Medium-Sized Cyclophanes, 25[1]

Bromination of [2.*n*]Metacyclophan-1-enes and Isolation of Two Isomers of 1-Bromo[2.*n*]metacyclophan-1-enes

Takehiko Yamato*[a], Jun-ichi Matsumoto[a], Seiji Ide[a], Kazuaki Suehiro[a], Kazumasa Kobayashi[b], and Masashi Tashiro[b]

Department of Industrial Chemistry, Faculty of Science and Engineering, Saga University[a], Honjo-machi 1, Saga-shi, Saga 840, Japan

Institute of Advanced Material Study, Kyushu University[b], Kasuga-kohen 6-1, Kasuga-shi, Fukuoka 816, Japan

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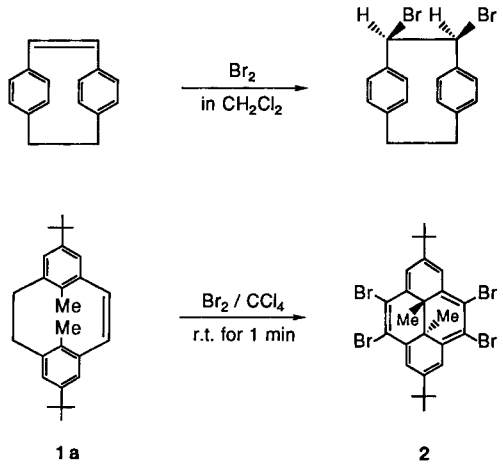
Bromination of dimethyl[2.3]metacyclophan-1-ene (**1b**) with bromine affords the *cis* adduct **6b** resulting from the addition to the bridging double bond; a similar reaction of dimethyl[2.4]metacyclophan-1-ene (**1c**) gives a mixture of the *cis* and *trans* adduct formed by the addition to the bridged double bond along with the products containing a brominated internal methyl group. On the other hand, bromination of dimethyl[2.*n*]metacyclophan-1-enes (**1**) with benzyltrimethylammonium tribromide affords exclusively the product of the *cis* addition **6** to the bridged double bond. Treatment of [3.2]metacyclophane **6b** with potassium *tert*-butoxide in refluxing *t*BuOH for 1 h gives the dehydrobrominated product (*E*)-**8b** in 95% yield; a similar reaction of [4.2]metacyclophane **6c** furnishes two isomers, (*E*)-**8c** and (*Z*)-**8c**, of 1-bromo[2.4]metacyclophan-1-ene along with [2.4]metacyclophan-1-one **9c** in 20% yield. The characterization and the reaction pathway of these products are discussed.

Cram et al. have reported that the bromination of [2.2]paracyclophan-1-ene with bromine affords the corresponding *cis* adduct[2]. On the other hand, we have previously reported[3,4] that the reaction of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophan-1-ene (**1a**) with bromine affords *trans*-4,5,9,10-tetrabromo-2,7-di-*tert*-butyl-10b,10c-dimethyl-10b,10c-dihydropyrene (**2**) in good yield, but not the product formed by the addition of the bromine to the bridged double bond (Scheme 1).

Scheme 1



1a **2**

r.t.: room temp.

This novel transannular reaction may be attributed to the electronic interaction between two benzene rings, the proximity of the 8,16-positions and the release of considerable strain energy to form the more stable annulene π-electron system 10b,10c-dihydropyrene. Thus, there is substantial interest in investigating the bromination of [2.*n*]metacyclophan-1-enes, which may afford the product resulting from the addition to the bridged double bond, because the formation of 14-π dihydropyrene derivatives is not possible.

We report in this paper on the bromination of dimethyl[2.*n*]metacyclophan-1-enes **1b–d** and the hydrobromination of bromine adducts **6b–c** with potassium *tert*-butoxide.

Results and Discussion

The preparation of 5,14-di-*tert*-butyl-8,17-dimethyl[2.3]metacyclophan-1-ene (**1b**) and 5,15-di-*tert*-butyl-8,18-dimethyl[2.4]metacyclophan-1-ene (**1c**) was previously reported[5]. 5,16-Di-*tert*-butyl-8,19-dimethyl[2.5]metacyclophan-1-ene (**1c**) was prepared as described in Scheme 2.

The intermediate thia compound **3** was prepared in a previous work[6]. Attempted Wittig reaction of **3** with *n*-butyllithium followed by treatment with methyl iodide under the same reaction conditions as used for the preparation of **1b** and **1c** failed. Only the starting compound **3** was recovered. However, when lithium diisopropylamide (LDA) was used as a base, the desired sulfide **4** was obtained in 79% yield. The conversion of **4** into **1d** was carried out by using a standard procedure[5].

Attempted bromination of 5,14-di-*tert*-butyl-8,17-dimethyl[2.3]metacyclophan-1-ene (**1b**) with 1.1 equiv. of bromine carried out in carbon tetrachloride solution at room temp. for 3 min in analogy to the bromination of **1a** led to

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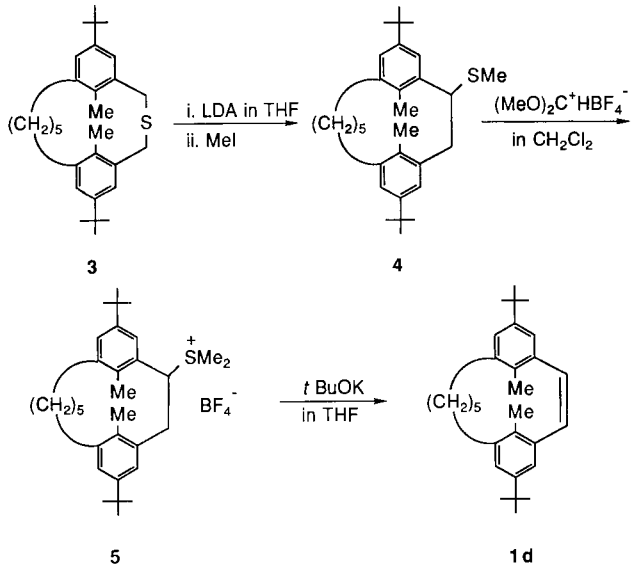
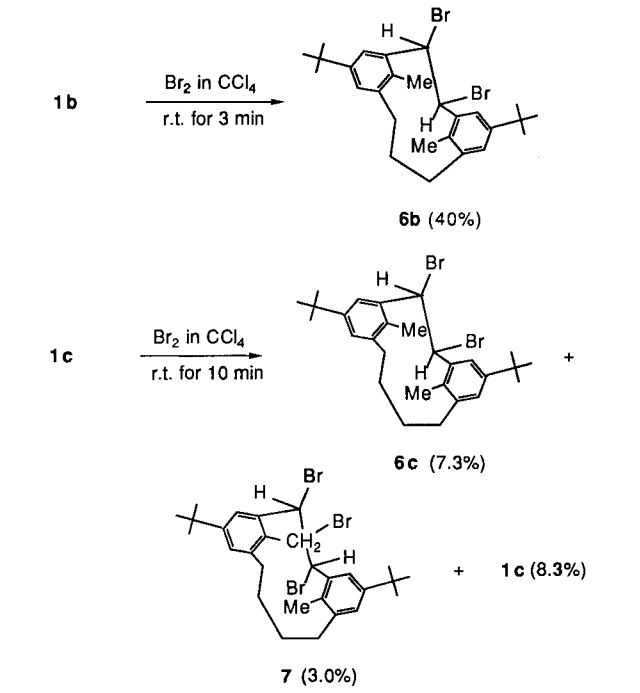
the expected product **6b** of the addition of the bromine to the bridged double bond in 40% yield along with the starting compound in 6% yield. The similar reaction of 5,15-di-*tert*-butyl-8,18-dimethyl[2.4]metacyclophan-1-ene (**1c**) for 10 min gave **6c** in only 7.3% yield, but instead, mainly bromination of the internal methyl group furnishing **7** occurred (Scheme 3).

Scheme 2



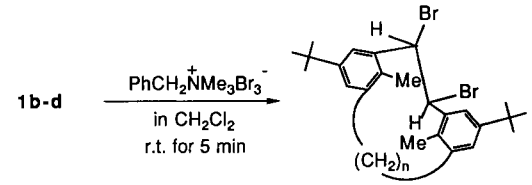
Scheme 3



r.t.: room temp.

In contrast, compounds **1b–d** were treated with an equimolar amount of benzyltrimethylammonium tribromide (BTMA Br_3) in dichloromethane, which was recently found to be a convenient solid brominating agent[7,8] to afford the corresponding adducts **6b–d** in 90, 95 and 95% yield, respectively (Scheme 4).

Scheme 4



6	n	Yield
b	3	90%
c	4	95%
d	5	95%

r.t.: room temp.

The structure of the products obtained was determined on the basis of their elemental analyses and spectral data. The ^{1}H-NMR spectrum of **6b** in $CDCl_3$ shows two sets of doublets (J = 4.2 Hz) at δ = 5.14 and 5.45 for the methine protons and a doublet (J = 2.0 Hz) at δ = 7.71 for one aromatic proton which is located in a strongly deshielding region of the *endo*-Br atom on the ethylene bridge.

These data are strongly supported by the fact that the two Br atoms exhibit an *exo* and *endo* arrangement, and therefore **6b** has been found to be the product of the *cis* addition of the brominating agent to the bridged double bond. This assignment is also applied to the adducts **6c** and **6d**.

In contrast, the ^{1}H-NMR spectrum of **7** in $CDCl_3$ shows two sets of doublets (J = 1.0 Hz) at δ = 6.03 and 6.10 for the methine protons, the coupling constant of which is smaller than that of the *cis* adduct **6c** (J = 4.3 Hz), and no deshielded aromatic proton as in **6c** has been observed. These data are strongly supported by the fact that the two Br atoms exhibit an *exo* arrangement, and therefore **7** has been found to be the *trans* adduct formed by the addition to the bridged double bond. Furthermore, the ^{1}H-NMR spectrum of **7** shows the methylene protons of the internal bromomethyl group as a pair of doublets (J = 10.8 Hz) at δ = 3.07 and 4.08; this is a consequence of the rigid cyclophane conformation which makes the CH_2 protons diastereotopic.

To the best of our knowledge, only a few examples of methylarenes in which the methyl group is brominated under the conditions used have been reported[9,10]. This result may be attributed to the cyclophane structure.

The fact that *cis* adducts like **6b** are exclusively obtained indicates the formation of a four-membered transition state **B**[12–13] rather than a nonclassic bromonium ion intermediate **A**[14] in the bromination. The absence of **A** might be attributed to the strain of this intermediate. When the number of the methylene bridges is increased by one, the *cis* addition of bromine to [2.4]metacyclophan-1-ene (**1c**) competes with the *trans* addition due to the decrease of strain of the intermediate **A** (Figure 1).

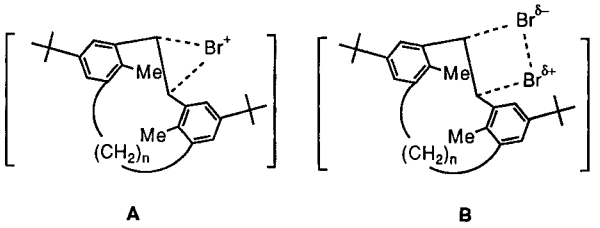


Figure 1. Bromination intermediates

Treatment of [3.2]metacyclophane **6b** with potassium *tert*-butoxide in refluxing THF or *tert*-butanol for 1 h gave the dehydrobrominated product (*E*)-**8b** in 90 and 95% yield, respectively. A similar reaction of [4.2]metacyclophane **6c** in refluxing *tert*-butanol afforded two isomers, (*E*)-**8c** und (*Z*)-**8c**, of 1-bromo[2.4]metacyclophan-1-ene along with [2.4]metacyclophan-1-one (**9c**) in 20% yield. These different results are attributed to the release of strain of the product (*Z*)-**8c** by increasing the length of the methylene bridge by one unit (Scheme 5, Table 1).

Scheme 5

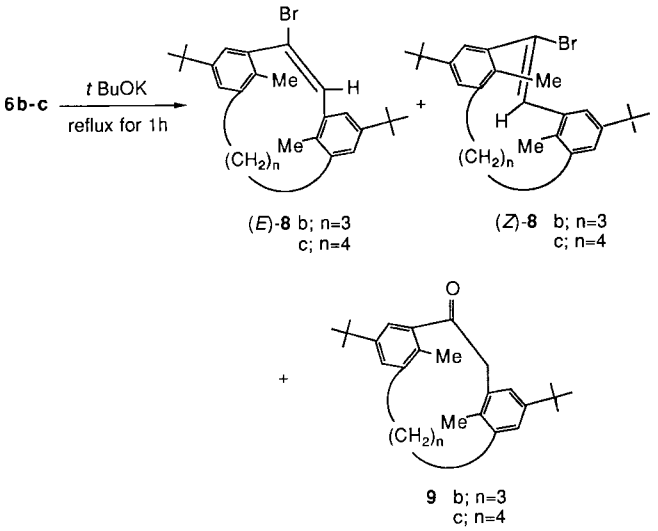


Table 1. Dehydrobromination of **6** with *t*BuOK

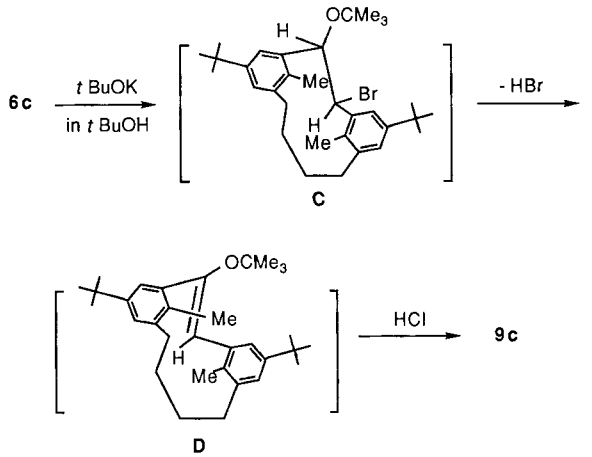
Run	Substrate	Solvent	Products (% yield)[a]
1[b]	**6b**	THF	(*E*)-**8b** (90)
2[c]	**6b**	*t*BuOH	(*E*)-**8b** (95)
3	**6c**	THF	(*Z*)-**8c** (70), **9c** (30)
4	**6c**	*t*BuOH	(*E*)-**8c** (15), (*Z*)-**8c** (65), **9c** (20)

[a] Relative yields determined by ^{1}H-NMR spectroscopy. — [b] Starting compound **6b** was recovered in 10% yield. — [c] Starting compound **6b** was recovered in 5% yield.

The ^{1}H-NMR spectrum of (*E*)-**8c** in $CDCl_3$ shows a singlet at $\delta = 7.26$ for the olefinic proton. In contrast, in compound (*Z*)-**8c** the olefinic proton is observed at higher field ($\delta = 6.42$) which is in a strongly shielding region due to folding into the π cavity formed by two benzene rings.

It was also found that when (*E*)-**8c** and (*Z*)-**8c** were treated with potassium *tert*-butoxide under the same reaction conditions, the starting compounds were recovered in quantitative yield. This result is strongly supported by the fact that (*E*)-**8c** and (*Z*)-**8c** are not intermediates in the formation of **9c**. Although the mechanism of the formation of **9c** has not yet been completely elucidated, it may be assumed that the reaction involves nucleophilic substitution of **6c** with a *tert*-butoxy anion to form **C** followed by HBr elimination as shown in Scheme 6 rather than the formation of a cyclophyne intermediate[15–17] followed by addition of *t*BuOH to the triple bond to form **D**. This assumption is also supported by the fact that the reaction of (*E*)-**8c** or (*Z*)-**8c** with 2,5-diphenylisobenzofuran[17] in the presence of potassium *tert*-butoxide under the same reaction conditions only leads to recovery of the starting compound.

Scheme 6



In conclusion, we have first isolated two isomers, (*E*)-**8c** and (*Z*)-**8c**, of 1-bromo[2.4]metacyclophan-1-ene of the metacyclophan-1-ene system. Furthermore, the present results of the dehydrobromination of the bromine adducts of [2.*n*]metacyclophan-1-enes with a base will open up new mechanistic aspects for cyclophane chemistry.

Further studies on the chemical properties of the two isomers, (*E*)-**8c** and (*Z*)-**8c** are presently being made.

Experimental

All melting and boiling points are uncorrected. — IR (KBr or NaCl): Nippon Denshi JIR-AQ2OM. — ^{1}H NMR: Nippon Denshi JEOL FT-270; in $CDCl_3$, TMS as reference. — UV: Hitachi 220A spectrophotometer. — MS: Nippon Denshi JMS-01SA-2. — Elemental analyses: Yanaco MT-5.

Wittig Rearrangement of **3** *to* **4**: To a stirred solution of 760 mg (1.77 mmol) of 6,17-di-*tert*-butyl-9,20-dimethyl-2-thia[3.5]metacyclophane (**3**) in 25 ml of dry THF was added under nitrogen 30 ml of a THF solution of LDA [prepared from 1.00 ml (4.60 mmol) of diisopropylamine and 5.00 ml of a 15% hexane solution of *n*-butyllithium (9.12 mmol)] with ice cooling. After stirring the reaction mixture for 10 min at room temp., 0.32 ml (5.14 mmol) of methyl iodide was added. The reaction mixture was worked up by the addition of H_2O and CH_2Cl_2. The CH_2Cl_2 extract was washed with

water, dried with Na_2SO_4, and concentrated. The remaining product was purified by filtration through silica gel with hexane/benzene (1:1) to give 610 mg (79%) of **4** as colorless prisms (hexane), m.p. 134–135°C. – ^{1}H NMR ($CDCl_3$): δ = 0.80–0.95 (2H, m), 1.21 (3H, s), 1.26 (3H, s), 1.30 (9H, s), 1.32 (9H, s), 1.20–1.50 (4H, m), 2.01 (3H, s), 2.20–2.35 (2H, m), 2.55–2.70 (3H, m), 3.16 (1H, dd, J = 12.8 Hz, J = 3.7 Hz), 4.37 (1H, dd, J = 12.8 Hz, J = 3.7 Hz), 6.89 (1H, d, J = 2.0 Hz), 6.90 (1H, d, J = 2.0 Hz), 7.17 (1H, d, J = 2.0 Hz), 7.78 (1H, d, J = 2.0 Hz). – MS (75 eV): m/z = 436 [M^+].

$C_{30}H_{44}S$ (436.7) Calcd. C 82.50 H 10.15
Found C 82.70 H 10.17

Preparation of the Sulfonium Salt **5**: A solution of 1.91 g (4.67 mmol) of **4** in 10 ml of CH_2Cl_2 was added with stirring to a suspension of 6.50 g (40.15 mmol) of dimethoxycarbonium tetrafluoroborate in 5 ml of CH_2Cl_2. The temp. of the reaction mixture was maintained at −30°C under nitrogen. The mixture was allowed to warm to room temp. and was stirred for an additional 4 h. Then, 150 ml of ethyl acetate was added and the mixture stirred for ca. 12 h. Subsequently, the solvent was decanted. The resulting crystalline precipitate was collected and dried to give 1.99 g (79%) of **5** as colorless crystals, m.p. >300°C. – ^{1}H NMR ([D_6]DMSO): δ = 0.65–0.80 (2H, m), 1.20–1.40 (4H, m), 1.28 (3H, s), 1.31 (9H, s), 1.32 (9H, s), 1.39 (3H, s), 2.20–2.38 (2H, m), 2.50–2.78 (2H, m), 2.79 (3H, s), 3.44 (3H, s), 3.30–3.50 (2H, m), 5.06 (1H, dd, J = 7.3 Hz, J = 14.5 Hz), 6.96 (1H, d, J = 2.2 Hz), 7.09 (1H, d, J = 2.2 Hz), 7.36 (2H, d, J = 2.2 Hz). – MS (75 eV): m/z = 538 [M^+].

$C_{31}H_{47}BF_4S$ (538.6) Calcd. C 69.13 H 8.79
Found C 68.86 H 8.22

5,16-Di-tert-butyl-8,19-dimethyl[2.5]metacyclophan-1-ene (**1d**): To a solution of 1.12 g (2.08 mmol) of **5** in 70 ml of THF was added with stirring 0.44 g (3.92 mmol) of potassium *tert*-butoxide. After stirring of the reaction mixture at room temp. under nitrogen for 4 h, benzene (200 ml) was added, and the mixture was acidified by the addition of dilute aqueous hydrochloric acid. The organic layer was separated, washed with water, dried with Na_2SO_4, and concentrated. The residue was recrystallized from methanol to give 0.57 g (70%) of **1d** as colorless prisms (hexane), m.p. 113–115°C. – ^{1}H NMR ($CDCl_3$): δ = 1.20–1.55 (6H, m), 1.25 (6H, s), 1.30 (18H, s), 2.22–2.37 (2H, m), 2.50–2.73 (2H, m), 6.81 (2H, s), 7.01 (2H, d, J = 2.0 Hz), 7.17 (2H, d, J = 2.0 Hz). – MS (75 eV): m/z = 388 [M^+].

$C_{29}H_{40}$ (388.6) Calcd. C 89.63 H 10.37
Found C 89.66 H 10.50

Reaction of [2.n]Metacyclophan-1-enes with Bromine. – Typical Procedure: To a stirred solution of 100 mg (0.28 mmol) of **1b** in 30 ml of carbon tetrachloride was added a solution of 0.02 ml (0.31 mmol) of bromine in 10 ml of carbon tetrachloride at room temp. After the reaction mixture had been stirred for 3 min, it was poured into 30 ml of ice-cold water. The organic layer was washed with aqueous 10% sodium thiosulfate (10 ml) and water, dried with Na_2SO_4, and concentrated. The residue was separated by silica gel column chromatography (eluent hexane) to give 6.20 mg (6.2%) of **1b** and 58.0 mg (40%) of **6b**.

10,11-Dibromo-6,14-di-tert-butyl-9,17-dimethyl[3.2]metacyclophane (**6b**): Colorless prisms (hexane), m.p. 222–224°C. – ^{1}H NMR ($CDCl_3$): δ = 0.69 (3H, s), 1.00 (3H, s), 1.19 (9H, s), 1.25 (9H, s), 1.68–2.11 (2H, m), 2.40–2.84 (4H, m), 5.14 (1H, d, J = 4.2 Hz), 5.45 (1H, d, J = 4.2 Hz), 6.89 (1H, d, J = 2.0 Hz), 7.02 (2H, br. s), 7.71 (1H, d, J = 2.0 Hz). – MS (75 eV): m/z = 518, 520, 522 [M^+].

$C_{27}H_{36}Br_2$ (520.4) Calcd. C 62.32 H 6.97
Found C 62.57 H 6.97

Compounds **6c** and **7** were prepared in the same manner as described above.

11,12-Dibromo-7,15-di-tert-butyl-10,18-dimethyl[4.2]metacyclophane (**6c**): Colorless prisms (methanol), m.p. 202–204°C. – ^{1}H NMR ($CDCl_3$): δ = 0.80–1.68 (4H, m), 0.95 (3H, s), 1.22 (3H, s), 1.28 (9H, s), 1.34 (9H, s), 1.96–2.41 (2H, m), 2.52–2.95 (2H, m), 5.50 (1H, d, J = 4.3 Hz), 5.68 (1H, d, J = 4.3 Hz), 6.96 (2H, d, J = 2.1 Hz), 7.06 (1H, J = 2.1 Hz), 7.89 (1H, d, J = 2.1 Hz). – MS (75 eV): m/z = 532, 534, 536 [M^+].

$C_{28}H_{38}Br_2$ (534.4) Calcd. C 62.93 H 7.17
Found C 63.07 H 7.17

11,12-Dibromo-10-bromomethyl-7,15-di-tert-butyl-18-methyl[4.2]metacyclophane (**7**): Colorless prisms (methanol), m.p. 212–214°C. – ^{1}H NMR ($CDCl_3$): δ = 0.94–1.76 (4H, m), 1.17 (3H, s), 1.31 (9H, s), 1.33 (9H, s), 1.96–2.44 (2H, m), 2.52–3.04 (2H, m), 3.07 (1H, d, J = 10.8 Hz), 4.08 (1H, d, J = 10.8 Hz), 6.03 (1H, d, J = 1.0 Hz), 6.10 (1H, d, J = 1.0 Hz), 6.94–7.08 (2H, m), 7.14–7.24 (2H, m). – MS (75 eV): m/z = 610, 612, 614, 616 [M^+].

$C_{28}H_{37}Br_3$ (613.3) Calcd. C 54.83 H 6.08
Found C 54.60 H 6.17

Reaction of [2.n]Metacyclophan-1-enes **1** *with BTMA* Br_3. – *Typical Procedure:* To a stirred solution of 100 mg (0.25 mmol) of **1d** in 10 ml of CH_2Cl_2 was added 110 mg (0.28 mmol) of BTMA Br_3 at room temp. After the reaction mixture had been stirred for 5 min, it was poured into 10 ml of ice-cold water. The organic layer was washed with aqueous 10% sodium thiosulfate (10 ml) and water, dried with Na_2SO_4, and concentrated. The residue was separated by silica gel column chromatography (eluent hexane) to give 58.0 mg (95%) of **6d**.

12,13-Dibromo-8,16-di-tert-butyl-11,19-dimethyl[5.2]metacyclophane (**6d**): Colorless prisms (methanol), m.p. 220–222°C. – ^{1}H NMR ($CDCl_3$): δ = 1.24 (3H, s), 1.29 (9H, s), 1.30 (3H, s), 1.35 (9H, s), 1.20–1.40 (6H, m), 2.27–2.48 (2H, m), 2.57–2.73 (2H, m), 5.73 (1H, d, J = 4.4 Hz), 5.77 (1H, d, J = 4.4 Hz), 6.91 (1H, d, J = 2.2 Hz), 7.04 (1H, d, J = 2.2 Hz), 7.07 (1H, d, J = 2.2 Hz), 8.02 (1H, d, J = 2.2 Hz). – MS (75 eV): m/z = 546, 548, 550 [M^+].

$C_{29}H_{40}Br_2$ (548.5) Calcd. C 63.51 H 7.35
Found C 63.78 H 7.44

Similarly, **6b** and **6c** were prepared in the same manner as described above in 90 and 95% yield, respectively.

Hydrobromination of **6** *with tBuOK. – Typical Procedure:* To a stirred solution of 0.30 g (0.56 mmol) of **6c** in 50 ml of *t*BuOH was added 2.40 g (21.4 mmol) of *t*BuOK at room temp. After the reaction mixture had been refluxed for 1 h, it was poured into 20 ml of ice-cold water and extracted with CH_2Cl_2. The organic layer was washed with water (3 × 20 ml), dried with Na_2SO_4, and concentrated. The residue was separated by silica gel column chromatography (eluent hexane and benzene) to give 0.13 g (50%) of (*Z*)-**8c**, 0.03 g (10%) of (*E*)-**8c**, and 0.04 g (18%) of **9c**.

(1Z)-1-Bromo-5,15-di-tert-butyl-8,18-dimethyl[2.4]metacyclophan-1-ene [(*Z*)-**8c**]: Colorless prisms (hexane), m.p. 162–164°C. – ^{1}H NMR ($CDCl_3$): δ = 1.02 (3H, s), 1.30 (3H, s), 1.30 (9H, s), 1.35 (9H, s), 2.16–2.30 (4H, m), 2.71–2.76 (4H, m), 6.42 (1H, s), 6.79 (1H, d, J = 1.8 Hz), 6.86 (1H, d, J = 1.8 Hz), 6.96 (1H, d, J = 1.8 Hz), 7.41 (1H, d, J = 1.8 Hz). – MS (75 eV): m/z = 452, 454 [M^+].

$C_{28}H_{37}Br$ (453.5) Calcd. C 74.16 H 8.22
Found C 73.96 H 8.03

(1E)-1-Bromo-5,15-di-tert-butyl-8,18-dimethyl[2.4]metacyclophan-1-ene [(*E*)-**8c**]: Colorless prisms (hexane), m.p. 162–164°C. – ^{1}H NMR ($CDCl_3$): δ = 1.02 (3H, s), 1.30 (3H, s), 1.30 (9H, s), 1.35 (9H, s), 2.16–2.30 (4H, m), 2.71–2.76 (4H, m), 6.42 (1H, s), 6.79 (1H, d, J = 1.8 Hz), 6.86 (1H, d, J = 1.8 Hz), 6.96 (1H, d,

J = 1.8 Hz), 7.41 (1H, d, J = 1.8 Hz). – MS (75 eV): m/z = 452, 454 [M^+]. $C_{28}H_{37}Br$ (453.5) Calcd. C 74.16 H 8.22
Found C 73.96 H 8.03

5,15-Di-tert-butyl-8,18-dimethyl[2.4]metacyclophan-1-one (**9c**): Colorless prisms (hexane), m.p. 180–184°C. – ^{1}H NMR ($CDCl_3$): δ = 0.84 (3H, s), 1.08 (3H, s), 1.20 (9H, s), 1.23 (9H, s), 1.40–1.50 (2H, m), 2.10–2.25 (2H, m), 2.68–2.86 (2H, m), 3.65 (1H, d, J = 12.6 Hz), 4.03 (1H, d, J = 12.6 Hz), 6.86 (1H, d, J = 1.6 Hz), 6.91 (1H, d, J = 1.6 Hz), 6.98 (1H, d, J = 1.6 Hz), 7.07 (1H, d, J = 1.6 Hz). – MS (75 eV): m/z = 390 [M^+].

$C_{28}H_{38}O$ (390.6) Calcd. C 86.10 H 9.81
Found C 86.31 H 9.75

Similarly, (*E*)-**8b** was prepared in the same manner as described above in 90% yield.

(1E)-1-Bromo-5,14-di-tert-butyl-8,17-dimethyl[2.3]metacyclophan-1-ene [(*E*)-**8b**]: Colorless prisms (hexane), m.p. 158–159°C. – ^{1}H NMR ($CDCl_3$): δ = 0.88 (6H, s), 1.28 (9H, s), 1.31 (3H, s), 1.95–2.00 (2H, m), 2.48–2.55 (4H, m), 2.57–2.73 (2H, m), 5.73 (1H, d, J = 4.4 Hz), 5.77 (1H, d, J = 4.4 Hz), 6.88 (1H, d, J = 2.0 Hz), 6.98 (1H, d, J = 2.0 Hz), 7.04 (1H, d, J = 2.0 Hz), 7.13 (1H, s), 7.30 (1H, d, J = 2.0 Hz). – MS (75 eV): m/z = 438, 440 [M^+]. $C_{27}H_{35}Br$ (439.5) Calcd. C 73.79 H 8.03
Found C 73.90 H 8.10

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