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<https://doi.org/10.15017/6510>

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出版情報：九州大学機能物質科学研究所報告. 1 (1), pp.1-10, 1987-12-28. 九州大学機能物質科学研究所  
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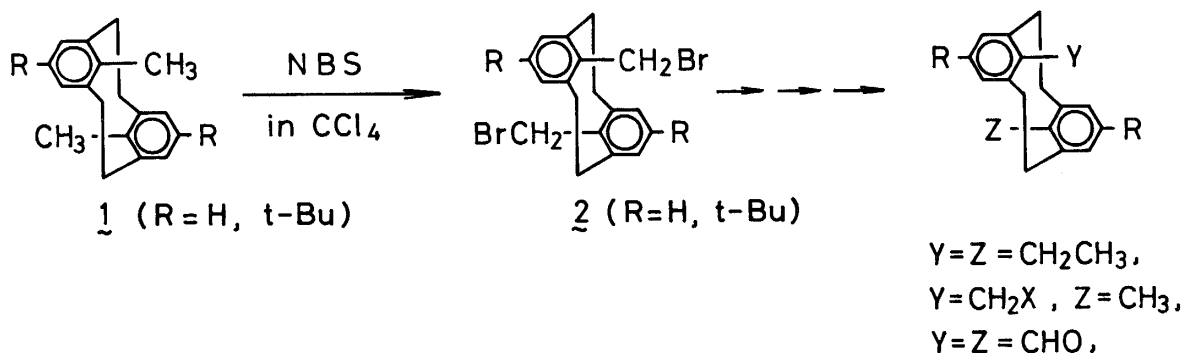


# Metacyclophanes and Related Compounds. 20. Reaction of Methyl [2.2] metacyclophanes with N-bromosuccinimide<sup>1</sup>

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Methyl[2.2]metacyclophanes were prepared and their bromination with NBS was carried out in order to obtain the corresponding bromomethyl derivatives. The desired bromomethyl derivatives were obtained in good yield in most cases. However, it was found that 5-bromomethyl-13-methoxy [2.2] metacyclophane was not formed in bromination of 5-methoxy-13-methyl [2.2] metacyclophane with NBS and that treatment of 5-tert-butyl-8-methoxy-13-methyl [2.2] metacyclophane with NBS afford 2-bromomethyl-7-tert-butylpyrene in good yield.

We previously reported that<sup>2</sup> the bromination of 8,16-dimethyl [2.2] metacyclophanes (MCPs) **1** with N-bromosuccinimide (NBS) gave the corresponding dibromides **2** in good yield, which are important synthetic key compounds for the preparation of [2.2] MCPs having various functions at 8 and 16 positions<sup>3-5</sup>.

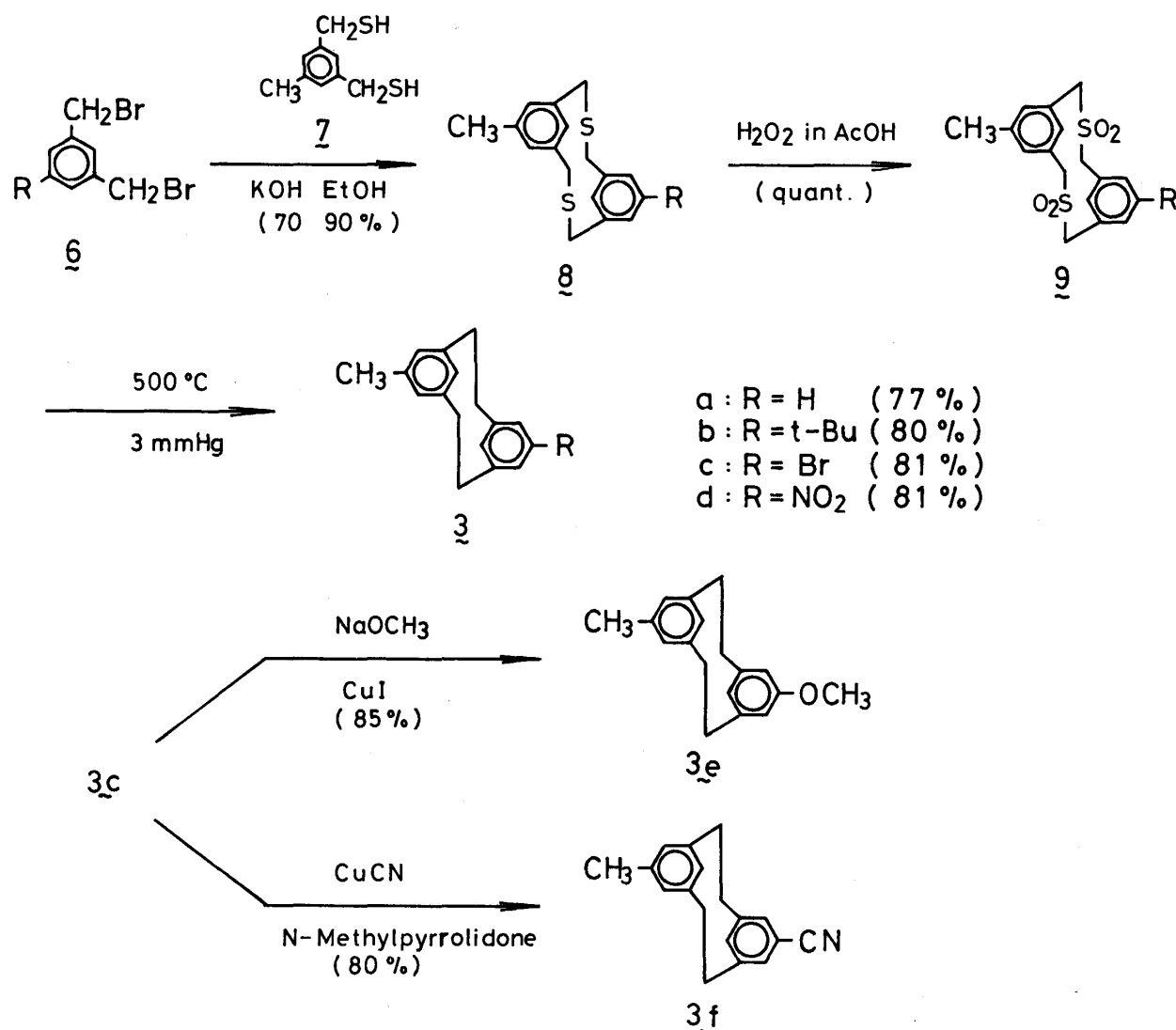


Scheme 1

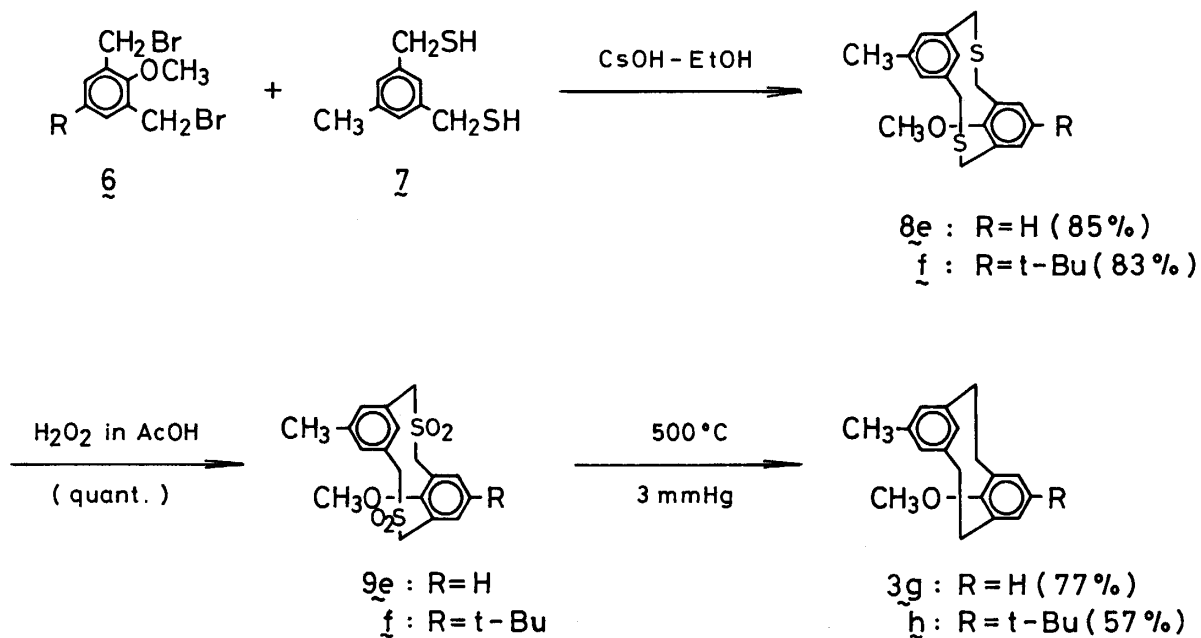
We now report the bromination of methyl [2.2] MCPs **3** with NBS, giving the corresponding bromomethyl [2.2] MCPs **4**, and the novel formation of 2-bromomethyl-7-tert-butylpyrene (**5**) in the reaction of 5-tert-butyl-8-methoxy-13-methyl [2.2] MCP (**3h**) with NBS.

## Results and Discussion

The preparative routes of **3a-3f** are shown in Scheme II and III. Compounds **6b<sup>2</sup>**, **6c<sup>6</sup>**, **6d<sup>7</sup>** and **7<sup>8</sup>** were prepared according to the reported methods, respectively. The desired **3a-3d** were prepared from the corresponding **6** and **7** via disulfides **8** and disulfones **9**. Compound **3e** and **3f** were obtained by the reaction of **3c** with MeONa and by the reaction with CuCN, respectively. Similarly, 5-methyl-16-methoxy [2.2] MCPs **3g** and **3h** were prepared by sulfur method.

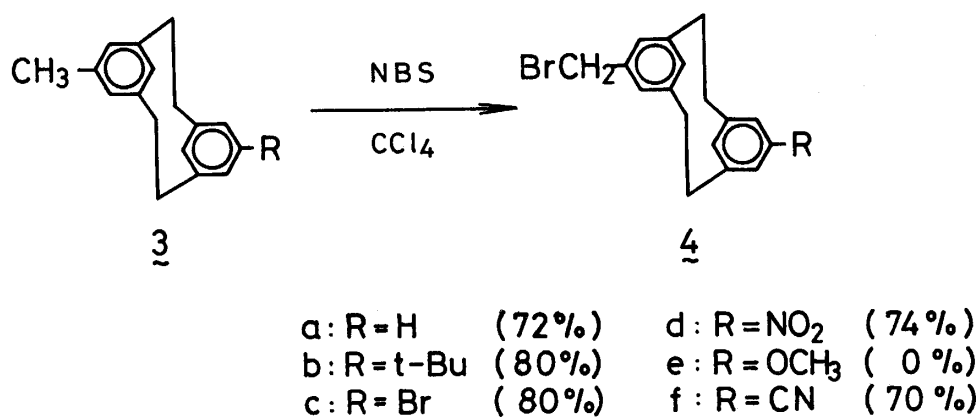


Scheme II



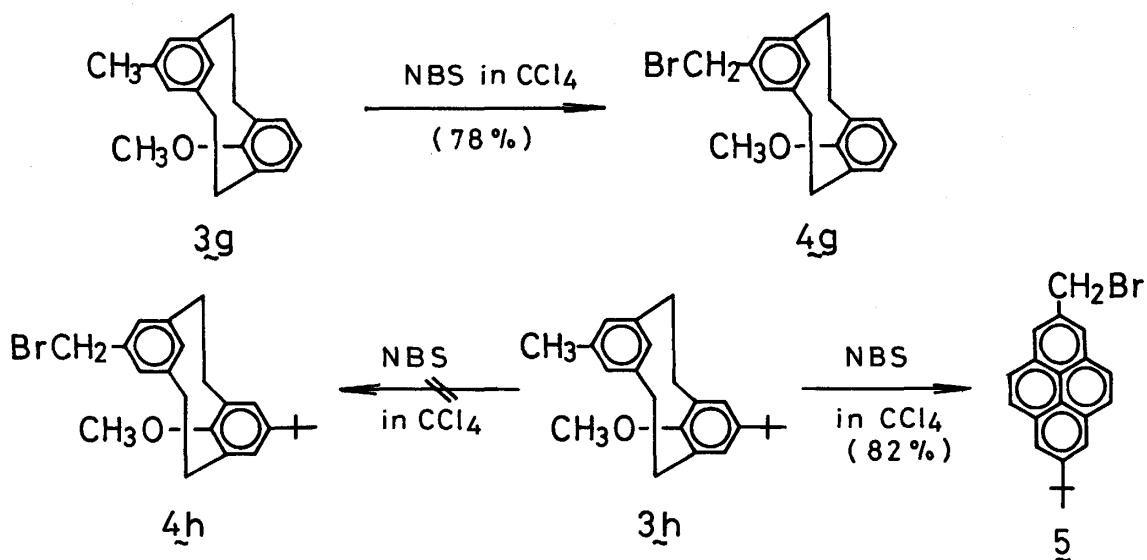
Scheme III

Compounds **3a-3d** and **3f** were treated with NBS in boiling carbon tetrachloride to afford the corresponding bromomethyl compounds **4a-4d** and **4f** in good yield, respectively. However, the bromination of **3e** with NBS did not afford any product under the same conditions, but **3e** was recovered in quantitative yield (Scheme IV).



Scheme IV

In the NBS-bromination of methoxy-methyl [2.2] MCP **3g**, the expected bromomethyl [2.2] MCP **4g** was obtained in 78% yield. On the other hand, tert-butyl derivative **3h** did not give the desired bromomethyl [2.2] MCP **4h** but unexpected compound, 2-bromomethyl-7-tert-butylpyrene (**5**) was obtained in 82% yield (Scheme V). This indicates that the tert-butyl group in **3h** plays an important role in the reaction with NBS to afford pyrene **5**.

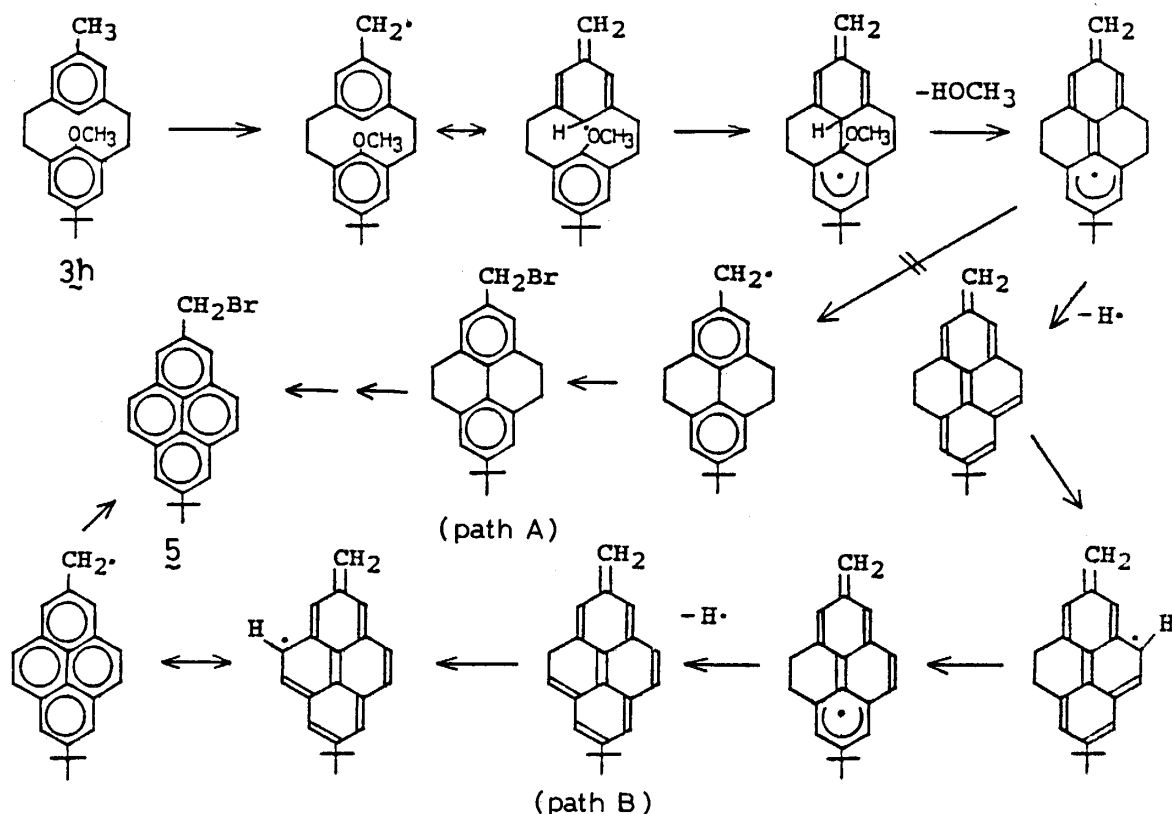


### Scheme V

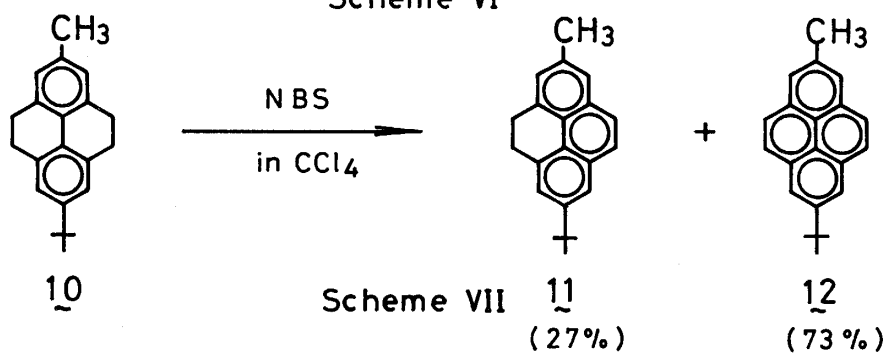
As shown in Scheme VI, two pathways are possible for the formation of **5** from **3h**. In path **A**, oxidation to pyrene skeleton precedes the bromination step and vice versa in path **B**.

Thus, tetrahydropyrene **10** was treated with NBS under the same conditions. Compound **5** was not obtained but the oxidation products, **11** and **12** were formed. From this result, path **B** was excluded and **5** might be formed via path **A**.

The scope of this novel preparative method of 2-bromomethylpyrenes is now under intense study.



Scheme VI



### Experimental Section

All melting points are uncorrected. NMR spectra were recorded at 100MHz with a Nippon Denshi JEOL FT-100NMR spectrometer with  $\text{Me}_4\text{Si}$  as an internal reference. IR spectra were measured on KBr pellets or as a liquid film on NaCl plates in a Nippon Bunko A-102 spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 spectrometer at 75 eV using a direct inlet system.

**Preparation of Methylthia [3.3] metacyclophanes (8). Typical Procedure.** A solution of 12.8g (50mmol) of 3,5-bis (mercaptomethyl) toluene (7)<sup>8</sup> and 16.0g (50mmol) of dibromo-*m*-xylene (6a) in 200mL of benzene was added dropwise, over a period of 24h from a Hershberg funnel with stirring under nitrogen, to a solution of 6.6g of potassium hydroxide in 4L of absolute ethanol. After the addition was completed, the reaction mixture was

concentrated and the residue was extracted with 500mL of dichloromethane. The dichloromethane extract was concentrated and chromatographed on  $\text{Al}_2\text{O}_3$  using a 1 : 1-mixture of hexane and benzene as an eluent to give colorless solid which, on recrystallization from a 1 : 1-mixture of hexane and benzene, afforded 11g (77%) of **8a** : 6-Methyl-2, 11-dithia [3.3] metacyclophane, colorless prisms ; mp 107-108°C (lit.,<sup>9</sup> 107-108°C).

Similarly, **8b-8f** were synthesized in the same manner as described above.

**8b** : 6-tert-Butyl-15-methyl-2,11-dithia [3.3] metacyclophane, colorless prisms (hexane); mp 86-89°C ; IR (KBr) 3010, 2950, 2900, 2850, 1595, 1450, 1410, 1355, 1220, 1180, 915, 890, 865, 730, 710, 695 $\text{cm}^{-1}$  ; NMR ( $\text{CDCl}_3$ )  $\delta$ 1.17 (9H, s), 2.10 (3H, s), 3.68 (4H, s), 3.73 (4H, s), 6.62 (3H, brs), 6.77 (1H, brs), 6.87 (2H, brs); mass spectrum, m/e 342 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{21}\text{H}_{21}\text{S}_2$  : C, 73.73 ; H, 7.63. Found : C, 73.63 ; H, 7.65.

**8c** : 6-Bromo-15-methyl-2, 11-dithia [3.3] metacyclophane, colorless prisms (a 1 : 1-mixture of hexane and benzene); mp 123-125°C (lit.,<sup>10</sup> 123-124°C).

**8d** : 6-Nitro-15-methyl-2, 11-dithia [3.3] metacyclophane, pale yellow prisms (benzene); mp 184-185°C (lit.,<sup>10</sup> 182-183°C).

**8e** : 9-Methoxy-15-methyl-2, 11-dithia [3.3] metacyclophane, colorless prisms (a 1 : 1-mixture of hexane and benzene); mp 183-184°C; IR (KBr) 2900, 1590, 1450, 1420, 1250, 1230, 1200, 1160, 1070, 1010, 880, 850, 810, 790, 760, 730, 700 $\text{cm}^{-1}$  ; NMR ( $\text{CDCl}_3$ )  $\delta$ 2.11 (3H, s) 3.72 (3H, s) 3.68 (4H, s), 3.47 and 4.25 (each 2H, d, J = 14Hz), 6.57-6.96 (6H, m); mass spectrum, m/e 316 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{18}\text{H}_{20}\text{OS}_2$  : C, 68.31 ; H, 6.37. Found : C, 68.48 ; H, 6.32.

**8f** : 6-tert-Butyl-9-methoxy-15-methyl-2,11-dithia [3.3] metacyclophane, colorless prisms (hexane); mp 150-151°C ; IR (KBr) 3040, 2950, 1600, 1480, 1460, 1430, 1410, 1260, 1225, 1200, 1170, 1100, 1015, 865, 740, 710 $\text{cm}^{-1}$  ; NMR ( $\text{CDCl}_3$ )  $\delta$ 1.10 (9H, s), 2.08 (3H, s) 3.67 (3H, s), 3.58 and 3.74 (each 2H, d, J = 16Hz), 3.44 and 4.22 (each 2H, d, J = 16Hz), 6.62 (2H, d, J = 2 Hz), 6.82 (1H, d, J = 2H.), 6.90 (2H, s); mass spectrum, m/e 372 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{22}\text{H}_{28}\text{OS}_2$  : C, 70.92 ; H, 7.58. Found : C, 71.21 ; H, 7.68.

#### Preparation of Methyl-2, 11-dithia [3.3] metacyclophane 2, 2, 11, 11-tetraoxides (**9**).

**Typical Procedure.** A mixture of 6.5mmol of **8**, 11 mL (about 100mmol) of 30% hydrogen peroxide, and 43mL of glacial acetic acid was refluxed for 12h. The reaction mixture was poured into a cold solution of 25g of sodium hydroxide in 100mL of water. The resulting paste was filtered and washed with a small amount of ethanol to afford colorless crystals of **9**.

**9a** : 6-Methyl-2, 11-dithia [3.3] metacyclophane-2, 2, 11, 11-teraoxide, colorless prisms (MeOH); mp > 300°C (lit.,<sup>10</sup> > 300°C). IR (KBr) 3010, 2980, 2930, 1600, 1400, 1319, 1270, 1175, 1120, 870, 700 $\text{cm}^{-1}$  ; mass m/e 350 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{17}\text{H}_{18}\text{S}_2\text{O}_4$  : C, 58.18 ; H, 5.18. Found : C, 58.23 ; H, 5.15

**9b** : 6-tert-Butyl-15-methyl-2, 11-dithia [3.3] metacyclophane-2, 2, 11, 11-teraoxide, colorless prisms ; mp > 300°C ; IR (KBr) 2960, 2920, 2870, 1595, 1455, 1405, 1360, 1320, 1300,

1260, 1175, 1110, 930, 905, 895, 875, 840, 795, 750, 700 $\text{cm}^{-1}$ ; NMR (DMSO- $\text{d}_6$ )  $\delta$ 1.14 (9H, s) 2.08 (3H, s), 4.52 (4H, brs), 4.57 (4H, brs), 6.89 (2H, s), 7.18 (2H, s), 7.29 (1H, s), 7.36 (1H, s); mass spectrum,  $m/e$  406 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{21}\text{H}_{26}\text{S}_2\text{O}_4$ : C, 62.04; H, 6.45. Found: C, 62.20; H, 6.50.

**9c**: 6-Bromo-15-methyl-2, 11-dithia [3.3] metacyclophane-2, 2, 11, 11-teraoxide, colorless prisms; mp  $> 300^\circ\text{C}$ ; IR (KBr) 2970, 2920, 1565, 1455, 1395, 1300, 1260, 1175, 1100, 900, 870, 815, 750, 715, 690 $\text{cm}^{-1}$ ; mass spectrum,  $m/e$  428, 430 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{17}\text{H}_{17}\text{BrS}_2\text{O}_4$ : C, 47.56; H, 3.99. Found: C, 47.89; H, 4.05.

**9d**: 6-Nitro-15-methyl-2, 11-dithia [3.3] metacyclophane-2, 2, 11, 11-teraoxide, colorless prisms; mp  $> 300^\circ\text{C}$  (lit., <sup>10</sup>  $> 300^\circ\text{C}$ ); IR (KBr) 3075, 2970, 2920, 1520, 1455, 1400, 1350, 1300, 1110, 970, 940, 910, 860, 840, 780, 755, 715, 685 $\text{cm}^{-1}$ ; mass  $m/e$  395 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{17}\text{H}_{17}\text{NS}_2\text{O}_6$ : C, 51.69; H, 4.33; N, 3.54. Found: C, 51.69; H, 4.41; N, 3.68.

**9e**: 9-Methoxy-15-methyl-2, 11-dithia [3.3] metacyclophane-2, 2, 11, 11-teraoxide, colorless prisms; mp  $> 300^\circ\text{C}$ ; IR (KBr) 2920, 2830, 1460, 1430, 1310, 1250, 1210, 1175, 1105, 1070, 990, 910, 870, 800, 770, 710 $\text{cm}^{-1}$ ; NMR (DMSO- $\text{d}_6$ )  $\delta$ 2.06 (3H, s), 3.71 (3H, s), 4.04-5.00 (8H, m), 6.85 (1H, s), 6.85-7.48 (6H, m); mass spectrum,  $m/e$  380 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{18}\text{H}_{20}\text{S}_2\text{O}_5$ : C, 56.82; H, 5.30. Found: C, 56.95; H, 5.46.

**9f**: 6-tert-Butyl-9-methoxy-15-methyl-2, 11-dithia [3.3] metacyclophane-2, 2, 11, 11-teraoxide, colorless prisms; mp  $> 300^\circ\text{C}$ ; IR (KBr) 3050, 2950, 1600, 1480, 1455, 1310, 1295, 1260, 1200, 1170, 1110, 985, 890, 860, 755, 715 $\text{cm}^{-1}$ ; NMR (DMSO- $\text{d}_6$ )  $\delta$ 1.13 (9H, s), 2.12 (3H, s), 3.72 (3H, s), 3.80-4.84 (8H, m), 7.00 (2H, s); mass spectrum,  $m/e$  435 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{22}\text{H}_{28}\text{O}_5\text{S}_2$ : C, 60.52; H, 6.46. Found: C, 60.22; H, 6.50

**Pyrolysis of Disulfones 9.** Pyrolysis of disulfones **9** was carried out in an apparatus consisting of horizontal tube (15mm in diameter) passing through two adjacent tube furnaces, each of which was 20cm long. The first furnace provided a temperature that would induce sublimation of disulfones **9**; the second was used at a higher temperature ( $500^\circ\text{C}$ ) that would assure pyrolysis. A vacuum pump was connected at the exit from the second furnace. Disulfone **9a** (1g) was placed in the first furnace and pyrolyzed at  $500^\circ\text{C}$  under reduced pressure (2-3mmHg) in the second furnace which was packed with small glass beads. The product which sublimed was collected and purified through chromatography on silica gel with hexane and recrystallization from methanol, affording 635mg (77%) of **3a**: 5-Methyl [2.2] metacyclophane, colorless prisms; mp  $64-65^\circ\text{C}$  (lit., <sup>9</sup>  $64.5-66^\circ\text{C}$ ).

Compounds **3b-3d** and **3g-3h** were synthesized in the same manner as described above.

**3b**: 5-tert-Butyl-13-methyl [2.2] metacyclophane, colorless oil; IR (NaCl) 3000, 3000, 22950, 2925, 2840, 1590, 1470, 1440, 1435, 1355, 1265, 1215, 1175, 950, 880, 840, 720 $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$ 1.24 (9H, s) 1.88-2.02 (4H, m), 2.26 (3H, s), 2.76-3.08 (4H, m), 3.96 (1H, brs), 4.07 (1H, t,  $J = 1\text{Hz}$ ), 6.94 (2H, d,  $J = 1\text{Hz}$ ); mass spectrum,  $m/e$  278 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{21}$



(1H, t,  $J = 1\text{Hz}$ ), 6.94 (2H, d,  $J = 1\text{Hz}$ ); mass spectrum,  $m/e$  278 ( $M^+$ ). Anal. Calcd. for  $C_{21}H_{26}$ : C, 90.59; H, 9.41. Found: C, 90.38; H, 9.42.

**3c**: 5-Bromo-13-methyl [2.2] metacyclophane, colorless prisms (hexane); mp 155-156°C (lit., <sup>10</sup> 153-154°C).

**3d**: 5-Methyl-13-nitro [2.2] metacyclophane, pale yellow prisms (hexane); mp 189-190°C (lit., <sup>10</sup> 188.5-190°C).

**3g**: 8-Methoxy-13-methyl [2.2] metacyclophane, colorless prisms (hexane); mp 72-73°C; IR (KBr) 2920, 2840, 1590, 1450, 1410, 1240, 1205, 1175, 1155, 1075, 1015, 950, 880, 840, 775, 750, 715 $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$ 2.29 (3H, s), 1.95-2.96 (8H, m), 3.01 (3H, s), 3.85 (1H, brs), 6.83 (2H, s), 7.02 (3H, s); mass spectrum,  $m/e$  251 ( $M^+$ ). Anal. Calcd. for  $C_{18}H_{20}O$ : C, 85.67; H, 7.99. Found: C, 85.97; H, 8.21

**3h**: 5-tert-Butyl-8-methoxy-13-methyl [2.2] metacyclophane, colorless prisms (methanol); mp 73-74°C, IR (KBr) 3040, 2930, 2860, 1600, 1475, 1460, 1435, 1290, 1235, 1200, 1180, 1100, 1015, 890, 840, 770, 720 $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$ 1.34 (9H, s), 1.92-2.20 (2H, s), 2.28 (3H, s), 2.40-3.00 (3H, s), 3.77 (1H, brs), 6.80 (2H, brs), and 7.00 (2H, s); mass spectrum  $m/e$  308 ( $M^+$ ); Anal. Calcd. for  $C_{22}H_{28}O$ : C, 85.66; H, 9.15. Found: C, 85.63; H, 9.15.

**Preparation of 3e.** To 72mL of methanol was added 2.18g (95mmol) of sodium and then a mixture of 0.7g of CuI and 1.7g (5.64mmol) of **4c** in 22mL of DMF was added. After the reaction mixture was refluxed for 26h, it was poured into a large amount of ice-water and extracted with dichloromethane. The dichloromethane solution was dried over sodium sulfate and evaporated in vacuo to leave the colorless solid which was recrystallized from hexane to give 1.2g (84.5%) of **4e**: 5-Methoxy-13-methyl [2.2] metacyclophane, colorless prisms (hexane); mp 111-112°C (lit., <sup>10</sup> 107-108°C).

**Von Braun Reaction with 3c. Preparation of 3f.** After a mixture of 5.0g (14.0mmol) of **4c** and 2.20g of cuprous cyanide in 20mL of N-methylpyrrolidone was heated at 180-185°C for 10h, it was then poured into 400mL of a 1:1-mixture of water and concentrated aqueous ammonia. After the resulting mixture had been stirred under cooling for 3c, the solid precipitates were collected by filtration, washed with water, and dried. The resulting solid was placed at the top of a silica gel column, and eluted with dichloromethane. From the eluent, it was isolated 3.4g (80%) of **3f**: 5-Cyano-13-methyl [2.2] metacyclophane, colorless prisms (hexane); mp 165-166°C (lit., <sup>10</sup> 167-167.5°C).

**Reaction of 3 with NBS. Typical Procedure.** After a mixture of 304mg (1.37mmol) of **4a**, 304 mg (1.7mmol) of NBS, and 50mg of dibenzoyl peroxide in 150mL of carbon tetrachloride was refluxed for 4h, the formed precipitates were filtered off. The filtrate was concentrated to give colorless solid which, on recrystallization from hexane, gave 297mg (72%) of **4a**: 5-Bromomethyl [2.2] metacyclophane, colorless prisms (hexane); mp 109-111°C; IR (KBr) 2940, 2850, 1475, 1450, 1430, 1310, 1285, 1205, 1180, 1160, 1110, 1080, 1030, 990, 950, 890,

850, 785, 755, 720, 700  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  1.97–3.23 (8H, m), 4.13 (1H, s), 4.27 (1H, s), 4.47 (2H, s), 6.73–7.63 (5H, m); mass spectrum,  $m/e$  300, 302 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{17}\text{H}_{17}\text{Br}$ : C, 67.78; H, 5.69. Found: C, 67.80; H, 5.61.

Compounds **4b–4d**, **4f**, were synthesized in the same manner as described above.

**4b**: 5-Bromomethyl-13-tert-butyl [2.2] metacyclophane, colorless prisms (hexane); mp 93–95°C; IR (KBr) 3025, 2940, 2850, 1585, 1470, 1440, 1390, 1360, 1330, 1270, 1210, 1175, 1150, 1050, 955, 890, 850, 725 $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  1.33 (9H, s), 1.96–2.20 (4H, m), 2.84–3.16 (4H, m), 4.10 (1H, t,  $J = 1\text{Hz}$ ), 4.17 (1H, t,  $J = 1\text{Hz}$ ), 4.50 (2H, s), 6.90–7.28 (4H, m); mass spectrum,  $m/e$  357, 359 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{21}\text{H}_{25}\text{Br}$ : C, 70.59; H, 7.05. Found: C, 70.63; H, 6.91.

**4c**: 13-Bromo-5-bromomethyl [2.2] metacyclophane, colorless prisms (hexane); mp 147–149°C; IR (KBr) 3010, 2950, 2850, 1585, 1555, 1430, 13330, 1285, 1275, 1210, 1175, 990, 955, 890, 875, 850, 785, 720, 705, 680 $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  1.88–2.32 (4H, m), 2.80–3.24 (4H, m), 4.15 (1H, t,  $J = 1\text{Hz}$ ), 4.28 (1H, t,  $J = 1\text{Hz}$ ), 4.41 (2H, s), 7.00 (2H, d,  $J = 1\text{Hz}$ ), 7.11 (2H, d,  $J = 1\text{Hz}$ ); mass spectrum,  $m/e$  377, 379, 381 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{17}\text{H}_{16}\text{Br}_2$ : C, 53.72; H, 4.24. Found: C, 53.39; H, 4.14.

**4d**: 5-Bromomethyl-13-nitro [2.2] metacyclophane, pale yellow prisms (hexane); mp 168–170°C; IR (KBr) 3020, 2920, 2850, 1580, 1510, 1430, 1340, 1210, 1175, 1085, 960, 920, 900, 850 $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  2.08–2.32 (4H, m), 3.04–3.38 (4H, m), 4.29 (1H, t,  $J = 1\text{Hz}$ ), 4.43 (1H, t,  $J = 1\text{Hz}$ ), 4.52 (2H, s), 7.13 (2H, d,  $J = 1\text{Hz}$ ), 7.92 (2H, d,  $J = 1\text{Hz}$ ); mass spectrum,  $m/e$  345, 347 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{17}\text{H}_{16}\text{NO}_2\text{Br}$ : C, 58.98; H, 4.66; N, 4.05. Found: C, 59.01, H, 4.82; N, 3.93.

**4f**: 5-Cyano-13-bromomethyl [2.2] metacyclophane, colorless prisms (AcOH); mp 190–192°C; IR (KBr) 3020, 2945, 2920, 2845, 2225, 1595, 1560, 1470, 14440, 1370, 1310, 1280, 1260, 1210, 1175, 1030, 990, 960, 890, 850, 790, 720, 700, 675 $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  2.00–2.24 (4H, M), 3.04–3.27 (4H, m), 4.25 (1H, s), 4.37 (1H, s), 4.51 (2H, s), 7.11 (2H, s), 7.35 (2H, s); mass spectrum,  $m/e$  325, 327 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{18}\text{H}_{16}\text{NBr}$ : C, 66.27; H, 4.94; N, 4.29. Found: C, 66.20; H, 5.20; N, 4.22.

**4g**: 5-Bromomethyl-16-methoxy [2.2] metacyclophane, colorless prisms (hexane); mp 170–172°C; IR (KBr) 2940, 2910, 2825, 1570, 1440, 1430, 1230, 1090, 855, 810, 770, 735, 715, 702 $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  2.31 (2H, s), 2.52 (3H, s), 2.78 (3H, s), 2.81 (3H, s), 3.22 (2H, s), 3.27 (1H, s), 6.87–8.00 (5H, m); mass spectrum,  $m/e$  329, 331 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{18}\text{H}_{19}\text{OBr}$ : C, 65.27; H, 5.78. Found: C, 65.58; H, 5.90.

**Reaction of 3h with NBS.** After a mixture of 422mg (1.37mmol) of **3h**, 304mg (1.7mmol) of NBS, and 50mg of dibenzoyl peroxide in 150mL of carbon tetrachloride was refluxed for 7h, it was treated as described above to give colorless solid which was recrystallized from hexane to give 394mg (82%) of **5**: 2-Bromomethyl-7-tert-butylpyrene, colorless

prisms (hexane); mp 213-214°C; IR (KBr) 2950, 2850, 1590, 1455, 1430, 1370, 1350, 1220, 1195, 1150, 1050, 985, 915, 875, 860, 790, 705cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>)  $\delta$  1.52 (4H, s), 2.76 (2H, s) 7.72-8.42 (8H, m); mass spectrum, m/e 350, 352 (M<sup>+</sup>). Anal. Calcd. for C<sub>21</sub>H<sub>19</sub>Br: C, 71.80; H, 5.45. Found: C, 71.69; H, 5.43.

**Reaction of 10 with NBS.** After a mixture of 210mg (0.76mmol) of **10**, 160mg (0.912mmol) of NBS, and 10mg of dibenzoyl peroxide in 20mL of carbon tetrachloride was refluxed for 1h, it was treated as described above to give colorless solid which was analyzed by GC to detect a 27:73-mixture of 2-tert-butyl-7-methyl-4,5-dihydropyrene (**11**) and 2-tert-butyl-7-methylpyrene (**12**). The structures of **11** and **12** were assumed by their <sup>1</sup>H-NMR spectra.

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