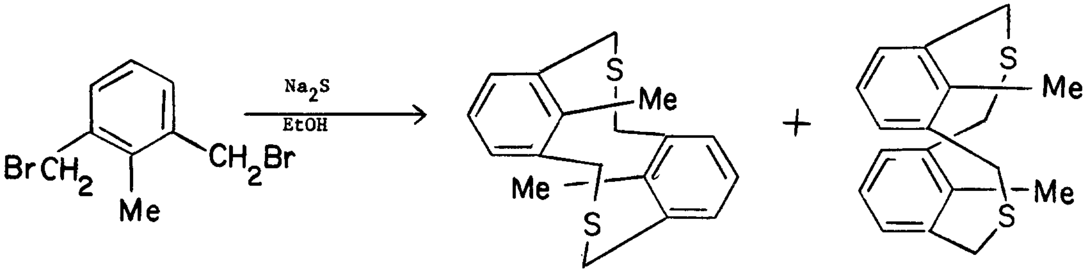
[a] For all new compounds being reported satisfactory elemental analyses and mass spectra have been obtained.

of 4 show the normal metacyclophane pattern at τ 2.6-3.0, whereas the aromatic protons of 5 are shifted upfield to τ 3.34, a common consequence of superimposing aromatic rings.(10-12)



3 4 5

The conversion of 4 to its corresponding disulfonium salt 6 was readily accomplished in quantitative yield using the very convenient methylating reagent popularized by Borch(13) and gave the fluoroborate of 6 as white crystals, m.p. 210° dec. When 6 was treated with sodium hydride in tetrahydrofuran, the Stevens rearrangement occurred smoothly in 90% yield to give the corresponding disulfide 7. Although 7 was a mixture of isomers,[b] as would be expected, the nmr spectrum of the mixture (internal methyl singlets between τ 9.0-9.5) clearly showed that all of these isomers were related to the *trans*-[2.2]metacyclophanes and so no conformational interconversion occurred during the Stevens rearrangement.

This mixture of isomers was again methylated with dimethoxycarbonium fluoroborate in methylene chloride at -30° to give the disulfonium salt 8. The final elimination of dimethyl sulfide from 8 has been investigated using a number of different bases and, with potassium *t*-butoxide in boiling

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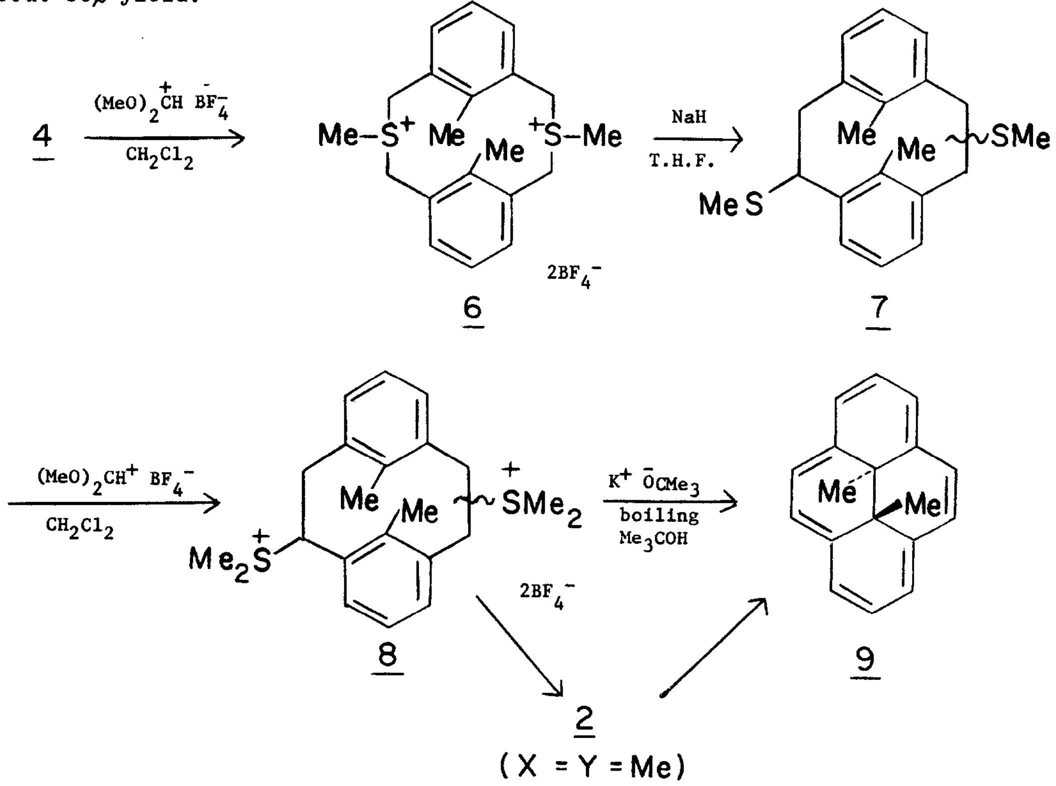
[b] The description of the separation of these isomers and their individual physical properties will be reported elsewhere.

t-butanol, the conversion of 8 to 15,16-dimethyldihydropyrene (9) occurs in about 80% yield.



Thus, the overall conversion of 2,11-Dithia[3.3]metacylophanes to 15,16-dihydropyrenes via a Stevens rearrangement and elimination is a simple and high yield procedure. As discussed in an accompanying communication,(14) this method has been applied to other systems and appears to be a general method for replacing a sulfide linkage by a carbon-carbon double bond.

The fact that the elimination of dimethyl sulfide from 8 first yields the diene 2 (X=Y= $-CH_3$), which then undergoes valence tautomerization to 15,16-dimethyldihydropyrene (9), has also been shown. When 8 was treated with sodium hydride in tetrahydrofuran at room temperature, it was converted in about 60% yield to a mixture of about equal parts of 2 (X=Y= $-CH_3$) and 9, as analyzed from its nmr spectrum. Either on heating or chromatography over silica gel the mixture was converted entirely to **9**.

It is of interest that the *cis* isomer **5**, after conversion to the corresponding sulfonium salt **6** (*cis*-geometry), also readily undergoes the Stevens rearrangement to provide a mixture of isomers corresponding to **7** but with *cis* geometry. The evidence for *cis* geometry is based on the nmr spectrum of the mixture which shows the internal methyl protons at τ 7.7-7.9, the normal region for a toluene methyl and showing the absence of ring current effects.[c]

The formation of **7** with *cis* geometry is the first instance of the preparation of a [2.2]metacyclophane in which the benzene rings are *cis* to each other. Molecular models suggest that the proximity of the two aromatic rings must be comparable to that for the case of [2.2]paracyclophane. In fact the ultraviolet spectra of the *cis* isomers of **7** show no long wave length absorption band comparable to that found for [2.2]paracyclophane(15) and this may be of some theoretical import.(16) Studies on *cis*-[2.2]metacyclophanes are continuing.

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[c] The description of the separation of these individual isomers and their physical properties will be reported elsewhere.

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