Anal. Calcd for $C_{16}H_{10}F_2$: C, 79.99; H, 4.19. Found: C, 79.85; H, 4.16.

When compound **12**, isomeric to **6**, was converted to the corresponding bis(sulfonium) fluoroborate and subjected to the same conditions for the Hofmann elimination, as described above for the preparation of **7**, the reaction mixture became a deep green but turned colorless during work-up. The material isolated was a complex mixture whose nmr spectrum suggested the presence of pyrene and fluoropyrene derivatives.

Bis(sulfone) 8.—A mixture of 25 mg of **7** in 10 mg of glacial acetic acid containing 1 ml of 30% aqueous hydrogen peroxide was boiled under reflux for 24 hr. When the solution was allowed to cool, a crystalline solid separated. This was collected, washed with methanol, and dried to give 30 mg (100%) of a white powder: mp >350°; nmr ($AsCl_3$), a multiplet at τ 2.68 (4 H, ArH), a triplet at 3.15 (2 H, ArH), and an AB quartet at 5.52 and 5.94 (8 H, J = 14 Hz, $-CH_2SO_2-$).

Anal. Calcd for $C_{16}H_{14}O_4F_2S_2$: C, 51.60; H, 3.79. Found: C, 51.56; H, 3.75.

Pyrolysis of 8 to Give 9.—The bis(sulfone) **8** (75 mg) was placed in a pyrolysis flow system modeled after that described by Haenel and Staab.[15] The first furnace was at 340° and the second at 500° with the pyrolysis requiring 12 hr. The solid pyrolysate was recrystallized from cyclohexane to give 31 mg (64%) of white crystals: mp 156–158°; uv (cyclohexane) 272 nm (ϵ 700) and 279 (600); nmr ($CDCl_3$), a multiplet at τ 2.78–3.10 (6 H, ArH) and a multiplet at 7.26 (8 H, $-CH_2$); fluorine nmr (acetone-d_6) signal at +123.1 ppm relative to $CFCl_3$ as an internal standard; mass spectrum (70 eV) m/e (rel intensity) 244 (100), 224 (24), 223 (19), 203 (16), 202 (10), 201 (23), and 122 (32).

(15) M. Haenel and H. A. Staab, *Tetrahedron Lett.*, 3585 (1970).

Anal. Calcd for $C_{16}H_{14}F_2$: mol wt, 244.106. Found (high-resolution mass spectrometry): mol wt, 244.104 ± 0.01.

Hydrogenation of 7 to Give 9.—A mixture of 9 mg of *syn*-8,16-difluoro[2.2]metacyclophane-1,9-diene (**7**) and 15 mg of a prereduced platinum catalyst in 5 ml of ethyl acetate was subjected to hydrogenation at room temperature and atmospheric pressure. After removal of the catalyst and solvent, the residual solid was recrystallized from cyclohexane to give white crystals, mp 156–158°, identical in all respects with the sample of **9** described previously.

Thermolysis of *syn*-8,16-Difluoro[2.2]metacyclophane-1,9-diene (7) to Give 1-Fluoropyrene (11).—A solution of 40 mg of *syn*-8,16-difluoro[2.2]metacyclophane-1,9-diene (**7**) in 5 ml of dry tetrahydrofuran was carefully degassed and sealed in a pyrolysis tube. This was then heated at 120° for 68 hr. The tube was then opened and the contents were concentrated to give a crystalline solid. This was taken up in petroleum ether and chromatographed over silica gel to give 36 mg (98%) of white crystals, mp 136.5–138.0°, nmr ($CDCl_3$), a multiplet at τ 1.8–2.52.

Anal. Calcd for $C_{16}H_9F$: mol wt, 220.069. Found (high-resolution mass spectrometry): 220.067 ± 0.01.

The picrate derived from this material melted at 207–209° [Bavin and Dewar[11] give 135–136° for the melting point of 1-fluoropyrene (**11**) and 208–210° for the melting point of the corresponding picrate].

Registry No.—**3**, 25006-86-4; **4**, 25117-62-8; **4** bis(sulfonium) fluoroborate, 41560-37-6; **5**, 30736-36-8; **6**, 41563-60-4; **6** bis(sulfonium) fluoroborate, 41560-38-7; **7**, 41563-61-5; **8**, 41563-62-6; **9**, 22506-31-6; **11**, 1691-65-2; **12**, 41563-65-9; 2-fluoro-*m*-xylene, 443-88-9; *N*-bromosuccinimide, 128-08-5; 2,6-bis(mercaptomethyl)toluene, 41563-67-1; dimethoxycarbonium fluoroborate, 18346-68-4; potassium *tert*-butoxide, 865-47-4.

Attempted Syntheses of *trans*-15-Methyl-15,16-dihydropyrene[1]

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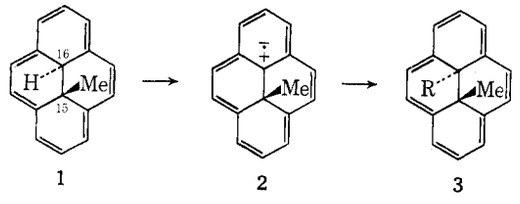
A possible synthesis of the potentially interesting *trans*-15-methyl-15,16-dihydropyrene (**1**) has been investigated by subjecting *anti*-9-methyl-2,11-dithia[3.3]metacyclophane to the two-step reaction sequence of a Stevens rearrangement and a Hofmann elimination. However, the only product isolated was pyrene. When the Hofmann elimination was conducted using a high vacuum train, the green mixture could be shown to contain radicals by esr measurements, and the loss of color accompanying the formation of pyrene resulted in evolution of methane, as shown by mass spectroscopy. Alternatively, the possible photoisomerization of 8-methyl[2.2]metaparacyclophane-1,9-diene (**18**) to **1** was attempted without success, even though the photoisomerization of 8-methyl[2.2]metaparacyclophane (**19**) to 8-methyl[2.2]metacyclophane (**21**) occurs smoothly and in good yield.

Theoretically, *trans*-15-methyl-15,16-dihydropyrene (**1**) is a molecule of high interest because of its possible conversion to the corresponding radical or ions (**2**). Not only would these species be of inherent interest for examination of their physical properties, but they could be valuable synthetic intermediates for preparing dihydropyrenes with substituents at the 16 position as shown by **3**. For these reasons we have studied several



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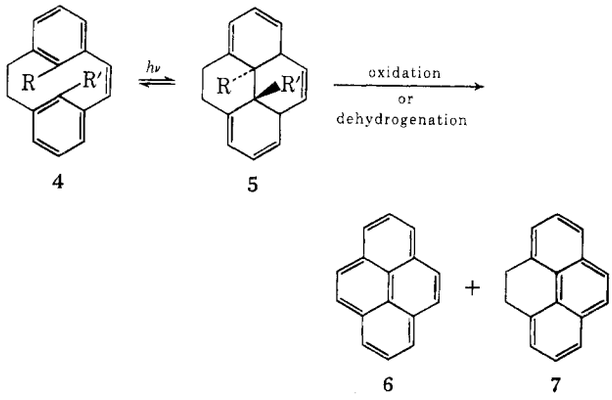
possible approaches which might lead to a synthesis of *trans*-15-methyl-15,16-dihydropyrene (**1**).

In an earlier study,[2,3] we had shown that [2,2]-metacyclophan-1-enes (**4**) are readily photoisomerized to the corresponding 4,5,15,16-tetrahydropyrenes (**5**). With both of the internal substituents being methyl (R = R′ = Me), dehydrogenation of **5** proceeded smoothly to give *trans*-15,16-dimethyldihydropyrene.



4 5 6 7

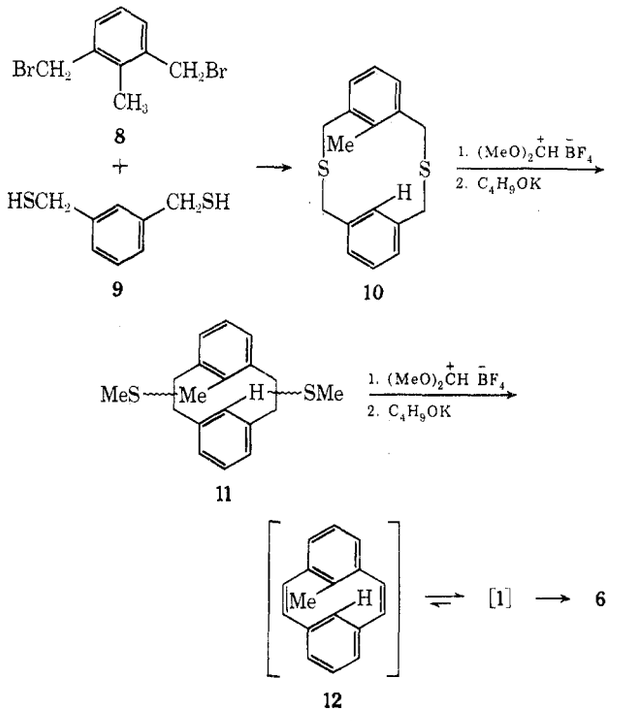
(1) We thank the National Science Foundation for their support of this investigation.

(2) H. Blaschke, C. E. Ramey, I. Calder, and V. Boekelheide, *J. Amer. Chem. Soc.*, **92**, 3675 (1970).

(3) C. E. Ramey and V. Boekelheide, *J. Amer. Chem. Soc.*, **92**, 3681 (1970).

However, when the internal substituents were both hydrogen (R = R′ = H) or hydrogen and methyl (R = H; R′ = Me), dehydrogenation as well as oxidation of **5** gave pyrene (**6**) and 4,5-dihydropyrene (**7**) as the major products. Thus, it was clear that the final step in a synthesis of **1** should be done with rigid exclusion of oxygen and should not require dehydrogenation agents.

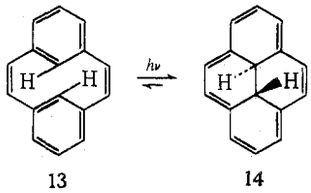
A method which appeared to fulfill these requirements was the two-step Stevens rearrangement and Hofmann elimination sequence developed for the synthesis of 15,16-dialkyldihydropyrenes.[4] For this purpose then, 9-methyl-2,11-dithia[3.3]metacyclophane (**10**) was prepared by the condensation of 2,6-bis(bromomethyl)toluene (**8**) and 1,3-bis(mercaptomethyl)-benzene (**9**).[5] Methylation of **10** using dimethoxycarbonium fluoroborate followed by reaction with potassium *tert*-butoxide in tetrahydrofuran gave the Stevens rearrangement product **11** in 65% yield as a mixture of stereoisomers. Methylation of **11** followed again by treatment with potassium *tert*-butoxide in tetrahydrofuran gave pyrene (**6**), presumably *via* **12** and **1** as intermediates.



In the case of *anti*-[2.2]metacyclophane-1,9-diene (**13**), where both internal substituents are hydrogen, valence tautomerization to *trans*-15,16-dihydropyrene does not occur spontaneously at room temperature and it is possible to isolate the pure compound and study its properties.[4,6] However, when both internal substituents are alkyl, valence tautomerization to the corresponding *trans*-15,16-dialkyldihydropyrene occurs spontaneously at room temperature.[7] In this respect, **12** appears to behave similarly to the *anti*-8,16-dialkyl[2.2]metacyclophane-1,9-dienes rather than to *anti*-[2.2]metacyclophane-1,9-diene (**13**) itself. To investigate whether oxygen was playing a role in the conversion of **12** to pyrene, the Hofmann elimination procedure was repeated using a high-vacuum train with rigid exclusion of oxygen. When the bis(methosulfonium) fluoroborate from **11** was added to potassium *tert*-butoxide in tetrahydrofuran under these conditions, a deep green solution developed, as might be expected for **1**. No useful nmr spectra of this solution were obtained, apparently because of broadening owing to the presence of radicals. An esr spectrum of the solution showed a broad symmetrical peak with a g value of 2.0059. As Bersohn and Thomas have shown,[8] peroxy radicals have g values in the range of 2.0140 to 2.0190, whereas alkyl and alkoxy radicals have g values of less than 2.0100. Although it was not possible to analyze the esr signal in terms of fine structure, the evidence is indicative of the presence of an R′ radical. The green color of the solution faded on standing and introduction of the gases from above the reaction mixture into a mass spectrometer produced an intense signal due to methane.

An attractive interpretation of these data is that **1** is being formed but is undergoing a rapid reaction with base to form the carbanion **2**. The carbanion **2**, in turn, can undergo loss of methyl radical to give the pyrene radical anion. The methyl radical by abstraction of hydrogen from **1** would give methane and the radical **2**, which could complete the cycle by giving pyrene and another methyl radical. Although attempts were made to avoid such a decomposition by using other bases or less than 1 equiv of base, these experiments were unsuccessful.

It would appear that a successful preparation of **1** and a study of its properties requires both the absence of oxygen and base. For the case of *trans*-15,16-dihydropyrene (**14**), a similarly sensitive compound, its synthesis was accomplished by irradiation of [2.2]-metacyclophane-1,9-diene (**13**) in carefully degassed

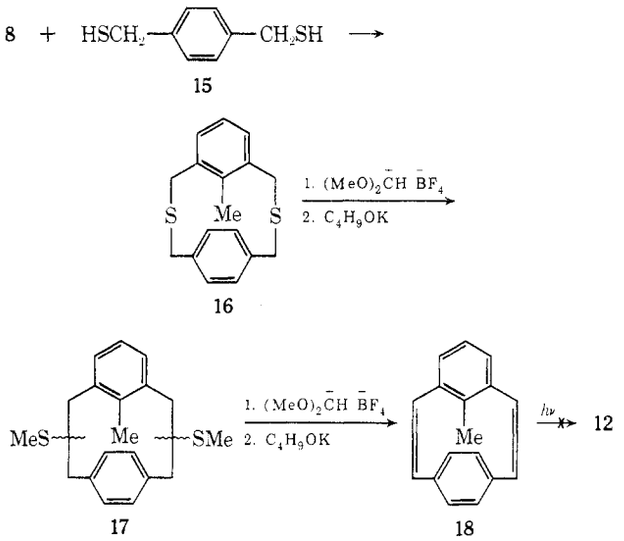


cyclohexane.[4,6] Recently, Cram and his collaborators have reported the photochemical rearrangement of [2.2]metaparacyclophanes to [2.2]metacyclophanes.[9] If a similar photochemical rearrangement of [2.2]metaparacyclophane-1,9-dienes were to occur, this would provide an attractive route to **1**, since the intermediate *anti*-8-methyl[2.2]metacyclophane-1,9-diene (**12**) could be generated under conditions of rigid exclusion of oxygen and base.

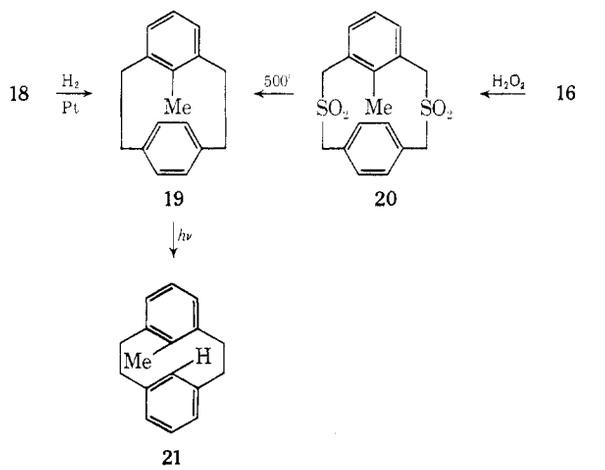
To investigate the possible synthesis of **1** by photochemical rearrangement, the synthesis of 8-methyl-[2.2]metaparacyclophane-1,9-diene (**18**) was undertaken. Condensation of 2,6-bis(bromomethyl)toluene (**8**) with 1,4-bis(mercaptomethyl)benzene (**15**) proceeded smoothly in good yield to give 9-methyl-2,11-

(4) R. H. Mitchell and V. Boekelheide, *Tetrahedron Lett.*, 1197 (1970).
(5) F. Vögtle and P. Neumann [*Tetrahedron*, **26**, 5299 (1970)] have previously reported syntheses of **10** and **16**.
(6) R. H. Mitchell and V. Boekelheide, *J. Amer. Chem. Soc.*, **92**, 3510 (1970).
(7) H.-R. Blattmann and W. Schmidt, *Tetrahedron*, **26**, 5885 (1970).
(8) M. Bersohn and J. R. Thomas, *J. Amer. Chem. Soc.*, **86**, 959 (1964).
(9) R. E. Gilman, M. H. Delton, and D. J. Cram, *J. Amer. Chem. Soc.*, **94**, 2478 (1972).

dithia[3.3]metaparacyclophane (**16**).[5] A Stevens rearrangement of **16** then led to **17**, as a mixture of stereoisomers, and a Hofmann elimination reaction with **17** readily gave the desired 8-methyl[2.2]metaparacyclophane-1,9-diene (**18**). Unfortunately, irradiation of a solution of **18** in carefully degassed cyclohexane with light of 254 nm was entirely without effect.[10]



To make certain that the conditions employed in the photochemical experiments were effective for the photochemical rearrangement of [2.2]metaparacyclophane to [2.2]metacyclophane, the synthesis was extended to prepare 8-methyl[2.2]metaparacyclophane (**19**) and study its behavior on irradiation. Catalytic hydrogenation of **18** readily gave 8-methyl[2.2]metaparacyclophane (**19**) in good yield. However, for preparing larger quantities of **19**, it was more convenient to oxidize **16** to the corresponding bis(sulfone) **20** and subject this to pyrolysis. Thermal decomposition of **20** proceeded smoothly at 500° to give **19** in 90% yield. Irradiation of a solution of **19** in cyclohexane with light of 254 nm for 4 hr readily gave 8-methyl[2.2]metacyclophane (**21**), identical in all respects with



an authentic sample,[2] in 47% yield. It is not clear why the [2.2]metaparacyclophane-1,9-dienes are unaffected by irradiation under conditions which cause a smooth rearrangement of the corresponding [2.2]metaparacyclophane to [2.2]metacyclophane.

(10) V. Boekelheide and P. H. Anderson (unpublished observations) have likewise observed that [2.2]metaparacyclophane-1,9-diene itself is unaffected by irradiation.

Experimental Section[11]

9-Methyl-2,11-dithia[3.3]metacyclophane (10).—A solution of 25.0 g of 2,6-bis(bromomethyl)toluene[4] (**8**) in 600 ml of benzene and a solution of 15.3 g of 1,3-bis(mercaptomethyl)benzene[12] (**9**) in 600 ml of 85% aqueous ethanol containing 7.2 g of sodium hydroxide were added separately, but simultaneously, from two Hershberg funnels, to 3 l. of boiling ethanol. When addition was complete (5 hr), the mixture was boiled under reflux for another 28 hr and then concentrated. The residual solid was extracted with dichloromethane and the dichloromethane extract was washed with aqueous base and water. After concentration of the organic extract, the residue was taken up in a 20% chloroform–petroleum ether (bp 30–60°) mixture and chromatographed over silica gel. The main fraction of eluate gave 9.5 g (38%) of white crystals: mp 105–106°; nmr ($CDCl_3$), a multiplet at τ 2.9–3.2 (6 H, ArH), a broad singlet at 4.50 (1 H, ArH at 18 position), a multiplet at 5.9–6.6 (8 H, $-CH_2-$), and a singlet at 7.82 (3 H, $ArCH_3$); mass spectrum (70 eV) *m/e* (rel intensity) 286 (100), 252 (25), 221 (20), 180 (30), 151 (25), 150 (90), 149 (125), 148 (125), and 147 (120).

Anal. Calcd for $C_{17}H_{18}S_2$: C, 71.28; H, 6.33; S, 22.39. Found: C, 71.18; H, 6.28; S, 22.56.

Bis(methosulfonium) Fluoroborate of 10.—A solution of 4.0 g of **10** in 100 ml of dichloromethane was added dropwise with stirring to a solution of 5.67 g of dimethoxycarbonium fluoroborate[13] in 50 ml of dichloromethane held at −30°. The mixture was allowed to warm to room temperature and was then stirred overnight. The crystalline precipitate was separated by decantation and triturated with ethyl acetate to give 6.0 g (88%) of a white solid, mp 206° dec.

Anal. Calcd for $C_{19}H_{24}S_2B_2F_8$: C, 46.56; H, 4.94. Found: C, 46.33; H, 4.94.

Stevens Rearrangement to Give 11.—A mixture of 6.0 g of the bis(methosulfonium) fluoroborate of **10** and 3.0 g of potassium *tert*-butoxide in 200 ml of dry tetrahydrofuran was stirred at room temperature for 5 hr. After addition of dichloromethane and dilute aqueous acid, the organic layer was separated, washed with water, dried, and concentrated. The residual oil was taken up in a 2:3 mixture of dichloromethane in petroleum ether and chromatographed over silica gel. The main fraction of eluate gave 2.87 g (76%) of a colorless oil: nmr ($CDCl_3$), a multiplet at τ 2.2–3.0 (6 H, ArH), a singlet at 6.0 (1 H, ArH at 16 position), a multiplet at 5.9–6.25 (2 H, $-CHSCH_3$), a multiplet at 6.6–8.1 (4 H, $-CH_2-$), a singlet at 7.9 (6 H, $-SCH_3$), and a narrow doublet at 9.5 (3 H, $ArCH_3$).

Anal. Calcd for $C_{19}H_{22}S_2$: C, 72.56; H, 7.05; S, 20.39. Found: C, 72.27; H, 7.13; S, 20.60.

Bis(methylsulfonium) Fluoroborate of 11.—A solution of 2.58 g of **11** in 100 ml of dichloromethane was added with stirring to a suspension of 4.4 g of dimethoxycarbonium fluoroborate in 20 ml of dichloromethane held at −30°. After the mixture had been stirred for 5 hr, 50 ml of ethyl acetate was added and the mixture was stirred for an additional 30 min. The crystalline precipitate was collected, triturated with ethyl acetate, and dried to give 3.53 g (84%) of white crystals: mp 260–261°; nmr ($CDCl_3$), a multiplet at τ 2.4–2.6 (6 H, ArH), a broad singlet at 6.1 (1 H, ArH at 16 position), a singlet at 6.6 (12 H, $-SCH_3$), a multiplet at 7.05 7.20 (6 H, $-CH_2$ and $-CHSCH_3$), and a singlet at 9.4 (3 H; $ArCH_3$).

Anal. Calcd. for $C_{21}H_{28}S_2B_2F_8$: C, 48.68; H, 5.45. Found: C, 48.67; H, 5.42.

Attempted Hofmann Eliminations with the Bis(methosulfonium) Fluoroborate of 11.—A mixture of 1.04 g of the bis(methosulfonium) fluoroborate of **11** and 667 mg of potassium *tert*-butoxide in 50 ml of dry tetrahydrofuran was stirred at room temperature for 3 hr. Then dilute aqueous acid and petroleum ether were added to the mixture. After the organic layer had been separated, it was washed with water, dried, and concentrated.

(11) Elemental and mass spectral analyses were determined by Dr. S. Rottschaefer, University of Oregon Microanalytical Laboratories. Infrared spectra were measured with a Beckman IR-5a; visible and ultraviolet spectra with a Cary 15; nmr with a Varian A-60 or HA-100 spectrometer; and mass spectra with a Consolidated Model 21-110 spectrometer.

(12) W. Autenreith and F. Beuttel, *Chem. Ber.*, **42**, 4357 (1901).

(13) R. F. Borch, *J. Org. Chem.*, **34**, 627 (1969).

The residual yellow solid was taken up in petroleum ether and chromatographed over silica gel to give 220 mg of pale yellow crystals, mp 156–157°, identical in all respects with an authentic specimen of pyrene.

When the experiment was repeated using various other bases, such as sodium hydride, *n*-butyllithium, or sodium hydroxide, the results were essentially the same. One experiment using potassium *tert*-butoxide as above, but in a high vacuum train, gave a green solution having a strong, broad esr signal (g 2.0059). A mass spectrum of the gases collected in the high-vacuum train showed a strong signal at m/e 16, indicating the presence of methane. The green color of the reaction mixture faded to a pale yellow over a short period of time.

9-Methyl-2,11-dithia[3.3]metaparacyclophane (16).—A solution of 12.0 g of 2,6-bis(bromomethyl)toluene (**8**) in 600 ml of benzene and a solution of 7.32 g of 1,4-bis(mercaptomethyl)-benzene (**15**) in 600 ml of 85% aqueous ethanol containing 3.5 g of sodium hydroxide were added simultaneously, but separately, from two Hershberg funnels to 3 l. of boiling ethanol. When the addition was complete, the mixture was boiled under reflux for an additional 30 hr and then concentrated. After the residual solid had been extracted with dichloromethane, the organic extract was washed with dilute base and dried. Concentration of the extract gave a yellow solid which was taken up in a 25% benzene–petroleum ether mixture and chromatographed over silica gel. The main eluate fraction gave 5.35 g (44%) of white crystals: mp 204–205° (lit.[5] mp 202°); nmr ($CDCl_3$), a multiplet at τ 2.7–3.2 (5 H, ArH), a multiplet at 3.7–3.8 (2 H, ArH), a multiplet at 6.15–6.55 (8 H, $-CH_2$), and a singlet at 8.1 (3 H, $ArCH_3$).

Bis(methosulfonium) Fluoroborate of 16.—A solution of 2.86 g of **16** in 50 ml of dichloromethane was added dropwise with stirring to a suspension of 4.55 g of dimethoxycarbonium fluoroborate in 20 ml of dichloromethane held at −30°. After the mixture warmed to room temperature, it was stirred overnight. The crystalline precipitate was collected, triturated with ethyl acetate, and dried. Recrystallization from water gave 4.90 g (100%) of a white powder, mp 200° dec.

Anal. Calcd for $C_{19}H_{24}S_2B_2F_8$: C, 46.56; H, 4.94. Found: C, 46.19; H, 5.02.

Stevens Rearrangement to Give 17.—A mixture of 3.76 g of the bis(methosulfonium) fluoroborate of **16** and 2.54 g of potassium *tert*-butoxide in 100 ml of dry tetrahydrofuran was stirred at room temperature overnight. Dilute aqueous hydrochloric acid and dichloromethane were then added with stirring and the organic layer was separated. Concentration of the organic extract gave an oily residue which was taken up in a 25% benzene–petroleum ether mixture and chromatographed over silica gel. The main fraction of eluate gave 870 mg (31%) of a colorless oil: nmr ($CDCl_3$), a multiplet at τ 2.5–3.0 (5 H, ArH), a multiplet at 4.06–4.12 (2 H, ArH), an AB pattern at 5.7–6.62 (4 H, $-CH_2$), a multiplet at 7.4–7.9 (2 H, $-CHSCH_3$), a singlet at 7.95 (6 H, $-SCH_3$), and a singlet at 8.18 (3 H, $ArCH_3$).

Anal. Calcd for $C_{19}H_{22}S_2$: C, 72.56; H, 7.05; S, 20.39. Found: C, 72.28; H, 7.04; S, 20.68.

Bis(methosulfonium) Fluoroborate of 17.—A solution of 670 mg of **17** in 50 ml of dichloromethane was added dropwise with stirring to a suspension of 1.03 g of dimethoxycarbonium fluoroborate in 50 ml of dichloromethane held at −30°. After the mixture had been stirred for 5 hr, 50 ml of ethyl acetate was added and stirring was continued overnight at room temperature. The crystalline precipitate was collected, washed with ethyl acetate, and dried. Recrystallization from water gave 800 mg (73%) of white crystals, mp 218° dec.

Anal. Calcd for $C_{21}H_{28}S_2B_2F_8$: C, 48.68; H, 5.45. Found: C, 48.98; H, 5.50.

8-Methyl[2.2]metaparacyclophane-1,9-diene (18).—A mixture of 1.64 g of the bis(methosulfonium) fluoroborate of **17** and 1.08 g of potassium *tert*-butoxide in 25 ml of dry tetrahydrofuran was stirred at room temperature for 24 hr. After addition of dilute aqueous hydrochloric acid and dichloromethane with shaking, the organic layer was separated, dried, and concentrated. The solid residue was taken up in petroleum ether and chromatographed over silica gel. The material from the main fraction of eluate was recrystallized from a benzene–petroleum ether mixture to give 184 mg (26%) of white crystals: mp 157–158°; nmr ($CDCl_3$), a multiplet at τ 2.9–3.4 (5 H, ArH), a quartet at 3.15 (4 H, $-CH{=}CH-$), a doublet at 3.9 (2 H, ArH), and a singlet at 8.55 (3 H, $ArCH_3$).

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.12; H, 6.61.

Hydrogenation of 18 to Give 19.—A solution of 125 mg of **18** in 10 ml of ethyl acetate containing 75 mg of a prereduced platinum catalyst was subjected to hydrogenation at room temperature and atmospheric pressure. After removal of the catalyst and solvent, the residue was recrystallized from a benzene–petroleum ether mixture to give 127 mg (100%) of white crystals: mp 218–219°; nmr ($CDCl_3$), a multiplet at τ 3.05–3.50 (5 H, ArH), a doublet at 4.28 (2 H, ArH), a multiplet at 6.2–8.2 (8 H, $-CH_2-$), and a singlet at 8.22 (3 H, $ArCH_3$).

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.87; H, 8.14.

9-Methyl-2,11-dithia[3.3]metaparacyclophane Bis(sulfone) (20).—To a solution of 150 mg of **16** in 30 ml of dichloromethane was added in portions with shaking 450 mg of *m*-chloroperbenzoic acid. When addition was complete, the mixture was stirred overnight. After the mixture was washed with dilute aqueous base and water, it was dried and concentrated to give 182 mg (100%) of a white powder: mp 400° dec; nmr (CF_3CO_2H) a multiplet at τ 2.2–2.8 (5 H, ArH), a broad singlet at 3.25 (2 H, ArH), a multiplet at 5.0–6.1 (8 H, $-CH_2-$), and a singlet at 8.0 (3 H, $ArCH_3$).

Anal. Calcd for $C_{17}H_{18}S_2O_4$: C, 58.26; H, 5.17. Found: C, 58.29; H, 5.13.

Pyrolysis of 20 to Give 19.—In a pyrolysis flow system, modeled after that described by Haenel and Staab,[14] was placed a 60-mg sample of **20**. The first furnace was set at 300° with the second at 500°, and the flow rate was such that the pyrolysis was complete in 24 hr. There collected on the cold finger 28 mg (90%) of white crystals, mp 218°, identical in all respects with the sample of **19** prepared previously.

Photoisomerization of [2.2]Metaparacyclophane (19) to [2.2]-Metacyclophane (21).—A carefully degassed solution of 30 mg of [2.2]metaparacyclophane (**19**) in 5 ml of cyclohexane sealed in a quartz tube was irradiated with 254-nm light for 72 hr. At this stage nmr monitoring indicated that the solution contained about a 50:50 mixture of **19** and **21**. The contents of the tube were then concentrated. The residue was taken up in hexane and chromatographed over silica gel. Analysis of the early fractions of eluate showed only the presence of starting material **19**. The product from the middle eluate fractions was recrystallized from methanol to give 14 mg (47%) of white crystals, mp 91.0–91.5°, identical in all respects with an authentic specimen of 8-methyl-[2.2]metacyclophane (**21**).[2]

When a degassed solution of 10 mg of **18** in 5 ml of cyclohexane was subjected to irradiation in exactly the same way, nmr monitoring showed no change in the spectrum after 43 hr. Work-up of the irradiated solution led to a complete recovery of the starting material (**18**).

Registry No.—**8**, 41563-68-2; **9**, 41563-69-3; **10**, 30736-35-7; **10** bis(methosulfonium) fluoroborate, 41560-40-1; **11**, 41583-10-2; **11** bis(methylsulfonium) fluoroborate, 41562-83-8; **15**, 105-09-9; **16**, 27453-78-7; **16** bis(methosulfonium) fluoroborate, 41611-00-1; **17**, 41562-84-9; **17** bis(methosulfonium) fluoroborate, 41562-85-0; **18**, 41563-70-6; **19**, 41563-71-7; **20**, 41563-72-8; **21**, 28746-30-7; dimethoxycarbonium fluoroborate, 18346-68-4; *m*-chloroperbenzoic acid, 937-14-4.

(14) M. Haenel and H. A. Staab, *Tetrahedron Lett.*, 3585 (1970).