Reaction of [2.2]Metacyclophanes Having an Internal C=C Bond with Brominating Agents

Tsutomu Ishi-i,[†] Tsuyoshi Sawada,[‡] Shuntaro Mataka,[‡] and Masashi Tashiro*[,‡]

Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-kohen, Kasuga-shi, Fukuoka 816 Japan, and Institute of Advanced Material Study, Kyushu University, 6-1 Kasuga-kohen, Kasuga-shi, Fukuoka 816, Japan

Received February 6, 1996[⊗]

Treatment of 5-*tert*-butyl-8-ethenyl[2.2]metacyclophane (**2**) with benzyltrimethylammonium tribromide or bromine exclusively gave the addition−elimination product, *β*-bromoolefin **6**. The bromination reactions of (*E*)-5-*tert*-butyl-8-(2-phenylethenyl)[2.2]metacyclophane ((*E*)-**3**) and its isomer (*Z*)-**3** were always stereoconvergent to give a mixture (40/60) of *β*-bromoolefins **8a** and **8b**, respectively. On the other hand, when (*E*)-8,8′-(ethene-1,2-diyl)bis(5-*tert*-butyl[2.2]metacyclophane) ((*E*)-**4**) and its isomer (*Z*)-**4** were treated with the brominating agents, none of the products arising from the electrophilic attack of a bromonium ion on the central etheno bridge was obtained; the reaction of (*E*)-**4** gave monotetrahydropyrene derivative **9** and bis(tetrahydropyrene) derivative **10**, products resulting from a transannular reaction-alkenyl migration sequence. In the reaction of (*Z*)-**4** the aromatic electrophilic substitution products 13-bromo compound **11** and 13,13′-dibromo compound **12** were obtained, along with a small amount of **9**. The reaction pathway of the brominations mentioned above is discussed.

1. Introduction

It is known that the electrophilic addition of bromine to C=C bond proceeds *via* cationic intermediates such as bridged bromonium ions and open *β*-bromocarbocations to give corresponding α,*β*-dibromo adducts.[1] The overall course of the reaction is strongly governed by the structure of the olefin. In the case of aryl-substituted ethenes such as styrene and stilbene with electron-donating groups that stabilize a cationic charge, bromination proceeds *via* *β*-bromocarbocation intermediates. In contrast, the bromination of olefins with electron-withdrawing groups favors the bromonium ion intermediate.[2−4] The addition of bromine is difficult in the case of sterically congested olefins, since the nucleophilic attack of the bromide ion to the cationic intermediate is hindered due to steric reasons, and monobromoolefins are often found.[5−7]

The bromination of the internal alkenyl groups of [2.2]metacyclophanes[8] ([2.2]MCPs) is of interest, since the internal substituents at 8 or 16 position of [2.2]MCP are surrounded by two etheno bridges and the opposing benzene ring at short distances.[9−12] Nevertheless, the chemical behavior of [2.2]MCPs with internal alkenyl groups toward brominating agents is not known. In this paper, the bromination reactions of 8-alkenyl[2.2]MCPs **2**−**4** were studied.

2. Results and Discussion

8-Ethenyl[2.2]MCP **2** was prepared by Wittig reaction of the corresponding 8-formyl[2.2]MCP **1**[11] with methyltriphenylphosphonium iodide (Scheme 1). Horner−Wadsworth−Emmons reaction of **1** with diethyl benzylphosphonate selectively gave (*E*)-8-(2-phenylethenyl)[2.2]MCP (*E*)-**3**, which isomerized to the corresponding *Z*-isomer (*Z*)-**3** on irradiation with a high-pressure mercury lamp (Scheme 1). The stereochemistry of (*E*)-**3** and (*Z*)-**3** was determined on the basis of the coupling constants of the olefinic methine protons (J = 16.5 Hz for (*E*)-**3** and J = 12.5 Hz for (*Z*)-**3**). The preparation of bis[2.2]MCPs (*E*)- and (*Z*)-**4** was reported previously.[12]

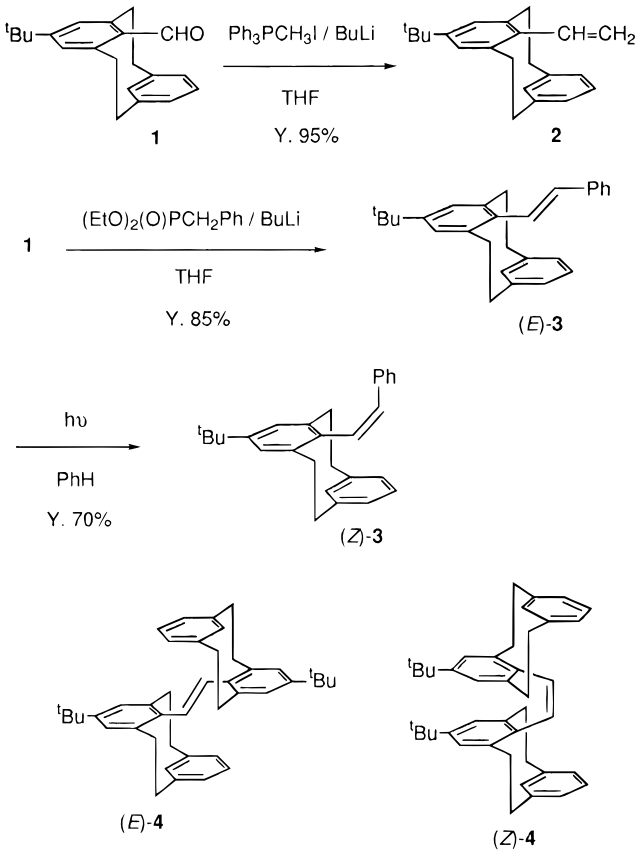
When [2.2]MCP **2** was treated with 1 equiv of bromine in carbon tetrachloride or with 1 equiv of benzyltrimethylammonium tribromide ($BTMABr_3$)[13] in dichloromethane at rt for 5 min, *β*-bromoolefin **6** was obtained in 99% yield, not the expected dibromo adduct **5** (Scheme

[†] Graduate School of Engineering Sciences.
[‡] Institute of Advanced Material Study.
[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1996.

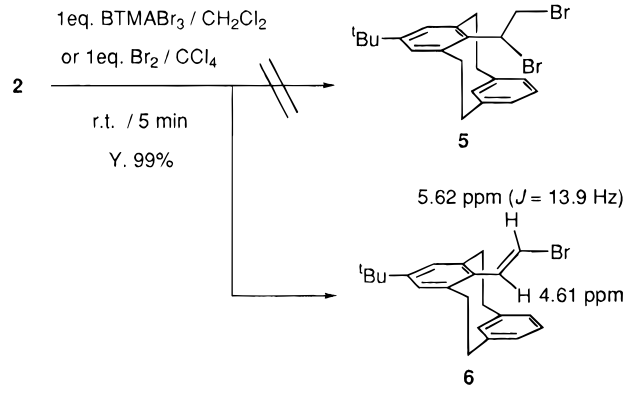
(1) (a) Ruasse, M. F. *Acc. Chem. Res.* **1990**, *23*, 87. (b) Ruasse, M. F. *Adv. Phys. Org. Chem.* **1993**, *28*, 207. (c) Herges, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 51.
(2) Bellucci, G.; Bianchini, R.; Chiappe, C.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1991**, *113*, 8012.
(3) (a) Ruasse, M. F.; Dubois, J. E. *J. Org. Chem.* **1972**, *37*, 1770. (b) Dubois, J. E.; Ruasse, M. F. *J. Org. Chem.* **1973**, *38*, 493. (c) Ruasse, M. F.; Dubois, J. E. *J. Org. Chem.* **1974**, *39*, 2441. (d) Argile, A.; Ruasse, M. F. *J. Org. Chem.* **1983**, *48*, 209.
(4) (a) Ruasse, M. F.; Argile, A.; Dubois, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 7645. (b) Ruasse, M. F.; Argile, A. *J. Org. Chem.* **1983**, *48*, 202.
(5) (a) Ruasse, M. F.; Motallebi, S.; Galland, B.; Lomas, J. S. *J. Org. Chem.* **1990**, *55*, 2298. (b) Ruasse, M. F.; Motallebi, S.; Galland, B. *J. Am. Chem. Soc.* **1991**, *113*, 3440. (c) Nagorski, R. W.; Slebocka-Tilk, H.; Brown, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 419. (d) Slebocka-Tilk, H.; Motallebi, S.; Nagorski, R. W.; Turner, P.; Brown, R. S.; McDonald, R. *J. Am. Chem. Soc.* **1995**, *117*, 8769.
(6) Hopf, H.; Hänel, R.; Jones, P. G.; Bubenitschek, P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1369.
(7) (a) Lenoir, D. *Chem. Ber.* **1978**, *111*, 411. (b) Mayr, H.; Will, E.; Heigl, U. W.; Schade, C. *Tetrahedron* **1986**, *42*, 2519. (c) Brown, R. S.; Slebocka-Tilk, H.; Bennet, A. J.; Bellucci, G; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1990**, *112*, 6310. (d) Slebocka-Tilk, H.; Zheng, C. Y.; Brown, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 1347. (e) Bellucci, G.; Bianchini, R.; Chiappe, C.; Lenoir, D.; Attar, A. *J. Am. Chem. Soc.* **1995**, *117*, 6243.
(8) For reviews, see: (a) Vögtle, F.; Neumann, P. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 73. (b) Keehn, M. P.; Rosenfeld, S. M. *Cyclophanes*; Academic Press: New York, 1983. (c) Vögtle, F. *Cyclophane Chemistry*; John Wiley and Sons: Chichester, 1993.
(9) (a) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1981**, *46*, 4556. (b) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1983**, *48*, 1461.
(10) Tashiro, M.; Arimura, T.; Yamato, T. *Chem. Pharm. Bull.* **1983**, *31*, 370.
(11) Tsuge, A.; Ishii, T.; Sawada, T.; Mataka, S.; Tashiro, M. *Chem. Lett.* **1994**, 1529.
(12) Ishii, T.; Sawada, T.; Mataka, S.; Tashiro, M.; Thiemann, T. *Chem. Ber.* **1996**, *129*, 289.
(13) (a) Kajigaeshi, S.; Kakinami, T.; Tokiyama, H.; Hirakawa, T.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2667. (b) Yamato, T.; Matsumoto, J.; Ide, S.; Suehiro, K.; Kobayashi, K.; Tashiro, M. *Chem. Ber.* **1993**, *126*, 447.

S0022-3263(96)00243-5 CCC: $12.00

Scheme 1



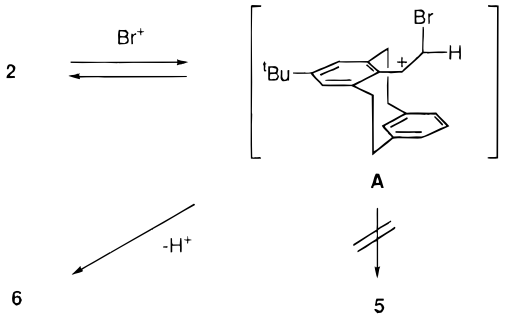
Scheme 2



2). The ^{1}H NMR spectrum of **6**, which shows for the olefinic methine protons as two sets of doublets at 4.61 and 5.62 ppm with $J = 13.9$ Hz, is strongly supportive of the proposed (*E*)-configuration.

Recently, Hopf *et al.* reported that in the bromination of a sterically hindered olefin such as 1,2,3-tri-*tert*-butylbutadiene, the cationic intermediate is stabilized by loss of a proton and the corresponding 4-bromo compound is afforded exclusively.[6] Similarly, in the reaction of **2** the electrophilic attack of the bromonium ion on the olefinic moiety affords the β-bromocarbocation intermediate **A**, which is stabilized by the π-electrons of the opposing benzene ring.[10] The nucleophilic attack of a bromide ion to **A** is inhibited due to the sterically crowded [2.2]MCP substructure. The intermediate **A** readily loses the β-proton to give **6**, and the dibromo adduct **5** is not formed (Scheme 3). The overall course of the reaction corresponds to a substitution by addition−elimination, which is observed for the conventional aromatic electrophilic substitution.

Scheme 3



Scheme 4

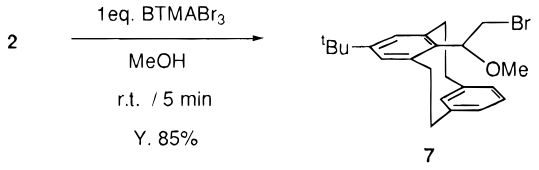
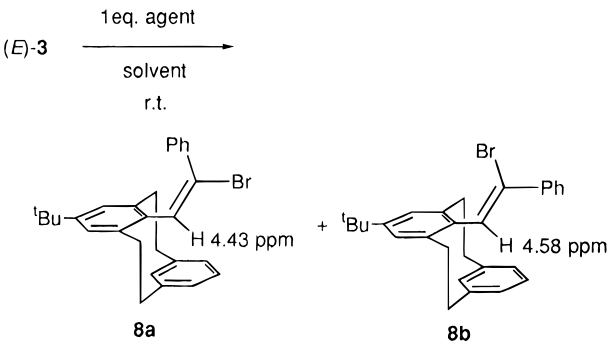


Table 1. Treatment of (*E*)-3 with $BTMABr_3$ or Br_2



			yield (%)			
agent	solvent	time (h)	(*E*)-**3**	**8a**	**8b**	**8a/8b**
$BTMABr_3$	CH_2Cl_2	45	13	25	38	40/60
$BTMABr_3$	CH_2Cl_2	90	0	34	51	40/60
Br_2	CCl_4	4	38	16	24	40/60

Table 2. Treatment of (*Z*)-3 with $BTMABr_3$ or Br_2

$$(Z)\text{-}\mathbf{3} \xrightarrow[\text{solvent, rt}]{\text{1 equiv of agent}} (E)\text{-}\mathbf{3} + \mathbf{8a} + \mathbf{8b}$$

			yield (%)			
agent	solvent	time (h)	(*E*)-**3**	**8a**	**8b**	**8a/8b**
$BTMABr_3$	CH_2Cl_2	45	54	14	20	41/59
$BTMABr_3$	CH_2Cl_2	90	14	28	44	39/61
Br_2	CCl_4	4	48	15	24	38/62

In order to trap the carbocation intermediate **A**, the reaction of **2** with $BTMABr_3$ was carried out in methanol (Scheme 4).[4,14] The expected α-methoxy-β-bromo derivative **7** was obtained exclusively, showing that the bromination of **2** proceeds *via* **A**.

Treatment of (*E*)-**3** with 1 equiv of $BTMABr_3$ or bromine at rt gave an isomeric mixture of β-bromoethenes **8a** and **8b**. (Table 1). Bromination of (*Z*)-**3** with $BTMABr_3$ or Br_2 also afforded **8a** and **8b** (Table 2). Both reactions of (*E*)-**3** and (*Z*)-**3** are stereoconvergent to give a mixture of **8a** and **8b** (40/60). In the reaction of (*Z*)-**3**, the starting material (*Z*)-**3** could not be recovered;

(14) (a) Dubois, J. E.; Chretien, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 3506. (b) Ruasse, M. F.; Dubois, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 3230. (c) Chretien, J. R.; Coudert, J. D.; Ruasse, M. F. *J. Org. Chem.* **1993**, *58*, 1917.

Scheme 5

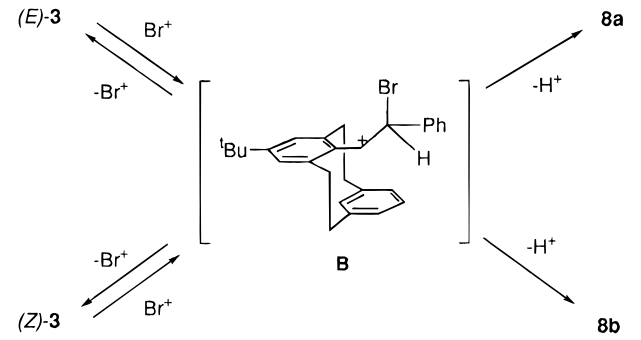
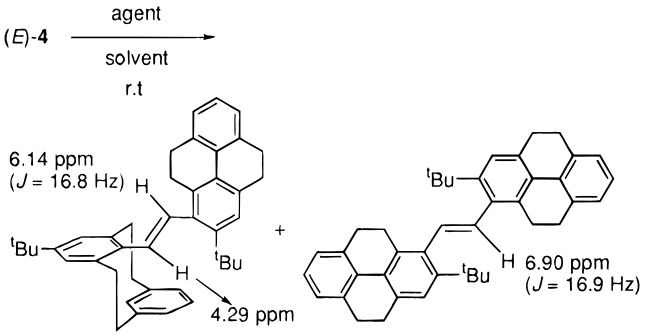


Table 3. Treatment of (*E*)-4 with $BTMBr_3$ or Br_2



			yield (%)		
agent	solvent	time (h)	(*E*)-**4**	**9**	**10**
1 equiv of $BTMABr_3$	CH_2Cl_2	4	29	50	0
2 equiv of $BTMABr_3$	CH_2Cl_2	110	0	26	54
3 equiv of $BTMABr_3$	CH_2Cl_2	230	0	0	72
1 equiv of Br_2	CCl_4	1	14	73	4

however, the corresponding isomer (*E*)-**3** was obtained. It was also found that the *β*-phenyl substituent of **3** retards the bromination, and it took >90 h to complete the bromination.

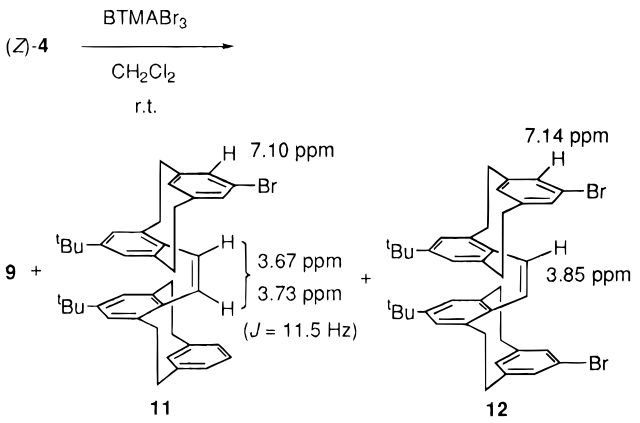
The ^{1}H NMR spectrum of **8a** shows the olefinic methine proton as a singlet at 4.43 ppm, while the corresponding proton of **8b** appears at 4.58 ppm as a singlet. The (*E*)-configuration of **8a** was determined by X-ray crystallographic analysis.[15]

Here, one might assume the reaction pathway for the formation of **8** to be as shown in Scheme 5. In the case of both (*E*)-**3** and (*Z*)-**3**, the *β*-bromocarbocation intermediate **B** is formed by an electrophilic attack of the bromonium ion on the olefinic moiety. Unstable (*Z*)-**3** can revert to stable (*E*)-**3** *via* **B**,[2] which loses the *β*-proton to give **8a** and **8b** in a ratio of *ca.* 40/60.

When bis[2.2]MCP (*E*)-**4** is treated with $BTMABr_3$ or bromine at rt, a transannular reaction between positions 8 and 16 results with a subsequent alkenyl migration to the position *ortho* to the *tert*-butyl groups to give monotetrahydropyrene derivative **9** and bis(tetrahydropyrene) derivative **10** (Table 3). No products arising from the electrophilic attack of a bromonium ion on the olefinic moiety of (*E*)-**4** could be obtained. The absence of such products is due to the steric shielding effect of the two [2.2]MCP substructures. It is known already that the aromatic electrophilic substitution of [2.2]MCPs affords

(15) The authors have deposited atomic coordinates for compounds **8a** and **9** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Table 4. Treatment of (*Z*)-4 with $BTMBr_3$

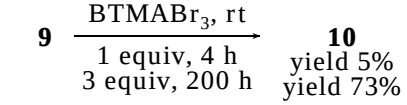


		yield (%)			
$BTMABr_3$ (equiv)	time (h)	(*Z*)-**4**	**9**	**11**	**12**
1	11	61	1	22	0
1	60	7	5	52	15
3	230	0	6	0	80

the corresponding tetrahydropyrenes.[16] To the best of our knowledge, a migration of an alkenyl group on a benzene ring has been reported for neither [2.2]MCPs nor aromatic compounds.

Bis[2.2]MCP (*E*)-**4** afforded **9** in 50% yield, when reacted with 1 equiv of $BTMABr_3$ for 4 h (Table 3). Under the same conditions **9** gave **10** in only 5% yield; however, under prolonged reaction times (200 h) **10** was obtained in 73% yield (Scheme 6). These findings suggest that conversion of **9** to **10** is slower than that of (*E*)-**4** to **9** and that the strain of **9** is smaller than that of (*E*)-**4**.

Scheme 6



X-ray crystallographic analysis[15] of **9** shows the (*E*)-arrangement of the [2.2]MCP unit and the tetrahydropyrene unit. The ^{1}H NMR spectrum of **9** shows the olefinic methine protons at 4.29 and 6.14 ppm as two sets of doublets with $J = 16.8$ Hz. The original upfield shift[9] at 4.29 ppm for the α-olefinic methine proton is due to the shielding effect of the opposing benzene ring of the [2.2]MCP unit. The signal at 6.14 ppm for the *β*-olefinic methine proton indicates a loss of the shielding effect by the transformation of a [2.2]MCP unit to a tetrahydropyrene unit. The assignment of the structure of **10** was made according to the ^{1}H NMR spectrum, which shows the olefinic methine proton in a normal region at 6.90 ppm as a singlet with a coupling constant of $J = 16.9$ Hz for the ^{13}C satellite peak.

Treatment of bis[2.2]MCP (*Z*)-**4** with $BTMABr_3$ preferentially gave the aromatic ring brominated products 13-bromide **11** and 13,13′-dibromide **12** (Table 4). Their yields are dependent on the reaction time and the amount

(16) (a) Fujimoto, M.; Sato, T.; Hata, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 600. (b) Sato, T.; Wakabayashi, M.; Okamura, Y.; Amada, T.; Hata, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2363. (c) Allinger, N. L.; Gorden, B. J.; Hu, S. E.; Ford, R. A. *J. Org. Chem.* **1967**, *32*, 2272. (d) Tashiro, M.; Mataka, S.; Takezaki, Y.; Takeshita, M.; Arimura, T.; Tsuge, A.; Yamato, T. *J. Org. Chem.* **1989**, *54*, 451. (e) Yamato, T.; Ide, S.; Tokuhisa, K.; Tashiro, M. *J. Org. Chem.* **1992**, *57*, 271.

of $BTMABr_3$ used. Interestingly, the (*E*)-olefin **9** was also obtained in the reaction of (*Z*)-**4**, though the yield is poor (1−6%). A finding that (*Z*)-**4** does not isomerize to (*E*)-**4** shows that **9** was directly formed from (*Z*)-**4**, but not *via* (*E*)-**4**, as will be mentioned later.

The structures of **11** and **12** were determined on the basis of the elemental analysis, spectral data, and chemical conversion. The ^1H NMR spectra of **11** and **12** show the original upfield shifts[9] of the internal olefinic protons at 3.67 and 3.73 ppm as doublets (J = 11.5 Hz) for **11** and at 3.85 ppm as a singlet for **12**. The signals of the aromatic protons of the brominated benzene rings (7.10 ppm for **11**, and 7.14 ppm for **12**) are shifted to lower magnetic field as compared to those[12] (6.97 ppm) of the parent bis[2.2]MCP (*Z*)-**4**. The bromides **11** and **12** were converted to (*Z*)-**4** as shown in Scheme 7.

Scheme 7

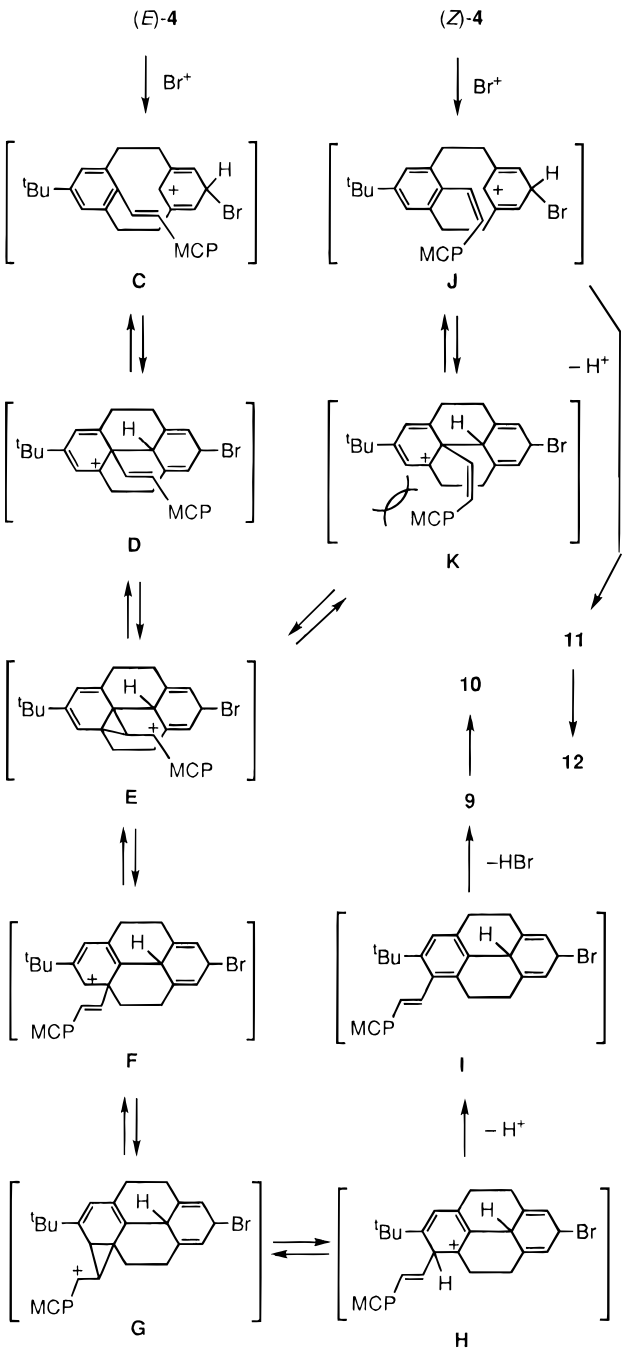
$$\mathbf{11},\ \mathbf{12} \xrightarrow[(2)\ H_2O]{(1)\ BuLi} (Z)\text{−}\mathbf{4}$$

yield 87−92%

Although the mechanisms for the formation of **9**−**12** are not clear, one might assume the reaction pathway to be as shown in Scheme 8. In the reaction of (*E*)-**4**, the initial electrophilic attack of the bromonium ion occurs at 13-position of the aromatic ring to give σ-complex **C**, which is converted to **D** by transannular reaction.[16] The alkenyl group migrates to an *ortho* position of a *tert*-butyl group *via* **E**, **F**, and **G** to give σ-complex **H**. During the migration, the olefinic moiety isomerizes to the thermodynamically stable (*E*)-configuration. σ-Complex **H** can be stabilized by deprotonation to give **I**, which produces **9** by elimination of hydrogen bromide. The transformation of **9** to **10** can be rationalized similarly.

In the reaction of (*Z*)-**4**, the formation of **11** competes with a sequence of transannular reaction and alkenyl migration leading to **9**; however, the transannular reaction of σ-complex **J** to **K** is made difficult by the steric repulsion between a [2.2]MCP unit and a cationic hydropyrenium unit in **K**. Thus, the deprotonation of **J** is facilitated to give **11**. Similarly, **12** is obtained from **11**.

Scheme 8



3. Conclusion

The chemical behavior of [2.2]MCPs **2**−**4** with an internal alkenyl group toward brominating agents was investigated in order to study the effect of the [2.2]MCP substructure.

The corresponding dibromo adducts were not obtained in the reaction of **2**−**4** with bromine or $BTMABr_3$. The reaction of **2** and **3** exclusively gave the β-bromoolefins **6** and **8** *via* an addition−elimination mechanism due to the steric crowding of the [2.2]MCP substructures. The reaction of β-phenylethenyl[2.2]MCP **3** is much slower than of ethenyl derivative **2**. In the reaction of **4**, the electrophilic attack of the bromonium ion occurs on the benzene ring due to the steric shielding of the double [2.2]-MCPs structure; (*E*)-**4** gives the transannular reaction−alkenyl migration products **9** and **10**, and (*Z*)-**4** affords the aromatic substitution products **11** and **12**.

In summary, the unusual chemical behavior of **2**−**4** mentioned above must be ascribed to the special geometrical and electronic characteristics of [2.2]MCP systems.

4. Experimental Section

All melting points are uncorrected. IR spectra were measured as KBr pellets. ^1H and ^{13}C NMR spectra were recorded on 270 MHz spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. Mass spectra were measured at 75 eV using a direct inlet method. Column chromatography was carried out on silica gel (200−300 mesh).

5-*tert*-Butyl-8-ethenyl[2.2]metacyclophane (2). To a suspension of methyltriphenylphosphonium iodide (3.03 g, 7.5 mmol) in dry tetrahydrofuran (20 mL) was added dropwise a hexane solution of *n*-butyllithium (5.0 mL, 1.5 M, 7.5 mmol) within 1 min at room temperature under argon. After the reaction mixture was stirred for 30 min, a solution of **1** (731 mg, 2.5 mmol) in dry tetrahydrofuran (2 mL) was added dropwise within 1 min. After the reaction mixture had been stirred for 5 min, it was poured into ice−water and extracted with ether. The extracts were washed with water, dried over magnesium sulfate, and evaporated in *vacuo*. The residue was purified by column chromatography (hexane), giving **2** in 95%

yield (688 mg, 2.37 mmol). An analytical sample was obtained as colorless prisms by recrystallization from hexane: mp 120−122 °C; IR (KBr) ν_{max} 2980, 2890, 1600, 1480, 1460, 1445, 1360, 1280, 1180, 990, 950, 920, 895, 865, 790, 760, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 9 H, ^{t}Bu), 2.18 (dt, J = 5.0, 11.9 Hz, 2 H, C_2H_4), 2.76 (dt, J = 4.3, 11.9 Hz, 2 H, C_2H_4), 2.89 (ddd, J = 2.6, 5.0, 11.9 Hz, 2 H, C_2H_4), 3.00 (ddd, J = 2.6, 4.3, 11.9 Hz, 2 H, C_2H_4), 3.86 (s, 1 H, ArH), 4.38 (dd, J = 10.9, 17.8 Hz, 1 H, olefin), 4.64 (dd, J = 2.6, 17.8 Hz, 1 H, olefin), 4.73 (dd, J = 2.6, 10.9 Hz, 1 H, olefin), 7.02−7.12 (m, 3 H, ArH), 7.10 (s, 2 H, ArH); MS m/z 290 (M$^+$, 39), 185 (100). Anal. Calcd for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 91.13; H, 9.02.

(*E*)-5-*tert*-Butyl-8-(2-phenylethenyl)[2.2]metacyclophane ((*E*)-3). To a solution of diethyl benzylphosphonate (913 mg, 4.0 mmol) in dry tetrahydrofuran (10 mL) was added dropwise a hexane solition of *n*-butyllithium solution (2.67 mL, 1.5 M, 4.0 mmol) within 1 min at room temperature under argon. After the reaction mixture was stirred for 10 min, a solution of **1** (585 mg, 2.0 mmol) in dry tetrahydrofuran (2 mL) was added dropwise within 1 min. After the reaction mixture had been stirred for 1 h, it was poured into ice−water and extracted with ether. The extracts were washed with water, dried over magnesium sulfate, and evaporated in *vacuo*. The residue was purified by column chromatography (hexane−ether 19:1), giving (*E*)-**3** in 85% yield (620 mg, 1.69 mmol). An analytical sample was obtained as colorless prisms by recrystallization from hexane: mp 105−106 °C; IR (KBr) ν_{max} 2980, 1590, 1475, 1440, 1360, 1180, 965, 865, 780, 760, 750, 740, 715, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 9 H, ^{t}Bu), 2.18−2.27, 2.76−3.04 (m, 8 H, C_2H_4), 4.00 (s, 1 H, ArH), 4.80, 5.94 (d, J = 16.5 Hz, each 1 H, olefin), 6.98−7.29 (m, 10 H, ArH); MS m/z 366 (M$^+$, 100), 309 (M$^+$ − ^{t}Bu, 31). Anal. Calcd for $C_{28}H_{30}$: C, 91.75; H, 8.25. Found: C, 91.41; H, 8.30.

(*Z*)-5-*tert*-Butyl-8-(2-phenylethenyl)[2.2]metacyclophane ((*Z*)-3). A solution of (*E*)-**3** (183 mg, 0.5 mmol) in degassed benzene (7 mL) was irradiated with a high-pressure mercury lamp at 5 °C for 1 h under argon. The reaction mixture was evaporated in *vacuo*, and the residue was purified by column chromatography (hexane−ether 39:1), giving (*Z*)-**3** in 70% yield (128 mg, 0.349 mmol) and unchanged (*E*)-**3** in 10% yield (18 mg, 0.049 mmol). An analytical sample of (*Z*)-**3** was obtained as colorless prisms by recrystallization from hexane: mp 105−106 °C; IR (KBr) ν_{max} 2980, 2870, 1595, 1495, 1475, 1440, 1355, 1180, 780, 715, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 9 H, ^{t}Bu), 2.20 (dt, J = 4.6, 12.2, 2 H, C_2H_4), 2.57 (dt, J = 4.0, 12.2 Hz, 2 H, C_2H_4), 2.78 (ddd, J = 3.0, 4.6, 12.2 Hz, 2 H, C_2H_4), 2.99 (ddd, J = 3.0, 4.0, 12.2 Hz, 2 H, C_2H_4), 3.81, 5.87 (d, J = 12.5 Hz, each 1 H, olefin), 3.94 (s, 1 H, ArH), 6.65−7.18 (m, 10 H, ArH); MS m/z 366 (M$^+$, 100), 351 (M$^+$ − Me, 25). Anal. Calcd for $C_{28}H_{30}$: C, 91.75; H, 8.25. Found: C, 92.11; H, 8.35.

General Procedure for Treatment of 2 with $BTMABr_3$. To a solution of **2** (581 mg, 2.0 mmol) in dichloromethane (20 mL) was added $BTMABr_3$ (780 mg, 2.0 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 5 min, it was poured into 10% aqueous sodium thiosulfate solution and extracted with ether. The extracts were washed with water, dried over $MgSO_4$, and evaporated in *vacuo*. The residue was purified by column chromatography (hexane), giving **6** in 99% yield (729 mg, 1.97 mmol).

General Procedure for Treatment of 2 with Br_2. To a solution of **2** (581 mg, 2.0 mmol) in carbon tetrachloride (20 mL) was added a solution of bromine in carbon tetrachloride (4 mL, 0.5 M, 2.0 mmol) at room temperature. After the reaction mixture was stirred for 5 min, it was poured into 10% aqueous sodium thiosulfate solution and extracted with ether. The extracts were washed with water, dried over magnesium sulfate solution, and evaporated in *vacuo*. The residue was purified by column chromatography (hexane), giving **6** in 99% yield (731 mg, 1.98 mmol).

(*E*)-8-(2-Bromoethenyl)-5-*tert*-butyl[2.2]metacyclophane (6): colorless prisms (hexane); mp 127−129 °C; IR (KBr) ν_{max} 2990, 2950, 2890, 1600, 1480, 1360, 1230, 1180, 935, 790, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 9 H, ^{t}Bu), 2.18 (dt, J = 5.0, 12.0 Hz, 2 H, C_2H_4), 2.66 (dt, J = 4.0, 12.0 Hz, 2 H, C_2H_4), 2.91 (ddd, J = 2.6, 5.0, 12.0 Hz, 2 H, C_2H_4), 3.02 (ddd, J = 2.6, 4.0, 12.0 Hz, 2 H, C_2H_4), 3.89 (s, 1 H, ArH), 4.61, 5.62 (d, J = 13.9 Hz, each 1 H, olefin), 7.10 (s, 2 H, ArH), 7.14 (s, 3 H, ArH); MS m/z 370 (M$^+$, 50), 368 (M$^+$, 40), 185 (100). Anal. Calcd for $C_{22}H_{25}Br$: C, 71.54; H, 6.82. Found: C, 71.28; H, 6.89.

8-(2-Bromo-1-methoxyethyl)-5-*tert*-butyl[2.2]metacyclophane (7). To a suspension of **2** (145 mg, 0.5 mmol) in methanol (5 mL) was added $BTMABr_3$ (195 mg, 0.5 mmol) at room temperature. After the reaction mixture was stirred for 5 min, it was poured into 10% aqueous sodium thiosulfate solution and extracted with ether. The extracts were washed with water, dried over magnesium sulfate, and evaporated in *vacuo*. The residue was purified by column chromatography (hexane−ether 79:1), giving **7** in 85% yield (170 mg, 0.424 mmol). An analytical sample was obtained as colorless prisms by recrystallization from hexane: mp 40−42 °C; IR (KBr) ν_{max} 2960, 2930, 2860, 1590, 1475, 1360, 1285, 1210, 1180, 1105, 870, 785, 715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 9 H, ^{t}Bu), 2.11−2.36 (m, 2 H, C_2H_4), 2.53 (dd, J = 3.0, 10.9 Hz, 1 H, CH_2Br) 2.69 (dt, J = 4.3, 12.2 Hz, 1 H, C_2H_4), 2.85−3.11 (m, 6 H, C_2H_4 and CH_2Br), 2.94 (s, 3 H, OMe), 3.42 (dd, J = 3.0, 7.6 Hz, 1 H, C*H*OMe), 3.52 (s, 1 H, ArH), 6.95−7.13 (m, 5 H, ArH); MS m/z 402 (M$^+$, 10), 400 (M$^+$, 10), 263 (100). Anal. Calcd for $C_{23}H_{29}BrO$: C, 68.82; H, 7.28. Found: C, 68.66; H, 7.41.

Treatment of (*E*)-3 with $BTMABr_3$. Using the procedure for the treatment of **2** with $BTMABr_3$, (*E*)-**3** (293 mg, 0.8 mmol) was converted to **8a** in 34% yield (121 mg, 0.272 mmol) and **8b** in 51% yield (182 mg, 0.409 mmol) by treatment with $BTMABr_3$ (390 mg, 0.8 mmol) in dichloromethane (8 mL) for 90 h. The products were separated by column chromatography (hexane).

Similarly, compounds **8a** and **8b** were obtained from (*Z*)-**3** as shown in Table 2.

(*E*)-8-(2-Bromo-2-phenylethenyl)-5-*tert*-butyl[2.2]metacyclophane (8a): colorless prisms (hexane); mp 140−141 °C; IR (KBr) ν_{max} 2970, 2940, 1590, 1475, 1435, 1360, 1175, 950, 890, 870, 790, 770, 720, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 9 H, ^{t}Bu), 2.15 (dt, J = 4.6, 12.2 Hz, 2 H, C_2H_4), 2.52 (dt, J = 4.0, 12.2 Hz, 2 H, C_2H_4), 2.72 (ddd, J = 2.6, 4,6, 12.2 Hz, 2 H, C_2H_4), 3.01 (ddd, J = 2.6, 4.0, 12.2 Hz, 2 H, C_2H_4), 3.90 (s, 1 H, ArH), 4.43 (s, 1 H, olefin), 6.80−7.23 (m, 10 H, ArH); MS m/z 446 (M$^+$, 59), 444 (M$^+$, 50), 57 (100). Anal. Calcd for $C_{28}H_{29}Br$: C, 75.50; H, 6.56. Found: C, 75.27; H, 6.56.

(*Z*)-8-(2-Bromo-2-phenylethenyl)-5-*tert*-butyl[2.2]metacyclophane (8b): colorless prisms (hexane); mp 38−40 °C; IR (KBr) ν_{max} 2975, 2930, 1590, 1490, 1470, 1435, 1360, 1230, 1180, 900, 870, 785, 750, 715, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 9 H, ^{t}Bu), 2.25, 2.56 (dt, J = 4.6, 12.2 Hz, each 2 H, C_2H_4), 2.98, 3.04 (ddd, J = 2.6, 4.6, 12.2 Hz, each 2 H, C_2H_4), 3.93 (s, 1 H, ArH), 4.58 (s, 1 H, olefin), 7.15−7.30 (m, 10 H, ArH); MS m/z 446 (M$^+$, 37), 444 (M$^+$, 31), 57 (100). Anal. Calcd for $C_{28}H_{29}Br$: C, 75.50; H, 6.56. Found: C, 75.36; H, 6.62.

(*E*)-5-*tert*-Butyl-8-[2-(2-*tert*-butyl-4,5,9,10-tetrahydro-1-pyrenyl)ethenyl][2.2]metacyclophane (9). Using the procedure for the reaction of **2** with $BTMABr_3$, (*E*)-**4** (750 mg, 1.357 mmol) was converted to **9** in 50% yield (372 mg, 0.675 mmol), along with unchanged (*E*)-**4** in 29% yield (219 mg, 0.396 mmol), by treatment with $BTMABr_3$ (529 mg, 1.357 mmol) in dichloromethane (14 mL) for 4 h. The products were separated by column chromatography (hexane−toluene 19:1). An analytical sample of **9** was obtained as colorless prisms by recrystallization from hexane: mp 222−223 °C; IR (KBr) ν_{max} 2970, 2940, 2870, 1480, 1430, 1360, 1260, 1180, 980, 870, 780, 750, 715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25, 1.41 (s, each 9 H, ^{t}Bu), 2.10−2.31 (m, 2 H, C_2H_4), 2.61−3.06 (m, 14 H, C_2H_4), 3.83 (s, 1 H, ArH), 4.29, 6.14 (d, J = 16.8 Hz, each 1 H, olefin), 6.85−7.20 (m, 9 H, ArH); ^{13}C NMR ($CDCl_3$) δ 27.15, 28.43, 28.77, 28.81 (t, CH_2), 31.47, 31.63 (q, $C(CH_3)_3$), 34.36, 36.08 (s, $C(CH_3)_3$), 37.14, 41.69 (t, CH_2), 123.36, 123.47, 125.46, 125.73, 125.98, 126.72, 126.83 (d, ArCH), 128.55, 130.91, 132.15 (s, ArC), 133.53 (d, α-olefin), 134.38, 134.52 (s, ArC), 134.57 (d, 16-ArCH), 134.84 (d, β-olefin), 135.27, 135.42, 137.02, 138.65, 144.13, 147.33, 151.03 (s, ArC); MS m/z 550 (M$^+$, 100), 57 (100). Anal. Calcd for $C_{42}H_{46}$: C, 91.58; H, 8.42. Found: C, 91.50; H, 8.23.

(*E*)-1,1′-(Ethene-1,2-diyl)bis(2-*tert*-butyl-4,5,9,10-tetrahydropyrene) (10). Using the procedure for the reaction of **2** with $BTMABr_3$, (*E*)-**4** (166 mg, 0.3 mmol) was converted to **10** in 72% yield (118 mg, 0.215 mmol) by treatment with $BTMABr_3$ (351 mg, 0.9 mmol) in dichloromethane (3 mL) for 230 h. The product was purified by column chromatography (hexane−toluene 9:1). An analytical sample of **10** was obtained as colorless prisms by recrystallization from hexane: mp 231−233 °C; IR (KBr) ν_{max} 2980, 1440, 1260, 1080, 1020, 870, 800, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (s, 18 H, ^{t}Bu), 2.78−2.95 (m, 12 H, C_2H_4), 3.20−3.35 (m, 4 H, C_2H_4), 6.90 (s, 2 H, olefin), 7.05−7.25 (m, 8 H, ArH); ^{13}C NMR ($CDCl_3$) δ 27.93, 28.39, 29.02, 29.17 (t, CH_2), 31.88 (q, $C(CH_3)_3$), 36.14 (s, $C(CH_3)_3$), 123.79, 125.39, 125.77, 126.83 (d, ArCH), 129.51, 132.67 (s, ArC), 132.67 (d, olefin), 133.96, 134.27, 134.34, 135.33, 135.58, 147.49 (s, ArC); MS *m*/*z* 548 (M^+, 53), 231 (100). Anal. Calcd for $C_{42}H_{44}$: C, 91.92; H, 8.08. Found: C, 91.64; H, 8.04.

Treatment of 9 with $BTMABr_3$ Affording 10. According to the procedure for the treatment of **2** with $BTMABr_3$, **9** (55 mg, 0.1 mmol) was converted to **10** in 73% yield (40 mg, 0.073 mmol) by treatment with $BTMABr_3$ (117 mg, 0.3 mmol) in dichloromethane (1 mL) for 200 h.

(*Z*)-13-Bromo-8,8′-(ethene-1,2-diyl)bis(5-*tert*-butyl[2.2]metacyclophane) (11). According to the procedure for the treatment of **2** with $BTMABr_3$, (*Z*)-**4** (166 mg, 0.3 mmol) was converted to **11** in 22% yield (42 mg, 0.067 mmol) along with **9** in 1% yield (2 mg, 0.004 mmol) and unchanged (*Z*)-**4** in 61% yield (101 mg, 0.183 mmol) by treatment with $BTMABr_3$ (117 mg, 0.3 mmol) in dichloromethane (3 mL) for 11 h. The products were separated by column chromatography (hexane−toluene 19:1). An analytical sample of **11** was obtained as colorless prisms by recrystallization from hexane: mp 245−246 °C; IR (KBr) ν_{max} 2970, 1590, 1550, 1430, 1350, 1280, 1170, 870, 780, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (s, 18 H, ^{t}Bu), 1.85−2.80 (m, 16 H, C_2H_4), 3.52, 3.65 (s, each 1 H, ArH), 3.67, 3.73 (d, J = 11.5 Hz, each 1 H, olefin), 6.66 (s, 4 H, ArH), 7.00 (s, 3 H, ArH), 7.10 (s, 2 H, ArH); MS *m*/*z* 632 (M^+, 100), 630 (M^+, 94). Anal. Calcd for $C_{42}H_{47}Br$: C, 79.85; H, 7.50. Found: C, 79.99; H, 7.58.

(*Z*)-8,8′-(Ethene-1,2-diyl)bis(13-bromo-5-*tert*-butyl[2.2]metacyclophane) (12). According to the procedure for the treatment of **2** with $BTMABr_3$, (*Z*)-**4** (332 mg, 0.6 mmol) was converted to **12** in 80% yield (342 mg, 0.481 mmol) along with **9** in 6% yield (20 mg, 0.036 mmol) by treatment with $BTMABr_3$ (702 mg, 1.8 mmol) in dichloromethane (6 mL) for 230 h. The products were separated by column chromatography (hexane−toluene 9:1). An analytical sample of **12** was obtained as colorless prisms by recrystallization from hexane: mp 248−249 °C; IR (KBr) ν_{max} 2950, 2850, 1590, 1555, 1430, 1170, 870, 840, 790, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (s, 18 H, ^{t}Bu), 1.96 (dt, J = 4.3, 11.9 Hz, 4 H, C_2H_4), 2.12 (dt, J = 3.6, 11.9 Hz, 4 H, C_2H_4), 2.47 (ddd, J = 2.6, 4.3, 11.9 Hz, 4 H, C_2H_4), 2.77 (ddd, J = 2.6, 3.6, 11.9 Hz, 4 H, C_2H_4), 3.52 (s, 2 H, ArH), 3.85 (s, 2 H, olefin), 6.66 (s, 4 H, ArH), 7.14 (s, 4 H, ArH); MS *m*/*z* 712 (M^+, 58), 710 (M^+, 100), 708 (M^+, 51). Anal. Calcd for $C_{42}H_{46}Br_2$: C, 70.99; H, 6.52. Found: C, 70.90; H, 6.62.

General Procedure for Reduction of 11 Affording (*Z*)-4. To a solution of **11** (63 mg, 0.1 mmol) in dry tetrahydrofuran (1 mL) was added a hexane solution of *n*-butyllithium (0.13 mL, 1.5 M, 0.2 mmol) at −60 °C. After the reaction mixture was stirred at −60 °C for 5 min, ether and water were added. The reaction mixture was extracted with ether, washed with water, dried over magnesium sulfate, and evaporated in vacuo. The residue was purified by column chromatography (hexane), giving (*Z*)-**4** in 87% yield (48 mg, 0.087 mmol).

Similarly, compound **12** (71 mg, 0.1 mmol) was converted to (*Z*)-**4** in 92% yield (51 mg, 0.092 mmol) by treatment with a hexane solution of *n*-butyllithium (0.27 mL, 1.5M, 0.4 mmol) in dry tetrahydrofuran (1 mL).

X-ray crystallographic analysis of 8a: $C_{28}H_{29}Br$, M = 445.44, triclinic, space group $P\bar{1}$ (No. 2), a = 9.115(2) Å, b = 16.124(3) Å, c = 8.432(4) Å, α = 94.40(2)°, β = 109.64(2)°, γ = 99.93(2)°, V = 1137.5(7) Å^3, Z = 2, D_c = 1.30 g/cm^3, monochromated Cu Kα radiation, λ = 1.541 84 Å. A colorless prism of compound **8a** (from hexane, approximate dimensions of 0.20 × 0.20 × 0.10 mm), mounted on a glass fiber in a random orientation, was used for X-ray data collection. Data were collected on an Enraf-Nonius CAD-4 diffractometer using $\omega - 2\theta$ scan at a temperature of 23 ± 1 °C. A total of 4124 reflections were collected, of which 3852 were unique. The structure was solved by direct methods (SIR 88)[17] and refined by full-matrix least-squares calculation to give R = 0.049, R_w = 0.062 for 2920 observed independent reflections [$|F_o^2| > 3\sigma(F_o^2)$, 2° < θ < 65°]. All non-hydrogen atoms were located in succeeding difference Fourier syntheses and anisotropically treated. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. All calculations were performed on a MicroVAX 3100 computer using MolEN.[18]

X-ray crystallographic analysis of 9: $C_{42}H_{46}$, M = 550.83, triclinic, space group $P\bar{1}$ (No. 2), a = 11.999(1) Å, b = 13.561(3) Å, c = 11.389(1) Å, α = 103.52(1)°, β = 114.50(1)°, γ = 96.38(1)°, V = 1593.6(5) Å^3, Z = 2, D_c = 1.15 g/cm^3, monochromated Cu Kα radiation, λ = 1.541 84 Å. A colorless prism of compound **9** (from hexane, approximate dimensions of 0.50 × 0.50 × 0.10 mm), mounted on a glass fiber in a random orientation, was used for X-ray data collection. Data were collected on an Enraf-Nonius CAD-4 diffractometer using $\omega - 2\theta$ scan at a temperature of 23 ± 1 °C. A total of 5660 reflections were collected, of which 5408 were unique. The structure was solved by direct methods (SIR 88)[17] and refined by full-matrix least-squares calculation to give R = 0.045, R_w = 0.065 for 4497 observed in dependent reflections [$|F_o^2| > 3\sigma(F_o^2)$, 2° < θ < 65°]. All non-hydrogen atoms were located in succeeding difference Fourier syntheses and anisotropically treated. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. All calculations were performed on a MicroVAX 3100 computer using MolEN.[18]

Acknowledgment. The authors are indebted to Dr. Thies Thiemann of Coimbra University for stimulating discussions and for his help in writing the manuscript.

JO9602433

(17) Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Vitebo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389.
(18) MolEN, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, The Netherlands, 1990.