Similar analysis of the isomeric mixture derived from the trans dialdehyde and ethylidenetriphenylphosphorane in DMSO indicated the ctc:ctt:ttt proportions 65:33:2.

Pure samples of these isomers for characterization, preparative scale thermolyses, and kinetic studies were obtained by preparative glpc on squalene columns.

cis,trans,cis-1,2-Di(prop-1'-enyl)cyclopropane had a strong infrared band at 713 cm⁻¹. The nmr spectral parameters are given above.

cis,trans,trans-1,2-Di(prop-1'-enyl)cyclopropane had strong infrared bands at 712 and 955 cm⁻¹; nmr, see above.

trans,trans,trans-1,2-Di(prop-1'-enyl)cyclopropane had a strong infrared band at 958 cm⁻¹. The nmr spectrum is discussed above.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.50; H, 11.52.

cis-6,7-Dimethylcyclohepta-1,4-diene. A 40-μl sample of the *trans,trans,trans*-dipropenylcyclopropane (98.6% pure) was degassed through three or four freeze–pump–thaw cycles at 10^{-4} Torr, then sealed under vacuum in a base-washed and thoroughly dried ampoule and heated in an oil bath at 178° for 4.2 hr. The reaction mixture contained one product (98.8%) and no starting material, according to glpc analyses. By thorough analysis of the nmr spectrum, as given above, the product was identified as *cis*-6,7-dimethylcyclohepta-1.4-diene.

trans-6,7-Dimethylcyclohepta-1,4-diene. An 18-μl sample of the *cis,trans,trans*-dipropenylcyclopropane (94.2%) pure) was sealed in a degassed ampoule and kept 4.2 hr at 179°. The product (95.0%) was identified through its nmr spectral properties (see above). The impurities in the original sample were unchanged by the thermolysis.

cis,cis,cis-1,2-Di(prop-1'-enyl)cyclopropane. A 35-μl sample of

the *cis,trans,cis*-dipropenylcyclopropane was heated in a sealed ampoule at 179° for 4.2 hr. Analysis by glpc using a $\beta\beta'$-ODPN column revealed three components having relative retention times 0.76:1.00:1.21. The first and second proved to be *cis*-6,7-dimethylcyclohepta-1,4-diene and unconverted starting material. The third was identified as *cis,cis,cis*-1,2-di(prop-1'-enyl)cyclopropane; nmr, see text above.

A pure sample of the ctc isomer kept at 178° for 4.2 hr gave rise to a 4:72:24 product distribution. Another sample kept at this temperature for 75 hr gave a 35:50:15.6 product ratio.

Pyrolysis of a mixture containing *cis*-6,7-dimethylcyclohepta-1,4-diene, *cis,trans,cis*-dipropenylcyclopropane, and *cis,cis,cis*-dipropenylcyclopropane in 11:6:84 proportions at 182° for 4.2 hr gave a 12:68:20 mixture of these isomers. Product identifications were confirmed nmr spectroscopically.

Gas-phase isomerization kinetics were obtained using a static reactor, vacuum line, pentane as diluent, and glpc to measure isomeric distributions as a function of time.[48] The isomeric purity of reactants was determined on the squalane capillary column, while product distiributions were measured on $\beta\beta'$-ODPN columns. The impurities in reactants (4% of the ctt isomer in the ttt material, 8% of ctc compound in the ctt, and 3% of ctt in ctc), persisting after two or three consecutive preparative glpc separations on squalene columns, contributed to the observed distributions of C_9H_{14} isomers as functions of time to a minor and easily corrected for extent. The rate constants determined are given in Table III above.

(48) J. E. Baldwin and R. H. Fleming, *J. Amer. Chem. Soc.*, **95**, 5249 (1973).

Transformation of Sulfide Linkages to Carbon–Carbon Double Bonds. Syntheses of *cis*- and *trans*-15,16-Dimethyldihydropyrene and *trans*-15,16-Dihydropyrene[1]

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Abstract: It is shown that the transformation of sulfide linkages to carbon–carbon double bonds in highly strained molecules can be effected conveniently and in high yield by a reaction sequence of a Stevens rearrangement followed by a Hofmann elimination. This route is of particular advantage for preparing cyclophane derivatives since the medium-sized ring sulfides required as starting materials are easy to prepare. When *m*-xylylene dibromide is treated with 1,3-bis(mercaptomethyl)benzene, 2,11-dithia[3.3]metacyclophane (**25**) is formed in 80% yield. Similarly, 2,6-bis(bromomethyl)toluene (**5**) can be converted to 2,11-dithia-9,19-dimethyl[3.3]metacyclophane, which exists in both the syn and anti conformations (**7** and **8**). Subjection of these three 2,11-dithia[3.3]metacyclophane derivatives to the Stevens rearrangement leads in each case to the corresponding ring-contracted bis(methylthio)-[2.2]cyclophane, isolated as a mixture of isomers. When the mixture of isomers **10**, resulting from the *anti*-9,18-dimethyl derivative, is subjected to a Hofmann elimination, *trans*-15,16-dimethyldihydropyrene (**14**) forms in excellent overall yield. Similarly, the mixture of isomers **18** from the *syn*-8,16-dimethyl derivative is converted to *cis*-15,16-dimethyldihydropyrene (**21**). Surprisingly, the Hofmann elimination reaction with the parent bis(methylthiomethyl)[2.2]metacyclophane (**26**) gives *anti*-[2.2]metacyclophane-1,9-diene (**31**), rather than the expected *trans*-15,16-dihydropyrene. Although *anti*-[2.2]metacyclophane-1,9-diene (**31**) is a stable compound and does not undergo spontaneous valence tautomerization, it is converted on irradiation to *trans*-15,16-dihydropyrene (**35**). Some of the physical and chemical properties of these bridged [14]annulenes are presented.

P revious syntheses of the interesting *trans*-15,16-dialkyldihydropyrenes have been lengthy and have not provided the possibility of preparing either the cis isomers or the parent substance, *trans*-15,16-dihydro-

pyrene (**35**).[2-4] Inasmuch as the formation of medium-

(2) V. Boekelheide and T. A. Hylton, *J. Amer. Chem. Soc.*, **92**, 3669 (1970).
(3) H. Blaschke, C. E. Ramey, I. Calder, and V. Boekelheide, *J. Amer. Chem. Soc.*, **92**, 3675 (1970).
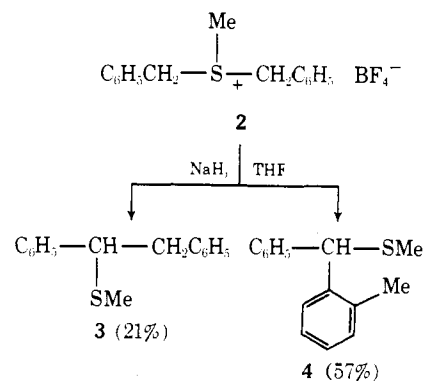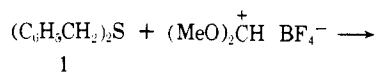(4) V. Boekelheide and J. B. Phillips, *J. Amer. Chem. Soc.*, **89**, 1695 (1967).

sized rings by closure of sulfide linkages is generally a facile reaction proceeding in good yield, a successful method for the transformation of sulfide linkages to carbon–carbon double bonds in highly strained molecules would provide a very attractive route to [2.2]metacyclophane-1,9-dienes, the valence tautomers of 15,16-dihydropyrenes.[5] Although the Ramberg–Bäcklund rearrangement is a well-known method for extruding sulfur with concomitant formation of a carbon–carbon double bond,[6,7] it is our own experience, as well as that of others,[8] that the Ramberg–Bäcklund rearrangement is unsatisfactory when applied to 2,11-dithia[3.3]cyclophanes.

The rigid geometry of the dithiacyclophanes requires that, when ring contraction and sulfur extrusion occurs, the new carbon–carbon bond be formed in a frontside manner. As Brewster and Kline have shown in the case of optically active ammonium salts,[9] the Stevens rearrangement occurs with retention of configuration and so fulfills this requirement. More recently, it has also been demonstrated that Stevens rearrangements exhibit chemically induced, dynamic nuclear polarization,[10,11] and so, at least in part, must also involve diradical intermediates. However, regardless of the mechanistic details, it seems clear that the Stevens rearrangement does meet the rigid requirements of cyclophane geometry, and thus a Stevens rearrangement followed by a Hofmann elimination might provide the desired transformation of a sulfide linkage to a carbon–carbon double bond.

The potential of this reaction sequence was first investigated with dibenzyl sulfide (1), as a model. Methylation of sulfides cannot be done in the usual way with methyl iodide because iodide ion, as an effective nucleophile, causes displacement and trimethylsulfonium iodide usually becomes the major product. Of the alternate methylating agents having nonnucleophilic counterions, we have employed in various experiments trimethyloxonium fluoroborate (Meerwein's reagents),[12] dimethoxycarbonium fluoroborate,[13] and methyl fluorosulfonate.[14] Although all three reagents perform quite satisfactorily, we have generally found the dimethoxycarbonium fluoroborate to give the cleanest product and to be the most convenient to use. When methyldibenzylsulfonium fluoroborate (2) was treated with sodium hydride in tetrahydrofuran, the Stevens rearrangement product 3 was formed in 21% yield and the Sommelet rearrangement product 4 in 57% yield.[15]

Examination of molecular models indicated that the

$(C_6H_5CH_2)_2S + (MeO)_2\overset{+}{C}H\ BF_4^-\longrightarrow$

1

Me
|
$C_6H_5CH_2\overset{+}{-}S-CH_2C_6H_5\ BF_4^-$

2

NaH, THF

$C_6H_5-CH-CH_2C_6H_5$
|
SMe

3 (21%)

$C_6H_5-CH-SMe$ (with o-Me aromatic ring)

4 (57%)

Stevens rearrangement, but not the Sommelet, would be possible in the cyclophane series, so we then turned to the preparation of the appropriate dithiacyclophanes. Treatment of 2,6-bis(bromomethyl)toluene (5)[16] with either 2,6-bis(mercaptomethyl)toluene (6) or sodium sulfide in an ethanol solution gave a mixture of the syn and anti conformers 7 and 8 in a ratio of about 7:1.[17,18] In his extensive studies on conformational flipping and temperature-dependent nmr spectra of dithiacyclophanes, Vögtle has likewise prepared mixtures of 7 and 8 and found that they are not spontaneously interconvertible.[19] The assignment of structure for the pure syn and anti isomers 7 and 8 is readily apparent from their nmr spectra. Thus, the protons of the internal methyl groups of 8 show an upfield shift due to the ring current of the opposite aromatic ring and appear as a singlet at τ 8.70, whereas the protons of the internal methyls of 7 are normal and appear at τ 7.46. In addition, the aromatic protons of 8 show the normal anti-metacyclophane pattern at τ 2.6–3.0, whereas the aromatic protons of 7 are shifted upfield to τ 3.34, a common consequence of superimposng two parallel aromatic rings.[20-22] Finally, Davis and Bernal have made an X-ray crystallographic analysis of 7, confirming its syn conformation.[23] The aromatic rings of 7 are more or less parallel but tilted toward each other, so that the intercarbon distances between the two rings vary from 3.28 to 3.76 Å.

Methylation of anti-2,11-dithia[3.3]cyclophane (8) with dimethoxycarbonium fluoroborate gave the corresponding anti-bis(sulfonium) salt 9 in 95% yield. Although various conditions for effecting the Stevens rearrangement have been investigated, the most generally satisfactory and convenient procedure appears to be its heterogeneous reaction with sodium hydride in tetrahydrofuran. Under these conditions 9 was converted to a mixture of isomers, as shown by structure 10, in yields ranging from 90 to 99%. For its use in the Hof-

(5) H.-R. Blattmann, D. Meuche, E. Heilbronner, R. J. Molyneux, and V. Boekelheide, J. Amer. Chem. Soc., 87, 130 (1965).

(6) L. A. Paquette and R. W. Houser, J. Amer. Chem. Soc., 91, 3870 (1969).

(7) E. J. Corey and E. Block, J. Org. Chem., 34, 1233 (1969).

(8) H. J. J.-B. Martel and M. Rasmussen, Tetrahedron Lett., 3843 (1971).

(9) J. H. Brewster and M. W. Kline, J. Amer. Chem. Soc., 74, 5179 (1952).
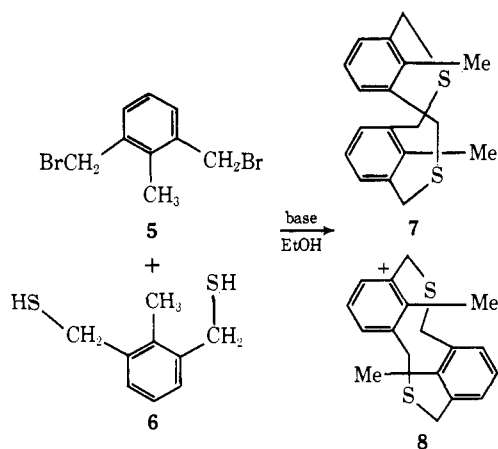
(10) A. R. Lepley, Chem. Commun., 1460 (1969).

(11) U. Schollkopf, U. Ludwig, G. Ostermann, and M. Patsch, Tetrahedron Lett., 3415 (1969).
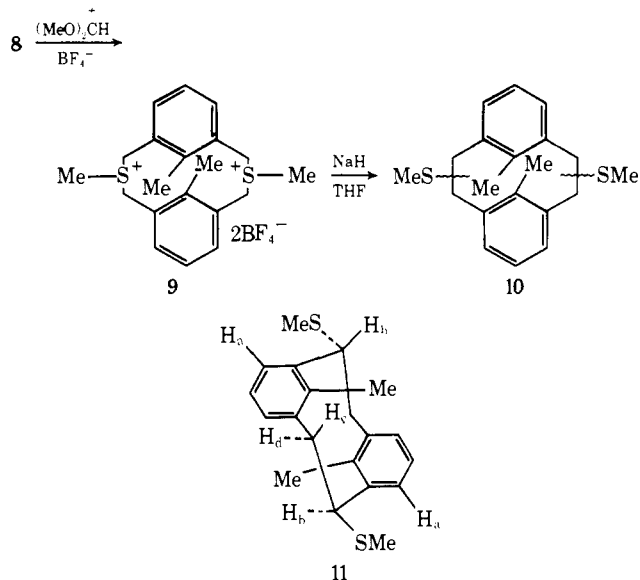
(12) H. Meerwein, Org. Syn., 46, 120 (1966).

(13) (a) H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert, and K. Wunderlich, Justus Liebigs Ann. Chem., 632, 38 (1960); (b) see also, R. F. Borch, J. Amer. Chem. Soc., 90, 5303 (1968); J. Org. Chem., 34, 627 (1969).

(14) Sold by Aldrich Chemical Co. under the trade name Magic Methyl.

(15) Y. Hayashi and R. Ada (Tetrahedron Lett., 5381 (1968)) have found similar results using aqueous base.

(16) See the Experimental Section for an improved synthesis of 5.

(17) The combined yield of 7 and 8 observed was in the range of about 15%, but conditions for optimizing the yield have not been thoroughly investigated.

(18) Preliminary publication of these results has been made: R. H. Mitchell and V. Boekelheide, Tetrahedron Lett., 1197 (1970).

(19) F. Vögtle and P. Neumann, Tetrahedron, 26, 5299 (1970).

(20) R. H. Mitchell and F. Sondheimer, J. Amer. Chem. Soc., 90, 530 (1968).

(21) D. J. Cram, C. K. Dalton, and G. R. Knox, J. Amer. Chem. Soc., 85, 1088 (1963).

(22) R. H. Martin, G. Morren, and J. J. Schurter, Tetrahedron Lett., 3683 (1969).

(23) B. R. Davis and I. Bernal, J. Chem. Soc. B, 2307 (1971).

BrCH₂ ... CH₂Br
CH₃

5

+

HS, CH₃ SH
CH₂ CH₂

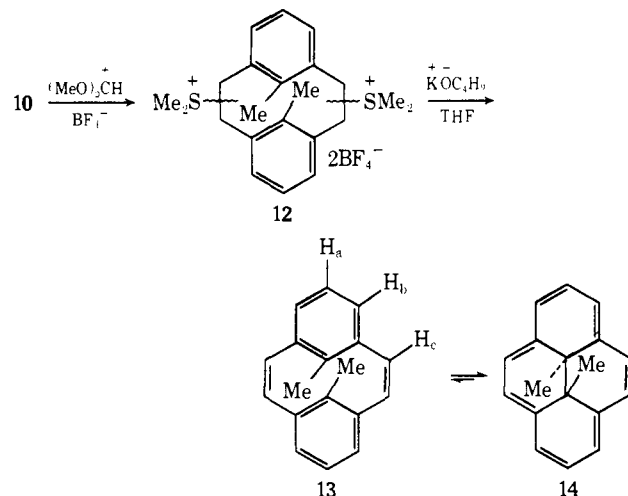**6**

base
EtOH →

S—Me
—Me
S

7

S—Me

Me—S

8

mann elimination reaction the mixture of isomers corresponding to **10** need not be separated. However, chromatography of **10** over silica gel gave the principle component (about 40% of the mixture) in a pure state, mp 213–214°. This isomer has been assigned structure **11** based on its nmr spectrum, which shows the molecule to have a center of symmetry with two of the aromatic protons being strongly deshielded by neighboring pseudoequatorial sulfur atoms.

8 $\xrightarrow[\text{BF}_4^-]{\text{(MeO)}_2\text{CH}}$

Me—S⁺ Me ⁺S—Me
Me
2BF₄⁻

9

$\xrightarrow[\text{THF}]{\text{NaH}}$

MeS Me SMe

10

Hₐ MeS Hᵦ
Me
Hₑ
H_d
Me
Hᵦ Hₐ
SMe

11

The mixture **10** was again methylated to give the *anti*-bis(sulfonium) salt **12** in 90% yield. Again various conditions were investigated for effecting the Hofmann elimination reaction but, in the case of **12**, the best procedure was the use of potassium *tert*-butoxide in boiling tetrahydrofuran. This gave, after isolation and purification, pure *trans*-15,16-dimethyldihydropyrene (**14**) in yields of 75–80%. Thus, the conversion of the *anti*-2,11-dithia-9,18-dimethyl[3.3]cyclophane (**8**) to *trans*-15,16-dimethyldihydropyrene (**14**) is conveniently accomplished by a two-stage operation (Stevens rearrangement and Hofmann elimination) in overall yields of 63–68%.

In all of the experiments on the Hofmann elimination of **12**, when the course of the reaction was monitored using nmr, it could be shown that the first product formed was the *anti*-8,16-dimethyl[2.2]metacyclophane-1,9-diene (**13**). The signals shown by **13** are an AB_2 triplet at τ 3.00 (2 H, $J = 7.5$ Hz, Hₐ), an AB_2 doublet at 3.40 (4 H, $J = 7.5$ Hz, Hᵦ), a singlet at 3.72

10 $\xrightarrow[\text{BF}_4^-]{\text{(MeO)}_2\text{CH}}$ Me₂S⁺ Me ⁺SMe₂
Me
2BF₄⁻ $\xrightarrow[\text{THF}]{\text{KOC}_4\text{H}_9}$

12

Hₐ
Hᵦ
Hₑ
Me
Me

⇌

Me Me

13 **14**

(4 H, Hₑ), and a singlet at 8.45 (6 H, CH₃). After chromatography over silica gel, the *trans*-15,16-dimethyldihydropyrene (**14**) is free of the presence of the diene **13**, as measured by nmr. On the other hand, as has been reported previously,[5,24] either irradiation or heating of **14** causes valence tautomerization to **13**.

In addition to **14** there could also be isolated from the Hofmann elimination reaction varying amounts of the sulfide **15**. Under the conditions cited above the yield of **15** was only 7%. However, when **12** was treated with potassium *tert*-butoxide in boiling *tert*-butyl alcohol, the yield of *trans*-15,16-dimethyldihydropyrene (**14**) was only 38% and the yield of **15** was 60%. It is somewhat surprising that the displacement reaction leading to **15** should be competitive with the elimination reaction. However, it was shown that **15** could be converted on to **14** by irradiation in the presence of base. Presumably, irradiation of **15** gives the valence tautomer **16**, which then readily undergoes a base-catalyzed elimination of methyl mercaptan to generate the aromatic **14**.

Hᵦ
Me
H_d
Hᵥ
Me
Hₑ
SMe

⇌

$\xleftarrow{h\nu}$ Me Me SMe
H

$\xrightarrow{-\text{CH}_3\text{SH}}$ **14**

15 **16**
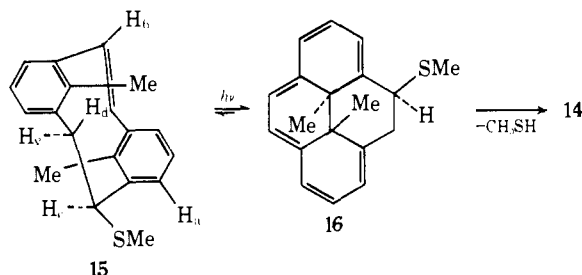
In view of the fact that previous studies with *syn*-[2.2]metacyclophane-1,9-dienes have not led to the isolation of cis dihydropyrenes as discrete entities,[25–28] it was of interest to see whether the syn isomer **7** could be converted *via* the two stage Stevens rearrangement–Hofmann elimination sequence to *cis*-15,16-dimethyldihydropyrene (**21**). Treatment of **7** with dimethoxy-carbonium fluoroborate gave the corresponding *syn*-bis(sulfonium) salt **17** in 83% yield. When **17** was stirred with sodium hydride in tetrahydrofuran, the Stevens rearrangement occurred in essentially quantita-

(24) H.-R. Blattmann and W. Schmidt, *Tetrahedron*, **26**, 5885 (1970).
(25) B. A. Hess, Jr., A. S. Bailey, B. Bartusek, and V. Boekelheide, *J. Amer. Chem. Soc.*, **91**, 1665 (1969).
(26) B. A. Hess, Jr., and V. Boekelheide, *J. Amer. Chem. Soc.*, **91**, 1672 (1969).
(27) H. B. Renfroe, *J. Amer. Chem. Soc.*, **90**, 2194 (1968).
(28) V. Boekelheide and R. A. Hollins, *J. Org. Chem.*, **36**, 2437 (1971).

tive overall yield, but the product was a mixture of the anti and syn isomers (**10** and **18**) in a ratio of 3:1, as measured by nmr. The differences in chemical shift for the internal methyls of the syn and anti isomers (τ 7.7–8.2 vs. 9.0–9.5) makes this an easy analysis.

7 $\xrightarrow[\text{BF}_4^-]{\text{(MeO)}_2\text{CH}}$ **17** $\xrightarrow[\text{THF}]{\text{NaH}}$ **18** + **10**
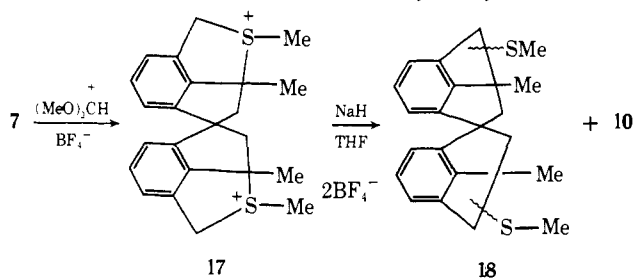
Although the isomerization of the major portion of the cyclophane **17** from syn to anti during the Stevens rearrangement was unexpected, it is in accord with the postulate of an open intermediate, diradical or ionic, which by flipping from syn to anti provides relief from the high degree of strain in the syn conformer. Invoking a diradical intermediate such as **19**, one can visualize the isomerization to **20** as shown below.


17 → **19** → **20** → **10**
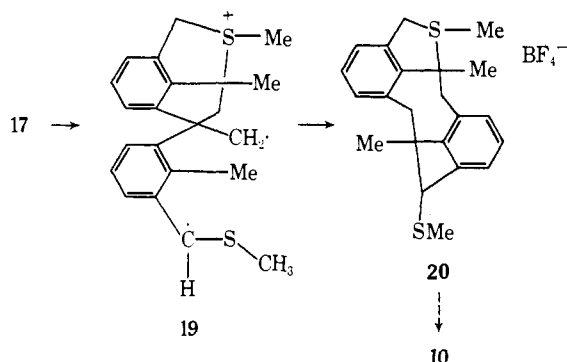
The mixture of **10** and **18** was again methylated and, without further purification, was subjected to a Hofmann elimination using potassium *tert*-butoxide in tetrahydrofuran. Isolation of the products by chromatography over alumina led to two separate green bands. The first of these was present in 28% yield and was shown to be *trans*-15,16-dimethyldihydropyrene (**14**). The second compound, isolated in 10% yield, proved to be the desired *cis*-15,16-dimethyldihydropyrene (**21**). Since the ratio of the trans to cis dihydropyrene isomers is approximately the same as the ratio of the anti to syn cyclophanes, it would appear that the Hofmann elimination has occurred without further conformational isomerization.

10 and 18 $\xrightarrow[\text{2. }t\text{-C}_4\text{H}_9\text{OK}]{\text{1. (MeO)}_2\text{CH}^+}$ **21** + **14**
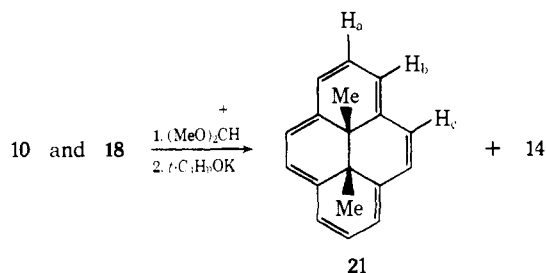
Molecular models of *cis*-15,16-dimethyldihydropyrene (**21**) indicate that the perimeter is quite planar with the molecule having the overall shape of a shallow saucer. The internal methyls of **21** would be expected to be farther out from the center of the plane than in the trans case, and in accord with this, the signal for the chemical

shift of their protons in the nmr appears as a singlet at τ 12.06, whereas the corresponding signal for the trans isomer is at τ 14.25. The aromatic peripheral protons of **21** appear as a singlet at τ 1.26 (4 H, H_c), an AB_2 doublet at 1.76 (4 H, $J = 8$ Hz, H_b), and an AB_2 triplet at 2.50 (2 H, $J = 8$ Hz, H_a), in close analogy to the values found for **14**. Likewise, the ultraviolet and visible spectrum of **21** is very similar to that of the trans isomer **14** but with lower extinction coefficients and a small shift of the maxima to shorter wavelengths. Thus, the absorption maxima for *cis*-15,16-dimethyldihydropyrene (**21**) are at 310 nm (ϵ 5300), 328 (22,400), 335 (15,800), 355 (11,600), 396 (1130), 420 (1740), 439 (3820), 506 (26), 564 (62), 581 (66), and 601 (70).[29] Again, similar to the trans isomer **14**, the fragmentation pattern of the mass spectrum of *cis*-15,16-dimethyldihydropyrene (**21**) showed sequential loss of the internal methyl groups with the molecular ion of pyrene providing the most intense peak.

One of the most striking features of *trans*-15,16-dimethyldihydropyrene (**14**) is its reversible valence tautomerization to the corresponding *anti*-cyclophane-1,9-diene (**14** $\rightleftharpoons$ **13**) on heating or exposure to light.[5,24] Even though both processes occur readily and, apparently, in a concerted fashion,[30] the rules regarding conservation of orbital symmetry[31] predict the photochemical process to be allowed and the thermal process to be forbidden. For the cis isomer **21**, the conservation of orbital symmetry rules would predict the reverse with the thermal valence tautomerization to *syn*-cyclophane-1,9-diene (**22**) being an allowed process whereas the photochemical isomerization would be forbidden. In fact, we have no experimental evidence that a reversible tautomerization to **22** occurs either thermally or photochemically. Irradiation of **21** led to a slow and irreversible loss of color, suggesting a photochemical decomposition but with no indication of any formation of **22**.[32]

21 $\nrightarrow$ **22**
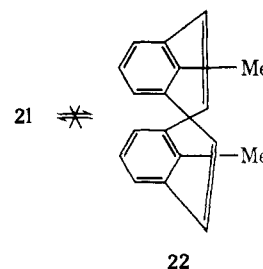
The preparation of the parent compound in this series, *trans*-15,16-dihydropyrene (**35**), has been long sought.[33]

(29) The comparative ultraviolet and visible spectra of *cis*- and *trans*-15,16-dimethyldihydropyrenes (**14** and **21**) are presented in the preliminary announcement describing the synthesis of **21**; see R. H. Mitchell and V. Boekelheide, *Chem. Commun.*, 1555 (1970).

(30) W. Schmidt, *Helv. Chim. Acta*, **54**, 862 (1971).

(31) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

(32) *trans*-15,16-Dimethyldihydropyrene (**14**) undergoes a thermal rearrangement [V. Boekelheide and E. Sturm, *J. Amer. Chem. Soc.*, **91**, 902 (1969)] which has been interpreted as a 1,5-sigmatropic shift. It would be expected that this type of thermal rearrangement would be even more facile in the cis series.

(33) W. Neunhoeffer and W. Woggen [*Angew. Chem.*, **68**, 386 (1956)] speculated that a blue-green substance resulting from a sodium reduction of pyrene might be **35**. Their subsequent investigations [*Justus Liebigs Ann. Chem.*, **600**, 34 (1956); *ibid.*, **612**, 98 (1958)], as well as our own experiments, gave no encouragement to the possibility of preparing **35** this way. In fact, the sodium reduction of pyrene followed by mild air oxidation gives the interesting 1,9-trimethylenephenalenyl radical: F. Gerson, E. Heilbronner, H. A. Reddoch, D. H. Paskovich, and N. C. Das, *Helv. Chim. Acta*, **50**, 813 (1967)).

It was of interest, therefore, to see whether the Stevens rearrangement–Hofmann sequence could be employed to achieve this goal. The reaction of *m*-xylylene dibromide (23) with 1,3-bis(mercaptomethyl)benzene (24) in aqueous ethanol gave 2,11-dithia[3.3]metacyclophane (25) in 80% yield. The fact that halides condense with mercaptide anions to give medium-sized rings in excellent yield without employing high dilution procedures is a very real advantage for using these cyclic sulfides as starting materials.[34] The nmr spectrum of 2,11-dithia[3.3]metacyclophane (25) shows the methylene protons as a singlet at τ 6.28, which remains unchanged even when the solution is cooled to −90°. Thus, the energy barrier to conformational flipping between the syn and anti isomers of 25 is quite small.[35]
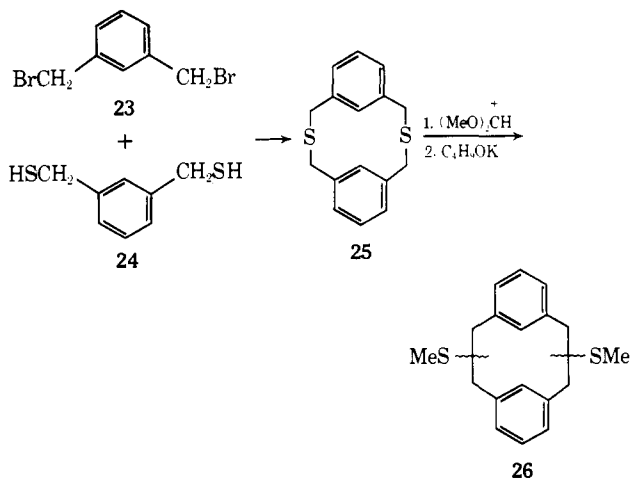

Methylation of 25 with dimethoxycarbonium fluoroborate gave the corresponding sulfonium salt and this, on treatment with potassium *tert*-butoxide in tetrahydrofuran, underwent the Stevens rearrangement to give 26 as a mixture of isomers in essentially quantitative yield overall. Chromatography of 26 permitted separation and isolation of each of the four components of the mixture in a pure state. Based on nmr spectral evidence (see Experimental Section), structures 27–30 have been assigned to the individual isomers with their relative percentage yields being 28, 45, 10, and 17%, respectively.

For further characterization, each of the individual isomers, 27–30, was converted to the corresponding bis(sulfonium) salt by reaction with dimethoxycarbonium fluoroborate. However, for preparative purposes, the mixture of isomers (26) was simply methylated directly and the resulting mixture of bis(sulfonium) salts was treated with potassium *tert*-butoxide in tetrahydrofuran. Chromatographic work-up gave the Hofmann elimination product, *anti*-[2.2]metacyclophane-1,9-diene

(34) The procedure described in the Experimental for preparing 25 has by now been employed for the syntheses of a number of different dithiacyclophanes with the yields observed being in the range of 75–90% [J. A. Lawson, R. DuVernet, and V. Boekelheide, *J. Amer. Chem. Soc.*, **95**, 956 (1973); V. Boekelheide, O. Wennerstrom, and R. DuVernet, unpublished work]. F. Vogtle [*Chem. Ind. (London)*, 346 (1972)] has described a high dilution apparatus which appears to be quite useful for synthesizing dioxocyclophanes but in our experience is not necessary in most instances for preparing dithiacyclophanes.

(35) T. Sato, M. Wakabayashi, M. Kainosho, and K. Hata, *Tetrahedron Lett.*, 4185 (1968), have previously described the preparation of 25 and reported on its ease of conformational flipping. This has also been described by F. Vögtle and L. Schunder, *Chem. Ber.*, **102**, 2677 (1969).
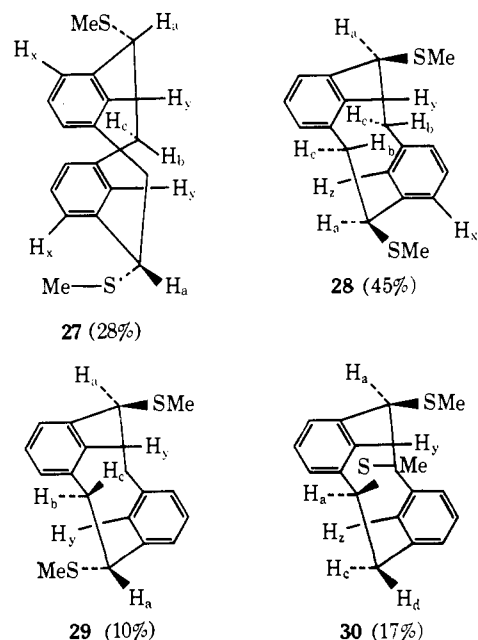
(31), in 35% yield, plus two other products corresponding to a single elimination–Stevens rearrangement (32, 31%) and a double Stevens rearrangement (33, 19%).
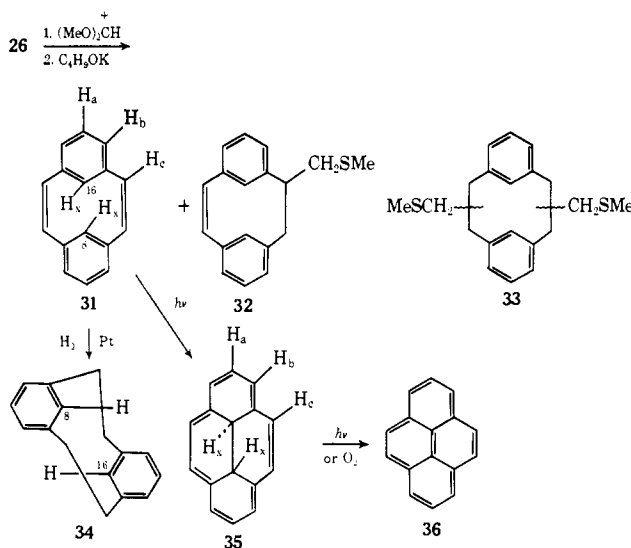
The spectral properties of 31 are clearly in agreement with its assignment as *anti*-[2.2]metacyclophane-1,9-diene. The compound shows a single absorption band at 280 nm (ε 28,000) in the ultraviolet. Its nmr spectrum has a singlet at τ 2.10 (2 H, H_x), an AB_2 multiplet at 2.99 (2 H, H_a), an AB_2 multiplet at 3.40 (4 H, H_b), and a singlet at 3.78 (4 H, H_c). The mass spectrum of 31 shows a signal for the parent molecular ion, followed by sequential loss of two hydrogens with the pyrene molecular ion being the most intense signal in the spectrum. Hydrogenation of 31 over a platinum catalyst gave the known *anti*-[2.2]metacyclophane (34) in quantitative yield.

Finally, an X-ray crystallographic examination of *anti*-[2.2]metacyclophane-1,9-diene (31) by Hansen and Röhrl has confirmed its structure.[36] The X-ray data show 31 to be much more flattened out than *anti*-[2.2]-

(36) A. W. Hanson and M. Röhrl, *Acta Crystallogr., Sect. B*, **28**, 2032 (1972).

metacyclophane (34). Thus, the distance between the 8 and 16 carbons of 34 is 2.69 Å,[37] whereas in 31 the separation is only 2.57 Å.[38] One of the striking spectral differences between 31 and 34 is the chemical shift of the internal protons at the 8 and 16 positions. In 34 the signal for these protons appears at τ 5.75, whereas in 31 it appears at τ 2.10. The magnitude of the downfield shift of these protons in going from 34 to 31 is too large to be simply explained as due to the anisotropy of the bridging olefinic linkages and a large part of the downfield shift must come from the flattening out of the molecule in 31 which moves the internal protons from being near the center of the opposite aromatic ring, as in 34, to a position nearer the edge where the ring current effect is smaller.

The fact that anti-[2.2]metacyclophane-1,9-diene (31) can be isolated after chromatography and be studied as a pure, crystalline compound is rather in contrast to the 8,16-dialkyl[2.2]metacyclophane-1,9-dienes which spontaneously isomerize to the corresponding trans-15,16-dihydropyrenes. It is not clear whether the equilibrium in the valence tautomerization of 31 $\rightleftharpoons$ 35 strongly favors 31 or whether the energy of activation for the valence tautomerization of 31 $\rightarrow$ 35 is very much higher than is the case for the 8,16-dialkyl derivatives. When the pale yellow crystals of 31 are sealed in a capillary melting point tube and placed in a bath at a temperature a few degrees from their melting point, they immediately become a deep green and melt sharply at 119–120°. If the bath is cooled to allow the melt to solidify and then reheated, the green solid melts over a range indicating the presence of a mixture. This suggests that at 120° thermal isomerization of 31 to 35 is occurring very readily. However, if the green melt is maintained at 120° for a few minutes, the green color is lost and the predominant product is pyrene plus some tetrahydro and higher hydrogenated pyrene derivatives. Heating a sample of 31 in the presence of air likewise results in a rapid conversion to pyrene (36).

The possible valence tautomerization of 31 by irradiation was next investigated. When a sample of 31 in carefully degassed cyclohexane was exposed to light of 2537 Å, the solution became a deep green. Nmr analysis of the solution after 1.5 hr of irradiation indicated the presence of a mixture containing 60% trans-15,16-dihydropyrene (35), 35% of pyrene (36), and 5% of the starting diene (31). The nmr spectrum of pure 36 could be simulated by computer subtraction of the pyrene signals from the observed spectrum, and it shows a singlet at τ 1.42 (4 H, H_c), an AB_2 doublet at 1.50 (4 H, $J = 7.5$ Hz, H_b), an AB_2 multiplet at 1.98–2.11 (2 H, $J = 7.5$ Hz, H_a), and a singlet at 15.49 (2 H, H_x).[39] The ultraviolet and visible spectrum of 35, based on measurements of irradiated, degassed cyclohexane solutions of 31, showed absorption maxima at 623 nm (ϵ 590), 607 (515), 595 (543), 582 (305), 571 (248), 566 (183), 553 (120), 523.5 (139), 516 (130), 506 (103), 497 (110), 444 (9700), 432 (9300), 412 (7300), 394 (7200),

361 (36,000), 355 (25,000), 325 (29,000), 305 (25,000), 272 (22,000), and 262 (15,000).

Prolonged irradiation of the degassed cyclohexane solutions resulted in the complete conversion of 35 to pyrene (36). Similarly, exposing solutions of 35 to air led to a rapid, but not instantaneous, oxidation to pyrene. On the other hand, sealed solutions of 35 in degassed cyclohexane can be stored more or less indefinitely at 0° without change. When solutions of 35 were warmed to 80° or higher, fairly rapid loss of color occurred, apparently due to a thermal rearrangement of the type mentioned previously.[32]

Although 26 was a mixture of both syn and anti isomers, only the anti-[2.2]metacyclophane-1,9-diene (31) was obtained by the Hofmann elimination and none of the corresponding syn isomer. Surprisingly, when the pure syn isomer 27, or each of the other pure anti isomers, was subjected separately to the conditions of Hofmann elimination, the results were the same, only the anti diene 31 is formed. Even though the energy barrier for the conformational flip of anti-[2.2]metacyclophane to syn-[2.2]metacyclophane is known to be quite large, being at least 28 kcal/mol,[35] the barrier for conformational flip from syn to anti is apparently rather small.[40] In the present instance it is not clear whether the transformation of syn isomer 27 to anti isomer 31 is the result of a conformational flip or a bond-breaking, bond-remaking process. Actually, the syn isomer 27 is unexpectedly stable thermally. In an nmr study a sample of 27 in perchlorobutadiene was heated to 190° and showed no change.

In the light of these results an attempt was made to convert 27 by desulfurization with Raney nickel to the syn-[2.2]metacyclophane, a still unknown, but much sought-after, compound. However, instead, the product, which formed in quantitative yield, was the anti-[2.2]metacyclophane (34).

In an attempt to avoid the possibility of conformational flip, the Raney nickel desulfurization of the syn-8,16-dimethyl derivative 18 was investigated. Again the resulting 8,16-dimethyl[2.2]metacyclophane was entirely the anti isomer 37 with no evidence for the presence of any of the syn isomer.
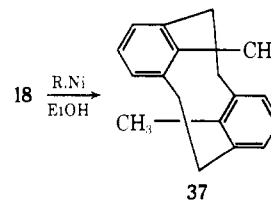
Since Raney nickel desulfurizations presumably involve radical intermediates and these radicals might undergo easy conformational flip, we investigated alternate methods of desulfurization. When the syn isomer 27 was allowed to react with sodium in liquid ammonia for 90 sec, it gave the anti isomer 34 plus compounds 38 and 39. With longer reaction times the yield of 34 fell and the yields of 38 and 39 increased. This is in accord with the postulate that 38 and 39 are actually being formed through the Birch reduction of anti-[2.2]metacyclophane (34).[41]

(37) C. J. Brown, J. Chem. Soc., 3278 (1953).

(38) It should be noted that prior to the availability of the X-ray results, W. Schmidt [Helv. Chim. Acta, 54, 862 (1971)] made an extended Hückel calculation of the energy surface of 31 as the distance between the 8 and 16 positions was varied from 1.53 to 2.70 A. By this calculation a minimum occurs at 2.55 Å.

(39) In a preliminary publication [R. H. Mitchell and V. Boekelheide J. Amer. Chem. Soc., 92, 3510 (1970)] the simulated and experimental spectra of 35 are presented.

(40) V. Boekelheide and R. A. Hollins, J. Amer. Chem. Soc., 95, 3201 (1973).

(41) J. Reiner and W. Jenny [Helv. Chim. Acta, 52, 1624 (1969)] have recently reported that the Birch reduction of 34 gives 39.

27 $\xrightarrow{\text{Na/NH}_3}$ 34 + [structure] + [structure]

38   39
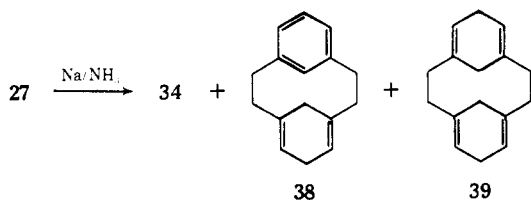
Experimental Section[42]

Stevens Rearrangement of Dibenzyl Sulfide (1). A solution of 2.14 g of dibenzyl sulfide[43] (10 mmol) in 5 ml of dichloromethane was added to 12.5 mmol of dimethoxycarbonium fluoroborate reagent[13b] in 3 ml of dichloromethane at room temperature under an atmosphere of nitrogen. This gave 3.15 g (100%) of **2** which, after recrystallization from ethyl acetate, melted at 115–116°. It decomposed on standing and so was used directly. A suspension of 500 mg of **2** and 84 mg of sodium hydride in 10 ml of dry tetrahydrofuran was stirred at room temperature under nitrogen for 22 hr. After addition of dilute aqueous acid the mixture was extracted with ether. The ether extract was washed with water, dried, and concentrated. The resulting oil was chromatographed over silica gel using a 1:9 benzene–petroleum ether (30–60°) mixture for elution. The first fraction (18 mg) was shown by its nmr spectrum to be bibenzyl. The second fraction gave 204 mg (57%) of a colorless oil whose spectral properties indicated it to be the Sommelet product **4**: nmr multiplet at τ 2.2–3.0 (9 H, ArH), a singlet at 4.75 (1 H, CH), a singlet at 7.70 (3 H, CH$_3$), and a singlet at 8.07 (3 H, SCH$_3$); mass spectrum (70 eV), m/e (rel intensity) 228 (8) and 181 (100).

Anal. Calcd for C$_{15}$H$_{16}$S: C, 78.92; H, 7.06; S, 14.02. Found: C, 79.03; H, 7.20; S, 13.89.

The third fraction from the chromatography gave 74 mg (21%) of a colorless oil, whose spectral properties are in accord with the Stevens rearrangement product **3**: nmr multiplet at τ 2.6–3.0 (10 H, ArH), a triplet at 4.08 (1 H, $J = 7$ Hz, CH), a doublet at 6.77 (2 H, $J = 7$ Hz, –CH$_2$–), and a singlet at 8.18 (3 H, SCH$_3$); mass spectrum (70 eV) m/e (rel intensity) 228 (8), 181 (14), 180 (9), and 137 (100).

Anal. Calcd for C$_{15}$H$_{16}$S: C, 78.92; H, 7.06. Found: C, 78.77; H, 7.25.

Alternate Synthesis of 2,6-Bis(bromomethyl)toluene (5). A. **2-Methylisophthalaldehyde.** To a solution of 24.2 g of 2,6-dicyanotoluene[44] in 200 ml of dry benzene under a nitrogen atmosphere there was added dropwise with stirring at room temperature 290 ml of a 20% solution of di(isobutyl)aluminum hydride in hexane. After the addition was complete, the deep orange solution was allowed to stir an additional hour at room temperature before being decomposed by the careful successive additions of 40 ml of methanol, 60 ml of a 1:1 aqueous methanol solution, and finally 220 ml of a 4 N aqueous solution of hydrochloric acid. After extraction of the resulting mixture with ether, the ether extract was washed with water, dried, and concentrated to give 25.2 g (99%) of colorless crystals. A sample, recrystallized from methanol, yielded colorless needles: mp 101–102°; nmr a singlet at τ −0.50 (2 H, CH=O), an AB$_2$ multiplet at 1.8–2.7 (3 H, ArH), and a singlet at 6.96 (3 H, CH$_3$).

Anal. Calcd for C$_9$H$_8$O$_2$: C, 72.96; H, 5.44. Found: C, 72.97; H, 5.54.

B. **2,6-Bis(hydroxymethyl)toluene.** A solution of 25.0 g of 2-methylisophthalaldehyde in 180 ml of dry tetrahydrofuran was added to a slurry of 4.3 g of sodium borohydride in 50 ml of dry tetrahydrofuran with stirring at room temperature. After the

mixture had been stirred at room temperature for 2 hr, it was decomposed by addition of 100 ml of 3 N aqueous hydrochloric acid. After extraction of the mixture with ether, the ether extract was washed with water, dried, and concentrated to give 23.2 g (92%) of colorless crystals, mp 123–124°, identical in all respects with an authentic sample of 2,6-bis(hydroxymethyl)toluene.[45] The conversion of 2,6-bis(hydroxymethyl)toluene to **5** proceeded in 95% yield following the procedure given previously.[45]

2,6-Bis(mercaptomethyl)toluene (6). A. 2,6-Bis(isothiouroniummethyl)toluene Dibromide. To a hot solution of 7.6 g of thiourea in 75 ml of alcohol there was added portionwise with stirring 13.9 g of 2,6-bis(bromomethyl)toluene (**5**). An exothermic reaction ensued and, after addition was complete, the mixture was boiled under reflux an additional 30 min. When the solution was concentrated to half-volume and cooled, there separated 19 g (89%) of white crystals, mp 242–243°.

Anal. Calcd for C$_{11}$H$_{18}$S$_2$N$_4$Br$_2$: C, 30.71; H, 4.22; N, 13.03. Found: C, 30.06; H, 4.37; N, 13.12.

B. **Hydrolysis of 2,6-Bis(isothiouroniummethyl)toluene Dibromide.** A solution of 12.7 g of 2,6-bis(isothiouroniummethyl)toluene dibromide in a mixture of 51.5 g of potassium hydroxide in 140 ml of water was boiled under reflux for 5 hr. The mixture was then cooled, 60 ml of 9 M aqueous sulfuric acid was added, and the whole was extracted with ether. The ether extract was washed with water, dried, and concentrated to give 5.3 g (99%) of a crystalline solid. A sample was recrystallized from a benzene–hexane mixture to yield colorless needles: mp 40–41°; nmr a singlet at τ 2.94 (3 H, ArH), a doublet at 6.36 (4 H, $J = 7$ Hz, –CH$_2$–), a singlet at 7.68 (3 H, CH$_3$), and a triplet at 8.39 (2 H, $J = 7$ Hz, SH); mass spectrum (70 eV) m/e (rel intensity) 184 (40), 151 (38), 150 (45), and 117 (100); ir (neat) 2560 cm^{-1} (–SH).

Anal. Calcd for C$_9$H$_{12}$S$_2$: C, 58.69; H, 6.57; S, 34.75. Found: C, 58.75; H, 6.35; S, 34.70.

Coupling of 5 and 6. A solution of 13.9 g of 2,6-bis(bromomethyl)toluene (**5**) in 350 ml of a 4:1 ethanol–benzene mixture was placed in one Hershberg funnel and 9.2 g of 2,6-bis(mercaptomethyl)toluene (**6**) in 300 ml of ethanol containing 4 g of sodium hydroxide dissolved in 65 ml of water was placed in a second Hershberg funnel. The solutions from the two Hershberg funnels were then added dropwise simultaneously, and at the same rate, to 1 l. of vigorously boiling ethanol. When the addition was complete (12 hr), the solution was boiled an additional 2 hr before being cooled and concentrated. Dichloromethane and water were added to the residue. The dichloromethane extract was washed with water, dried, and concentrated. The residue was preabsorbed on a silica gel column and eluted using a 1:1 mixture of benzene–petroleum ether (bp 30–60°). This chromatography gave four fractions: the first consisted of a mixture of **7** and **8** while the remaining three were products of higher molecular weight.

A. *anti*-9,18-Dimethyl-2,11-dithia[3.3]metacyclophane (8). The mixture of **7** and **8** obtained from the first fraction from the chromatography experiment above was recrystallized from benzene. This gave the principal portion as pure crystals of the anti isomer **8**. The residue from them other liquors was then rechromatographed over silica gel using a 3:7 benzene–petroleum ether (30–60°) mixture for elution. The crystals from the first fraction eluted were combined with the previous sample of **8** and recrystallized from benzene to give 2.35 g (15.7%) of colorless crystals, mp 260–265°; uv (EtOH) 256 nm (ϵ 2340), 278 (1580), 300 (895), and 350 (35, tail); nmr a multiplet at τ 2.6–3.0 (6 H, ArH), a singlet at 6.32 (8 H, –CH$_2$–), and a singlet at 8.70 (6 H, CH$_3$); mass spectrum (70 eV) m/e (rel intensity) 300 (100), 266 (8), 151 (54), 150 (30), 149 (48), 148 (45), and 147 (42).

Anal. Calcd for C$_{18}$H$_{20}$S$_2$: C, 71.98; H, 6.71; S, 21.31. Found: C, 72.02; H, 6.78; S, 21.61.

B. *syn*-9,18-Dimethyl-2,11-dithia[3.3]metacyclophane (7). The solid isolated from the second fraction of the above experiment was recrystallized from a 1:9 benzene–hexane mixture to give 215 mg (1.4%) of colorless crystals: mp 238–240°; uv (EtOH) 235 nm (ϵ 5600), 260 (3500), 295 (247), and 350 (28, tail); nmr a singlet at τ 3.41 (6 H, ArH), an AB quartet with the A doublet at 6.00 (4 H, $J = 14$ Hz, –CH$_2$–) and the B doublet at 6.20 (4 H, $J = 14$ Hz, –CH$_2$–), and a singlet at 7.49 (6 H, CH$_3$); mass spectrum (70 eV) m/e (rel intensity) 300 (100), 266 (29), 235 (18), 180 (18), 150 (125), 149 (85), 148 (130), 147 (115), and 146 (111).

(42) Elemental and mass spectral analyses were determined by Dr· S. Rottschaefer, University of Oregon Microanalytical Laboratories. Melting points are uncorrected and were taken with a Mel-Temp apparatus; infrared spectra were measured with a Beckman IR-5$_a$ or IR-7 instrument; visible and ultraviolet spectra with a Cary 15; nmr spectra were measured using deuteriochloroform with tetramethylsilane as an internal standard, unless otherwise specified, and were obtained with a Varian A-60, HA-100, or XL-100 instrument; and mass spectra with a Consolidated Model 21-110 spectrometer. We thank the National Science Foundation for funds used toward the purchase of the Varian XL-100.

(43) R. L. Shriner, *J. Amer. Chem. Soc.*, **52**, 2066 (1930).

(44) Prepared in 57% yield by the von Braun reaction of 2,6-dichlorotoluene with cuprous cyanide following the procedure of M. S. Newman, "Organic Syntheses," Collect. Vol. 3, Wiley, New York, N. Y., 1955, p 631.

(45) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *J. Amer. Chem. Soc.*, **83**, 943 (1961).

Anal. Calcd for C₁₈H₂₀S₂: C, 71.98; H, 6.71; S, 21.31. Found: C, 71.89; H, 6.73; S, 21.42.
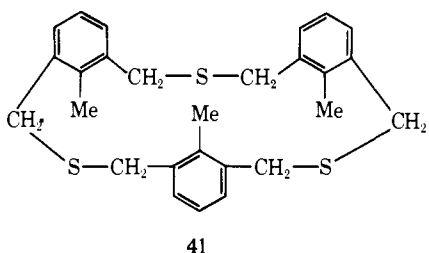
C. Cyclic Trimer Disulfide 40.

The second fraction from the

40
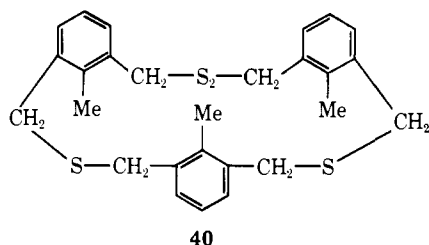
original chromatography described above gave a crystalline solid to which structure **40** has been assigned based on its composition and spectral properties. Recrystallization from a benzene–hexane mixture gave 150 mg (1%) of white crystals: mp 208–209°; nmr a singlet at τ 2.86 (9 H, Ar*H*), three singlets at 6.25, 6.38, and 6.43 (4 H each, CH₂), a singlet at 7.80 (3 H, CH₃ remote from –SS–), and a singlet at 8.24 (6 H, CH₃ near –SS–); mass spectrum (70 eV) *m/e* (rel intensity) 482 (100).

Anal. Calcd for C₂₇H₃₀S₄: C, 67.20; H, 6.27; S, 26.53. Found: C, 67.37; H, 6.31; S, 26.76.

D. Cyclic Trimer 41.

The third fraction eluted from the

41

original chromatography described above gave a crystalline solid to which structure **41** has been assigned. Recrystallization from a benzene–hexane mixture gave 1.23 g (8%) of colorless needles: mp 220–221°; nmr, a singlet at τ 2.89 (9 H, Ar*H*), a singlet at 6.37 (12 H, –CH₂–), and a singlet at 8.20 (9 H, CH₃); mass spectrum (70 eV) *m/e* (rel intensity) 450 (100).

Anal. Calcd for C₂₇H₃₀S₃: C, 71.98; H, 6.27; S, 21.31. Found: C, 72.16; H, 6.69; S, 21.54.

E. Cyclic Tetramer 42.

The fourth fraction from the original

42
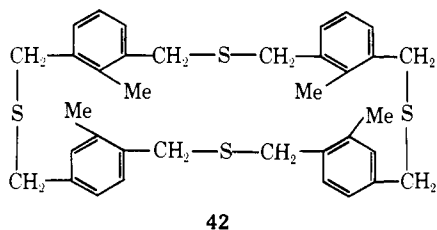
chromatography described above gave crystals to which structure **42** has been assigned. Recrystallization from benzene gave 600 mg (4%) of colorless crystals: mp 200–202°; mass spectrum (70 eV) *m/e* (rel intensity) 600 (69), 481 (40), 449 (50), and 270 (100).

Anal. Calcd for C₃₆H₄₀S₄: C, 71.98; H, 6.71; S, 21.31. Found: C, 71.84; H, 6.74; S, 21.25.

Although the coupling of **5** and **6** to give **7** and **8** appears to be the preferred procedure, their preparation can also be accomplished by the reaction of 2,6-bis(bromomethyl)toluene (**5**) with sodium sulfide. When 27.8 g of **5** in 700 ml of benzene was added dropwise with stirring simultaneously with addition from a second Hershberg funnel of a solution of 26 g of sodium sulfide nonahydrate in 700 ml of aqueous ethanol (200 ml of water and 500 ml of ethanol) to a boiling solution of 1 l. of ethanol and the reaction mixture was worked up as before, there was obtained 1.81 g of **8** and 252 mg (1.7%) of **7**.

anti-Bis(sulfonium) Salt (**9**). A solution of 4.0 g of *anti*-8,16-dimethyl-2,11-dithia[3.3]metacyclophane (**8**) in 150 ml of dichloromethane was added slowly with stirring to a suspension of 6.7 g of dimethoxycarbonium fluoroborate in 10 ml of dichloromethane held at −30° under a nitrogen atmosphere. When the addition was complete, the mixture was allowed to warm to room temperature and was stirred another 4 hr. After addition of 30 ml of

ethyl acetate to dissolve excess reagent, the solid product was collected by filtration, giving 6.65 g (99%) of an off-white powder, mp 210° dec (turns red); nmr (DMSO-*d*₆) a multiplet at τ 2.1–2.8 (6 H, Ar*H*), multiplet at 4.6–5.9 (8 H, –CH₂–), a singlet at 6.72 (6 H, SCH₃), and a singlet at 8.95 (6 H, CH₃).

Anal. Calcd for C₂₀H₂₆S₂B₂F₈: C, 47.65; H, 5.20; S, 12.70. Found: C, 46.86; H, 5.19; S, 13.02.

Stevens Rearrangement of 9 to give 10. To a stirred suspension of 6.65 g of **9** in 250 ml of dry tetrahydrofuran under a nitrogen atmosphere there was added 3.25 g of solid potassium *tert*-butoxide. The mixture was stirred for 5 min and then aqueous 6 *N* hydrochloric acid, water, and dichloromethane were added. The dichloromethane layer was separated, washed with water, dried, and concentrated. The crystalline residue **10** weighed 4.08 g (94%) and could be used directly in the next step, the Hofmann elimination. When a portion of the product, the mixture of isomers represented by **10**, was chromatographed over silica gel using a 2:5 benzene–petroleum ether (30–60°) mixture for elution, the first main fraction of eluate gave crystals consisting of single isomer (**11**). Recrystallization of these from a cyclohexane–hexane mixture gave colorless needles (about 40% of **10**): mp 213–214°; nmr a triplet at τ 2.24 (2 H, $J = 7$ Hz, H$_a$, deshielded by SMe), a multiplet at 2.7–3.2 (4 H, Ar*H*), a double doublet at 5.98 (2 H, $J_{b-c} = 3.5$ Hz, $J_{b-d} = 12$ Hz, H$_b$), a double doublet at 6.79 (2 H, $J_{c-b} = 3.5$ Hz, $J_{c-d} = 12$ Hz, H$_c$), a coincidental double doublet at 7.38 (2 H, $J_{d-c} = 12$ Hz, $J_{d-b} = 12$ Hz, H$_d$), a singlet at 7.87 (6 H, SCH₃), and a singlet at 9.36 (6 H, CH₃); mass spectrum (70 eV) *m/e* (rel intensity) 328 (100), 280 (43), and 265 (33).

Anal. Calcd for C₂₀H₂₄S₂: C, 73.14; H, 7.37; S, 19.49. Found: C, 73.03; H, 7.32; S, 19.51.

The Stevens rearrangement of **9** to **10** was also carried out by allowing 151 mg of **9** to react with a suspension of 30 mg of sodium hydride in dry tetrahydrofuran. Work-up, as before, gave 98 mg (100%) of **10**, identical in its properties with that prepared above.

anti-Bis(sulfonium)Salt (**12**). A solution of 4.08 g of the mixture of isomers **10** in 60 ml of dichloromethane was added with stirring to a suspension of 5.6 g of dimethoxycarbonium fluoroborate in 10 ml of dichloromethane held at −30° under an atmosphere of nitrogen. The mixture was allowed to warm to room temperature and was stirred an additional 4 hr. Then 40 ml of ethyl acetate was added, the mixture was stirred, and the solvent was decanted. Fresh ethyl acetate (100 ml) was added to the oily residue and it was stirred for 2 hr more. The resulting crystalline precipitate was collected and dried, giving 5.90 g (90%) of off-white crystals, mp dec at 300° with loss of dimethyl sulfide; nmr (DMSO-*d*₆) a multiplet at τ 2.5–3.3 (6 H, Ar*H*), a double doublet at 5.50 (2 H, $J_1 = 11$ Hz, $J_2 = 4$ Hz, –CHS–), a multiplet at 6.6–7.5 (4 H, –CH₂–), singlets at 6.89 and 7.31 (6 H each, –S(Me$_a$)Me$_b$), and a singlet at 9.49 (6 H, CH₃).

Anal. Calcd for C₂₂H₃₀S₂B₂F₈: C, 49.64; H, 5.68; S, 12.05. Found: C, 49.53; H, 5.72; S, 12.28.

Hofmann Elimination of 12 to give *trans*-15,16-Dimethyldihydropyrene (14) and *anti*-10-Methylthio[2.2]metacyclophan-1-ene (15). To a solution of 3.75 g of potassium *tert*-butoxide in 200 ml of tetrahydrofuran there was added with stirring 5.9 g of **12**. After the mixture has been stirred at room temperature under a nitrogen atmosphere for 4 hr, benzene was added and the mixture was made acidic by addition of dilute aqueous hydrochloric acid. The organic layer was separated, washed with water, dried, and concentrated. An nmr spectrum of the crystalline green residue showed the expected signals for *trans*-15,16-dimethyldihydropyrene (**14**),[46] but in addition showed strong signals of an *AB*₂ triplet at τ 3.00 (2 H, $J = 7.5$ Hz, H$_a$), an *AB*₂ doublet at 3.40 (4 H, $J = 7.5$ Hz, H$_b$), a singlet at 3.72 (4 H, H$_c$), and a singlet at 8.45 (6 H, CH₃), corresponding to the presence of *anti*-8,16-dimethyl[2.2]metacyclophane-1,9-diene (**13**).

The crystalline residue was taken up in a few ml of benzene, impregnated on a silica gel column, and eluted with petroleum ether. The first main fraction of eluate contained 1.93 g (75%) of dark green crystals, mp 119–120°, identical in all respects with an authentic sample of **14**.[46] Later fractions gave 162 mg (6%) of a yellow oil corresponding to **15**. When the Hofmann reaction with **12** was carried out using sodium hydride in boiling tetrahydrofuran, the yield of **14** was 80%.

However, when 50 mg of **12** was stirred with 112 mg of potassium *tert*-butoxide in boiling *tert*-butyl alcohol for 30 min and the mixture

(46) V. Boekelheide and J. B. Phillips, *J. Amer. Chem. Soc.*, **89**, 1695 (1967).

was worked up as before, the yield of **14** was only 8 mg (38%) whereas that of **15** was 27 mg (60%). Finally, repetition of this last experiment at room temperature gave almost entirely **15**: nmr a double doublet at τ 2.41 (1 H, $J_1 = 7$ Hz, $J_2 = 1.5$ Hz, H$_a$), a multiplet at 2.8–3.3 (5 H, ArH), a singlet at 3.44 (2 H, H$_b$), a double doublet at 6.26 (1 H, $J_{c-e} = 11$ Hz, $J_{c-d} = 3.5$ Hz, H$_c$), a double doublet at 6.92 (1 H, $J_{d-e} = 12$ Hz, $J_{d-c} = 3.5$ Hz, H$_d$), a double doublet at 7.58 (1 H, $J_{e-d} = 12$ Hz, $J_{e-c} = 11$ Hz, H$_e$), a singlet at 7.92 (3 H, SCH$_3$), and a singlet at 9.24 (6 H, CH$_3$); mass spectrum (70 eV) m/e 280.

Anal. Calcd for C$_{19}$H$_{20}$S: C, 81.40; H, 7.19; S, 11.41. Found: C, 80.54; H, 7.03; S, 11.09.

A solution of 60 mg of **15** and 500 mg of potassium *tert*-butoxide in 250 ml of *tert*-butyl alcohol was irradiated in a quartz tube under nitrogen with light of wavelength 2537 Å for 6 hr. Removal of solvent followed by chromatography of the residue over silica gel gave 18 mg (36%) of **14** as green crystals, mp 119–120°, identical in all respects with an authentic sample.[46]

Stevens Rearrangement and Hofmann Elimination Sequence with 7 to give *cis*-15,16-Dimethyldihydropyrene (21). A. *syn*-Bis(sulfonium) Salt 17. A solution of 252 mg of **7** in 7 ml of dichloromethane was added with stirring to a suspension of 425 mg of dimethoxycarbonium fluoroborate in 2 ml of dichloromethane held at −30° under a nitrogen atmosphere. The mixture was warmed to room temperature and stirred for 4 hr before adding 5 ml of ethyl acetate to dissolve excess methylating agent. The white granular precipitate was collected by filtration, washed with ethyl acetate, and dried to give 350 mg (83%) of crystals: mp dec with loss of dimethyl sulfide; nmr (DMSO-d_6) a multiplet at τ 3.0–3.2 (6 H, ArH), an AB quartet at 4.86 and 5.15 (8 H, $J_{AB} = 13.5$ Hz, –CH$_2$–), a singlet at 6.81 (6 H, SCH$_3$), and a singlet at 7.37 (6 H, CH$_3$). Due to the easy loss of dimethyl sulfide **17** did not give a satisfactory elemental analysis.

B. Stevens Rearrangement of 17. To a stirred suspension of 32 mg of sodium hydride in 60 ml of dry tetrahydrofuran there was added 220 mg of **17**. The mixture was stirred for 9 hr before acidifying with aqueous hydrochloric acid and adding dichloromethane. The organic layer was separated, washed with water, dried, and concentrated. The oily residue weighed 145 mg (100%) and its spectral properties indicated it to be a mixture of the isomers represented by **10** and **18**. Since the signals for the internal methyl protons of the anti isomer **18** appear between τ 9.0–9.5, integration of the areas of these signals made readily possible the conclusion that the ratio of anti to syn isomers (**10–18**) was 3:1. Because of the large number of isomers present and the difficulties of their separation, the mixture of **10** and **18** was used directly in the Hofmann elimination step.

C. Hofmann Elimination of 10 and 18 to give 14 and 21. A solution of 145 mg of the mixture of isomers (**10** and **18**) from the above experiment in 5 ml of dichloromethane was added with stirring to a suspension of 220 mg of dimethoxycarbonium fluoroborate held at −30° under a nitrogen atmosphere. The mixture was allowed to warm to room temperature and stirred an additional 4 hr before adding 10 ml of ethyl acetate. The solvent was decanted and an additional 20 ml of ethyl acetate was added to the oily residue. After this suspension had been stirred for 2 hr, the white powdery precipitate was collected and dried to give 205 mg (88%) of a mixture of the bis(sulfonium) salts of **10** and **18** as an off-white powder.

To a solution of 100 mg of the mixture of bis(sulfonium) salts of **10** and **18** in 50 ml of dry tetrahydrofuran there was added 55 mg of potassium *tert*-butoxide and the resulting mixture was stirred under nitrogen at room temperature for 1 hr. Then, 50 ml of petroleum ether (30–60°) and 60 ml of 2 N aqueous hydrochloric acid were added successively. The organic layer was separated, washed with water, dried, and concentrated. The resulting green, crystalline residue was taken up in petroleum ether and chromatographed over alumina (Woelm neutral, activity II). The fraction of eluate containing the first bright green band was collected and concentrated to give 12.3 mg (28%) of dark green crystals, mp 119–120°, identical in all respects with an authentic specimen of *trans*-15,16-dimethyldihydropyrene (**14**).[46]

The fraction of eluate containing the second green band from the column was collected and concentrated to give 4.3 mg (10%) of *cis*-15,16-dimethyldihydropyrene (**21**). Sublimation at room temperature of the crystalline residue gave dark green crystals: mp 90–95°; uv (cyclohexane) 310 nm (ϵ 5300), 328 (22,400), 335 (15,800), 355 (11,600), 396 (1130), 420 (1740), 439 (15,800), 506 (26), 564 (62), 581 (66), and 6.02 (70); nmr a singlet at τ 1.26 (4 H, H$_c$), an AB_2 doublet at 1.76 (4 H, $J = 8$ Hz, H$_b$), an AB_2 triplet at 2.50

(2 H, $J = 8$ Hz, H$_a$), and a singlet at 12.06 (6 H, CH$_3$); mass spectrum, m/e (rel intensity) 232 (20), 217 (47), and 202 (100).

Anal. Calcd molecular weight for C$_{18}$H$_{16}$: 232.125. Found (high resolution mass spectrum): 232.124.

2,11-Dithia[3.3]metacyclophane (25).[47] To a solution of 3.2 g of sodium hydroxide in a mixture of 30 ml of water and 50 ml of ethanol there was added 7.3 g of 1,3-bis(mercaptomethyl)benzene (**24**) under nitrogen and the mixture was warmed gently until it became clear. It was then diluted by addition of 500 ml of ethanol and placed in a Hershberg funnel attached to one arm of a three-necked flask. A solution of 10.0 g of *m*-xylylene dibromide (**23**) in 500 ml of benzene was then placed in a Hershberg funnel attached to the second side arm. The solutions from the two Hershberg funnels were added simultaneously and dropwise with vigorous stirring to 1.5 l. of boiling ethanol under nitrogen in the flask. When the addition was complete (12 hr), the reaction mixture was concentrated and the residue was extracted with dichloromethane. After the dichloromethane extract was washed with water, dried, and concentrated, the crystalline residue was chromatographed over silica gel using a 1:1 benzene–petroleum ether (30–60°) mixture for elution. The main eluate fraction gave 8.2 g (80%) of white crystals, mp 119–121°. Recrystallization of a sample from cyclohexane gave long, colorless needles: mp 122–123°; nmr an apparent doublet at τ 3.12 (6 H, $J = 1$ Hz, ArH), a singlet at 3.24 (2 H, internal ArH), and a singlet at 6.28 (8 H, CH$_2$); mass spectrum (70 eV) m/e (rel intensity) 272 (100), 167 (20), 137 (54), 136 (46), and 135 (28).

Anal. Calcd for C$_{16}$H$_{16}$S$_2$: C, 70.57; H, 5.92; S, 23.50. Found: C, 70.44; H, 5.71; S, 23.78.

The formation of 2,11-dithia[3.3]metacyclophane (**25**) could also be accomplished by the reaction of *m*-xylylene dibromide (**23**) with sodium sulfide. In this case a solution of 25.0 g of **23** in 600 ml of benzene was added from one Hershberg funnel and 25 g of sodium sulfide nonahydrate in 550 ml of 70% aqueous ethanol from the other to 1 l. of boiling ethanol. Work-up as before gave 6.0 g (48%) of **25** as colorless needles, mp 122–123°, identical in all respects with the previous specimen. In this case, though, further elution of the column gave 1.3 g (10%) of fluffy, colorless needles: mp 124–125°; nmr an apparent doublet at τ 2.74 (9 H, $J = 1.5$ Hz, ArH), a singlet at 2.91 (3 H, internal ArH), and a singlet at 6.48 (12 H, –CH$_2$–); mass spectrum (70 eV) m/e (rel intensity) 408 (100), 303 (35), and 271 (100). On the basis of this spectral data and its elemental composition this product has been assigned the cyclic trimer structure **43**.
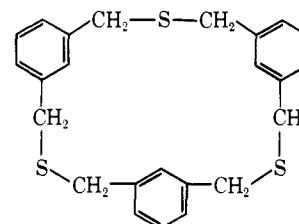

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Anal. Calcd for C$_{24}$H$_{24}$S$_3$: C, 70.57; H, 5.92; S, 23.50. Found: C, 70.34; H, 5.89; S, 23.69.

Still further elution of the column yielded a third product. This, after recrystallization from a benzene–cyclohexane mixture, gave 260 mg (2%)·of colorless needles: mp 161–162°; nmr a multiplet at τ 2.8–2.9 (12 H, ArH), a singlet at 2.97 (4 H, internal ArH), and a singlet at 6.43 (16 H, –CH$_2$–); mass spectrum (70 eV) m/e (rel intensity) 544 (100). This has been assigned the structure of the cyclic tetramer **44**.

Anal. Calcd for C$_{32}$H$_{32}$S$_4$: C, 70.57; H, 5.92; S, 23.50. Found: C, 69.75; H, 6.04; S, 23.68.

Stevens Rearrangement of 25 to 26. A. 2,11-Dithia[3.3]metacyclophane Bis(methosulfonium) Fluoroborate. A solution of 5.6 g of 2,11-dithia[3.3]metacyclophane (**25**) in 30 ml of dichloromethane was added to a stirred suspension of 11.6 g of dimethoxycarbonium fluoroborate in 10 ml of dichloromethane at −30° under nitrogen. After the mixture had stirred for 4 hr, 30 ml of ethyl acetate was added and the mixture was stirred an additional 30 min. The crystalline precipitate was collected, washed with ethyl acetate, and dried, giving 9.8 g of a white powder: mp 200° dec; nmr, broad

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(47) We thank Mr. C.-T. Tsai for repeating this procedure and providing some improvements.

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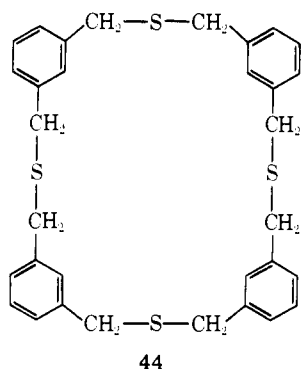
singlet at τ 2.48 (2 H, internal ArH), a multiplet at 2.6–3.0 (6 H, ArH), an AB double doublet at 5.04 and 5.19 (8 H, J = 13 Hz, CH$_2$S$^+$), and singlets at 6.73 and 6.86 (6 H, S$^+$CH$_3$).

Anal. Calcd for C$_{18}$H$_{22}$S$_2$B$_2$F$_8$: C, 45.41; H, 4.66; S, 13.47. Found: C, 45.32; H, 4.71; S, 13.19.

B. Stevens Rearrangement. To a stirred suspension of 9.5 g of 2,11-dithia[3.3]metacyclophane bis(methosulfonium) fluoroborate in 250 ml of dry tetrahydrofuran there was added with stirring 6.7 g of potassium *tert*-butoxide. After the mixture had been stirred at room temperature for 10 min, it was made acidic with aqueous hydrochloric acid and dichloromethane was added. The organic layer was separated, washed with water, dried, and concentrated. The residue was taken up in benzene, impregnated on a short silica gel column, and eluted with a 1:1 benzene–petroleum ether (30–60°) mixture. This gave 6.0 g (100%) of **26** as crystals consisting of a mixture of isomers **27–30**. For use in the next step the mixture of crystals (**26**) could be used directly.

However, to separate the individual components a 1.0-g sample of **26** was chromatographed over silica gel using a 1:3 benzene–petroleum ether (30–60°) mixture for elution. The first eluate fraction provided a crystalline solid (**27**) which, after recrystallization from a cyclohexane–hexane mixture, gave 280 mg (28%) of colorless needles: mp 166–167°; uv (Et$_2$O) 277 nm (ϵ 480); nmr a multiplet at τ 2.3–2.5 (2 H, H$_x$), a triplet at 2.66 (2 H, J = 7 Hz, H$_y$), a multiplet at 2.8–3.1 (4 H, ArH), a double doublet at 5.70 (2 H, J_{a-b} = J_{a-c} = 15 Hz, H$_a$), a multiple at 6.6–6.9 (4 H, H$_b$ and H$_c$), and a singlet at 7.90 (6 H, SCH$_3$); mass spectrum (70 eV) m/e (rel intensity) 300 (17), 285 (3), 206 (17), 205 (73), 204 (100), 203 (52), and 202 (94). This isomer has been assigned the syn conformation **27** because the internal aromatic protons are in the normal region and do not show the dramatic upfield shift characteristic of the anti isomers. Since this isomer shows a single SCH$_3$ signal, the environment of the two SCH$_3$ groups must be the same. Furthermore, the H$_x$ protons show a marked downfield shift as would be expected for deshielding by a neighboring pseudoequatorial sulfur atom. These data are best accommodated by structure **27**.

Anal. Calcd for C$_{18}$H$_{20}$S$_2$: C, 71.98; H, 6.71; S, 21.31. Found: C, 71.78; H, 6.90; S, 21.12.

The second eluate fraction gave 460 mg (46%) of **28** which, after recrystallization from a cyclohexane–hexane mixture, was obtained as colorless needles: mp 132–133°; nmr a doublet of triplets at τ 2.38 (1 H, J_{ortho} = 7 Hz, J_{meta} = 1.5 hz, H$_x$], a multiplet at 2.6–3.1 (5 H, ArH), singlets at 5.16 and 5.61 (1 H each, H$_y$ and J$_z$), a multiplet at 5.6–5.8 (2 H, H$_a$), a multiplet at 6.6–6.9 (3 H, H$_b$), a quartet at 7.47 (1 H, J_{b-c} = 12 Hz, J_{a-c} = 4.5 Hz, H$_c$), a singlet at 7.89 (3 H, SCH$_3$ equatorial), and a singlet at 8.11 (3 H, SCH$_3$ axial); mass spectrum (70 eV) m/e (rel intensity) 300 (46), 285 (6), 206 (31), 205 (38), 204 (58), 203 (100), and 202 (58). This isomer has been assigned the anti conformation **28**. The upfield shift of the internal protons (H$_y$ and H$_z$ at τ 5.16 and 5.61) clearly require the anti conformation. The two SCH$_3$ groups are clearly different—the equatorial SCH$_3$ deshielding an aromatic proton (H$_x$) and the axial SCH$_3$ deshielding an internal aromatic proton (H$_y$). These data are best accommodated by structure **28**.

Anal. Calcd for C$_{18}$H$_{20}$S$_2$: C, 71.98; H, 6.71; S, 21.31. Found: C, 71.96; H, 6.58; S, 21.39.

The third eluate fraction gave 100 mg (10%) of **29** which, after recrystallization from cyclohexane, was obtained as colorless crystals: mp 219–220° dec; uv (Et$_2$O) 272 nm (ϵ 835); nmr multiplet at τ 2.7–3.0 (6 H, ArH), singlet at 5.02 (2 H, H$_y$), a double doublet at 5.68 (2 H, J_{a-c} = 5 Hz, J_{a-b} = 2.5 Hz, H$_a$), a quartet at 6.79 (2 H, J_{b-c} = 13.5 Hz, J_{b-a} = 2.5 Hz, H$_b$), a quartet at 7.39 (2 H, J_{c-b} = 13.5 Hz, J_{c-a} = 5 Hz, H$_c$), and a singlet at 8.08 (6 H, SCH$_3$); mass spectrum (70 eV) m/e (rel intensity) 300 (42), 285 (5), 206 (31),

205 (43), 204 (60), 203 (100), and 202 (56). The upfield shift of the internal protons and their appearance as a singlet require this isomer to have a symmetrical anti conformation. Since there is no downfield aromatic signal as would be expected if an equatorial SCH$_3$ group were present, the SCH$_3$ groups must be axial and so the only isomer accommodating these data is **29**.

Anal. Calcd for C$_{18}$H$_{20}$S$_2$: C, 71.98; H, 6.71; S, 21.31. Found: C, 71.93; H, 6.54; S, 21.13.

The fourth fraction of eluate gave 180 mg (18%) of **30** which, after recrystallization from a cyclohexane–hexane mixture, was obtained as colorless crystals: mp 216–218° dec; uv (Et$_2$O) 258 nm (ϵ 1060), 273 (660, sh), 318 (60, sh), and 354 (47); nmr a multiplet at τ 2.7–3.1 (6 H, ArH), singlet at 4.43 (1 H, H$_y$), singlet at 5.67 (1 H, H$_z$), a quartet at 5.68 (2 H, J_{a-c} = 5 Hz, J_{a-b} = 2.5 Hz, H$_a$), a double doublet at 6.82 (2 H, J_{b-c} = 13 Hz, J_{b-a} = 2.5 Hz, H$_b$), a quartet at 7.45 (2 H, J_{c-b} = 13 Hz, J_{c-a} = 5 Hz, H$_c$), and a singlet at 8.09 (6 H, SCH$_3$). The singlet for the SCH$_3$ groups indicates the molecule is symmetrical, while the high field signal for the internal protons confirms the anti conformation. The fact that H$_y$ is at markedly lower field than H$_z$ indicates both SCH$_3$ groups are adjacent to the same ring. Since there is no downfield aromatic proton signal due to pseudoequatorial SCH$_3$ deshielding, both SCH$_3$ groups must be pseudoaxial. These data are best accommodated by structure **30**.

Anal. Calcd for C$_{18}$H$_{20}$S$_2$: C, 71.98; H, 6.71; S, 21.31. Found: C, 71.68; H, 6.69; S, 21.38.

Hofmann Elimination of 26 to give *anti*-[2.2]Metacyclophane-1,9-diene (31) plus 32 and 33. A solution of 6.8 g of the mixture of isomers **26** in 40 ml of dichloromethane was added at −30° to a stirred suspension of 12.9 g of dimethoxycarbonium fluoroborate in 10 ml of dichloromethane under nitrogen. After the mixture had stirred for 4 hr while warming to room temperature, 20 ml of ethyl acetate was added with continued stirring for an additional 15 min. The solvent was removed by decantation and the oily residue was triturated with ethyl acetate effecting the separation of 10.9 g (96%) of the bis(sulfonium) salt as white crystals. These were employed directly in the next step. To a solution of 10.9 g of the bis(sulfonium) salt in 300 ml of dry tetrahydrofuran there was added 14.0 g of potassium *tert*-butoxide. The mixture was allowed to stir at room temperature for 3 hr.

Benzene was added and the mixture was acidified with aqueous hydrochloric acid. After the organic layer was separated, it was washed with water, dried, and concentrated. The pale green residue was taken up in petroleum ether (30–60°) and chromatographed over silica gel. The first fraction of eluate contained 1.54 g of *anti*-[2.2]metacyclophane-1,9-diene (**31**). This was carefully recrystallized from petroleum ether (45°) under nitrogen to give large, pale-yellow crystals: mp 119–120° (sealed capillary placed in the bath at 112°), instantly turning green; uv (cyclohexane) 280 nm (ϵ 28,000); nmr a singlet at τ 2.10 (2 H, H$_x$), an AB_2 multiplet at 2.99 (2 H, H$_a$), an AB_2 multiplet at 3.40 (4 H, H$_b$), and a singlet at 3.78 (4 H, H$_c$); mass spectrum (70 eV) m/e (rel intensity) 204 (25), 203 (62), 202 (100), 102 (5), 101.5 (9), 101 (42), 100.5 (8), and 100 (20).

Anal. Calcd for C$_{16}$H$_{12}$: C, 94.08; H, 5.92. Found: C, 94.00; H, 6.11.

The second fraction of eluate gave 1.70 g of an unstable yellow oil which has been assigned structure **32**, as a mixture of isomers. Its spectral properties were: nmr a multiplet at τ 2.2–3.8 (7 H, ArH), a multiplet at 4.0–4.3 (3 H, two vinyl protons plus a shielded ArH), two doublets at 6.06 and 6.27 (1 H, J = 7.5 Hz, J = 6.5 Hz, –CHCH$_2$S–), a multiplet at 6.67–7.2 (2 H, –CH$_2$–), multiplet at 7.4–7.9 (2 H, –CH$_2$S–), and a singlet at 8.51 (3 H, SCH$_3$); mass spectrum (70 eV) m/e (rel intensity) 266 (70), 205 (100), 204 (27), 203 (93), and 202 (83). The compound rapidly decomposed to a black oil and satisfactory elemental analyses were not obtained.

The next fraction of eluate gave 1.36 g (19%) of a yellow oil which, on treatment with ethanol, yielded pale yellow crystals, mp 144–150°. On the basis of their spectral properties these crystals have been assigned the mixture of isomers represented by **33**. The nmr spectrum of **33** showed a multiplet at τ 2.5–4.5 (8 H, ArH), a multiplet at 5.0–6.4 (2 H, –CHCH$_2$–), a multiplet at 6.5–7.4 (4 H, ArCH$_2$), a multiplet at 7.4–8.1 (4 H, –CH$_2$S–), and singlets at 7.94 and 8.32 (3 H each, SCH$_3$); mass spectrum (70 eV) m/e (rel/intensity) 328 (35), 267 (55), 220 (100), 205 (48), 204 (41), 203 (66), and 202 (53). These crystals were unstable, darkening quickly, and satisfactory elemental analyses were not obtained.

When the Hofmann elimination, as described above, was carried out with 100 mg of the pure *syn*-bis(sulfonium) salt derived from **27**, there was isolated 16 mg (35%) of *anti*-[2.2]metacyclophane-1,9-

diene (30) but no evidence of the corresponding *syn*-[2.2] metacyclo-phane-1,9-diene could be found. Similarly, subjecting the other pure isomers (28, 29, and 30) to the conditions of the Hofmann elimination gave essentially the same results as with 27.

Hydrogenation of *anti*-[2.2]Metacyclophane-1,9-diene (31) to *anti*-[2.2]Metacyclophane (34). A solution of 10 mg of 31 in 15 ml of ethyl acetate was subjected to hydrogenation over a prereduced platinum catalyst at room temperature and atmospheric pressure. After removed of the solvent and catalyst, the residual crystals melted at 131–132° and were identical in all respects with an authentic specimen of *anti*-[2.2]metacyclophane (34).

Irradiation of 31 to Give *trans*-15,16-Dihydropyrene (35). A sample of 6 mg of *anti*-[2.2]metacyclophane-1,9-diene (31) was sealed under vacuum in 0.5 ml of carefully degassed cyclohexane. The tube was irradiated with light of 2537 Å from a 6 W source (Ultraviolet Products PCOXI). The course of the reaction was monitored by nmr and after 1.5 hr the maximum concentration of 35 had developed. At that point the nmr analysis indicated the relative constituents as 60% *trans*-15,16-dihydropyrene (35), 35% pyrene (36), and 5% of unchanged *anti*-[2.2]metacyclophane-1,9-diene (30). By computer subtraction the nmr spectra of 36 and 31 could be removed from the experimental spectrum and a simulated spectrum of 35 obtained.[39] The simulated nmr spectrum of 35 showed a singlet at τ 1.42 (4 H, H$_c$), a doublet at 1.50 (4 H, J = 7.5 Hz, H$_b$), a multiplet at 1.98–2.11 (2 H, H$_a$), and a singlet at 15.49 (2 H, H$_x$).

To obtain the ultraviolet and visible spectra of 35 samples of various sizes of 30 were sealed in carefully degassed cyclohexane in quartz ultraviolet cells. The individual samples were then irradiated for varying lengths of time and their spectra taken. By combining and analyzing these data minimal extinction coefficients could be projected for each maximum as follows: 623 nm (ϵ 590), 607 (515), 595 (543), 582 (305), 571 (248), 566 (183), 553 (120), 523.5 (139), 516 (130), 506 (103), 497 (110), 444 (9700), 432 (9300), 412 (7300), 394 (7200), 361 (36,000), 355 (25,000), 325 (29,000), 305 (25,000), 272 (22,000), and 262 (15,000).

When sample tubes of 1 in degassed cyclohexane were irradiated for prolonged periods, the green color of 35 disappeared and the only product to be isolated was pyrene in quantitative yield.

Similarly, when a sample tube containing maximal amounts of 35 was opened and air was allowed to enter, the green color of the solution turned clear starting from the surface and extending to the bottom. Again the only product to be isolated was pyrene, formed in essentially quantitative yield.

When a sample of 31 sealed in degassed cyclohexane was irradiated to give about 60% of 35, as measured by nmr, warming the sealed sample at 80° for 12 hr caused a complete loss of color. The nmr spectrum of the product showed a multiplet at τ 2.6–2.9 (3 H, ArH), a multiplet at 2.9–3.2 with a singlet at 3.42 (7 H, CH=C), and a broad singlet at 4.39 (2 H, CHCH=C). This nmr spectrum is in reasonable accord with structure 45, the logical thermal product by

analogy to the thermal rearrangement of the *trans*-15,16-dialkyl-dihydropyrenes.[32]

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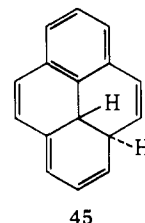
Raney Nickel Desulfurization of 27. A solution of 150 mg of 27 in 30 ml of ethanol containing W-7 Raney nickel was boiled under reflux for 6 hr. After removal of the catalyst and solvent, the residue was taken up in petroleum ether and chromatographed over silica gel. This gave 103 mg (99%) of colorless crystals, mp 131–132°, identical in all respects with an authentic sample of *anti*-[2.2]metacyclophane (34).

Raney Nickel Desulfurization of 10 and 18. A solution of 20 mg of the 3:1 mixture of 10 and 18 (see earlier experiment for the preparation of 18) in 15 ml of ethanol containing W-7 Raney nickel was boiled under reflux for 5 hr. After removal of the catalyst and solvent, the residue was recrystallized from hexane to give 11.5 mg (90%) of white crystals, mp 204–205°, identical in all respects with an authentic sample of *anti*-8,16-dimethyl[2.2]metacyclophane.[45]

Birch Reduction of 27. A solution of 50 mg of 27 in 5 ml of dry ether was added to 40 ml of a blue solution of liquid ammonia containing a chip of sodium. After 5 min ammonium chloride was added to discharge the blue color and the flask was warmed to room temperature. The residue was taken up in ether, washed successively with aqueous acid and water, dried, and concentrated. This residue was taken up in petroleum ether (30–60°) and chromatographed over silica gel. The first fraction of eluate gave 10.1 mg (20%) of colorless crystals, mp 106–107°; the melting point and nmr spectrum of this product are in full accord with the properties of 39, as reported by Reiner and Jenny.[41]

The second fraction of eluate gave 22 mg (66%) of an oil: nmr multiplet at τ 2.8–3.2 (4 H, ArH), a broad singlet at 4.25–4.45 (2 H, CH=C), and a multiplet at 7.0–8.6 (12 H, –CH$_2$–); mass spectrum (70 eV) m/e (rel intensity) 210 (49), 195 (7), 182 (30), 105 (100), and 91 (100). These spectral data are in accord with our assignment of structure 38 to this product. As further proof, a solution of 38 in benzene containing dichlorodicyanoquinone was boiled for 3 hr to effect aromatization and the only product to be isolated was *anti*-[2.2]metacyclophane in 91% yield.

The third fraction of eluate gave only a trace of 34.

When the Birch reduction of 27, as described above, was repeated but the reaction time was cut from 5 min to 60 sec, the yields of products were 38 (55%), 34 (42%), and 39 (trace).