H, OCH_2CH_3 side chain), 4.19 and 4.20 (2 q, 1 H each, OCH_2CH_3), 4.6–5.2 (m, 1 H, CH), 7.40 (s, 5 H, C_6H_5); IR ($CHCl_3$) 1725 (ester), 1630 (benzamide) cm^{-1}. Anal. Calcd for $C_{23}H_{31}NO_5S_2$: C, 59.35; H, 6.66; N, 3.01; S, 13.76. Found: C, 59.03; H, 6.93; N, 3.37; S, 14.20.

Ethyl 1-Benzoyl-4-(ethoxycarbonyl)-4-methyl-2-piperidinepropionate (8). A suspension of 46.5 g (0.1 mol) of thioketals 7 and 440 g of freshly prepared W-4 Raney nickel in 2 L of EtOH was heated under reflux. After being stirred for 15 h, it was cooled, the solution filtered, and the nickel washed with EtOH. The combined filtrates were eluted through SiO_2, and the catalyst was extracted (Soxhlet) overnight with EtOH. Concentration of the combined ethanol solutions yielded an oil which was chromatographed. Elution with benzene/$CHCl_3$ (4:1) gave 1.5 g (4%) of **ethyl 1-benzoyl-4-(ethoxycarbonyl)-4-methyl-1,4,5,6-tetrahydropyridine-2-propionate (16)**: bp 220–230 °C (0.2 mm); NMR δ 1.22 and 1.25 (2 t, 3 H each, OCH_2CH_3), 1.30 (s, 3 H, CH_3), 1.5–3.0 (m, 6 H, CH_2), 3.5 (deformed t, 2 H, NCH_2), 4.03 and 4.09 (2 q, 2 H each, OCH_2CH_3), 5.20 (br s, 1 H, C=CH), 7.40 (m, 5 H, C_6H_5); IR ($CHCl_3$) 1725 (ester), 1650 (benzamide) cm^{-1}. Anal. Calcd for $C_{21}H_{27}NO_5$: C, 67.54; H, 7.29; N, 3.75. Found: C, 67.46; H, 7.55; N, 3.64. On elution with benzene/$CHCl_3$ (1:9) a *cis*-8 and *trans*-8 mixture (25 g, 67%) was obtained: bp 235–240 °C (0.15 mm); NMR δ 1.1–1.4 (m, 9 H, OCH_2CH_3 and CH_3), 1.5–2.8 (m, 8 H, CH_2), 3.25 (m, 1 H, C_6H_{ax}), 3.6 (m, 1 H, C_6H_{eq}), 3.9–4.3 (m, 4 H, OCH_2CH_3), 4.5 (m, 1 H, C_2H_{eq}), 7.3 (s, 5 H, C_6H_5); IR ($CHCl_3$) 1720 (ester), 1615 (benzamide) cm^{-1}. Anal. Calcd for $C_{21}H_{29}NO_5$: C, 67.20; H, 7.73; N, 3.73. Found: C, 67.29; H, 7.93; N, 3.58. When the mixture was allowed to stand, *trans*-8 crystallized from the more polar fractions: mp 74–75 °C (hexane–Et_2O); NMR δ 1.22 and 1.23 (2 t, 3 H each, OCH_2CH_3), 1.28 (s, 3 H, CH_3(ax)), 4.04 and 4.11 (2 q, 2 H each, OCH_2CH_3); IR (KBr) 1735 (ester), 1615 (benzamide) cm^{-1}. Anal. Calcd for $C_{21}H_{29}NO_5$: C, 67.20; H, 7.73; N, 3.73. Found: C, 67.16; H, 7.74; N, 3.68.

Ethyl 2-Benzoyl-5-methyl-6-oxo-2-azabicyclo[3.3.1]nonane-7-carboxylate (9). A sodium hydride oil dispersion (55%, 2.4 g, 55 mmol) was suspended in anhydrous toluene (80 mL) under nitrogen and a 2:1 *cis*-8 and *trans*-8 mixture (6.94 g, 18.5 mmol) in anhydrous toluene (80 mL) containing a few drops of EtOH was added dropwise with stirring at room temperature. The resulting mixture was refluxed with vigorous stirring for 8 h. After evaporation the residue was dissolved in 1 N HCl and extracted with $CHCl_3$. The combined organic extracts were evaporated to give an oil which on chromatography (SiO_2, 2:1 benzene/$CHCl_3$) gave 2.2 g (54% based on *cis*-8) of 9: bp 220–230 °C (0.4 mm); NMR δ 1.20 (s, 3 H, CH_3), 1.30 (t, 3 H, OCH_2CH_3), 1.65 (br peak, 4 H, 4- and 9-CH_2), 2.45 (br peak, 2 H, 8-CH_2), 2.9–3.9 (m, 2 H, 3-CH_2), 4.20 (q, 2 H, OCH_2CH_3), 4.0–4.4 (masked, 0.6 H, C_1H), 5.15 (br peak, 0.4 H, C_1H), 7.30 (s, 5 H, C_6H_5), 12.3 (s, 1 H, OH); IR ($CHCl_3$) 1650 (enol ester), 1615 (benzamide) cm^{-1}. Anal. Calcd for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.01; H, 7.17; N, 4.15. **Ethyl 2-(cyclohexylcarbonyl)-5-methyl-6-oxo-2-azabicyclo[3.3.1]nonane-7-carboxylate (18)** was obtained as a byproduct in the above Dieckmann cyclization when the crude desulfurization mixture was used without further purification. Compound 18 was isolated as a colorless oil from chromatography (SiO_2, 9:1 benzene/$CHCl_3$): NMR δ 1.20 (s, 3 H, CH_3), 1.30 (t, 3 H, OCH_2CH_3), 1.4–3.0 (m, 17 H, COC_6H_{11} and CH_2), 2.9–3.9 (m, 2 H, 3-CH_2), 4.20 (q, 2 H, OCH_2CH_3), 4.0–4.4 (masked, 0.6 H, C_1H), 5.05 (br peak, 0.4 H, C_1H), 12.3 (s, 1 H, OH); mass spectrum, *m/e* (relative intensity) 335 (3), 263 (4), 207 (80), 96 (100), 83 (86).

2-Benzoyl-5-methyl-2-azabicyclo[3.3.1]nonan-6-one (1). Sodium chloride (410 mg, 7 mmol), water (360 mg, 20 mmol), and Me_2SO (5 mL) were added to 9 (2.1 g, 6.38 mmol), and the heterogeneous reaction mixture was heated to 155–160 °C for 3 h. The mixture was extracted with Et_2O, and the ethereal extracts were washed exhaustively with brine. After the organic layer had been dried and concentrated, the residual oil was chromatographed on silica gel with a benzene–$CHCl_3$ (1:9) eluent to separate 1.25 g (76%) of 1: bp 220–230 °C (0.6 mm); NMR δ 1.10 (s, 3 H, CH_3), 1.5–2.3 (m, 6 H, CH_2), 2.4 (m, 2 H, $COCH_2$), 3.2 (m, 1 H, C_3H_{ax}), 3.8 (br peak, 0.4 H, C_3H_{eq}), 4.3 (br, 0.6 H, C_3H_{eq}), 4.6 (br, 0.4 H, C_1H), 5.25 (br, 0.6 H, C_1H), 7.4 (s, 5 H, C_6H_5); IR (NaCl) 1705 (ketone), 1625 (benzamide) cm^{-1}. Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.87; H, 7.38; N, 5.40. Found: C, 74.68; H, 7.70; N, 5.44.

Acknowledgment. We are indebted to Mrs. Isabel Serret for her helpful assistance.

Registry No. 1, 76359-07-4; 2, 16450-41-2; 3, 76359-08-5; 3 oxalate, 76359-09-6; 4, 75274-00-9; 5, 76359-10-9; *cis*-6, 76359-11-0; *trans*-6, 76359-12-1; *cis*-7, 76359-13-2; *trans*-7, 76419-57-3; *cis*-8, 76359-14-3; *trans*-8, 76359-15-4; 9, 76359-16-5; 10, 76359-17-6; 11, 76359-18-7; 12, 76359-19-8; 13, 75144-74-0; 14, 76359-20-1; *cis*-15, 76359-21-2; *trans*-15, 76359-22-3; 16, 76359-23-4; 18, 76359-24-5; ethyl 4-bromobutyrate, 2969-81-5; benzoyl chloride, 98-88-4; diethyl *N*-benzoylglutamate, 42807-47-6; phenylhydrazine, 100-63-0; ICH_3, 74-88-4; ethanedithiol, 540-63-6.

Selective Preparation. 30.[1] A Convenient Preparation of 5,13-Di-*tert*-butyl-8,16-disubstituted-[2.2]metacyclophanes and Their Trans-*tert*-butylation and Halogenation Reactions

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Received July 29, 1980

The preparation of 5,13-di-*tert*-butyl-8,16-disubtituted-[2.2]metacyclophanes (**16a–k**) from the corresponding 4-substituted-*tert*-butylbenzenes was described. The $AlCl_3$–CH_3NO_2-catalyzed trans-*tert*-butylation of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophane (**16b**) in benzene afforded 8,16-dimethyl[2.2]metacyclophane (**28a**) in good yield. However, the similar reaction of diethyl derivative **16c** gave only a complex mixture of products. Treatment of **16b** and **28a** with NBS in CCl_4 afforded the corresponding dibromides **38** and **39** in 86% and 95% yields, respectively. The bromination of **16b** and **16c** with bromine in CCl_4 afforded the corresponding *anti*-10b,10c-dialkyl-4,5,9,10-tetrabromo-2,7-di-*tert*-butyl-10b,10c-dihydropyrenes **41a** and **41b** in good yields, respectively. However, it was also found that the bromination of **16b** and **16c** in the presence of Fe powder in the same solvent afforded 4,5,9,10-tetrabromo-2,7-di-*tert*-butylpyrene (**40**) in good yield in all cases. On the other hand, the bromination of **28a** with bromine in the presence of Fe powder gave 2,7-dimethyl-3,6,8,11-tetrabromo-4,5,9,10-tetrahydropyrene (**42**). The reaction pathway of the bromination of **16** is discussed.

Although Boekelheide and his co-workers[2-11] have reported the synthesis of interesting 8-mono- and 8,16-di-substituted-[2.2]metacyclophanes in low total yields from simple starting compounds, their preparative routes seem

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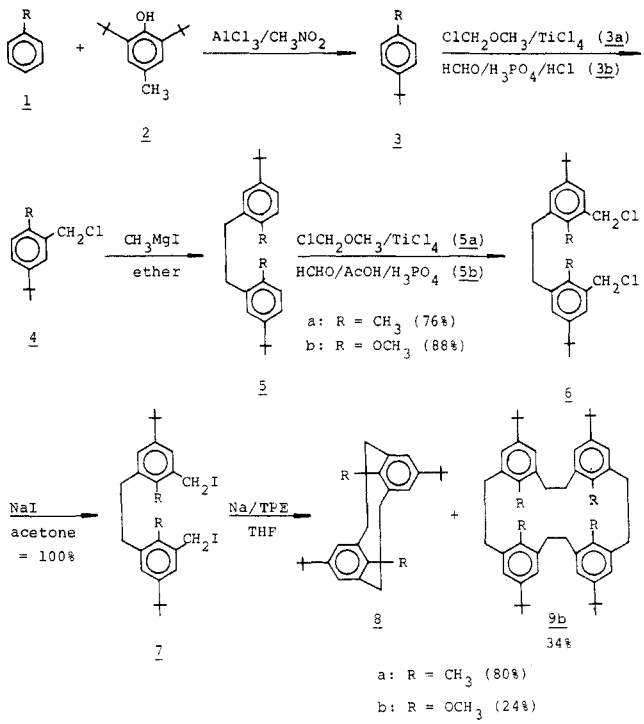
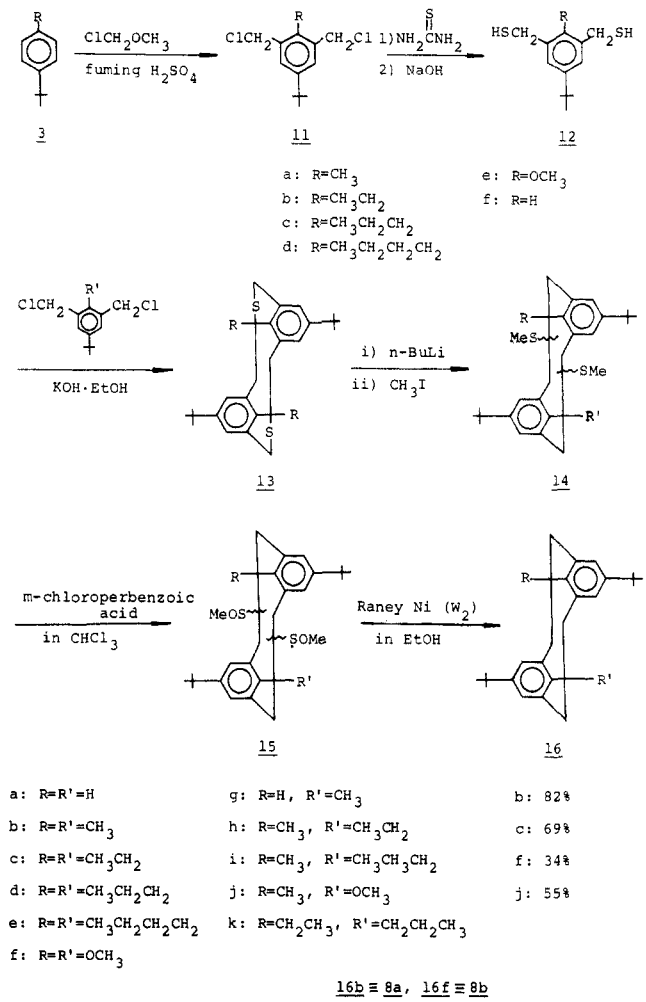
Scheme I



Scheme II



to be too long for practical purposes.

The [2.2]metacyclophanes are so highly strained compounds that they may be reactive toward many reagents. However, the chemistry of [2.2]metacyclophanes is very limited since their preparation from easily available compounds was very difficult.

We previously reported that[12,13] the *tert*-butyl group can be used as a positional protective group for the preparation of some phenolic compounds, diarylalkanes, 1,2-di- and 1,2,3-trisubstituted benzenes, 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene, and carbazoles.

We report here some convenient preparative routes for the title compounds, using the *tert*-butyl function as a positional protective group, and the results of $AlCl_3$–CH_3NO_2-catalyzed trans-*tert*-butylation and halogenation reactions of the title compounds.

Results and Discussion

Preparation of 5,13-Di-*tert*-butyl-8,16-disubstituted-[2.2]metacyclophanes. The title compounds were prepared by the three routes A, B, and C.

Route A. The preparative routes to 8,16-dimethyl (**8a** ≡ **16b**) and 8,16-dimethoxy-5,13-di-*tert*-butyl[2.2]metacyclophane (**8b** ≡ **16f**) are summarized in Scheme I.

The preparation of 1,2-bis(2-methyl- (**5a**) and 1,2-bis(2-methoxy-5-*tert*-butylphenyl)ethane (**5b**) from toluene and anisole was described in the previous report.[15] The chloromethylation of these 1,2-diphenylethanes **5** afforded the corresponding dichlorides **6a** and **6b** in 76% and 88% yields, respectively. The halogen-exchange reaction of **6** with sodium iodide in acetone gave the corresponding diiodides **7** in almost quantitative yields.

When the diiodide **7a** was added to a mixture of finely divided sodium and tetraphenylethylene (TPE) in dry tetrahydrofuran (THF) according to the reported method,[19] ring closure occurred smoothly in 80% yield to give the expected **8a**. However, similar cyclization of **7b** af-

(1) (a) Part 29. M. Tashiro and T. Yamato, *Org. Prep. Proced. Int.*, in press. (b) A part of this paper was published in a preliminary communication: M. Tashiro and T. Yamato, *Synthesis.*, 435 (1978).
(2) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961).
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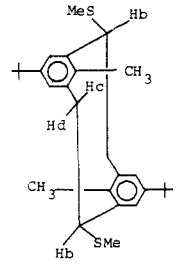
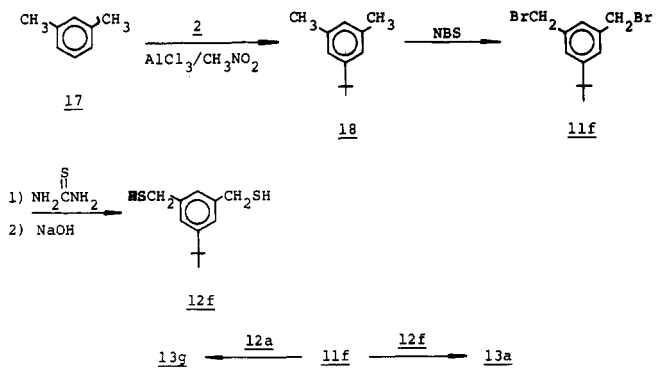
(10) V. Kamp and V. Boekelheide, *J. Org. Chem.*, **43**, 3470 (1978).
(11) R. H. Michell, T. Otsubom, and V. Boekelheide, *Tetrahedron Lett.* 219 (1975).
(12) M. Tashiro and G. Fukata, *Org. Prep. Proced. Int.*, **8**, 51 (1976).
(13) M. Tashiro, *Synthesis*, 921 (1979). Component **14b'** [about 33% of the mixture; mp 261–262 °C; colorless needles; NMR ($CDCl_3$) δ 0.60 (6 H, s), 1.30 (18 H, s), 2.14 (6 H, s), 2.63 (2 H, dd, J_{dc} = 12 Hz, J_{db} = 12 Hz), 3.21 (2 H, dd, J_{cb} = 4.5 Hz, J = 3 Hz), 7.79 (2 H, d, J = 3 Hz)] was isolated in a pure state.



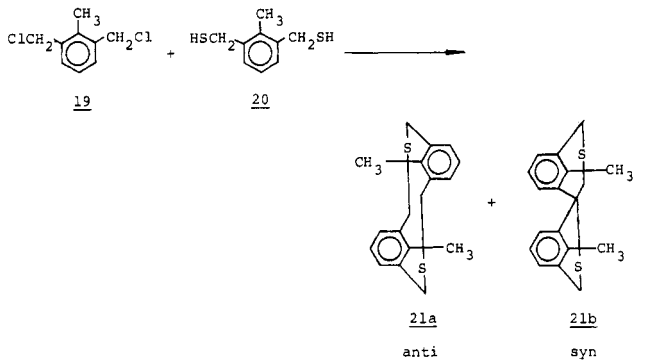
14b'

(14) M. Haenel and H. A. Staab, *Tetrahedron Lett.*, 3585 (1970).
(15) M. Tashiro and T. Yamato, *Synthesis*, 214 (1978).

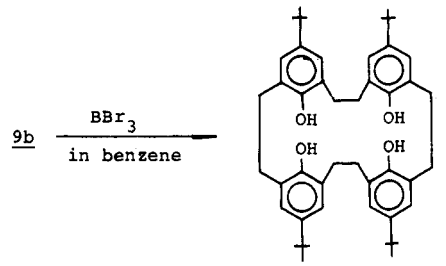
Scheme III



Scheme IV



forded the expected **8b** in only 24% yield together with formation of the cyclic tetramer **9b** which was demethylated with boron tribromide in a benzene solution to give the corresponding tetrahydroxy derivative **10**.



The separation of product **8** and tetraphenylethane (TPA), produced from TPE used in the cyclization of **7**, was difficult by means of recrystallization and column chromatography. In addition, asymmetric [2.2]metacyclophanes can not be prepared by this route A.

Route B. Some symmetric and asymmetric 8,16-disubstituted-5,13-di-*tert*-butyl[2.2]metacyclophanes (**16**) were prepared according to route B (Scheme II).

Although 2,6-bis(chloromethyl)- (**11a–e**) and 2,6-bis(mercaptomethyl)-4-substituted-*tert*-butylbenzenes (**12a–e**) were prepared according to the previous work,[1a] 2,6-bis(bromomethyl)- (**11f**) and 2,6-bis(mercaptomethyl)-*tert*-butylbenzene (**12f**) were obtained by the alternative route shown in Scheme III.

Mitchell and Boekelheide[7] reported that reaction of 2,6-bis(chloromethyl)toluene (**19**) and 2,6-bis(mercaptomethyl)toluene (**20**) afforded a mixture of anti conformer **21a** and syn conformer **21b** in a ratio of 7:1 (Scheme IV).

The assignment of structure for the anti conformer was readily apparent from its NMR spectrum.[7] Thus, the internal aromatic and alkyl protons should show an upfield shift due to ring current of the opposite aromatic ring. The NMR spectra of the dithia[3.3]metacyclophanes **13** prepared in the present paper show that their structures are exclusively the anti conformers. The NMR spectral data of **13** are summarized in Table I. The bulkiness of the *tert*-butyl groups of **13'** might inhibit the formation of **13'**.

Table I. Chemical Shifts (δ) of Internal Aromatic and Alkyl Protons of Dithia[3.3]metacyclophanes 13 and [2.2]Metacyclophanes 16[a]

compd	aromatic protons	methyl proton	methylene proton
13a	6.48 (2 H, s)		
13b		1.25 (6 H, s)	
13c		0.63 (6 H, t, J = 8 Hz)	1.58 (4 H, q, J = 8 Hz)
13d		0.68 (6 H, t, J = 7 Hz)	0.80–1.07 (4 H, m, β-CH_2), 1.52–1.68 (4 H, m, α-CH_2)
13e		0.76 (6 H, t, J = 6.5 Hz)	0.86–1.12 (4 H, m, β,γ-CH_2), 1.55–1.70 (4 H, m, α-CH_2)
13f		3.20 (6 H, s, OCH_3)	
13g	5.00 (1 H, d, J = 2 Hz)	2.00 (3 H, s)	
13h		0.62 (3 H, t, J = 7.5 Hz), 1.27 (3 H, s)	1.59 (2 H, q, J = 7.5 Hz, α-CH_2)
13i		0.69 (3 H, t, J = 7 Hz), 1.26 (3 H, s)	0.80–1.07 (2 H, m, CH_2)
13j		1.44 (3 H, s), 3.11 (3 H, s, OCH_3)	
16a	4.05 (2 H, d, J = 15 Hz)		
16b		0.56 (6 H, s)	
16c		0.32 (6 H, t, J = 8 Hz)	1.03 (4 H, q, J = 8 Hz)
16d		0.48 (6 H, t, J = 6 Hz)	0.40–1.08 (8 H, m, α,β-CH_2)
16e		0.64 (6 H, t, J = 6 Hz)	0.55–1.08 (12 H, m, α,β,γ-CH_2)
16f		2.62 (6 H, s, OCH_3)	
16g	3.56 (1 H, t, J = 1.5 Hz)	0.47 (3 H, s)	
16h		0.31 (3 H, t, J = 7.5 Hz), 0.56 (3 H, s)	1.05 (2 H, q, J = 7.5 Hz)
16i			
16j		0.59 (3 H, s), 2.64 (3 H, s, OCH_3)	
16k		0.31 (3 H, t, J = 7.5 Hz), 0.45 (3 H, t, J = 5 Hz)	0.60–0.80 (2 H, m, β-CH_2), 0.99 (4 H, t, J = 7.5 Hz, α,α-CH_2)

[a] Other signals are given in Experimental Section.

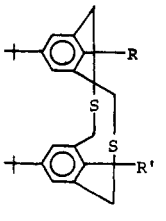
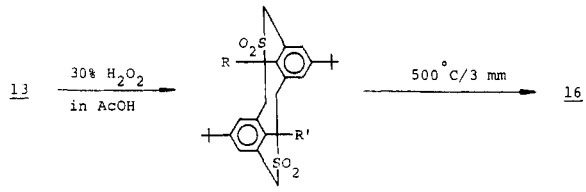


Table II. Yields of 13, 14, and 16

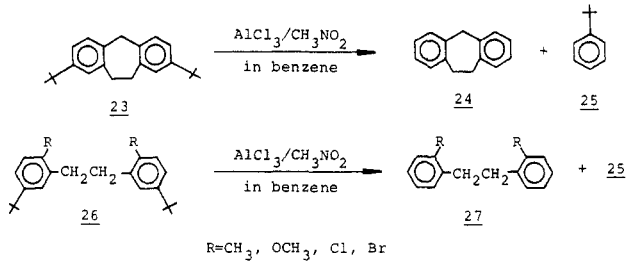
compd	% yield	compd	% yield
13a	67.9	**14c**	98.9
13b	88.6	**14d**	99.7
13c	50.7	**14e**	93.8
13d	73.9	**14f**	98.9
13e	70.7	**14g**	67.6
13f	56.3	**14h**	99.3
13g	85.8	**14i**	99.6
13h	84.6	**14j**	93.4
13i	77.7	**14k**	99.1
13j	67.7	**16b**	82.0
13k	79.4	**16c**	69.0
14a	96.0	**16f**	34.0
14b	97.4	**16j**	55.0

Scheme V



a: R=R'=H, 12%
b: R=R'=CH_3, 59%
c: R=R'=CH_3CH_2, 70%
d: R=R'=$CH_3CH_2CH_2$, 70%
e: R=R'=$CH_3CH_2CH_2CH_2$, 49%
f: R=R'=OCH_3, 63%
g: R=H, R'=CH_3, 10%
h: R=CH_3, R'=CH_3CH_2, 73%
i: R=CH_3, R'=$CH_3CH_2CH_2$, 86%
j: R=CH_3, R'=OCH_3, 95%
k: R=CH_3CH_2, R'=$CH_2CH_2CH_3$, 93%

Scheme VI



Treatment of the dithia[3.3]metacyclophanes **13** with *n*-butyllithium in dry THF at 0 °C followed by methylation of the resulting thiolate with methyl iodide gave good yields of the corresponding bis(methylthio)[2.2]metacyclophanes **14**, as a mixture of structural isomers[14] and stereoisomers.

Oxidation of **14** with *m*-chloroperbenzoic acid at 0 °C afforded the corresponding disulfoxides **15** in almost quantitative yields, again as a mixture of structural isomers and stereoisomers, which, without purification, were treated with freshly prepared W-2 Raney Ni to give only the [2.2]metacyclophanes **16b**, **16c**, **16f**, and **16j**.

Unfortunately, in the other cases, the expected **16** was not formed but the corresponding starting compounds or monomethylmercapto compounds were obtained (see Experimental Section).

Based on the above results, it is concluded that route B is also not a generally useful preparative route to **16**. The yields of **13**, **14**, and **16** prepared according to route B are summarized in Table II.

Route C. Pyrolysis of the dithia[3.3]metacyclophane tetraoxides **22**, which were easily obtained by oxidation of **13**, was carried out according to the reported method[16] and the results are summarized in Scheme V.

Except for **16a** and **16g**, the expected **16** was obtained in good yield. This result suggests that route C is the most useful preparative route for **16** among the three routes mentioned above. The structure of **16** as well as that of **13** can be easily determined by their NMR spectral data, as it is well-known that the internal aromatic and alkyl protons of the anti conformers appear upfield (Table I).

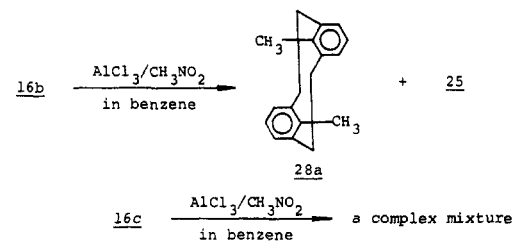
$AlCl_3$–CH_3NO_2-Catalyzed Trans-*tert*-butylation of 16b. It has been previously reported that the trans-*tert*-butylation of 2,8-di-*tert*-butyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptane (**23**)[13] and bis(*tert*-butylaryl)ethanes (**26**)[15] afforded the corresponding de-*tert*-butylated compounds **24** and **27** in good yields, respectively (Scheme VI).

These results suggest that the $AlCl_3$–CH_3NO_2-catalyzed trans-*tert*-butylation of **16** might afford the corresponding metacyclophanes **28** (Scheme VII).

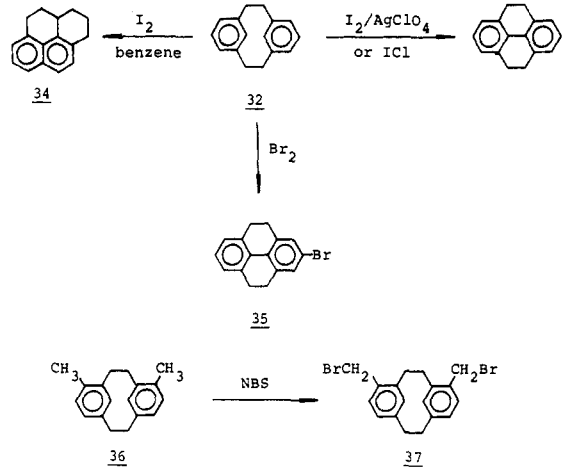
Indeed, the $AlCl_3$–CH_3NO_2-catalyzed trans-*tert*-butylation of **16b** afforded the expected 8,16-dimethyl[2.2]metacyclophane (**28a**) in a good yield. However, similar reaction of **16c** gave a mixture of many products which were tentatively identified by GC–mass spectra (Figure 1 and Table III).

The formation of **28b'**, **29**, and **30** indicated the occurrence of isomerization as well as trans-*tert*-butylation

Scheme VII



Scheme VIII



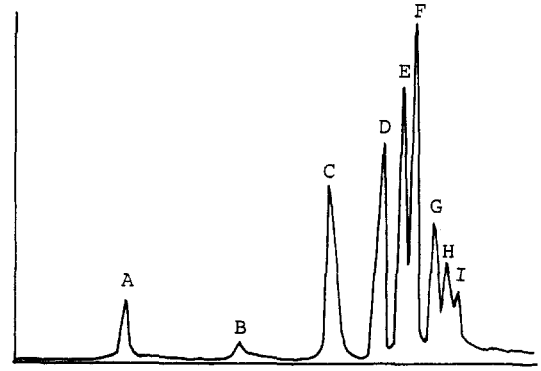
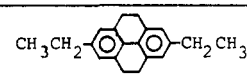
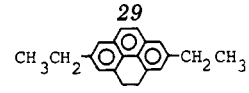
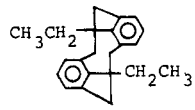
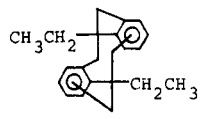
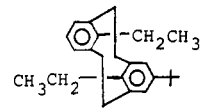


Figure 1. GC of the reaction mixture.

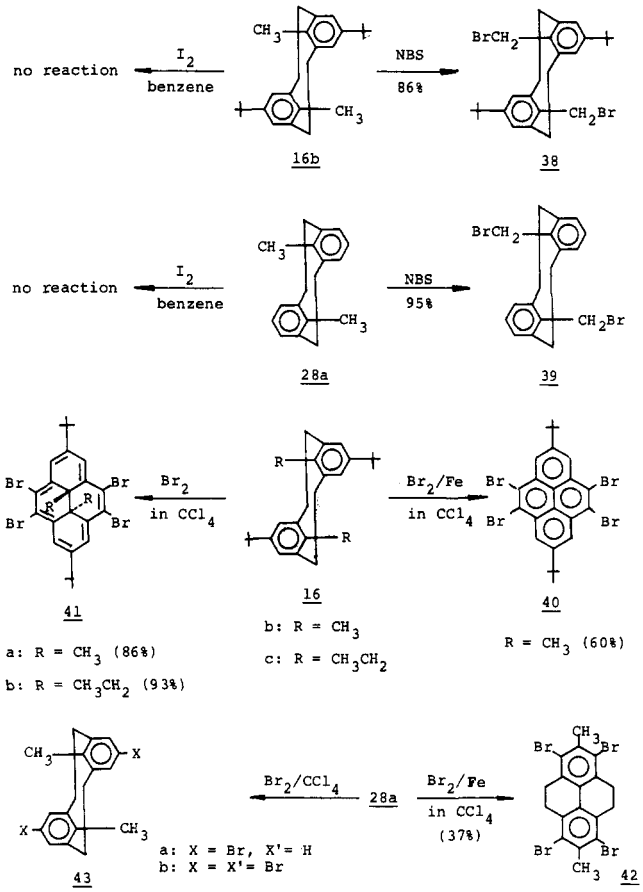
(16) T. Sato, E. Yamada, Y. Okamura, T. Amada, and K. Hata, *Bull. Chem. Soc. Jpn.*, **38**, 1049 (1965); *40*, 2363 (1967).

Table III. GC-Mass Spectroscopy of the Reaction Mixture

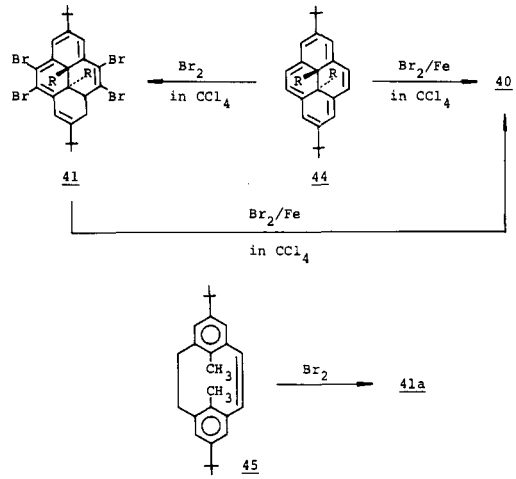
peak	M⁺, m/e	structure	peak	M⁺, m/e	structure
A[a]	160		F	262	 29
B[a]	216		G	260	 30
C	264	 28b			
D[a]	268		H[a]	278	
E	264	 28b′	I	320	

[a] Unidentified peak.

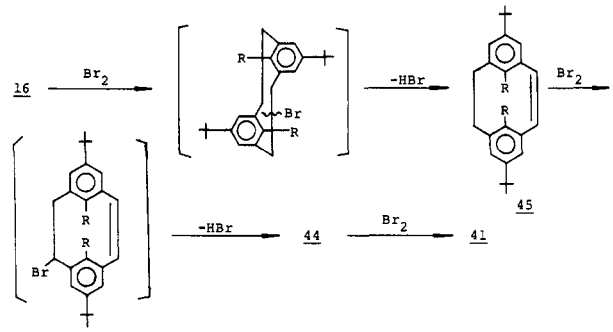
Scheme IX



Scheme X



Scheme XI



under the conditions used. The detailed investigation of the trans-*tert*-butylation of **16**, except **16a**, should be done in order to obtain the desired compound **28**.

Halogenation of 16. Recently, the reactions of some [2.2]metacyclophanes with halogen have been reported (Scheme VIII).[16-18] However, no halogenation of 8,16-disubstituted [2.2]metacyclophanes has been reported. Therefore, the reactions of **16** and **28a** with iodine and bromine were carried out under various conditions and the results are summarized in Scheme IX.

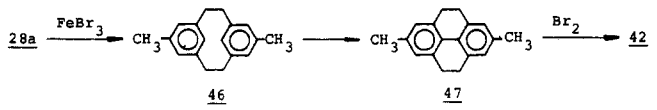
Treatment of **16b** or **28a** with iodine under the same conditions as reported[17] did not give any product, but the starting compound **16b** or **28a** was recovered almost quantitatively. The bromination of **16b** and **28a** with NBS afforded good yields of the expected dibromides **38** and **39**, respectively.

However, the bromination of **16b** and **16c** with bromine in a carbon tetrachloride solution surprisingly afforded the corresponding *anti*-10b,10c-dialkyl-4,5,9,10-tetrabromo-2,7-di-*tert*-butyl-10b,10c-dihydropyrenes **41a** and **41b** in good yields, while the bromination of **16b** with bromine in the presence of Fe powder in the same solvent afforded 4,5,9,10-tetrabromo-2,7-di-*tert*-butylpyrene (**40**) in 60% yield.

It was previously found that[20] the bromination of dialkyldihydropyrenes (**44**) with bromine in the presence of

(17) T. Sato and K. Nishiyama, *J. Org. Chem.*, **37**, 3254 (1972).
(18) N. L. Allinger, B. J. Gorden, S. Hu, and R. A. Ford, *J. Org. Chem.*, **32**, 2272 (1967).
(19) S. Akabori, T. Sato, and H. Hata, *J. Org. Chem.*, **33**, 3277 (1968).
(20) M. Tashiro and T. Yamato, *Chem. Lett.*, 1127 (1980).
(21) M. Tashiro and T. Yamato, to be published.

Scheme XII



or in absence of Fe powder afforded **40** or **41** in good yields, respectively, and that[21] the bromination of [2.2]metacyclophan-1-ene **45** with bromine gave also **41**. It was also found that[20] when **41** was treated with bromine in the presence of Fe powder, **40** was formed in good yield (Scheme X).

These results suggest that compounds **44** and **45** should be intermediates for the formation of **41** in the bromination of **16**. That is, the reaction pathway of the formation of **41** might be proposed as shown in Scheme XI.

On the other hand, the bromination of **28a** with bromine afforded a mixture of the expected bromo (**43a**) and dibromo derivatives (**43b**). However, the bromination of **28a** in the presence of Fe powder gave the unexpected product, 2,7-dimethyl-3,6,8,11-tetrabromo-4,5,9,10-tetrahydropyrene (**42**) which might be produced via isomerization, cyclization, and bromination as shown in Scheme XII. The catalyst for the isomerization from **28a** to **46** and for the oxidative cyclization of **46** might be $FeBr_3$ which should be produced from bromine and Fe powder present in this reaction.

It should be noted that **16b** and **28a** show very different behavior for the bromination in the absence of or in the presence of Fe powder.

Experimental Section

All melting and boiling points are uncorrected. NMR spectra were determined at 100 MHz with Nippon Denshi JEOL FT-100 NMR spectrometer with Me_4Si as an internal reference and IR spectra were measured as KBr pellets or liquid films on NaCl plates on a Nippon Bunko IR-A-102 spectrometer. Mass spectra were obtained on a Nippon Denshi, JMS-01SA-2 spectrometer at 75 eV, using a direct-inlet system or using GC.

Preparation of 1,2-Bis[5-*tert*-butyl-3-(chloromethyl)-2-methoxyphenyl]ethane (6b). After a mixture of 13.3 g (37.6 mmol) of 1,2-bis(2-methoxy-5-*tert*-butylphenyl)ethane (**5b**),[13] 2.8 g of paraformaldehyde, 75 mL of acetic acid, 25 mL of phosphoric acid, and 100 mL of concentrated hydrochloric acid (36%) was heated at 85–90 °C under vigorous stirring for 14 h, it was cooled to room temperature. The reaction mixture was extracted with benzene. the benzene solution was washed with water and 10% K_2CO_3 solution, dried over Na_2SO_4, and evaporated in vacuo to leave the residue which was solidified by addition of small amount of cold hexane to give 15 g (88.4%) of **6b**: colorless needles (hexane); mp 139–140 °C; NMR (CCl_4) δ 1.25 (18 H, s), 2.89 (4 H, s), 3.80 (6 H, s), 4.56 (4 H, s), 6.99–7.18 (4 H, m). Anal. Calcd for $C_{26}H_{36}O_2Cl_2$: C, 69.17; H, 8.04. Found: C, 69.34; H, 8.16.

Preparations of **6a**, **7a**, and **8a** were described in a previous communication.[1]

Preparation of 1,2-Bis[5-*tert*-butyl-3-(iodomethyl)-2-methoxyphenyl]ethane (7b). To a hot solution of 2.26 g (50 mmol) of **6b** in 100 mL of acetone was slowly added powered NaI (8.4 g). After the reaction mixture was refluxed for 2 h, it was concentrated in vacuo to leave the residue which was washed with 100 mL of warm water to give 2.85 g (90%) of **7b**: colorless needles (hexane); mp 171–172 °C; NMR (CCl_4) δ 1.24 (18 H, s), 2.94 (4 H, s), 3.85 (6 H, s), 4.51 (4 H, s), 7.02–7.22 (4 H, m); IR (KBr) 2960, 1475, 1210, 850 cm^{-1}. Anal. Calcd for $C_{26}H_{36}O_2I_2$: C, 49.23; H, 5.72. Found: C, 49.58; H, 5.82.

Cyclization of 7b. To a suspension of sodium (5 g) and tetraphenylethylene (400 mg) in 100 mL of tetrahydrofuran at −80 °C under a stream of nitrogen was added a solution of 5.33 g (8.4 mmol) of **7b** in 500 mL of tetrahydrofuran over a period of 36 h. After filtration of unchanged sodium from the reaction mixture, the filtrate was concentrated in vacuo to leave a residue which was dissolved in dichloromethane (500 mL). The dichloromethane solution was washed with dilute hydrochloric acid and concentrated to leave the residue which on column chromatography (active Al_2O_3), with hexane, a mixture of hexane and benzene (1:1), benzene, and chloroform as eluants, afforded 0.76 g (23.8%) of crude **8b** (from hexane fraction), 1.60 g (34.4%) of **9**, and 0.3 g of tetraphenylethane [mp 211–212 °C (lit. mp 212 °C)]. An unidentified compound (0.8 g) was obtained as a colorless solid (mp 280–285 °C) from the benzene and chloroform fractions. The structure of **8b** is based on the following physical properties: colorless prisms (hexane); mp 242–243 °C; IR (KBr) 3040, 2960, 1475, 1360, 1280, 1195, 1100, 1020, 885, 860, 805, 770, 710 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (18 H, s), 2.62 (6 H, s), 2.88 (8 H, s), 7.00 (4 H, s) ; mass spectrum, m/e 380 (M^+). Anal. Calcd for $C_{28}H_{36}O_2$: C, 82.06; H, 9.54. Found: C, 81.99; H, 9.67.

The structure of **9** is based on the following physical properties: colorless prisms (hexane–benzene, 1:1); mp 240–242 °C; IR (KBr) 3040, 2960, 1480, 1450, 1200, 1015, 880, 745, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.18 (36 H, s), 2.88 (16 H, s), 3.03 (12 H, s), 6.90 (8 H, s); mass spectrum, m/e 760 (M^+). Anal. Calcd for $C_{52}H_{72}O_4$: C, 82.06; H, 9.54. Found: C, 82.22; H, 9.45.

Demethylation of 8b. To a solution of 500 mg (0.657 mmol) of **9** in 60 mL of benzene was added 1.2 mL of BBr_3. After the reaction mixture was stirred at room temperature for 24 h, it was washed with water, dried over Na_2SO_4, and concentrated in vacuo to leave the residue which was washed with hot hexane to give 230 mg (50%) of 5,13,21,29-tetra-*tert*-butyl-8,16,24,32-tetrahydroxy[2.2.2.2]metacyclophane (**10**): mp >300 °C; IR (KBr) 3240, 2040, 2960, 1600, 1480, 1360, 1230, 1200, 1110, 1020, 880, 825 cm^{-1}; NMR ($CDCl_3$) δ 1.33 (36 H, s), 2.16 (4 H, s, exchanged with D_2O), 2.92 (16 H, s), 4.08 (8 H, s); mass spectrum, m/e 704 (M^+). Anal. Calcd for $C_{48}H_{64}O_8$: C, 81.77; H, 9.15. Found: C, 81.22; H, 8.99.

Preparation of 4-*tert*-Butyl-*n*-butylbenzene (3d). To a mixture of 200 g (1.49 mol) of *n*-butylbenzene and 110.2 g (0.5 mol) of 2,6-di-*tert*-butyl-*p*-cresol was added at 15 °C at once a solution of 99 g (0.75 mol) of aluminum chloride in 200 mL of nitromethane. The reaction mixture was stirred for 1 min and treated as previously reported[12] to give 175 g (92.1%) of **3d** as colorless oil, bp 77–79 °C (1 mm), and 50 g (92.6%) of *p*-cresol. The IR spectra of these compounds agreed with those of authentic samples.

Preparation of 2,6-Bis(chloromethyl)-4-*tert*-butylbutylbenzene (11d). To a mixture of 40 g (0.21 mol) of **3d** and 150 mL of $ClCH_2OCH_3$ under gentle reflux was added 50 mL of fuming H_2SO_4 over a period of 40 min. After the reaction mixture had been stirred for an additional 30 min, it was poured into a large amount of ice–water and treated as previously reported[1] to give 25 g of crude **11d**, which on recrystallization from hexane afforded 17 g (28.1%) of **11d**: bp 152–157 °C (1 mm); mp 60–62 °C; IR (KBr) 3040, 2960, 1605, 1480, 1450, 1260, 1235, 1200, 1150, 980, 915, 890, 780, 720, 680 cm^{-1}; NMR ($CDCl_3$) δ 0.89–1.04 (3 H, m), 1.32 (9 H, s), 1.40–1.64 (4 H, m), 2.70–2.86 (2 H, m), 4.61 (4 H, s), 7.33 (2 H, s). Anal. Calcd for $C_{16}H_{24}Cl_2$: C, 66.90; H, 8.42. Found: C, 66.90; H, 8.40.

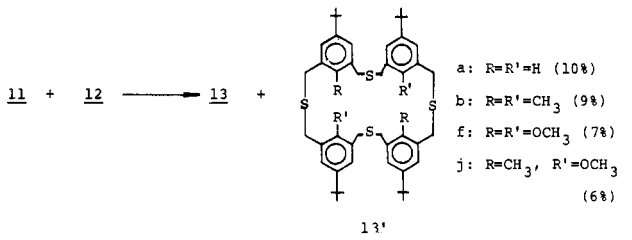
Preparation of 2,6-Bis(mercaptomethyl)-4-*tert*-butylbutylbenzene (12d). A solution of 14.35 g (50 mmol) of **11d** and 8.37 g (110 mmol) of thiourea in 75 mL of Me_2SO was worked up and treated as previously reported[1] to give 11.8 g (83.7%) of **12d** as colorless oil: bp 160–161 °C (4 mm); IR (NaCl) 3040, 2960, 2560, 1605, 1480, 1460, 1360, 1245, 1100, 880, 770, 745, 680 cm^{-1}; NMR ($CDCl_3$) δ 0.88–1.03 (3 H, m), 1.30–1.59 (4 H, m), 1.71 (2 H, t, J = 7 Hz, exchangeable with D_2O), 2.56–2.80 (2 H, m), 2.73 (4 H, d, J = 7 Hz), 7.17 (2 H, s). Anal. Calcd for $C_{16}H_{26}S_2$: C, 68.02; H, 9.28. Found: C, 67.55; H, 9.23.

Preparation of 3,5-Bis(bromomethyl)-*tert*-butylbenzene (11f). A solution of 16.1 g (0.1 mol) of 5-*tert*-butyl-*m*-xylene (**18**),[12] 42.72 g (0.24 mol) of NBS, and 0.5 g of benzoyl peroxide in 300 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 18.5 g (58%) of **11f** as colorless needles: mp 118–119 °C; IR (KBr) 3040, 2960, 1600, 1470, 1360, 1230, 1210, 970, 880, 705 cm^{-1}; NMR ($CDCl_3$) δ 1.33 (9 H, s), 4.48 (4 H, s), 7.28 (1 H, d, J = 2 Hz), 7.37 (2 H, d, J = 2 Hz). Anal. Calcd for $C_{12}H_{16}Br_2$: C, 45.03; H, 5.04. Found: C, 44.79; H, 5.07.

Preparation of 3,5-Bis(mercaptomethyl)-*tert*-butylbenzene (12f). A solution of 12.76 g (40 mmol) of **11f** and 6.7

g of thiourea in 50 mL of Me_2SO was worked up and treated as previously reported[1] to give 8.35 g (92.4%) of **12f**: colorless prisms; mp 42–43 °C; bp 137–138 °C (1 mm); IR (KBr) 3040, 2960, 2530, 1600, 1460, 1430, 1360, 1240, 875, 710 cm^{-1}; NMR ($CDCl_3$) δ 1.33 (9 H, s), 1.77 (2 H, t, J = 10 Hz, exchangeable with D_2O), 3.76 (4 H, d, J = 10 Hz), 7.18 (1 H, s), 7.26 (2 H, s). Anal. Calcd for $C_{12}H_{18}S_2$: C, 63.66; H, 8.01. Found: C, 63.75; H, 8.04.

General Procedure for Reaction of 11 with 12. A solution of 7.43 g (23.3 mmol) of **11** and 5.24 g (23.3 mmol) of **12** in 700 mL of benzene was added dropwise from a Hershberg funnel with stirring under nitrogen to a solution of 4.2 g of potassium hydroxide in 2.0 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 over Al_2O_3, using a suitable solvent as an eluant, to give the corresponding **13**. Some cases afforded the corresponding tetramer **13′** besides **13**.



The yields of **13** obtained by this method are summarized in Table II.

13a: colorless prisms (hexane); mp 120–121 °C; IR (KBr) 3040, 2960, 1600, 1475, 1450, 1405, 1360, 1245, 1220, 940, 870, 740, 730, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (18 H, s), 3.68 (8 H, s), 6.48 (2 H, br s, internal H), 6.93 (4 H, d, J = 1.5 Hz); mass spectrum, m/e 384 (M^+). Anal. Calcd for $C_{24}H_{32}S_2$: C, 74.94; H, 8.39. Found: C, 75.51; H, 8.65.

13b: colorless prisms (benzene); mp 255–256 °C; IR (KBr) 3040, 2960, 1480, 1360, 1220, 950, 880, 750 cm^{-1}; NMR ($CDCl_3$) δ 1.25 (6 H, s), 1.34 (18 H, s), 7.25 (4 H, s); mass spectrum, m/e 412 (M^+). Anal. Calcd for $C_{26}H_{35}S_2$: C, 75.67; H, 8.79. Found: C, 75.75; H, 8.72.

13c: colorless prisms (hexane–benzene, 1:1); mp 270–271 °C; IR (KBr) 3040, 2960, 1600, 1480, 1460, 1450, 1430, 1400, 1360, 1220, 885, 775, 630, 610 cm^{-1}; NMR ($CDCl_3$) δ 0.63 (6 H, t, J = 8 Hz), 1.34 (18 H, s), 1.58 (4 H, q, J = 8 Hz), 3.67 (8 H, s), 7.26 (4 H, s); mass spectrum, m/e 440 (M^+). Anal. Calcd for $C_{28}H_{40}S_2$: C, 76.30; H, 9.15. Found: C, 76.16; H, 9.14.

13d: colorless prisms (hexane–benzene, 1:1); mp 271–272 °C; IR (KBr) 3040, 2960, 1600, 1480, 1460, 1400, 1360, 1295, 1220, 1190, 1090, 940, 880, 875, 780, 750, 710 cm^{-1}; NMR ($CDCl_3$) δ 0.68 (6 H, t, J = 7 Hz), 0.80–1.07 (4 H, m), 1.34 (18 H, s), 1.52–1.68 (4 H, m), 3.64 (8 H, s), 7.23 (4 H, s); mass spectrum, m/e 468 (M^+). Anal. Calcd for $C_{30}H_{44}S_2$: C, 76.86; H, 9.46. Found: C, 76.64; H, 9.48.

13e: colorless prisms (hexane–benzene, 1:1); mp 210–212 °C; IR (KBr) 3040, 2960, 1600, 1475, 1460, 1430, 1400, 1360, 1220, 880, 870, 780, 750 cm^{-1}; NMR ($CDCl_3$) δ 0.76 (6 H, t, J = 6.5 Hz), 0.86–1.12 (8 H, m), 1.36 (18 H, s), 1.55–1.70 (4 H, m), 3.64 (8 H, s), 7.25 (4 H, s); mass spectrum, m/e 496 (M^+). Anal. Calcd for $C_{32}H_{48}S_2$: C, 77.35; H, 9.74. Found: C, 77.12; H, 9.76.

13f: colorless prisms (hexane–benzene, 1:1); mp 257–258 °C; IR (KBr) 3040, 2960, 1480, 1255, 1200, 1100, 1015, 880, 790 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (19 H, s), 3.20 (6 H, s), 3.56 (8 H, AB pattern, J_{AB} = 14 Hz), 7.28 (4 H, s); mass spectrum, m/e 444 (m^+). Anal. Calcd for $C_{26}H_{36}S_2O_2$: C, 70.22; H, 8.16. Found: C, 70.09; H, 7.99.

13g: colorless prisms (hexane); mp 101–102 °C; IR (KBr) 3040, 2960, 1590, 1480, 1460, 1360, 1225, 1200, 895, 870, 750, 715 cm^{-1}; NMR ($CDCl_3$) δ 1.24 (9 H, s), 1.28 (9 H, s), 2.00 (3 H, s), 3.54 (4 H, AB pattern, J_{AB} = 15 Hz), 3.85 (4 H, AB pattern, J_{AB} = 14 Hz), 5.00 (1 H, t, J = 2 Hz), 6.88 (2 H, d, J = 2 Hz), 7.08 (2 H, s); mass spectrum, m/e 398 (Ma^+). Anal. Calcd for $C_{25}H_{34}S_2$: C, 75.32; H, 8.60. Found: C, 75.19; H, 8.53.

13h: colorless prisms (hexane–benzene, 1:1); mp 232–233 °C; IR (KBr) 3040, 2960, 1600, 1480, 1460, 1420, 1400, 1360, 1215, 880, 770, 740 cm^{-1}; NMR ($CDCl_3$) δ 0.62 (3 H, t, J = 7.5 Hz), 1.27 (3 H, s), 1.34 (9 H, s), 1.36 (9 H, s), 1.58 (2 H, q, J = 7.5 Hz), 3.65 (4 H, s), 3.67 (4 H, s), 7.07 (2 H, s), 7.09 (2 H, s); mass spectrum m/e 426 (M^+). Anal. Calcd for $C_{27}H_{38}S_2$: C, 75.99; H, 8.98. Found: C, 75.75; H, 9.06.

13i: colorless prisms (hexane–benzene, 1:1); mp 176–178 °C; IR (KBr) 3040, 2960, 1600, 1475, 1450, 1390, 1355, 1220, 880, 870 cm^{-1}; NMR ($CDCl_3$) δ 0.69 (3 H, t, J = 7 Hz), 0.80–1.07 (2 H, m), 1.26 (3 H, s), 1.33 (9 H, s), 1.35 (9 H, s), 1.47–1.64 (2 H, m), 3.63 (4H, s), 3.65 (4 H, s), 7.25 (2 H, s), 7.27 (2 H, s); mass spectrum, m/e 441 (M^+). Anal. Calcd for $C_{28}H_{40}S_2$: C, 76.30; H, 9.15. Found: C, 76.30; H, 9.22.

13j: colorless prisms (hexane); mp 199–200 °C; IR (KBr) 3040, 2960, 1475, 1455, 1255, 1220, 1200, 1100, 1020, 880, 810, 780, 750 cm^{-1}; NMR ($CDCl_3$) δ 1.32 (9 H, s), 1.36 (9 H, s), 1.44 (3 H, s), 3.11 (3 H, s), 3.54 (4 H, AB pattern, J = 15 Hz), 3.68 (4 H, s), 7.24 (4 H, s); mass spectrum, m/e 428 (M^+). Anal. Calcd for $C_{26}H_{36}S_2O$: C, 72.84; H, 8.47. Found: C, 72.73; H, 8.53.

13k: colorless prisms (hexane–benzene, 1:1); mp 249–251 °C; IR (KBr) 3040, 2960, 1600, 1480, 1460, 1400, 1360, 1220, 885, 775, 710 cm^{-1}; NMR ($CDCl_3$) δ 0.62 (3 H, t, J = 8 Hz), 0.69 (3 H, t, J = 7 Hz), 0.80–1.07 (2 H, m), 1.49–1.72 (4 H, m), 1.34 (18 H, s), 3.65 (8 H, s), 7.26 (4 H, s); mass spectrum, m/e 454 (M^+). Anal. Calcd for $C_{39}H_{42}S_2$: C, 76.59; H, 9.31. Found: C, 76.51; H, 9.41.

13a′: colorless prisms (hexane–benzene, 2:1); mp 136–138 °C; IR (KBr) 3040, 2960, 1595, 1475, 1360, 1220, 880, 740, 700; NMR ($CDCl_3$) δ 1.32 (36 H, s), 3.63 (16 H, s), 7.10–7.30 (12 H, m); mass spectrum, m/e 769 (M^+). Anal. Calcd for $C_{48}H_{64}S_4$: C, 74.94; H, 8.39. Found: C, 75.51; H, 8.65.

9,18,27,36-Tetramethyl-2,11,20,29-tetrathia[3.3.3.3]metacyclophane (**13b′**): colorless prisms (benzene); mp 280–281 °C; IR (KBr) 3040, 2960, 1480, 1360, 1235, 1190, 940, 880, 870, 755, 675 cm^{-1}; NMR ($CDCl_3$) δ 1.25 (36 H, s), 1.65 (12 H, s), 3.57 (16 H, s), 7.04 (8 H, s). Anal. Calcd for $C_{52}H_{72}S_4$: C, 75.67; H, 8.79. Found: C, 75.60; H, 8.95.

9,18,27,36-Tetramethoxy-2,11,20,29-tetrathia[3.3.3.3]metacyclophane (**13f′**): colorless needles (hexane–benzene, 1:1); mp 247–248 °C; IR (KBr) 3040, 2960, 1485, 1365, 1250, 1205, 1100, 1000, 880, 680 cm^{-1}; NMr ($CDCl_3$) δ 1.30 (36 H, s), 3.20 (12 H, s), 3.66 (16 H, s), 7.20 (8 H, s). Anal. Calcd for $C_{52}H_{72}S_4O_4$: C, 70.22; H, 8.16. Found: C, 69.96; H, 7.95.

9,27-Dimethyl-18,36-dimethoxy-2,11,20,29-tetrathia[3.3.3.3]-metacyclophane (**13j′**): colorless prisms (benzene); mp 241–212 °C; IR (KBr) 3040, 2960, 1600, 1470, 1420, 1355, 1220, 1095, 1000, 880, 785, 670 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (36 H, s), 1.88 (6 H, s), 3.29 (6 H, s), 3.65 (16 H, s), 7.09 (4 H, s), 7.16 (4 H, s). Anal. Calcd for $C_{52}H_{72}S_4O_2$: C, 72.84; H, 8.47. Found: C, 72.81; H, 8.49.

Wittig Rearrangement of 13 To Give 14. The following experimental procedure was applied in all cases. To a stirred solution of 6 mmol of **13** 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.

14b: colorless crystals; mp 259–263 °C; IR (KBr) 3040, 2960, 1590, 1480, 1450, 1360, 1270, 1260, 1235, 1090, 1025, 880, 825, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.6–1.0 (6 H, CH_3), 1.29–1.35 [18 H, C(CH_3)$_3$], 2.15 (6 H, s, SCH_2), 2.65–2.83 (2 H, CH_2), 3.10–3.32 (2 H, CH_2), 4.00–4.17 (2 H, CH), 7.20–2.90 (4 H, Ar H). Anal. Calcd for $C_{28}H_{40}S_2$: C, 76.30; H, 9.15. Found: C, 76.04; H, 9.21.

14c: colorless crystals; mp 185–195 °C; IR (KBr) 3040, 2960, 1590, 1470, 1450, 1360, 1265, 1230, 1200, 1050, 995, 890, 840, 740 cm^{-1}; NMR ($CDCl_3$) δ 0.24–0.43 (6 H, CH_2CH_3), 0.90–1.30 (4 H, CH_2CH_3), 1.30–1.36 [18 H, C(CH_3)$_3$], 2.17 (6 H, s, SCH_3), 2.65–2.83 (2 H, CH_2), 3.07–3.27 (2 H, CH_2), 4.07–4.25 (2 H, CH), 7.15–7.87 (4 H, Ar H). Anal. Calcd for $C_{30}H_{44}S_2$: C, 76.86; H, 9.46. Found: C, 77.02; H, 9.80.

14d: colorless crystals; mp 165–200 °C; IR (KBr) 3040, 2960, 1590, 1470, 1450, 1360, 1270, 1235, 1080, 980, 880, 830, 735 cm^{-1}; NMR ($CDCl_3$) δ 0.37–0.53 (6 H, $CH_2CH_2CH_3$), 0.60–1.16 (8 H, $CH_2CH_2CH_3$), 1.30–1.36 [18 H, C(CH_3)$_3$], 2.16 (6 H, s, SCH_3), 2.66–2.78 (2 H, CH_2), 3.06–3.25 (2 H, CH_2), 4.08–4.25 (2 H, CH), 7.14–7.86 (4 H, Ar H). Anal. Calcd for $C_{32}H_{48}S_2$: C, 77.35; H, 9.74. Found: C, 77.40; H, 9.75.

14j: colorless crystals; mp 195–200 °C; IR (KBr) 3040, 2960, 1595, 1475, 1460, 1420, 1360, 1270, 1085, 1100, 1015, 885, 835, 740, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.69–0.71 (3 H, CH_3), 1.30–1.35 (18 H, *t*-Bu), 2.14 (6 H, s, SCH_3), 2.60–2.73 (2 H, CH_2), 2.85–2.88 (3 H, OCH_3), 3.05–3.25 (2 H, CH_2), 3.83–4.03 (2 H, CH), 7.13–7.79 (4 H, Ar H). Anal. Calcd for $C_{28}H_{40}OS_2$: C, 73.63; H, 8.83. Found: C, 73.70; H, 8.93.

14f: colorless crystals; mp 207–235 °C; IR (KBr) 3040, 2960, 1470, 1460, 1420, 1275, 1250, 1190, 1100, 1020, 880, 840, 810, 740 cm^{-1}; NMR ($CDCl_3$) δ 1.30–1.36 [18 H, $C(CH_3)_3$], 2.04 (6 H, s, SMe), 2.26–3.00 (4 H, CH_2), 3.01 (6 H, s, OCH_3), 3.80–4.00 (2 H, CH), 7.11–7.71 (4 H, Ar H). Anal. Calcd for $C_{28}H_{40}S_2O_2$: C, 71.14; H, 8.53. Found: C, 70.58; H, 8.50.

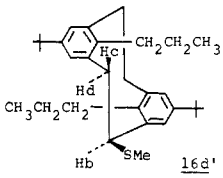
Oxidation of 14 To Give 15. The cyclophane **14** (3 mmol) and *m*-chloroperbenzoic acid (85%, 1.28 g, 6.30 mmol) were dissolved in chloroform (300 mL) at 0 °C under nitrogen and the solution was stirred for 24 h at room temperature. The solution was washed with 10% sodium bicarbonate solution and water, dried over Na_2SO_4, and concentrated. Disulfoxide **15** was obtained in almost quantitative yields as colorless crystals. The product was used without further purification.

Raney Nickel Reduction of 15 To Give 16. Reduction of 15b. Freshly prepared W-2 Raney nickel (7.2 g) was added to a solution of the crude sulfoxide **15b** (920 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 1:1 benzene–hexane mixture for elution. The crystals isolated from the eluate were recrystallized from hexane to give 570 mg (82%) of **16b**.

Reduction of 15c. To a solution of 1.63 g of the crude sulfoxide **15c** in 50 mL of ethanol was added 10.8 g of freshly prepared W-2 Raney nickel. After the reaction mixture was heated under reflux for 3 h, it was treated and worked up as described above to afford 780 mg (69%) of **16c**.

16c: colorless prisms (hexane); mp 262–264 °C; IR (KBr) 3040, 2960, 2860, 1595, 1480, 1450, 1360, 1280, 1180, 1050, 960, 885, 860, 760, 700 cm^{-1}; NMR ($CDCl_3$) δ 0.32 (6 H, t, J = 8 Hz), 1.03 (4 H, q, J = 8 Hz), 1.28 (18 H, s), 2.76, 2.88 (8 H, A_2B_2 pattern, J_{AB} = 8 Hz), 7.00 (4 H, s); mass spectrum, m/e 376 (M^+). Anal. Calcd for $C_{28}H_{40}$: C, 89.29; H, 10.71. Found: C, 89.18; H, 10.91.

Reduction of 15d. To a solution of 1.65 g of crude sulfoxide **15d** in 500 mL of ethanol was added 10.8 g of freshly prepared W-2 Raney nickel. After the reaction mixture was heated under reflux for 3 h, it was treated and worked up as described above to afford 948 mg (70.2%) of colorless crystals to which structure **16d′** has been assigned.



16d'

16d′: colorless prisms (MeOH); mp 140–143 °C; IR (KBr) 3040, 2960, 1585, 1470, 1450, 1355, 1270, 1260, 1180, 1080, 880, 730 cm^{-1}; NMR ($CDCl_3$) δ 0.47 (6 H, t, J = 6 Hz), 0.60–0.80 (4 H, m), 0.88–1.08 (4 H, m), 1.30 (9 H, s), 1.32 (9 H, s), 2.15 (3 H, s), 2.62 (1 H, dd, J_{dc} = 12 Hz, J_{db} = 12 Hz, Hd), 2.76–2.88 (4 H, m), 3.10 (1 H, dd, J_{cb} = 4.5 Hz, J_{cd} = 12 Hz, Hc), 4.10 (1 H, dd, J_{bc} = 4.5 Hz, J_{bd} = 12 Hz, Hb), 7.00–7.08 (3 H, m), 7.68 (1 H, d, J = 3 Hz, deshielded by SMe); mass spectrum, m/e 450 (M^+). Anal. Calcd for $C_{31}H_{46}S$: C, 82.60; H, 10.29. Found: C, 82.22; H, 10.30.

Reduction of 15f. To a solution of 1.13 g of crude sulfoxide **15f** in 300 mL of ethanol was added 7.2 g of freshly prepared W-2 Raney nickel. After the reaction mixture was heated under reflux for 3 h, it was treated and worked up as described above to afford 260 mg (34%) of **16f**.

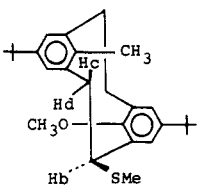
16f: colorless prisms (hexane); mp 242–243 °C; IR (KBr) 3040, 2960, 1475, 1360, 1280, 1195, 1100, 1020, 885, 860, 805, 770, 710 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (18 H, s), 2.62 (6 H, s), 2.88 (8 H, s), 7.00 (4 H, s); mass sppctrum, m/e 380 (M^+). Anal. Calcd for $C_{26}H_{36}O_2$: C, 82.06; H, 9.54. Found: C, 81.99; H, 9.67.

Preparation of 5,13-Di-*tert*-butyl-8-methyl-16-methoxy-[2.2]metacyclophane (16j). To a solution of 970 mg of the crude sulfoxide **15j** in 300 mL of ethanol was added 7.2 g of freshly prepared W-2 Raney nickel. After the reaction mixture was heated under reflux for 3 h, it was chromatographed on silica gel, using a mixture of hexane and benzene (1:1) and benzene as eluants, to afford 407 mg (54.8%) of **16j** and 104 mg (42.6%) of colorless prisims to which were assigned structure **16j′** or **16j″**.

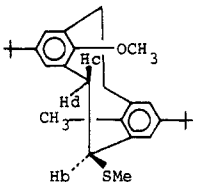
16j: colorless prisms (hexane); mp 215–216 °C; IR (KBr) 3040, 2960, 1475, 1360, 1205, 1180, 1100, 1025, 880, 850, 770, 710 cm^{-1}; NMR ($CDCl_3$) δ 0.59 (3 H, s), 1.28 (9 H, s), 1.32 (9 H, s), 2.58–2.80 (4 H, m), 2.64 (3 H, s), 2.85 (4 H, s), 7.00 (2 H, s), 7.05 (2 H, s); mass spectrum, m/e 364 (M^+). Anal. Calcd for $C_{26}H_{36}O$: C, 85.66; H, 9.95. Found: C, 85.45; H, 10.14.

The physical properties of **16b**, **16c**, **16f**, and **16j** are described elsewhere in the text.

16j′ or **16j″**: colorless prisms (hexane); mp 163–154 °C; IR (KBr) 3040, 2960, 1600, 1480, 1420, 1270, 1180, 1100, 1020, 880, 850, 800, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.58 (3 H, q), 1.32 (18 H, s), 2.13 (3 H, s), 2.44–2.76 (4 H, m), 2.62 (1 H, dd, J_{dc} = 12 Hz, J_{db} = 12 Hz, Hd), 3.10 (1 H, dd, J_{cb} = 4.5 Hz, J_{cd} = 12 Hz, Hc), 3.90 (1 H, dd, J_{bc} = 4.5 Hz, J_{cd} = 12 Hz, Hb), 7.04 (2 H, br s), 7.15 (1 H, d, J = 3 Hz), 7.79 (1 H, d, J = 3 Hz, deshield by SMe); mass spectrum, m/e: 410 (M^+). Anal. Calcd for $C_{27}H_{38}OS$: C, 78.97; H, 9.33. Found: C, 78.92; H, 9.37.



16j'



16j"

Preparation of 6,15-Di-*tert*-butyl-9,18-dialkyl-2,11-dithia[3.3]metacyclophane 2,2,11,11-Tetroxide (22). A mixture of 6.5 mmol of **13**, 11 mL (about 100 mmol) of 30% hydrogen peroxide, and 43 mL of glacial acetic acid was refluxed for 20 h. The reaction mixture was poured into a cold solution of 25 g of sodium hydroxide in 100 mL of water and the resulting paste was allowed to cool to room temperature. When was filtered off the crude sulfone and washed with a small amount of ethanol, colorless crystals were obtained.

22a: colorless needles (benzene); mp >300 °C; IR (KBr) 3040, 2960, 1600, 1475, 1320, 1260, 1180, 1110, 925, 900, 890, 750, 705, 680 cm^{-1}; NMR ($CDCl_3$) δ 1.25 (18 H, s), 4.29 (8 H, s), 6.61 (2 H, br s), 7.37 (2 H, s), 7.38 (2 H, s); mass spectrum, m/e 448 (M^+). Anal. Calcd for $C_{24}H_{32}S_2O_4$: C, 64.25; H, 7.19. Found: C, 64.55; H, 7.24.

22b: colorless prisms (benzene); mp >300 °C; IR (KBr) 3040, 2960, 2900, 1600, 1480, 1400, 1300, 1235, 1100, 890, 860, 780, 710 cm^{-1}; NMR ($CDCl_3$) δ 0.82 (6 H, s), 1.22 (18 H, s), 3.93 (8 H, AB pattern, J_{AB} = 15 Hz), 7.40 (4 H, s); mass spectrum, m/e 476 (M^+). Anal. Calcd for $C_{26}H_{36}S_2O_4$: C, 65.51; H, 7.61. Found: C, 65.36; H, 7.50.

22c: colorless prisms (benzene); mp >300 °C; IR (KBr) 3040, 2960, 1600, 1480, 1460, 1410, 1360, 1300, 1235, 1100, 890, 800, 750, 690 cm^{-1}; NMR ($CDCl_3$) δ 0.61 (6 H, t, J = 7.5 Hz), 1.35 18 H, s), 1.61 (4 H, q, J = 7.5 Hz), 4.37 (8 H, AB pattern, J_{AB} = 14.5 Hz), 7.61 (4 H, s); mass spectrum, m/e 504 (M^+). Anal. Calcd for $C_{28}H_{40}S_2O_4$: C, 66.63; H, 7.99. Found: C, 66.55; H, 7.99.

22d: colorless prisms; mp >300 °C; IR (KBr) 3040, 2960, 2860, 1600, 1480, 1305, 1235, 1160, 1105, 900, 765, 715 cm^{-1}; NMR ($CDCl_3$) δ 0.73 (6 H, t, J = 6 Hz), 0.84–1.06 (4 H, m), 1.37 (18 H, s), 1.54–1.69 (4 H, m), 4.39 (8 H, AB pattern, J_{AB} = 14.5 Hz), 7.65 (4 H, s); mass spectrum, m/e 532 (M^+). Anal. Calcd for $C_{30}H_{44}S_2O_4$: C, 67.63; H, 8.32. Found: C, 67.55; H, 8.39.

22e: colorless prisms; mp >300 °C; IR (KBr) 3040, 2960, 2870, 1605, 1480, 1360, 1310, 1265, 1240, 1110, 900, 765, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.80 (6 H, t, J = 6 Hz), 0.92–1.16 (8 H, m), 1.40 (18 H, s), 1.55–1.70 (4 H, m), 4.39 (8 H, AB pattern, J_{AB} = 14.5 Hz, 7.65 (4 H, s); mass spectrum, m/e 560 (M^+). Anal. Calcd for $C_{32}H_{45}S_2O_4$: C, 68.53; H, 8.63. Found: C, 68.37; H, 8.73.

22f: colorless prisms; mp >300 °C; IR (KBr) 3040, 2980, 1475, 1310, 1260, 1110, 1000, 900, 775 cm^{-1}; NMR ($CDCl_3$) δ 1.36 (18 H, s), 3.19 (6 H, s), 4.26 (8 H, AB pattern, J_{AB} = 15 Hz), 7.66 (4 H, s); mass spectrum, m/e 509 (M^+). Anal. Calcd for $C_{26}H_{36}S_2O_6$: C, 61.39; H, 7.13. Found: C, 61.40; H, 7.11.

22g: colorless prisms; mp >300 °C; IR (KBr) 3040, 2960, 1600, 1480, 1360, 1320, 1260, 1180, 1110, 890, 715 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (9 H, s), 1.39 (9 H, s), 1.62 (3 H, s), 4.13 (4 H, s), 4.44 (4 H, AB pattern, J_{AB} = 14.5 Hz), 5.25 (1 H, br s), 7.46 (2 H, d, J = 2 Hz), 7.59 (2 H, s); mass spectrum, m/e 462 (M^+). Anal. Calcd for $C_{25}H_{34}S_2O_4$: C, 64.90; H, 7.41. Found: C, 64.09; H, 7.30.

22h: colorless prisms; mp >300 °C; IR (KBr) 3040, 2960, 2900, 1600, 1480, 1300, 1240, 1105, 890, 800, 765, 735 cm^{-1}; NMR ($CDCl_3$) δ 0.65 (3 H, t, J = 7 Hz), 1.31 (3 H, s), 1.37 (9 H, s), 1.38 (9 H, s), 1.64 (2 H, q, J = 7 Hz), 4.41 (4 H, AB pattern, J_{AB} 14.5 Hz), 4.44 (4 H, AB pattern, J_{AB} = 14.5 Hz), 7.66 (2 H, s), 7.68 (2 H, s); mass spectrum, m/e 490 (M^+). Anal. Calcd for $C_{27}H_{38}S_2O_4$: C, 66.08; H, 7.81. Found: C, 65.75; H, 7.86.

22i: colorless prisms; mp >300 °C; IR (KBr) 3040, 2960, 1600, 1480, 1410, 1305, 1235, 1105, 895, 780, 735, 710 cm^{-1}; NMR ($CDCl_3$) δ 0.72 (9 H, s), 1.51–1.66 (2 H, m), 4.40 (4 H, AB pattern, J = 14.5 Hz), 4.42 (4 H, AB pattern, J. = 14.5 Hz), 7.63 (2 H, s), 7.67 (2 H, s); mass spectrum, m/e 504 (M^+). Anal. Calcd for $C_{28}H_{40}S_2O_4$: C, 66.63; H, 7.99. Found: C, 66.09; H, 8.01.

22j: colorless prisms; mp >300 °C; IR (KBr) 3040, 2960, 1605, 1480, 1460, 1360, 1300, 1260, 1240, 1100, 1000, 895, 780, 735, 680 cm^{-1}; NMR ($CDCl_3$) δ 1.32 (3 H, s), 1.34 (9 H, s), 1.37 (9 H, s), 3.17 (3 H, s), 4.20 (4 H, AB pattern, J_{AB} = 14 Hz), 4.38 (4 H, AB pattern, J_{AB} = 14 Hz), 7.50 (2 H, s), 7.70 (2 H, s); mass spctrum, m/e 492 (M^+). Anal. Calcd for $C_{26}H_{36}S_2O_5$: C, 63.38; H, 7.37. Found: C, 63.54; H, 7.40.

22k: colorless prisms; mp >300 °C; IR (KBr) 3040, 2960, 2860, 1600, 1480, 1300, 1235, 1100, 890, 800, 760, 740, 715, 700 cm^{-1}; NMR ($CDCl_3$) δ 0.64 (3 H, t, J = 6 Hz), 0.73 (3 H, t, J = 6 Hz), 0.90–1.06 (2 H, m), 1.37 (9 H, s), 1.38 (9 H, s), 4.39 (4 H, AB pattern, J_{AB} = 14.5 Hz), 1.61 (4 H, t, J = 6 Hz), 4.41 (4 H, AB pattern, J_{AB} = 14.5 Hz), 1.61 (4 H, t, J = 6 Hz), 4.41 (4 H, AB pattern, J_{AB} = 14.5 Hz), 7.65 (4 H, s); mass spectrum, m/e 518 (M^+). Anal. Calcd for $C_{29}H_{42}S_2O_4$: C, 67.14; H, 8.16. Found: C, 67.11; H, 8.25.

Pyrolysis of Disulfones 22. Pyrolysis of disulfones of [2.2]metacyclophanes (**22**) 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 **22** (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 and chloroform to yield the desired [2.2]metacyclophane and recovered disulfone (**22**), respectively.

16a: colorless prisms (hexane); mp 177–178 °C; IR (KBr) 3040, 2960, 1590, 1440, 1360, 1275, 1180, 945, 855, 725 cm^{-1}; NMR ($CDCl_3$) δ 1.36 (18 H, s), 2.07, 3.04 (8 H, A_2B_2 pattern, J_{AB} = 8 Hz), 4.05 (2 H, t, J = 1.5 Hz), 7.03 (4 H, s, J = 1.5 Hz); mass spectrum, m/e 320 (M^+). Anal. Calcd for $C_{24}H_{32}$: C, 89.94; H, 10.06. Found: C, 89.82; H, 10.07.

16b: colorless prisms (hexane); mp 254–255 °C; IR (KBr) 3040, 2960, 1470, 1450, 1350, 1180 cm^{-1}; NMR ($CDCl_3$) δ 0.56 (6 H, s), 1.27 (18 H, s), 2.65–2.92 (8 H, m), 7.05 (4 H, s); mass spectrum, m/e 348 (M^+). Anal. Calcd for $C_{26}H_{36}$: C, 89.59; H, 10.41. Found: C, 89.68; H, 10.44.

16c: colorless prisms (hexane); mp 262–264 °C; IR (KBr) 3040, 2960, 2860, 1595, 1480, 1450, 1420, 1360, 1280, 1180, 1050, 960, 885, 860, 760, 700 cm^{-1}; NMR ($CDCl_3$) δ 0.32 (6 H, t, J = 8 Hz), 1.03 (4 H, q, J = 8 Hz), 1.28 (18 H, s), 2.76, 2.88 (8 H, A_2B_2 pattern, J_{AB} = 8 Hz), 7.00 (4 H, s); mass spectrum, m/e 376 (M^+). Anal. Calcd for $C_{28}H_{40}$: C, 89.29; H, 10.71. Found: C, 89.18; H, 10.91.

16d: colorless plates (hexane); mp 205–206 °C; IR (KBr) 3040, 2960, 2870, 1595, 1480, 1450, 1360, 1280, 1180, 1090, 880, 860, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.48 (6 H, t, J = 6 Hz), 0.40–1.08 (8 H, m), 1.31 (18 H, s), 2.81 (8 H, s), 7.01 (4 H, s); mass spectrum, m/e 404 (M^+). Anal. Calcd for $C_{30}H_{44}$: C, 89.04; H, 10.96. Found: 89.11; H, 11.05.

16e: colorless prisms (hexane); mp 166–168 °C; IR (KBr) 3040, 2960, 2860, 1590, 1465, 1360, 1275, 1180, 855, 730 cm^{-1}; NMR ($CDCl_3$) δ 0.64 (6 H, t, J = 6 Hz), 0.52–1.08 (12 H, m), 1.29 (18 H, s), 2.80 (8 H, s), 7.02 (4 H, s); mass spectrum, m/e 432 (M^+). Anal. Calcd for $C_{32}H_{48}$: C, 88.82; H, 11.18. Found: C, 88.56; H, 11.10.

16f: colorless prisms (hexane); mp 242–243 °C; IR (KBr) 3040, 2960, 1475, 1360, 1280, 1195, 1100, 1020, 885, 860, 805, 770, 710 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (18 H, s), 2.62 (6 H, s), 2.88 (8 H, s), 7.00 (4 H, s); mass spectrum, m/e 380 (M^+). Anal. Calcd for $C_{26}H_{36}O_2$: C, 82.06; H, 9.54. Found: C, 81.99; H, 9.67.

16g: colorless prisms (hexane); mp 127–130 °C; IR (KBr) 3040, 2960, 1580, 1470, 1355, 1270, 1180, 880, 850, 730 cm^{-1}; NMR ($CDCl_3$) δ 0.47 (3 H, s), 1.27 (9 H, s), 1.33 (9 H, s), 2.00–3.06 (8 H, m), 3.56 (1 H, t, J = 1.5 Hz), 7.00 (2 H, s), 7.05 (2 H, d, J = 1.5 Hz); mass spectrum, m/e 334 (M^+). Anal. Calcd for $C_{25}H_{34}$: C, 89.75; H, 10.24. Found: C, 88.63; H, 10.27.

16h: colorless prisms (hexane); mp 226–228 °C; IR (KBr) 3040, 2960, 2850, 1590, 1470, 1450, 1385, 1275, 1180, 880, 850, 755, 730, 705 cm^{-1}; NMR ($CDCl_3$) δ 0.31 (3 H, t, J = 7.5 Hz), 0.56 (3 H, s), 1.05 (2 H, q, J = 7.5 Hz), 1.27 (9 H, s), 1.28 (9 H, s), 2.70–2.95 (8 H, m), 7.04 (2 H, s), 7.07 (2 H, s); mass spectrum, m/e 362 (M^+). Anal. Calcd for $C_{27}H_{38}$: C, 89.44; H, 10.56. Found: C, 89.23; H, 10.56.

16i: colorless plates (MeOH); mp 112–114 °C; IR (KBr) 3040, 2960, 1590, 1460, 1360, 1280, 1180, 880, 860, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.48 (3 H, t, J = 6 Hz), 0.56 (3 H, s), 0.60–0.80 (2 H, m), 0.94–1.10 (2 H, m), 1.26 (9 H, s), 2.70–2.96 (8 H, m), 7.04 (4 H, s); mass spectrum, m/e 376 (M^+). Anal. Calcd for $C_{28}H_{40}$: C, 89.29; H, 10.71. Found: C, 89.00; H, 10.72.

16j: colorless prisms (hexane); mp 215–216 °C; IR (KBr) 3040, 2960, 1475, 1360, 1205, 1180, 1100, 1025, 880, 850, 770, 710 cm^{-1}; NMR ($CDCl_3$) δ 0.59 (3 H, s), 1.28 (9 H, s), 1.32 (9 H, s), 2.58–2.80 (4 H, m), 2.64 (3 H, s), 2.85 (4 H, s), 7.00 (2 H, s), 7.05 (2 H, s); mass spectrum, m/e 364 (M^+). Anal. Calcd for $C_{26}H_{36}O$: C, 85.66; H, 9.95. Found: C, 85.45; H, 10.14.

16k: colorless prisms (hexane; mp 208–209 °C; IR 3040, 2960, 2860, 1590, 1480, 1450, 1360, 1275, 1180, 890, 860, 855, 765, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.31 (3 H, t, J = 7.5 Hz), 0.45 (3 H, t, J = 5.0 Hz), 0.60–0.80 (2 H, m), 0.99 (4 H, t, J = 7.5 Hz), 1.28 (9 H, s), 1.29 (9 H, s), 2.80 (8 H, br s), 7.02 (2 H, s), 7.04 (2 H, s); mass spectrum, m/e 390 (M^+). Anal. Calcd for $C_{28}H_{40}$: C, 89.29; H, 10.71. Found: C, 89.00; H, 10.72.

Preparation of 8,16-Dimethyl[2.2]metacyclophane (28a). To a solution of **16b** (4.5 g, 12.9 mmol) in benzene (600 mL) was added a solution of aluminum chloride (511 mg, 387 mmol) in nitromethane (1 mL). After the reaction mixture was stirred for 2 h at 50 °C, it was poured into ice/water and extracted with benzene. The benzene solution was dried over sodium sulfate and evaporated in vacuo to give the crude **28a** in almost quantitative yield, which was recrystallized from hexane to afford 2.6 g (85%) of **28a**: colorless prisms; mp 205–206 °C (hexane) (lit.[2] mp 205 °C). The formation of *tert*-butylbenzene (**25**) was confirmed by GLC.

Trans-*tert*-butylation of 5,13-Di-*tert*-butyl-8,16-diethyl-[2.2]metacyclophane (16c). To a solution of **16c** (100 mg, 0.266 mmol) in benzene (20 mL) was added a few drops of aluminum chloride–nitromethane (1 g–2 mL) solution. After the reaction mixture was stirred for 2 h at 50 °C, it was worked up as described above. The reaction mixture was analyzed by GC–mass spectrometry and the results are shown in Figure 1 and Table III.

Reaction of 16b with *N*-Bromosuccinimide. A mixture of 1.03 g (3 mmol) of **16b**, 1.32 g (7.42 mmol) of *N*-bromosuccinimide, and 100 mg of benzoyl peroxide in 600 mL of carbon tetrachloride was refluxed for 4 h. After the reaction mixture had cooled, it was filtered. The filtrate was concentrated to give colorless solid. This solid was washed with dichloromethane to give 1.30 g (85.5%) of **38**: colorless prisms (benzene); mp >300 °C; IR (KBr) 3040, 2960, 1585, 1475, 1360, 1225, 1220, 1190, 890, 760, 665 cm^{-1}; NMR ($CDCl_3$) δ 1.33 (18 H, s), 2.75–3.11 (8 H, m), 3.04 (4 H, s), 7.16 (4 H, s); mass spectrum, m/e 504, 506, 508 (M^+). Anal. Calcd for $C_{26}H_{34}Br_2$: C, 61.67; H, 6.37. Found: C, 61.25; H, 6.72.

Reaction of 28a with *N*-Bromosuccinimide. A mixture of 708 mg (3 mmol) of **28a**, 1.32 g (7.42 mmol) of *N*-bromosuccinimide, and 100 mg of benzoyl peroxide in 600 mL of carbon tetrachloride was refluxed for 4 h. The reaction mixture was treated as described above to give 1.12 g (95%) of **39**: colorless prisms (benzene); mp >300 °C; IR (KBr) 3040, 2960, 1460, 1455, 1220, 1185, 890, 775, 640 cm^{-1}; NMR ($CDCl_3$) δ 2.67–3.18 (8 H,

m), 3.00 (4 H, s), 6.98–7.40 (6 H, m); mass spectrum, *m/e* 392, 394, 396 (M^+). Anal. Calcd for $C_{18}H_{18}Br_2$: C, 54.85; H, 4.60. Found: C, 55.05; H, 4.65.

Bromination of 28a with Bromine. In the Absence of Iron Powder. To a solution of 100 mg (0.424 mmol) of **28a** in 50 mL of carbon tetrachloride was added a solution of 0.41 g (2.54 mmol) of bromine in 10 mL of carbon tetrachloride while stirring with a magnetic stirrer at room temperature. After 4 h, the reaction mixture was poured into a large amount of ice–water. The organic layer was extracted with dichloromethane. The dichloromethane solution was dried over Na_2SO_4 and evaporated in vacuo to leave a residue which was analyzed by liquid chromatography. The pure products, **43a** and **43b**, were not isolated. The structures were determined by NMR.

In the Presence of Iron Powder. To a solution of 100 mg (0.424 mmol) of **28a** and 50 mg of iron powder, in 50 mL of carbon tetrachloride was added a solution of 0.41 g (2.54 mmol) of bromine in 10 mL of carbon tetrachloride while stirring with a magnetic stirrer at room temperature. After the reaction mixture was stirred for 9 h, it was treated as described above to give 86.8 mg (37.2%) of **42**: pale yellow prisms (benzene); mp >300 °C; IR (KBr) 2940, 1580, 1545, 1430, 1360, 1250, 1205, 1020, 705, 780; NMR ($CDCl_3$) δ 2.18 (6 H, s), 2.50–3.20 (8 H, m); mass spectrum, *m/e* 550 (M^+). Anal. Calcd for $C_{18}H_{14}Br_4$: C, 39.31; H, 2.57. Found: C, 38.81; H, 2.12.

Bromination of 16b with Bromine. In the Absence of Iron Powder. To 100 mg (0.29 mmol) of **16b** in 50 mL of carbon tetrachloride was added 0.28 g (1.74 mmol) of bromine in 10 mL of carbon tetrachloride while stirring with a magnetic stirrer at room temperature. After 4 h, the reaction mixture was poured into a large amount of ice–water. The organic layer was extracted with dichloromethane. The dichloromethane solution was dried over Na_2SO_4 and evaporated in vacuo and the residue was chromatographed on silica gel, using petroleum ether for elution. The deep green crystals isolated from the eluate were recrystallized from hexane to give 164.4 mg (85.9%) of **41a**: green prisms (hexane); mp 228–230 °C (lit.[20] mp 228–230 °C). Compound **41b** was also obtained in this manner in 93% yield: deep brown prisms (hexane); mp 165–166 °C (lit.[20] mp 165–166 °C).

In the Presence of Iron Powder. To a solution of 100 mg (0.29 mmol) of **16b** and 50 mg of iron powder in 50 mL of carbon tetrachloride was added a solution of 0.28 g (1.74 mmol) of bromine in 10 mL of carbon tetrachloride while stirring with a magnetic stirrer at room temperature. After the reaction mixture was stirred for 4 h, it was treated as described above to give 110 mg (60%) of **40**: colorless plates (hexane); mp 287–288 °C; IR (KBr) 3040, 2960, 1600, 1425, 1360, 1245, 1040, 980, 870, 720 cm^{-1}; NMR ($CDCl_3$) δ 1.61 (18 H, s), 8.90 (4 H, s); mass sppctrum, *m/e* 630 (M^+). Anal. Calcd for $C_{24}H_{22}Br_4$: C, 45.75; H, 3.52. Found: C, 45.78; H, 3.56.

Registry No. 3d, 14011-00-8; **5b**, 65276-11-1; **6a**, 67691-33-2; **6b**, 76447-56-8; **7a**, 67691-34-3; **7b**, 76447-57-9; **9b**, 76447-58-0; **10**, 76447-59-1; **11d**, 76447-60-4; **11f**, 76447-61-5; **12d**, 76447-62-6; **12f**, 76447-63-7; **13a**, 76447-64-8; **13a'**, 76447-65-9; **13b**, 76447-66-0; **13b'**, 76447-67-1; **13c**, 76447-68-2; **13d**, 76447-69-3; **13e**, 76447-70-6; **13f**, 76447-71-7; **13f'**, 76447-72-8; **13g**, 76447-73-9; **13h**, 76447-74-0; **13i**, 76447-75-1; **13j**, 76447-76-2; **13j'**, 76447-77-3; **13k**, 76466-36-9; **14a**, 76466-29-0; **14b**, 76446-96-3; **14c**, 76446-97-4; **14d**, 76446-98-5; **14e**, 76466-30-3; **14f**, 76446-99-6; **14g**, 76466-31-4; **14h**, 76447-00-2; **14i**, 76447-01-3; **14j**, 76447-02-4; **14k**, 76447-03-5; **15b**, 76447-04-6; **15c**, 76466-32-5; **15d**, 76447-05-7; **15f**, 76447-06-8; **15j**, 76447-07-9; **16a**, 76497-11-5; **16b**, 67691-35-4; **16c**, 76447-78-4; **16d**, 76447-79-5; **16d'**, 76447-80-8; **16e**, 76466-37-0; **16f**, 72523-20-7; **16g**, 76447-81-9; **16h**, 76447-32-0; **16i**, 76447-33-1; **16j**, 76447-34-2; **16j'**, 76497-62-6; **16j''**, 76447-35-3; **16k**, 76447-36-4; **18**, 98-19-1; **22a**, 76447-37-5; **22b**, 76447-38-6; **22c**, 76447-39-7; **22d**, 76466-33-6; **22e**, 76447-40-0; **22f**, 76447-41-1; **22g**, 76447-42-2; **22h**, 76447-43-3; **22i**, 76447-44-4; **22j**, 76447-45-5; **22k**, 76447-46-6; **25**, 98-06-6; **28a**, 51689-61-3; **28b**, 76447-47-7; **28b'**, 76549-93-4; **29**, 76447-48-8; **30**, 76447-49-9; **38**, 76447-50-2; **39**, 76497-10-4; **40**, 76466-34-7; **41a**, 76447-51-3; **41b**, 76466-35-8; **42**, 76447-52-4; **43a**, 76447-53-5; **43b**, 76447-54-6; 5-*tert*-butyl-8,6-dimethyl[2.2]metacyclophane, 76447-55-7; *n*-butylbenzene, 104-51-8; 2,6-di-*tert*-butyl-*p*-cresol, 128-37-0; thiourea, 62-56-6; $ClCH_2OCH_3$, 107-30-2.

Lithium Aluminum Hydride Reduction of *peri*-Alkoxy-9,10-anthraquinones

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The outcome of $LiAlH_4$ reduction of 9,10-anthraquinones is greatly influenced by electronegative substituents in positions peri to the carbonyl groups of the quinone. Reductions of 1,4-, 1,5-, and 1,8-dimethoxyanthraquinones proceed to the anthrone stage. The critical role of the *peri*-methoxy group is evident from the comparison with the reduction of 2,6-dimethoxyanthraquinone and the parent anthraquinone, which give dihydro diols and no anthrone. $LiAlH_4$ reduction of *peri*-diethoxyanthraquinones differs from the reduction of the *peri*-dimethoxy derivatives, and dihydro diols are formed, rather than anthrones. A similar product dependency on the peri substituent is evident from reduction of 1,8- and 1,5-dichloroanthraquinones. The former leads to 4,5-dichloro-9-anthrone, and the latter gives dihydro diol exclusively. These differences are determined by the fate of the intermediate addition products of the quinone and lithium aluminum hydride. Anthrone formation is seen as the result of a carbanionic 1,4-elimination reaction from these *meso*-dihydroanthracene derivatives. Electronic and steric effects of peri substituents on this elimination reaction are discussed.

Reduction of 9,10-anthraquinones may lead to a series of products ranging from anthrahydroquinones to *meso*-dihydroanthracenes and including the intermediate oxidation states of anthrones, 9,10-dihydro-9,10-anthracenediols, and anthracenes. These transformations may be accomplished by several different reducing systems, many of which had found widespread use before the discovery of metal hydride reducing agents. Although the reductive properties of lithium aluminum hydride toward functional groups have been exhaustively documented,[1] use of this reagent for the reduction of 9,10-anthraquinones remains virtually unexplored and has resulted in conflicting reports for its reaction with the parent compound. Reduction of 9,10-anthraquinone with lithium aluminum hydride in ether/benzene resulted in the formation of

(1) H. C. Brown, P. M. Weissman, and N. M. Yoon, *J. Am. Chem. Soc.*, 88, 1458 (1966), and references cited therein.

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