316.1462, calcd for $C_{22}H_{20}O_2$ 316.1462.

1,4,7,10-Tetramethylnaphthacene (25). To a magnetically stirred solution of **23** (90 mg, 0.28 mmol) in CH_2Cl_2/MeOH (1:10, 11 mL) was added 10% Pd/C (20 mg) and oven-dried Mg turnings (100 mg, 4.1 mmol). The mixture was stirred at room temperature overnight to complete the formation of **24**. The mixture was poured into ice-cold 3 N HCl (20 mL), resulting in the immediate formation of an orange solid. The mixture was extracted with CH_2Cl_2 and the usual workup followed by column chromatography (silica gel, hexane) gave 45 mg (56%) of **25** as an orange powder: mp 269–273 °C; ^1H NMR ($CDCl_3$) δ 2.8 (s, 12 H), 7.05 (s, 4 H), 8.65 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 19.8, 123.4, 124.8, 131.4, 132.2; IR (KBr) 1622 (w), 885 (s), 813 (m) cm^{-1}; mass spectrum, *m/e* 284 (100%), 269, 253, 239, 142, 135, 127.

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.54; H, 7.30.

13,14-Dimethyl-1,4,7,10-tetrahydronaphthacene-1,4:7,10-diimine (26). The same procedure as described for the preparation of **11**, but with bromo tosylate **9** and a solution of freshly distilled *N*-methylpyrrole in THF (1:2), gave **26** (26%) as a bright yellow powder after column chromatography (activity III basic Al_2O_3, 95:5 EtOAc/Et_3N): mp >160 °C dec; ^1H NMR ($CDCl_3$) δ 2.2 (broad s, 6 H), 4.5 (broad s, 4 H), 6.8 (broad s, 4 H), 7.5 (s, 4 H); IR (KBr) 2950 (m), 1309 (m), 1270 (m), 928 (m), 798 (s), 705 (m) cm^{-1}; mass spectrum, *m/e* 286 (M^+), 271, 257, 244, 215, 202, 143, 84 (100%).

17,18-Dimethyl-1,2,3,4,9,10,11,12-octafluoro-5,8,13,16-tetrahydrohexacene-5,16:8,13-diimine (27). The same procedure as described for the preparation of **11**, but with bromo tosylate **9** and a solution of *N*-methyl-4,5,6,7-tetrafluoroisoindole (5 mmol) in THF (25 mL), gave **27** (16%) as a brown solid after flash chromatography (95:5 EtOAc/Et_3N), mp 155–165 °C; ^1H NMR ($CDCl_3$) δ 2.3 (s, 6 H), 5.4 (broad s, 4 H), 7.7 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 36.2, 69.5, 121.0, 128.2, 128.4, 130.1, 131.0, 142.8; IR (KBr) 1495 (s), 1481 (s), 1261 (m), 1045 (m), 740 (m) cm^{-1}; high resolution mass spectrum *m/e* 530.1009 (M^+, 100%), calcd for $C_{28}H_{14}F_8N_2$ 530.1029, 515, 501, 486, 472, 459.

Crystallographic Data and X-ray Structure Analysis of the Anti Isomer of 23. Crystal data: $C_{22}H_{20}O_2$, M_r = 316.4, monoclinic, a = 8.393 (2) Å, b = 8.019 (2) Å, c = 13.656 (2) Å, β = 112.45 (1)°, U = 849.4 (3) Å^3, D_c = 1.237 g cm^{-3}, Z = 2, Cu Kα radiation (λ = 1.5418 Å), μ = 6.2 cm^{-1}. Space group $P2_1/c$ (C_{2h}^5) from systematic absences: $0k0$ when $k \neq 2n$ and $h0l$ when $l \neq 2n$.

Data were collected ($4° < 2\theta < 130°$) with a variable speed, $\theta/2\theta$ scanning technique on a Syntex $P2_1$ diffractometer. Of the 1344 unique reflections collected, the 1023 with $I > 2\sigma(I)$ were used in structure solution and refinement. The structure was solved by using the MULTAN80 suite of programs[25] and refined with full-matrix least-squares iterations (anisotropic C, O; isotropic H).[26] The final R was 0.056.

Acknowledgment. This investigation was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, PHS Grant GM-30761 awarded by the National Institutes of Health, and Merck Sharp and Dohme Research Laboratories. We also thank Dr. Catherine E. Costello (Massachusetts Institute of Technology) for high-resolution mass spectra (NIH Resource Grant FR00317 from the Division of Research Facilities and Resources), the National Science Foundation for funds to purchase a Varian XL-300 NMR spectrometer, and Daniel J. Keavy for running some of the ^{13}C NMR spectra.

Registry No. **1**, 96965-60-5; **2**, 96998-98-0; **3**, 96965-61-6; **4**, 217-59-4; **5**, 56-55-3; **6**, 92-24-0; **7**, 96965-62-7; **8**, 96965-63-8; **9**, 96965-64-9; **10**, 110-00-9; **11**, 97058-39-4; **12**, 97058-40-7; **13**, 77037-26-4; **14**, 625-86-5; **15**, 96965-65-0; **16**, 96965-66-1; **17**, 96965-67-2; **18**, 96965-68-3; **19**, 96965-69-4; **20**, 96965-70-7; **21**, 96965-71-8; **22**, 96965-72-9; *anti*-**23**, 96965-73-0; **24**, 96965-74-1; **25**, 96965-75-2; **26**, 96965-76-3; **27**, 96965-77-4; 1,4-dibromo-2,3-dihydroxynaphthalene, 52864-96-7; 1,6-dibromo-2,7-dihydroxynaphthalene, 96965-78-5; 3,6-dibromo-2,7-dihydroxynaphthalene, 96965-79-6; *N*-methyl-4,5,6,7-tetrafluoroisoindole, 38053-09-7; *N*-methylpyrrole, 96-54-8.

Supplementary Material Available: Tables II–IV listing thermal parameters for non-hydrogen atoms, hydrogen atom parameters, bond lengths, valency angles, and torsion angles, all with estimated standard deviations (4 pages). Ordering information is given on any current masthead page.

(25) Main, P.; Fiske, S. J.; Hall, S. E.; Lessinger, G.; Declercq, J. P.; Woolfson, M. M. MULTAN 80, Universities of York, England, and Louvain, Belgium, 1980.

(26) All calculations were carried out on a VAX 11/780 computer. The least-squares refinement program was based on FMLS (Ganzel, P. L.; Sparks, R. A.; Trueblood, K. N.), UCLA, and modified by McPhail, A. T., Duke University. Figure 1 was drawn with ORTEP, crystallographic illustration programs, Johnson, C. K., Oak Ridge, ORNL-3794.

Metacyclophanes and Related Compounds. 14. Preparation of 8,16-Difluoro[2.2]metacyclophane[1]

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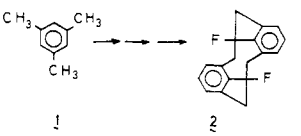
Although preparation of 8,16-difluoro-, 8,16-dichloro-, and 8,16-dibromo[2.2]metacyclophanes was attempted, only 8,16-difluoro[2.2]metacyclophane was obtained from fluorobenzene in seven steps by using a *tert*-butyl group as a positional protective function.

Although some [2.2]metacyclophanes ([2.2]MCP) having functional groups such as alkyl,[2-5] halomethyl,[5] alkoxy,[6] hydroxy,[7] and formyl[8] at their 8,16-positions have been prepared, there are few reports concerning the preparation

Scheme I



1 2

(1) Part 13: Tashiro, M.; Yamato, T. *Org. Prep. Proced. Int.*, in press.
(2) Boekelheide, V.; Phillips, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 1695.
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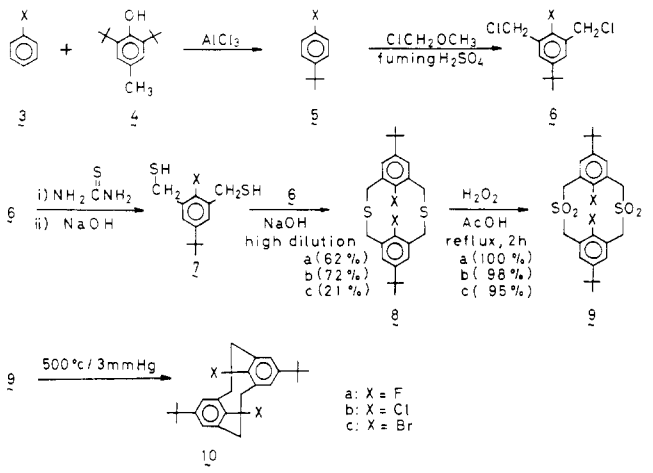
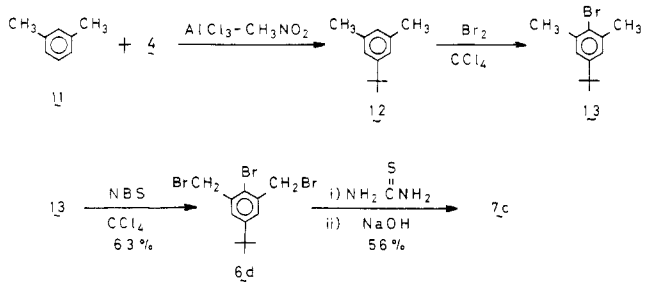
0022-3263/85/1950-2939$01.50/0

Scheme II



Scheme III



of [2.2]MCP having halogen atoms other than fluorine at their internal positions.

Boekelheide et al.[9] reported the preparation of *syn*-8,16-difluoro[2.2]MCP (**2**) from mesitylene (**1**) in 11 steps (Scheme I). However, Hanson pointed out that **2** was the anti form rather than the syn isomer.[10]

We previously reported that the *tert*-butyl group can be used as a positional protective group for a synthesis of *anti*-8,16-dimethyl[2.2]MCP[5] and *anti*-8,16-dihydroxy-[2.2]MCP.[7] Here we report a convenient preparation of **2** by using the *tert*-butyl function as a positional protective group.

Results and Discussion

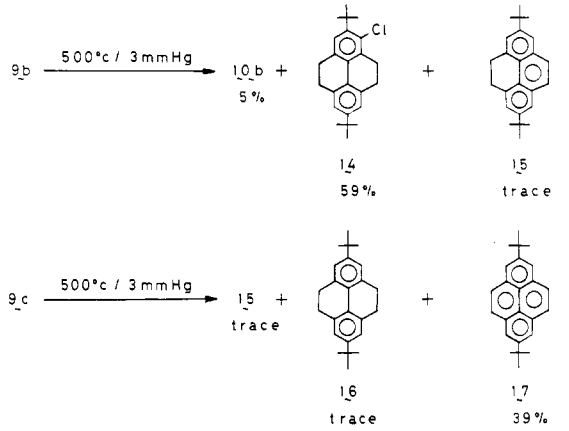
The preparation of 5,13-di-*tert*-butyl-8,16-dihalogeno-[2.2]MCPs (**10a–c**) was attempted by two routes as outlined in Schemes II and III.

The preparation of **10a–c** via pyrolysis of the corresponding disulfoxide derivatives **9a–c** is summarized in Scheme II.

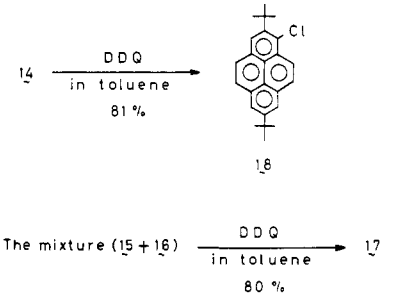
The preparations of 4-halo-*tert*-butylbenzenes **5a,b**,[11] 2,6-bis(chloromethyl)-4-substituted-*tert*-butylbenzenes **6a,b**,[12] and 2,6-bis(mercaptomethyl)-4-substituted-*tert*-butylbenzenes **7a,b**[12] were described in previous works. The 2,6-bis(bromomethyl)-4-bromo-*tert*-butylbenzene (**6d**) was obtained by the alternative route shown in Scheme III, since 2,6-bis(chloromethyl)-4-bromo-*tert*-butylbenzene (**6c**) could not be prepared by chloromethylation.

Compound **7c** was prepared from **6d** by the reported method.

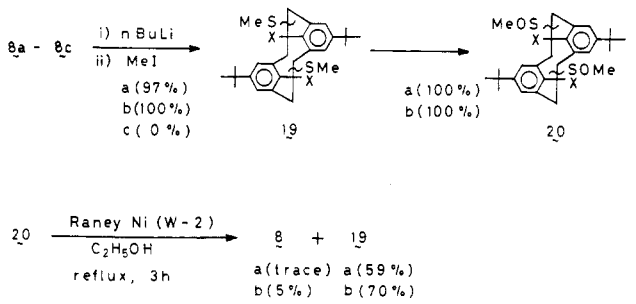
Scheme IV



Scheme V



Scheme VI



The preparation of **13** from **11** has been described in a previous paper.[13] The disulfides **8a,b** were prepared according the reported method.[5] Oxidation of **8a,b** with hydrogen peroxide in acetic acid afforded the corresponding disulfoxides **9a,b** in almost quantitative yields.

Although pyrolysis of **9a** afforded the desired **10a** in 36% yield, pyrolysis of **9b** and **9c** gave only a mixture of the products as shown in Scheme IV.

The structures of compounds **15** and **17** were identified by comparison with known samples.[14]

Oxidation of **14** with DDQ and the mixture of **15** and **16** afforded the corresponding pyrene derivatives **18** and **17** in good yields (Scheme V).

On the basis of the above results and an analysis of the spectral data, the structures of **14** and **16** seem fairly well established.

The preparation of **8a,b** was also attempted according to the route shown in Scheme VI.

Treatment of **8a** and **8b** with *n*-butyllithium in dry tetrahydrofuran at 0 °C followed by methylation of the resulting thiolate with methyl iodide gave the corresponding analogues **19a** and **19b** as a mixture of structural and stereoisomers in good yield. However, similar treat-

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(9) Boekelheide, V.; Anderson, P. H. *J. Org. Chem.* **1983**, *38*, 3928.
(10) Hanson, A. W. *Acta Crystallogr., Sect. B.* **1975**, *B31*, 2352. Form of **2** was determined by X-ray analysis.
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(12) Tashiro, M.; Yamato, T. *Org. Prep. Proced. Int.* **1981**, *13*, 1.
(13) Tahsiro, M.; Tamato, T. *J. Chem. Soc., Perkin Trans. 1* **1979**, 176.
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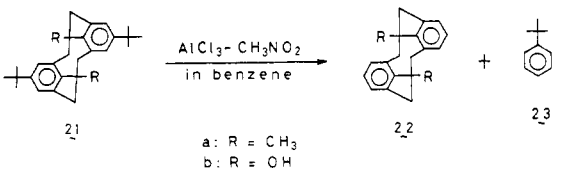
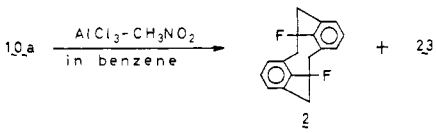
Scheme VII



Scheme VIII



and stereoisomers in good yield. However, similar treatment of **6c** gave only unidentified resinous materials.

Oxidation of **19a** and **19b** with *m*-chloroperbenzoic acid at 0 °C afforded **20a** and **20b** in almost quantitative yields, again as a mixture of structural and stereoisomers. These, without purification, were treated with freshly prepared W-2 Raney Ni to give the expected **8a** and **8b**, together with formation of dithia[2.2]MCPs **19a** and **19b**, respectively, but only in low yield.

$AlCl_3$–CH_3NO_2 Catalyzed Trans-*tert*-butylation of 10a. As mentioned above, it has been previously reported that $AlCl_3$–CH_3NO_2 mixtures catalyzes the trans-*tert*-butylation of *anti*-5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP (**21a**)[5] and *anti*-5,13-di-*tert*-butyl-8,16-dihydroxy[2.2]MCP (**21b**)[7] to afford the corresponding de-*tert*-butylated compounds **22a** and **22b** in good yield (Scheme VII).

These results suggest that the use of $AlCl_3$–CH_3NO_2 mixtures with **10a** might afford the desired compound **2** (Scheme VIII). Indeed, treatment of **10a** with an $AlCl_3$–CH_3NO_2 mixture gave **2** in good yield. Unfortunately the amount of **8b** obtained was too small to carry out a similar conversion. Although the attempts to prepare *anti*-8,16-dichloro[2.2]MCP and *anti*-8,16-dibromo[2.2]-MCP failed, a preparation of **2** from fluorobenzene (**3a**) in seven steps was achieved.

Experimental Section

2,6-Bis(bromoethyl)-4-*tert*-butylbromobenzene (6d). A solution of 24.1 g (0.1 mol) of 2,6-dimethyl-4-*tert*-butylbromobenzene (**13**),[12] 42.7 g (0.24 mol) of NBS, and 0.5 g of benzoyl peroxide in 400 mL of carbon tetrachloride was refluxed for 6 h. After filtration of insoluble materials from the reaction mixture, the filtrate was concentrated in vacuo to leave the residue, which on recrystallization from hexane gave 25 g (62.7%) of **6d** as colorless prisms: mp 91–92 °C; IR (KBr) 3040, 2960, 1580, 1430, 1360, 1230, 1210, 1140, 1110, 1020, 970, 880, 730, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (9 H, s), 4.64 (4 H, s), 7.45 (2 H, s). Anal. Calcd for $C_{12}H_{15}Br_3$: C, 36.12; H, 2.81. Found: C, 36.25; H, 2.90.

2,6-Bis(mercaptomethyl)-4-*tert*-butylbromobenzene (7c). A solution of 19.95 g (50 mmol) of **6d** and 8.37 g (110 mmol) of thiourea in 75 mL of Me_2SO was treated as previously reported[11] to give 8.53 g (55.9%) of **7c** as colorless prisms (hexane): mp 55–57 °C; IR (KBr) 3050, 2950, 2540, 1580, 1440, 1420, 1360, 1250, 1220, 1140, 1020, 880, 735 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (9 H, s), 2.01 (2 H, t, J = 8 Hz, exchangeable with D_2O), 3.84 (4 H, d, J = 8 Hz), 7.24 (2 H, s); mass spectrum, m/e 304, 306 (M^+). Anal. Calcd for $C_{12}H_{17}S_2Br$: C, 47.21; H, 5.61. Found: C, 46.88; H, 5.37.

***anti*-6,15-Di-*tert*-butyl-9,18-dihalodithia[3.3]metacyclophanes (8).** A solution of 10.58 g (42.5 mmol) of 2,6-bis(chloromethyl)-4-*tert*-butylfluorobenzene (**6a**) and 10.37 g (42.5 mmol) of 2,6-bis(mercaptomethyl)-4-*tert*-butylfluorobenzene (**7a**) in 700 mL of benzene was added dropwise from a Hershberg funnel with stirring under nitrogen to a solution of 8.4 g of potassium hydroxide in 4.0 L of absolute ethanol. When the addition was complete (3 days), the mixture was concentrated and the residue was extracted with 700 mL of dichloromethane. The dichloromethane extract was concentrated and the residue was chromatographed on Al_2O_3, using a mixture of hexane/benzene (1:1) as an eluent to give 12.78 g of crude **8a** as a coloroless solid which was recrystallized from hexane to afford 11 g (61.6%) of **8a** as colorless prisms: mp 108–111 °C; IR (KBr) 3040, 2950, 1475, 1405, 1355, 1260, 1200, 1170, 1095, 900, 870, 755, 725 cm^{-1}; NMR ($CDCl_3$) δ 1.12 (18 H, s), 3.83 (8 H, AB pattern, J_{AB} = 15 Hz), 6.85 (1 H, d, J = 3 Hz), 6.92 (1 H, d, J = 3 Hz); mass spectrum, m/e 420 (M^+). Anal. Calcd for $C_{24}H_{30}F_2S_2$: C, 68.53; H, 7.19. Found: C, 68.46; H, 7.00.

Compounds **8b** and **8c** were synthesized in the same manner as described above. Their yields are given in Scheme II.

8b: colorless prisms (hexane/benzene, 2:1); mp 264–266 °C; IR (KBr) 3050, 2960, 1580, 1460, 1440, 1390, 1360, 1220, 1140, 1040, 880, 755 cm^{-1}; NMR ($CDCl_3$) δ 1.36 (18 H, s), 3.80 (8 H, AB pattern, J_{AB} = 15 Hz), 7.46 (4 H, s); mass spectrum, m/e 453 (M^+). Anal. Calcd for $C_{24}H_{30}Cl_2S_2$: C, 63, 56; H, 6.67. Found: C, 63.38; H, 6.62.

8c: colorless prisms (hexane/benzene, 1:1); mp 226–267 °C; IR (KBr) 3040, 2960, 1580, 1450, 1420, 1390, 1360, 1220, 1210, 1140, 1020, 880, 750 cm^{-1}; NMR ($CDCl_3$) δ 1.34 (18 H, s), 3.81 (8 H, AB pattern, J_{AB} = 15 Hz), 7.36 (4 H, s); mass spectrum, m/e 539, 541, 543 (M^+). Anal. Calcd for $C_{24}H_{30}Br_2S_2$: C, 53.14; H, 5.58. Found: C, 53.26; H, 5.53.

***anti*-6,15-Di-*tert*-butyl-9,18-dihalo-2,11-dithia[3.3]metacyclophane 2,2,11,11-Tetroxide (9).** A mixture of 712 mg (1.7 mmol) of **8a**, 1.7 mL of 30% hydrogen peroxide, and 14 mL of glacial acetic acid was refluxed for 20 h. The reaction mixture was poured into a cold solution of 4 g of sodium hydroxide in 20 mL of water, and the resulting paste was allowed to cool to room temperature. The crude sulfone was filtered and washed with a small amount of ethanol to give colorless crystals of **9a**, 820 mg (99.6%): mp > 270 °C dec; IR (KBr) 3040, 2960, 1485, 1400, 1320, 1265, 1210, 1170, 1110, 890, 860, 730, 715 cm^{-1}; NMR ($CDCl_3$) δ 1.16 (18 H, s), 4.40 (8 H, AB pattern, J_{AB} = 15 Hz), 7.26 (1 H, d, J = 3 Hz), 7.31 (1 H, d, J = 3 Hz); mass spectrum, m/e 484 (M^+). Anal. Calcd for $C_{24,}H_{30}F_2S_2O_4$: C, 59.48; H, 6.24. Found: C, 59.01; H, 6.22.

Compounds **9a** and **9b** were synthesized in the same manner as described above. Their yields are given in Scheme II.

9b: colorless prisms; mp > 300 °C; IR (KBr) 3040, 2960, 2900, 1585, 1440, 1400, 1310, 1240, 1140, 1105, 885, 800, 720 cm^{-1}; NMR ($CDCl_3$) δ 1.36 (18 H, s), 4.56 (8 H, AB pattern, J_{AB} = 45 Hz). Anal. Calcd for $C_{24}H_{30}Cl_2S_2O_4$: C, 55,70; H, 5.84. Found: C, 55.43; H, 5.94.

9c: colorless prisms; mp > 300 °C; IR (KBr) 3040, 2960, 2900, 1580, 1480, 1440, 1400, 1295, 1240, 1100, 1015, 880, 800, 715 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (18 H, s), 4.62 (8 H, AB pattern, J_{AB} = 15 Hz), 7.72 (4 H, s); mass spectrum, m/e 605, 607, 609 (M^+). Anal. Calcd for $C_{24}H_{30}B_2S_2O_4$: C, 47.53; H, 4.99. Found: C, 47,63; H, 4.92.

Pyrolysis of Disulfone 9a. Pyrolysis of the disulfone **9a** was carried out in an apparatus consisting of a horizontal tube (15 mm in diameter) passing through two adjacent tube furnaces, each of which was 20-cm long. The first furnace provided a temperature that would induce sublimation of the disulfone; the second was used at a higher temperature (500 °C) that would assure pyrolysis. A vacuum pump was connected at the exit from the second furnace.

Pyrolysis of 9a. The disulfone **9a** (800 mg) was pyrolyzed at 500 °C under reduced pressure (2–3 mmHg) in the above apparatus as follows. The sample of disulfone was placed in the tube and small glass beads were packed into the second one. The sublimed product was collected and chromatographed on silica gel with hexane and chloroform to yield 140 mg (17.5%) and 210 mg (35.6%) of the desired *anti*-8,16-difluoro[2.2]MCP **2** and the recovered disulfone, respectively.

2: colorless prisms (hexane); mp 220–222 °C; IR (KBr) 3040, 2960, 2850, 1475, 1360, 1285, 1180, 885, 860, 750, 720 cm^{-1}; NMR ($CDCl_3$) δ 1.29 (18 H, s), 2.55–2.77 (8 H, m), 7.01 (4 H, d, J = 6 Hz); mass spectrum, m/e 356 (M^+). Anal. Calcd for $C_{24}H_{30}F_2$: C, 80.86; H, 8.48. Found: C, 80.73; H, 8.30.

Pyrolysis of Disulfone 9b. The disulfone **9b** (500 mg, 0.967 mmol) was pyrolyzed at 500 °C under reduced pressure (2–3 mmHg) in the same manner as described above. The sublimed product was collected and chromatographed on silica gel with

hexane and a mixture of hexane/benzene (1:1) as an eluent to give a mixture of **10b** **14**, and **15**.

The product obtained from the former eluent was recrystallized from hexane to afford 20 mg (5%) of **10b** as colorless prisms. Although, compound **15** could not be purified, it was identified by NMR and GC–MS.

The product obtained from the latter eluent was recrystallized from MeOH to afford 200 mg (59%) of **14** as colorless prisms.

10b: colorless prisms (hexane); mp 200–203 °C; IR (KBr) 3040, 2960, 2860, 1580, 1440, 1425, 1360, 1280, 1125, 1030, 885, 860, 730, 665 cm^{-1}; NMR ($CDCl_3$) δ 1.29 (18 H, s), 2.78–3.17 (8 H, m), 7.19 (4 H, s); mass spectrum, *m/e* 388, 390, 392 (M^+). Anal. Calcd for $C_{24}H_{32}Cl_2$: C, 74.03; H, 7.77. Found: C, 74.03; H, 7.72.

15: NMR ($CDCl_3$) δ 1.42 (18 H, s), 3.26 (4 H, s), 7.40 (2 H, d, J = 2 Hz), 7.62 (2 H, d, J = 2 Hz), 7.63 (2 H, s); GC–mass spectrum, *m/e* 316 (M^+).

14: colorless prisms (MeOH); mp 205–206 °C; IR (KBr) 3040, 2950, 1600, 1435, 1420, 1380, 1350, 1150, 1020, 870, 750 cm^{-1}; NMR ($CDCl_3$) δ 1.32 (9 H, s), 1.50 (9 H, s), 2.83 (4 H, s), 2.84–3.08 (4 H, m), 7.05 (2 H, s), 7.10 (1 H, s); mass spectrum, *m/e* 352, 354 (M^+). Anal. Calcd for $C_{24}H_{24}Cl$: C, 81.67; H, 8.28. Found: C, 81.79; H, 8.27.

Pyrolysis of Disulfone 9c. Disulfone **9c** (500 mg, 0.825 mmol) was pyrolyzed at 500 °C under reduced pressure (2–3 mmHg) in the same manner as described above. The sublimed product was collected and chromatographed on silica gel with hexane and a mixture of hexane/benzene (1:1) as eluent to yield a mixture of **17**, **16**, and **15**, respectively. The product obtained from the first eluate fraction was recrystallized from MeOH to afford a trace of **16** as colorless plates, mp 234–235 °C (lit.[15] mp 223–224 °C). The product obtained from the last eluate fraction was recrystallized from hexane to afford 100 mg (38.5%) of **17** as pale yellow prisms, mp 210–212 °C (lit.[14] mp 210–212 °C).

Oxidation of 14 with DDQ. A solution of 100 mg (0.284 mmol) of **14** and 200 mg (0.882 mmol) of DDQ in 50 mL of toluene was refluxed for 4 h. After the reaction mixture was cooled and concentrated, the residue was extracted with benzene, and the benzene solution was chromatographed on silica gel with hexane/benzene (1:1) mixture as eluent to give 80 mg (81%) of **18** as colorless prisms.

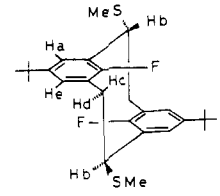
18: colorless prisms (MeOH); mp 172–175 °C; IR (KBr) 3040, 2960, 1600, 1360, 1225, 1025, 880, 805, 725 cm^{-1}; NMR ($CDCl_3$) δ 1.56 (9 H, s), 1.73 (9 H, s), 7.90–8.56 (7 H, m); mass spectrum, *m/e* 348, 350 (M^+). Anal. Calcd for $C_{24}H_{25}Cl$: C, 82.62; H, 7.22. Found: C, 82.67; H, 7.30.

Reaction of the Mixture (15 + 16) with DDQ. A solution of 100 mg of the mixture of **15** and **16** and 100 mg (0.441 mmol) of DDQ in 50 mL of toluene was refluxed for 4 h. After the reaction mixture was cooled and chromatographed on silica gel with hexane/benzene (1:1) mixture as eluent, there was isolted 80 mg (about 80%) of **17**.

Wittig Rearrangement of 8 to 19. To a solution of 2.52 g (6 mmol) of **8a** in 30 mL of dry tetrahydrofuran under nitrogen was added 9 mL of a 15% hexane solution of *n*-butyllithium (14.4 mmol) with ice cooling. After the solution had been stirred for 10 min at room temperature, 1.89 mL (30 mmol) of methyl iodide was added to the reaction mixture. The reaction mixture was worked up by the addition of H_2O and CH_2Cl_2. After the dichloromethane extract had been washed with water, dried, and concentrated, the products were purified by chromatography on silica gel with hexane/benzene (1:1) mixture as eluent to give 2.64 g (97.4%) of **19a** as a mixture of structural and stereoisomers.

19a: mixture of colorless crystals and oil; IR (KBr) 3040, 2960, 1475, 1460, 1435, 1360, 1280, 1250, 1200, 1180, 1090, 875, 835, 750, 735 cm^{-1}; NMR ($CDCl_3$) δ 1.04–1.42 (18 h, *t*-Bu), 2.08–2.26 (6 H, SMe), 2.43–2.67 (2 H, CH_2), 2.84–3.06 (2 H, CH_2), 3.60–4.12 (2 H, CHSMe), 7.00–7.24 (2 H, m, Ar H), 7.54–7.74 (2 H, m, Ar H); mass spectrum, *m/e* 448 (M^+). Anal. Calcd for $C_{26}H_{34}F_2S_2$: C, 69.90; H, 7.64. Found: C, 70.15; H, 7.79.

Component **19a'** was isolated by recrystallization of the mixture with hexane [about 40% of the mixture]: colorless prisms (hexane): mp 223–225 °C; IR (KBr) 3040, 2960, 1475, 1460, 1435, 1360, 1280, 1250, 1180, 1090, 880, 835, 750, 730 cm^{-1}; NMR ($CDCl_3$) δ 1.36 (18 H, s), 2.12 (6 H, s), 2.55 (2 H, dd, J_{dc} = 12 Hz, J_{db} = 12 Hz, Hd), 2.96 (2 H, dd, J_{cb} = 4 Hz, J_{cd} = 12 Hz, J_{e-F} = 3 Hz, J_{ae} = 5.5 Hz, He), 7.61 (2 H, dd, J_{a-F} = 3 Hz, J_{ae} = 5.5 Hz, deshieled by SMe, Hz); mass spectrum, *m/e* 448 (M^+), Anal. Calcd for $C_{26}H_{34}F_2S_2$: C, 69.60; H, 7.64. Found: C, 70.18; H, 7.84.



19a'

Similarly, compound **19b** was synthesized in the same manner as described above. However, similar reaction of **8c** gave a mixture of many products which could not be identified.

19b: colorless crystals; mp 230–235 °C; IR (KBr) 3040, 2960, 1590, 1460, 1360, 1240, 1170, 1090, 890, 830, 740, 730 cm^{-1}; NMR ($CDCl_3$) δ 1.32 (18 H, s), 2.14 (16 H, s), 2.80–3.30 (4 H, CH_2), 4.33–4.50 (2 H, CHSMe), 7.30–7.37 (2 H, m), 7.85–7.93 (2 H, m); mass spectrum, *m/e* 480, 482 (M^+). Anal. Calcd for $C_{26}H_{34}S_2Cl_2$: C, 64.84; H, 7.12. Found: C, 65.25; H, 7.12.

Oxidation of 19. The cyclophane **19** (3 mmol) and *m*-chloroperbenzoic acid 85%, 1.28 g, 6.30 mmol) were disolved in chloroform (300 mL) at 0 °C under nitrogen and the solution was stirred for 24 h at room temperature. The solution was washed with 10% sodium bicarbonate solution and water, dried over Na_2SO_4; and concentrated. Disulfoxide **10** was obtained in almost quantitative yield as colorless crystals. The product was used without further purification.

Reduction of 20a. Freshly prepared W-2 Raney nickel (7.2 g) was added to a solution of the crude sulfoxide **20** (960 mg) in ethanol (300 mL), and the mixture was heated under reflux for 3 h. After the solution was filtered and concentrated, the residue was chromatographed on silica gel, using a hexane a mixture of benzene/hexane (1:1) as eluent to give trace of **8a** and 528 mg (58.9%) of **19a**, respectively.

Reduction of 20b. To a solution of 1.03 g of the crude sulfoxide **20b** in 300 mL of ethanol was added 7.2 g of freshly prepared W-2 Ranney nickel. After the reaction mixture was heated under reflux for 3 h, it was treated and worked up as described above to afford 39 mg (5%) of **8b** and 674 mg (70%) of **19b**.

Trans-*tert*-butylation of *anti*-5,13-Di-*tert*-butyl-8,16-difluoro[2.2]metacyclophane (10a). To a solution of **10a** (159 mg, 0.5 mmol) in benzene (30 mL) was added a solution of aluminum chloride (200 mg, 1.5 mmol) in nitromethane (0.1 mL). After the reaction mixture was stirred for 20 h at room temperature, it was poured into ice/water and extracted with benzene. The benzene solution was dried over sodium sulfate and evaporated in vacuo to give crude **2**, which was recrystallized from hexane to afford 100 mg (82%) of **2** as colorless prisms; mp 154–155 °C (lit.[9] mp 157–158 °C).

The formation of *tert*-butylbenzene (**23**) was confirmed by GLC.

Registry No. **2**, 96997-83-0; **4**, 128-37-0; **6a**, 77180-43-9; **6b**, 77180-44-0; **6c**, 96929-81-6; **6d**, 96929-82-7; **7a**, 77180-50-8; **7b**, 77180-49-5; **7c**, 96929-83-8; **8a**, 92661-24-0; **8b**, 96929-84-9; **8c**, 96929-85-0; **9a**, 96929-86-1; **9b**, 96929-87-2; **9c**, 96929-88-3; **10a**, 96929-89-4; **10b**, 96929-90-7; **10c**, 96929-91-8; **11**, 108-38-3; **12**, 98-19-1; **13**, 5345-05-1; **14**, 96929-92-9; **15**, 69618-61-7; **16**, 69080-03-1; **17**, 24300-91-2; **18**, 78751-85-6; **19a**, 96929-93-0; **19b**, 96929-94-1; **19c**, 96929-95-2; **20a**, 96929-96-3; **20b**, 96929-97-4.

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