^{1}H NMR ($CDCl_3$) δ 2.10 (s, 3 H), 1.90–2.60 (m, 6 H), 3.00–3.20 (d, 2 H), 3.70 (s, 3 H); MS, *m/e* (relative intensity) 198 (M^+), 166 (45), 95 (35), 43 (100); IR (neat) 3000, 1760 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.34; H, 7.34.

In an another run, the allylation reaction was also carried out in the presence of patassium iodide (18 g, 2.0 equiv to CDOH). The reaction time was shortened to 2 h, and product **19** was obtained in a yield of 60%.

Ethyl Acetonylacetylacetate (20). By the general procedure B described above, **20** was obtained in a yield of 68% (6.4 g, 0.05-mol scale) as a colorless liquid by the reaction of ethyl acetylacetate with 1:1 equiv of **2**, bp 60 °C/0.1 Torr: ^{1}H NMR ($CDCl_3$) δ 1.20–1.35 (t, 3 H), 2.18 (s, 3 H), 2.37 (s, 3 H), 2.98–3.45 (m, 2 H), 3.95–4.35 (m, 3 H); MS, *m/e* (relative intensity) 187 ($M^+ + 1$), 101 (30), 55 (25), 43 (100); IR (neat) 3000, 1750, 1400, 1080 cm^{-1}. Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.65; H, 7.66.

With 2.2 equiv of **2**, ethyl diacetonylacetylacetate was also obtained in a yield of 17% as a colorless liquid by distillation at reduced pressure, bp 80 °C/0.1 Torr: ^{1}H NMR ($CDCl_3$) δ 1.02–1.49 (t, 3 H), 2.13 (s, 9 H), 3.35 (s, 4 H), 3.39–4.44 (q, 2 H); MS, *m/e* (relative intensity) 242 (M^+), 199 (30), 111 (100), 43 (60); IR (neat) 2950, 1720, 1360, 1200, 1020 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.23; H, 7.56. In this reaction, 10% of monoacetonylacetylacetate was also obtained together with a substantial amount of unidentified substances.

3-Acetonylacetylacetone (21). By the general procedure B described above, **21** was obtained in a yield of 64% (5.0 g) as a colorless liquid, bp 130 °C/10 Torr: ^{1}H NMR ($CDCl_3$) δ 2.00–2.40 (m, 9 H), 2.70 (s, 0.2 H), 2.99–3.02 (d, 1.6 H), 3.40 (s, 0.4 H), 4.10–4.28 (t, 0.8 H); MS, *m/e* (relative intensity) 156 (M^+), 96 (20), 71 (40), 43 (100); IR (neat) 2950, 1720, 1380, 1180 cm^{-1}. Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.15; H, 7.85.

3-Acetonylindene (22). By the same procedure used for **18**, **22** was obtained in a yield of 70% (6.0 g, 0.05-mol scale) as a slightly yellowish liquid, bp 80 °C/0.05 Torr: ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 3 H), 3.40 (s, 2 H), 3.64 (s, 2 H), 6.40 (s, 1 H), 7.10–7.52 (m, 4 H); MS, *m/e* (relative intensity) 172 (M^+), 129 (100), 43 (65); IR (neat) 3100, 2900, 1750, 1640, 1400 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83,21; H, 7.07.

9,9-Diacetonylfluorene (23). The diacetonylation was carried out by treating fluorene (8.3 g, 0.05 mol) with **2** (15.0 g, 0.11 mol) at 30 °C for 4 h in the presence of the PT catalyst and conditions similar to those used for **18**, followed by hydrolysis with a mixture of dilute aqueous sulfuric acid and dioxane at 60 °C for 1 h to afford **23** in a yield of 78% (10.9 g) as a yellowish waxy solid, bp 130 °C/0.05 Torr; mp 61–62 °C: ^{1}H NMR ($CDCl_3$) δ 1.90 (s, 6 H), 3.21 (s, 4 H), 7.20–7.40 (m, 4 H), 7.50–7.80 (m, 4 H); MS, *m/e* (relative intensity) 278 (M^+), 221 (25), 179 (30), 43 (100); IR (neat) 3050, 2925, 1740, 1480, 1360, 1200, 1140, 980, 800, 760 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 82.03; H, 6.41.

Diacetonylphenylacetonitrile (24). The diacetonylation was carried out at 60 °C for 3 h, and hydrolysis was accomplished in a manner similar to that used for **23**. **24** was obtained in a yield of 61% (7.0 g, 0.05-mol scale) as a yellowish waxy solid, bp 120 °C/0.05 Torr; mp 105–106 °C: ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 6 H), 3.40 (s, 4 H), 7.20–7.60 (m, 5 H); MS, *m/e* (relative intensity) 229 (M^+), 143 (40), 82 (50), 43 (100); IR (neat) 2900, 2240, 1740, 1180 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.60; N, 6.11. Found: C, 73.72; H, 6.53; N, 6.04.

Bis(2-methylene-3,5-dioxahexyl)decylamine (25). Decylamine (4.7 g, 0.03 mol) was treated with **2** (9.5 g, 0.07 mol) under the same conditions used for **10**. After the usual workup, the diallylic amine (bis(2-methylene-3,5-dioxahexyl)decylamine) was obtained by Kugelrohr distillation at reduced pressure in a yield of 50% (5.4 g) as a colorless liquid, bp 140 °C/0.07 Torr: ^{1}H NMR ($CDCl_3$) δ 0.74–1.00 (t, 3 H), 1.10–1.80 (m, 16 H), 2.40–2.60 (m, 2 H), 3.17 (s, 4 H), 3.43 (s, 6 H), 4.25 (s, 4 H), 4.96 (s, 4 H); MS, *m/e* (relative intensity) 357 (M^+), 230 (75), 45 (100); IR (neat) 2950, 1640, 1460, 1160, 1110, 1040 cm^{-1}.

Treatment of bis(2-methylene-3,5-dioxahexyl)decylamine in acidic water–dioxane (H_2SO_4) afforded a complicated mixture (by GLC).

Registry No. 1, 70905-45-2; **2**, 105104-40-3; **5**, 108270-19-5; **7**, 105104-43-6; **9**, 108270-20-8; **10**, 23982-57-2; **11**, 20233-08-3; **12**, 5042-53-5; **13**, 108270-21-9; **14**, 108270-22-0; **15**, 40657-11-2; **16**, 621-87-4; **17**, 108270-23-1; **18**, 24889-15-4; **19**, 92825-45-1; **20**, 41892-81-3; **21**, 42781-07-7; **22**, 103556-85-0; **23**, 108270-24-2; **24**, 108270-25-3; **25**, 108270-26-4; $C_{11}H_{23}COOH$, 143-07-7; $C_8H_{17}SH$, 111-88-6; $C_{10}H_{21}OH$, 112-30-1; $(CH_3OCO)_2CH_2$, 108-59-8; $CH_3C(O)CH_2COOC_2H_5$, 141-97-9; $CH_3C(O)CH_2C(O)CH_3$, 123-54-6; n-$C_{10}H_{21}NH_2$, 2016-57-1; methylbenzylamine, 103-67-3; benzenethiol, 108-98-5; (hydroxymethyl)-15-crown-5, 75507-25-4; tetraethylene glycol, 112-60-7; phenol, 108-95-2; phenyl glycidyl sulfide, 5296-21-9; 2-(methoxycarbonyl)cyclopentanone, 10472-24-9; ethyl diacetonylacetylacetate, 85288-60-4; indene, 95-13-6; fluorene, 86-73-7; phenylacetonitrile, 140-29-4.

Metacyclophanes and Related Compounds. 19. Reaction of 8-Methoxy[2.2]metacyclophanes with Iodine in Benzene Solution. A Preparative Route of Pyrenes[1]

Masashi Tashiro,* Takehiko Yamato, Kazumasa Kobayashi, and Takashi Arimura

Research Institute of Industrial Science and Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University 86, 6-1 Kasuga-kohen, Kasuga-shi, Fukuoka 816, Japan

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When 8-methoxy[2.2]metacyclophanes are treated with iodine in boiling benzene, the corresponding tetrahydropyrenes (**8**) are obtained in good yield. The $AlCl_3$-catalyzed trans-*tert*-butylation of **8** effected loss of the *tert*-butyl group to give **10a–c**, which were easily dehydrogenated with DDQ to afford the corresponding pyrene derivatives.

Although reaction of 8,16-unsubstituted [2.2]metacyclophanes with iodine in boiling benzene afforded the corresponding hexahydropyrenes,[2,3] 8,16-disubstituted [2.2]metacyclophanes did not react with iodine under similar conditions.[4] These results prompted us to investigate the reaction of 8-monosubstituted [2.2]metacyclophanes with iodine.

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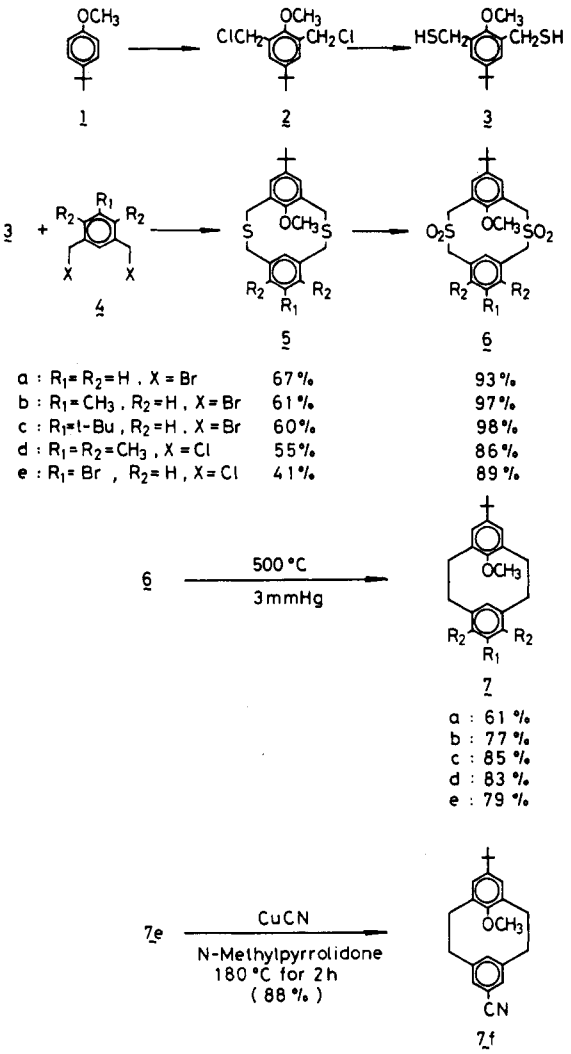
0022-3263/87/1952-3196$01.50/0

Scheme I



We report here the reaction of 8-methoxy[2.2]metacyclophanes **7a–f** with iodine in boiling benzene.

Results and Discussion

The preparative route of **7a–f** is shown in Scheme I, and the preparation of **2** and **3** is described in a previous paper.[5] Compounds **4b**,[6] **4c**,[4] **4d**,[7] and **4e**[8] were prepared according to the reported methods, respectively. The desired **7a–e** were prepared from the corresponding **3** and **4** via the disulfides **5** and bissulfones **6**. Compound **7f** was obtained by the reaction of **7e** with CuCN in *N*-methylpyrrolidone.

Compounds **7a–f** were treated with iodine in boiling benzene. The results are summarized in Table I.

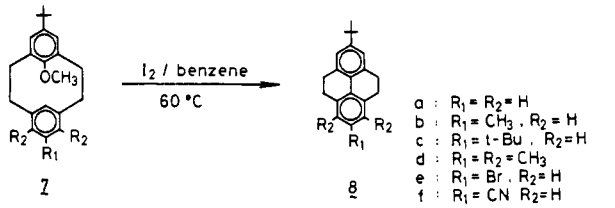
As shown in Table I, the reaction of **7e** and **7f**, having electron-withdrawing groups such as bromo and cyano, with iodine did not afford any product, but **7e** and **7f** were recovered in quantitative yield, respectively. Contrary, **7a–d** gave the corresponding tetrahydropyrenes **8a–d**, respectively . The order of reactivity of **7a–d** to iodine is estimated as follows: **7d > 7b ≃ 7c > 7a**.

Although the detailed mechanism of formation of 8 is not clear, one might assume the reaction pathway shown in Scheme III.

Iodo cation attacks the ipso position of 7 to form intermediate A, from which 8 might be produced via intermediates B and C. In the cases of **7e** and **7f**, which have electron-attracting groups such as Br and CN, the intermediate B might be labile, so that the reacton of **7e** and **7f** with iodine might not occur.

Dehydrogenation of **8a–c** with DDQ in benzene afforded the corresponding pyrenes **9** in good yields. The trans-

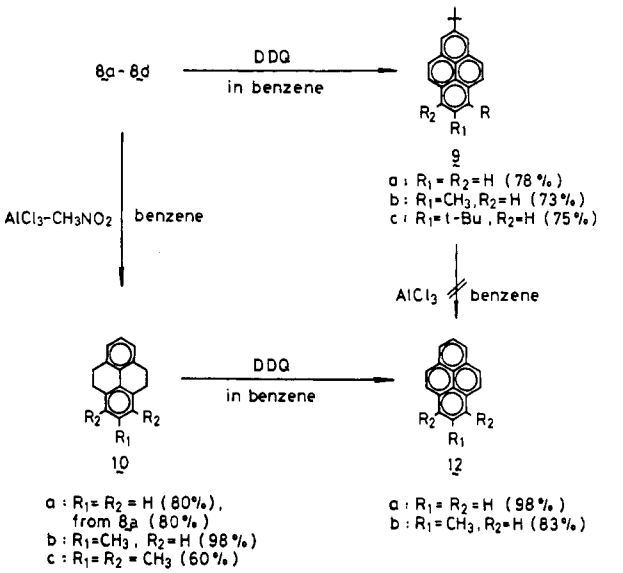
Table I. Reaction of 8-Methoxy[2.2]metacyclophanes 7a–f with Iodine in Benzene at 60 °C



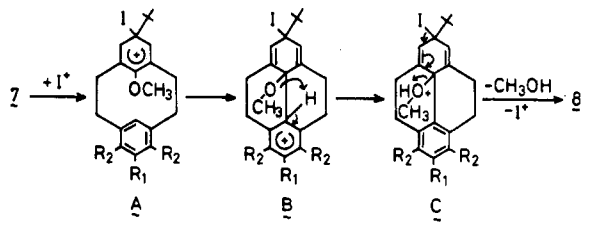
run	substr	I_2/7 (mol/mol)	time (h)	product (%)[a]	recovd 7 (%)[a]
1	**7a**	0.7	16	**8a** (3)	**7a** (96)
2	**7a**	2.0	16	**8a** (20)	**7a** (78)
3	**7a**	2.0	72	**8a** (88) (84)[b]	**7a** (4)
4	**7b**	2.0	3	**8b** (94)	**7b** (5)
5	**7b**	2.0	6	**8b** (100) (91)[b]	
6	**7c**	2.0	3	**8c** (89)	**7c** (10)
7	**7c**	2.0	6	**8c** (94) (85)[b]	**7c** (2)
8	**7d**	0.7	16	**8d** (96)	**7d** (2)
9	**7d**	2.0	1	**8d** (88)	**7d** (10)
10	**7d**	2.0	3	**8d** (100) (89)[b]	
11	**7e**	2.0	16	no reaction	**7e** (100)
12	**7f**	2.0	16	no reaction	**7f** (100)

[a] The product yields were determined by GC analyses. [b] Isolated yields are shown.

Scheme II



Scheme III



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tert-butylation[9] of **9** in benzene did not afford any product. However, a similar reaction of **8a–d** effected removal of the *tert*-butyl group to give **10a–c** together with *tert*-butylbenzene (**11**). The same product **10a** was obtained from both **8a** and **8c**.

The dehydrogenation of **10a** and **10b** with DDQ in benzene afforded the corresponding pyrenes **12a,b** in good yield. The above results suggest that the reaction routes **7** → **8** → **10** → **12** might be useful for the preparation of pyrene derivatives having alkyl groups.

Experimental Section

Preparation of 9-Methoxydithia[3.3]metacyclophanes 5. Typical Procedure. A solution of 12.8 g (50 mmol) of 2,6-bis(mercaptomethyl)-4-*tert*-butylanisol (**3**)[5] and 16.0 g (50 mmol) of α,α'-dibromo-*m*-xylene (**4a**) in 200 mL of benzene was added dropwise from a Hershberg funnel with stirring under nitrogen to a solution of 6.6 g of potassium hydroxide in 4.0 L of absolute ethanol. When addition was completed (24 h), the mixture was concentrated and the residue was extracted with 500 mL of dichloromethane. The dichloromethane extract was concentrated and the residue was chromatographed over Al_2O_3, using a 1:1 mixture of hexane and benzene as an eluent to give a colorless solid, which was recrystallized from a 10:1 mixture of hexane and benzene to afford 10.9 g (67%) of **6-*tert*-butyl-9-methoxy-2,11-dithia[3.3]metacyclophane (5a)** as colorless prisms (hexane/benzene 10:1): mp 182.5–183 °C; IR (KBr) 2950, 1585, 1480, 1455, 1430, 1410, 1400, 1355, 1305, 1255, 1220, 1200, 1170, 1100, 1005, 900, 885, 790, 730, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.10 (9 H, s), 3.66 (3 H, s), 3.38–4.30 (8 H, m), 6.84–6.86 (3 H, m), 6.90 (2 H, s), 6.99 (1 H, br s); mass spectrum, *m/e* 358 (M^+). Anal. Calcd for $C_{21}H_{26}OS_2$: C, 70.35; H, 7.31. Found: C, 70.39; H, 7.32.

Similarly, compounds **5b–e** were synthesized in the same manner as described above.

6-*tert*-Butyl-15-methyl-9-methoxy-2,11-dithia[3.3]metacyclophane (5b): 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 cm^{-1}; NMR ($CDCl_3$) δ 1.10 (9 H, s), 2.08 (3 H, s), 3.58, 3.74 (4 H, AB pattern, J_{AB} = 16 Hz), 3.44, 4.22 (4 H, AB pattern, J_{AB} = 16 Hz), 6.62 (2 H, d, J = 2 Hz), 6.82 (1 H, d, J = 2 Hz), 6.90 (2 H, s); mass spectrum, *m/e* 372 (M^+). Anal. Calcd for $C_{22}H_{28}OS_2$: C, 70.92; H, 7.58. Found: C, 71.21; H, 7.68.

6,15-Di-*tert*-butyl-9-methoxy-2,11-dithia[3.3]metacyclophane (5c): colorless prisms (hexane); mp 118–119 °C; IR (KBr) 3050, 2970, 2900, 1600, 1480, 1460, 1430, 1360, 1260, 1220, 1200, 1170, 1100, 1015, 875, 710 cm^{-1}; NMR ($CDCl_3$) δ 1.08 (9 H, s), 1.14 (9 H, s), 3.46 (2 H, d, J = 15 Hz), 3.60 (2 H, d, J = 15 Hz), 3.66 (3 H, s), 3.78 (2 H, d, J = 15 Hz), 4.19 (2 H, d, J = 15 Hz), 6.84–6.90 (5 H, m); mass spectrum, *m/e* 414 (M^+). Anal. Calcd for $C_{25}H_{34}OS_2$: C, 72.41; H, 8.27. Found: C, 72.19; H, 8.17.

6-*tert*-Butyl-9-methoxy-14,15,16-trimethyl-2,11-dithia[3.3]metacyclophane (5d): colorless prisms (hexane/benzene, 2:1); mp 242–244 °C; IR (KBr) 3050, 2950, 1600, 1475, 1425, 1255, 1200, 1170, 1100, 1000, 920, 880, 860, 810, 780, 760 cm^{-1}; NMR ($CDCl_3$) δ 1.00 (9 H, s), 1.95 (3 H, s), 2.05 (6 H, s), 3.43, 4.30 (4 H, AB pattern, J_{AB} = 14 Hz), 3.68 (7 H, s), 6.71 (1 H, br s), 6.91 (2 H, s); mass spectrum, *m/e* 400 (M^+). Anal. Calcd for $C_{24}H_{32}OS_2$: C, 71.95; H, 8.05. Found: C, 72.24; H, 8.24.

15-Bromo-6-*tert*-butyl-9-methoxy-2,11-dithia[3.3]metacyclophane (5e): colorless prisms (hexane/benzene, 1:1); mp 218–219 °C; IR (KBr) 3050, 2950, 1600, 1560, 1475, 1430, 1410, 1250, 1220, 1200, 1170, 1100, 1000, 875, 860, 735, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.66 (9 H, s), 3.45, 4.20 (4 H, AB pattern, J_{AB} = 16 Hz), 3.56, 3.73 (4 H, AB pattern, J_{AB} = 16 Hz), 3.68 (3 H, s), 6.84–7.00 (5 H, m); mass spectrum, *m/e* 435, 437 (M^+). Anal. Calcd for $C_{21}H_{25}BrOS_2$: C, 57.65; H, 5.76. Found: C, 57.72; H, 5.61.

Preparation of 9-Methoxy-2,11-dithia[3.3]metacyclophane 2,2,11,11-Tetraoxide 6. Typical Procedure. To a solution of 2.97 g (8.3 mmol) of **5a** in a 150 mL of chloroform was added 8.4 g (41.5 mmol, 85% purity) of *m*-chloroperbenzoic acid at 0 °C, while stirring with a magnetic stirrer. After the solution was stirred for 48 h at room temperatue, the solvent was evaporated in vacuo to leave the residue that was washed with 10% aqueous sodium bicarbonate, water, and ethanol to afford 3.26 g (93%) of **6-*tert*-butyl-9-methoxy-2,11-dithia[3.3]metacyclophane *S,S,S',S'*-tetraoxide (6a)**: colorless prisms; mp >300 °C; IR (KBr) 2950, 1485, 1390, 1360, 1315, 1265, 1205, 1180, 1110, 990, 910, 890, 855, 810, 750, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.14 (9 H, s), 3.74 (3 H, s), 3.84–4.86 (8 H, m), 6.89–7.37 (6 H, m); mass spectrum, *m/e* 422 (M^+). Anal. Calcd for $C_{21}H_{26}O_5S_2$: C, 59.69; H, 6.20. Found: C, 59.35; H, 6.16.

Similarly, compounds **6b–e** were synthesized in the same manner as described above.

6-*tert*-Butyl-15-methyl-9-methoxy-2,11-dithia[3.3]metacyclophane *S,S,S',S'*-tetraoxide (6b): colorless prisms; mp >300 °C; IR (KBr) 3050, 2950, 1600, 1480, 1455, 1310, 1295, 1260, 1200, 1170, 1110, 985, 890, 860, 755, 715 cm^{-1}; NMR ($CDCl_3$) δ 1.13 (9 H, s), 2.12 (3 H, s), 3.72 (3 H, s), 3.80–4.84 (8 H, m), 7.00 (2 H, d, J = 2 Hz), 7.18 (1 H, d, J = 2 Hz), 7.29 (2 H, s); mass spectrum, *m/e* 435 (M^+). Anal. Calcd for $C_{22}H_{28}O_5S_2$: C, 60.52; H, 6.46. Found: C, 60.31; H, 6.31.

6,15-Di-*tert*-butyl-9-methoxy-2,11-dithia[3.3]metacyclophane *S,S,S',S'*-tetraoxide (6c): colorless prisms (benzene); mp 268.5–269.5 °C; IR (KBr) 3040, 2970, 2930, 1600, 1485, 1480, 1360, 1320, 1260, 1220, 1205, 1180, 1170, 1115, 1000, 895, 885, 850, 710 cm^{-1}; NMR ($CDCl_3$) δ 1.12 (9 H, s), 1.16 (9 H, s), 3.74 (3 H, s), 3.83–4.85 (8 H, m), 7.20–7.30 (5 H, m); mass spectrum, *m/e* 478 (M^+). Anal. Calcd for $C_{25}H_{34}O_5S_2$: C, 62.73; H, 7.16. Found: C, 62.03; H, 6.72.

6-*tert*-Butyl-9-methoxy-14,15,16-trimethyl-2,11-dithia[3.3]metacyclophane *S,S,S',S'*-tetraoxide (6d): colorless prisms; mp >300 °C; IR (KBr) 3050, 2950, 1600, 1480, 1310, 1300, 1260, 1175, 1110, 985, 920, 890, 850, 740 cm^{-1}; NMR ($CDCl_3$) δ 1.04 (9 H, s), 1.99 (3 H, s), 2.17 (6 H, s), 3.75 (3 H, s), 3.84–4.48 (4 H, m), 3.19, 3.86 (4 H, AB pattern, J_{AB} = 15 Hz), 7.02 (1 H, br s), 7.40 (2 H, s); mass spectrum, *m/e* 464 (M^+), 336 ($M^+ - 2SO_2$). Anal. Calcd for $C_{24}H_{32}O_5S_2$: C, 62.04; H, 6.94. Found: C, 61.48; H, 6.90.

15-Bromo-6-*tert*-butyl-9-methoxy-2,11-dithia[3.3]metacyclophane *S,S,S',S'*-tetraoxide (6e): colorless prisms; mp >300 °C; IR (KBr) 3050, 2950, 1600, 1565, 1440, 1320, 1270, 1170, 1115, 1000, 900, 875, 860, 750, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (9 H, s), 3.74 (3 H, s), 3.83–4.13 (4 H, m), 4.32, 4.76 (4 H, AB pattern, J_{AB} = 14 Hz), 7.28–7.39 (5 H, m); mass spectrum, *m/e* 499, 501 (M^+). Anal. Calcd for $C_{21}H_{25}BrO_5S_2$: C, 50.30; H, 5.03. Found: C, 50.13; H, 4.90.

Pyrolysis of Disulfones 6. Pyrolysis of disulfones of [2.2]metacyclophanes **6** 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. Disulfone **6a** (1 g) 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 first furnace and small glass beads were packed into the second furnace. The product which sublimed was collected and chromatographed on silica gel with hexane to yield the desired [2.2]metacyclophane. Recrystallization from methanol afforded 425 mg (61%) of 5-*tert*-butyl-8-methoxy[2.2]metacyclophane (**7a**): colorless prisms (methanol); mp 96–99 °C; IR (KBr) 2950, 2925, 1595, 1480, 1430, 1360, 1290, 1205, 1180, 1100, 1020, 950, 890, 870, 790, 770, 720 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (9 H, s), 2.00–3.00 (8 H, m), 3.00 (3 H, s), 3.94 (1 H, br s), 7.02 (5 H, s); mass spectrum, *m/e* 294 (M^+). Anal. Calcd for $C_{21}H_{26}O$: C, 85.67, H, 8.90. Found: C, 85.48; H, 8.99.

Similarly, compounds **4b–e** were synthesized in the same manner as described above.

5-*tert*-Butyl-13-methyl-8-methoxy[2.2]metacyclophane (7b): colorless prisms (methanol); mp 73–74 °C; IR (KBr) 3040, 2930, 2860, 1600, 1475, 1460, 1435, 1290, 1235, 1200, 1180, 1100, 1015, 890, 860, 840, 770, 720, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.34 (9 H, s), 1.92–2.20 (2 H, m), 2.28 (3 H, s), 2.40–3.00 (6 H, m), 3.00 (3 H, s), 3.77 (1 H, br s), 6.80 (2 H, br s), 7.00 (2 H, s); mass spectrum, *m/e* 308 (M^+). Anal. Calcd for $C_{22}H_{28}O$: C, 85.66; H,

(9) Tashiro, M. *Synthesis* **1979**, 921.

9.15. Found: C, 85.63; H, 9.15.

5,13-Di-*tert*-butyl-8-methoxy[2.2]metacyclophane (7c): colorless prisms (methanol); mp 118–120 °C; IR (KBr) 3050, 2950, 1590, 1470, 1420, 1360, 1270, 1240, 1200, 1180, 1100, 1020, 880, 845, 720, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (9 H, s), 1.32 (9 H, s), 1.94–3.16 (8 H, m), 2.93 (3 H, s), 3.88 (1 H, br s), 7.00 (4 H, s); mass spectrum, m/e 350. Anal. Calcd for $C_{25}H_{34}O$: C, 85.66; H, 9.78. Found: C, 86.04; H, 9.71.

5-*tert*-Butyl-8-methoxy-12,13,14-trimethyl[2.2]metacyclophane (7d): colorless prisms (methanol); mp 96–97 °C; IR (KBr) 3050, 2950, 2870, 1590, 1480, 1455, 1430, 1285, 1240, 1200, 1170, 1100, 1015, 940, 870, 770, 710 cm^{-1}; NMR ($CDCl_3$) δ 1.32 (9 H, s), 1.58–1.87 (2 H, m), 2.16 (3 H, s), 2.24 (6 H, s), 2.34–2.68 (4 H, m), 2.93 (3 H, s), 3.20–3.40 (2 H, m), 3.91 (1 H, br s), 6.97 (2 H, s); mass spectrum, m/e 336 (M^+). Anal. Calcd for $C_{24}H_{32}O$: C, 85.66; H, 9.59. Found: C, 85.93; H, 9.80.

13-Bromo-5-*tert*-butyl-8-methoxy[2.2]metacyclophane (7e): colorless prisms (methanol); mp 113–114 °C; IR (KBr) 3050, 2950, 2870, 1585, 1560, 1480, 1420, 1290, 1240, 1200, 1180, 1160, 1100, 1015, 880, 850, 790, 705 cm^{-1}; NMR ($CDCl_3$) δ 1.33 (9 H, s), 1.90–2.17 (2 H, m), 2.42–3.00 (6 H, m), 3.03 (3 H, s), 3.88 (1 H, br s), 7.00 (2 H, s), 7.12 (2 H, d, J = 1.5 Hz); mass spectrum, m/e 372, 374 (M^+). Anal. Calcd for $C_{21}H_{25}BrO$: C, 67.57; H, 6.73. Found: C, 67.69; H, 6.70.

Von Braun Reaction with 7e To Give 7f. A solution of 932.5 mg (2.5 mmol) of **7e** and 4.0 g of cuprous cyanide in 30 mL of *N*-methylpyrrolidone was heated at 180–185 °C for 21 h. It was then poured into 400 mL of a 1:1 mixture of water and concentrated aqueous ammonium hydroxide. After the resulting mixture had been stirred with cooling for 3 h, the solid precipitate was 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 eluate there was isolated 700 mg (87.6%) of 5-*tert*-butyl-13-cyano-8-methoxy[2.2]metacyclophane (**7f**): colorless prisms (methanol); mp 169–170 °C; IR (KBr) 3050, 2950, 2860, 2230, 1580, 1480, 1460, 1440, 1290, 1270, 1240, 1205, 1180, 1100, 1015, 895, 870, 855, 720, 705 cm^{-1}; NMR ($CDCl_3$) δ 1.33 (9 H, s), 1.94–3.10 (8 H, m), 2.98 (3 H, s), 4.10 (1 H, br s), 7.05 (2 H, s), 7.30 (2 H, d, J = 2 Hz); mass spectrum, m/e 319 (M^+). Anal. Calcd for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.39. Found: C, 82.50; H, 7.97; N, 4.53.

Reaction of 7 with Iodine. Typical Procedure. A solution of 153 mg (0.52 mmol) of **7a** and 262 mg (1.04 mmol) of iodine in 3 mL of benzene was stirred for 72 h at 60 °C. The reaction mixture was washed with 10% sodium thiosulfate solution and then with water. The benzene solution was dried over Na_2SO_4 and concentrated to give the mixture of **8a** and **7a** in 88.0% and 3.5% yields, respectively. (The yields were determined by GLC analyses.)

The mixture was taken up with dichloromethane and chromatographed over silica gel, using a hexane as an eluent, to give colorless solid, which was recrystallized from hexane to give 90 mg (83.7%) of **2-*tert*-butyl-4,5,9,10-tetrahydropyrene (8a)**: colorless plates (hexane); mp 108–109.5 °C; IR (KBr) 2930, 1600, 1460, 1450, 1430, 1420, 1355, 1240, 870, 770, 735 cm^{-1}; NMR ($CDCl_3$) δ 1.34 (9 H, s), 2.86 (8 H, s), 7.02–7.06 (5 H, m); mass spectrum, m/e 262 (M^+). Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.09; H, 8.42.

Similarly, compounds **8b**, **8c**, and **8d** were obtained in the same manner as described above.

2-*tert*-Butyl-7-methyl-4,5,9,10-tetrahydropyrene (8b): colorless prisms (methanol); mp 116–117 °C; IR (KBr) 3040, 2960, 2950, 2900, 2850, 1610, 1460, 1420, 1360, 1245, 870, 860, 740 cm^{-1}; NMR ($CDCl_3$) δ 1.32 (9 H, s), 2.30 (3 H, s), 2.84 (4 H, s), 6.83 (2 H, s), 7.04 (2 H, s); mass spectrum, m/e 276 (M^+). Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.17; H, 8.69.

2,7-Di-*tert*-butyl-4,5,9,10-tetrahydropyrene (8c): colorless prisms (methanol); mp 234–235 °C (lit.[10] mp 223–224 °C).

2-*tert*-Butyl-6,7,8-trimethyl-4,5,9,10-tetrahydropyrene (8d): colorless prisms (hexane); mp 190–191 °C; IR (KBr) 3040, 2960, 2900, 2850, 1600, 1430, 1360, 1280, 1230, 1200, 870, 715 cm^{-1}; NMR ($CDCl_3$) δ 1.31 (9 H, s), 2.24 (9 H, s), 2.81 (8 H, s), 7.02 (2 H, s); mass spectrum, m/e 304 (M^+). Anal. Calcd for $C_{23}H_{28}$: C, 90.73; H, 9.27. Found: C, 90.34; H, 9.51.

Reaction of 8 with DDQ. Typical Procedure. A solution of 262 mg (1 mmol) of **8a** and 322 mg of DDQ (90% purity) in 30 mL of benzene was refluxed for 4 h. After the reaction mixture was cooled and concentrated, the residue was extracted and chromatographed on silica gel with hexane/benzene (1:1) as eluant to give 200 mg (77.5%) of **2-*tert*-butylpyrene (9a)**: colorless prisms (methanol); mp 109–110 °C; IR (KBr) 3050, 2970, 1600, 1480, 1460, 1440, 1390, 1380, 1360, 1215, 1180, 875, 840, 815, 750, 710 cm^{-1}; NMR ($CDCl_3$) δ 1.57 (9 H, s), 7.82–8.16 (9 H, m); mass spectrum, m/e 258 (M^+). Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.81; H, 6.89.

Similarly, compounds **9b,c** were synthesized in the same manner as described above.

2-*tert*-Butyl-7-methylpyrene (9b): colorless prisms (methanol); mp 119–120 °C; IR (KBr) 3040, 2950, 1600, 1440, 1355, 1200, 875, 860, 710 cm^{-1}; NMR ($CDCl_3$) δ 1.56 (9 H, s), 2.76 (3 H, s), 7.90–8.13 (8 H, m); mass spectrum, m/e 272 (M^+). Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.85; H, 7.35.

2,7-Di-*tert*-butylpyrene (9c): pale yellow prisms (hexane); mp 210–212 °C (lit.[11] mp 210–212 °C).

Trans-*tert*-butylation of 8. Typical Procedure. To a solution of 500 mg (1.9 mmol) of **8a** in 20 mL of benzene was added a solution of 30 mg (0.22 mmol) in 0.1 mL of nitromethane. After the reaction mixture was stirred for 2 h at room temperature, it was poured into ice/water and extracted with benzene. The benzene solution was dried over Na_2SO_4 and evaporated in vacuo to give crude **10a**, which was recrystallized from hexane to afford 310 mg (80%) of **4,5,9,10-tetrahydropyrene (10a)**, colorless prisms (hexane): mp 136–138 °C (lit.[12] mp 137–138 °C). The formation of *tert*-butylbenzene (**11**) was confirmed by GLC.

Similarly, compounds **10b,c** were obtained in the same manner as described above.

2-Methyl-4,5,9,10-tetrahydropyrene (10b): colorless prisms (methanol); mp 97–98 °C; IR (KBr) 3040, 2950, 2850, 1605, 1450, 1240, 860, 820, 760, 740, 720 cm^{-1}; NMR ($CDCl_3$) δ 2.31 (3 H, s), 2.83 (8 H, s), 6.86 (2 H, s), 7.02 (3 H, s); mass spectrum, m/e 220 (M^+). Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 93.04; H, 7.32.

6,7,8-Trimethyl-4,5,9,10-tetrahydropyrene (10c): colorless prisms (methanol); mp 76–78 °C; IR (KBr) 3050, 2940, 2880, 2840, 1600, 1420, 1200, 820, 770, 730 cm^{-1}; NMR ($CDCl_3$) δ 2.26 (9 H, s), 2.82 (8 H, s), 7.03 (3 H, s); mass spectrum, m/e 248 (M^+). Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.37; H, 7.84.

Reaction of 10 with DDQ. Typical Procedure. A solution of 60 mg (0.29 mmol) of **10a** and 161 mg of DDQ (90% purity) in 30 mL of benzene was refluxed for 4 h. After the reaction mixture was cooled and concentrated, the residue was extracted and chromatographed on silica gel with hexane/benzene (1:1) as eluant to give 58 mg (98%) of **12a**, colorless prisms (methanol): mp 145–148 °C (lit.[13] mp 149–150 °C).

Similarly, compound **12b** was synthesized in the same manner as described above.

2-Methylpyrene (**12b**): colorless prisms (methanol); mp 145–146 °C (lit.[14] mp 143–143.5 °C).

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