Metacyclophanes and Related Compounds. 21. Nitration of [2.2]Metacyclophanes[1]

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Various [2.2]metacyclophanes were prepared from the corresponding benzene derivatives by using the *tert*-butyl group as a positional protective function and their nitrations were carried out under various conditions. It was found that nitration of 8,16-dimethyl[2.2]metacyclophane with fuming HNO_3 afforded only 5-nitro-8,16-dimethyl[2.2]metacyclophane but not 5,13-dinitro-8,16-dimethyl[2.2]metacyclophane. 5-Iodo-13-nitro-8,16-dimethyl[2.2]metacyclophane was obtained by nitration of 5-iodo- and 5,13-diiodo-8,16-dimethyl[2.2]metacyclophane. It was also found that nitration of the [2.2]metacyclophanes having methoxy groups at internal positions 5 and/or 13 afforded the corresponding tetrahydropyrenes. The reaction mechanisms of the above reactions are also described.

Although many [2.2]metacyclophanes and related compounds were prepared and these compounds have been worthy of remark among organic chemists,[2] there are few investigation about their chemical natures. Recently, we reported that[3] bromination of 8,16-dimethyl[2.2]metacyclophane (**1a**) (MCP = metacyclophane) with bromine in the presence or absence of Fe powder as a catalyst afforded different types of products, **2** or **3**, and that similar reactions of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP (**1b**) also gave different types of products, **4** or **5**. It was also found that[3] bromination of both **1a** and **1b** with NBS afforded the corresponding bis(bromomethyl)[2.2]MCPs **6a** and **6b** (Scheme I).

Nitration of [2.2]MCPs was investigated in order to obtain information about their chemical natures for electrophilic substitution reactions in the present work.

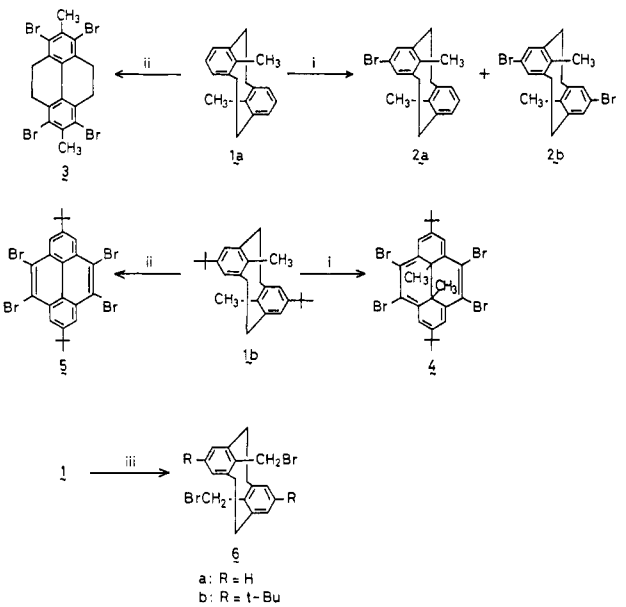
Results and Discussion

Nitration of 8,16-Dimethyl[2.2]MCPs. Allinger and his co-workers reported that[4] nitration of [2.2]MCP (**7**) afforded 2-nitro-4,5,9,10-tetrahydropyrene (**8**) (PRN = pyrene). It was expected from the results of the bromination of **1a** described above that nitration of **1a** might afford 8,16-dimethyl-5-nitro[2.2]MCP (**9**) and 8,16-dimethyl-5,13-dinitro[2.2]MCP (**10**) (Scheme II).

However, nitration of **1a** with fuming HNO_3 in AcOH at room temperature for 1 h afforded only one of the expected products (**9**) in 84% yield together with very small amount of 2,7-dioxo-4,10-dinitro-10b,10c-dimethyl-2,7,10b,10c-tetrahydroPRN (**11a**). The other isomer (**11b**) was cancelled by ^1H NMR spectral data from the possible structures. Treatment of **1a** with $Cu(NO_3)_2$ in Ac_2O at room temperature for 12 h also gave in 54% yield. The other expected product (**10**) could not be obtained even under more severe conditions than those described above. These results suggested that the nitro group of **9** should intramolecularly reduce the π-electron density of the benzene ring of the other side since the group has a very strong electron attraction.

Nitration of **1b** with fuming HNO_3 under similar conditions afforded 4,9-dinitro-10b,10c-dimethyl-10b,10c-dihydroPRN **12**, which was previously obtained by nitration of 10b,10c-dimethyl-10b,10c-dihydroPRN **13**[5] with $Cu(NO_3)_2$, in 21% yield with a large amount of resinous materials, and **12** was also obtained in only 7.2% yield by treatment of **1b** with $Cu(NO_3)_2$. Compound **13** might be, therefore, an intermediate for the formation of **12**.

Scheme I[a]



[a] (i) Br_2/CCl_4; (ii) $Br_2/Fe/CCl_4$; (iii) NBS/benzoyl peroxide/CCl_4.

As described above, **10** was not obtained by nitration of **1a**, but it was expected that nitration of 5-amino-8,16-dimethyl[2.2]MCP (**14**), which was easily prepared by reduction of **9**, might afford 5-amino-8,16-dimethyl-13-nitro[2.2]MCP (**15**). However, nitration of **14** did not afford the expected **15** but only a large amount of resinous materials was formed. Nitrations of 5-(acetylamino)-8,16-dimethyl[2.2]MCP (**16**) and 5-[(trifluoroacetyl)-amino]-8,16-dimethyl[2.2]MCP (**17**), which were easily prepared from **14** in the usual manner, were carried out under the conditions shown in Scheme III. The reaction of **16** did not afford the expected 5-(acetylamino)-8,16-dimethyl-13-nitro[2.2]MCP (**18**) but the unexpected 2-(acetylamino)-4,7,9-trinitro-10b,10c-dimethyl-10b,10c-di-

† Saga University.

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(2) Boekelheide, V. *Topics in Current Chemistry*; Boschke, F. L., Ed., Springger-Verlag: Berlin, 1983; Vol. 113, p 87.

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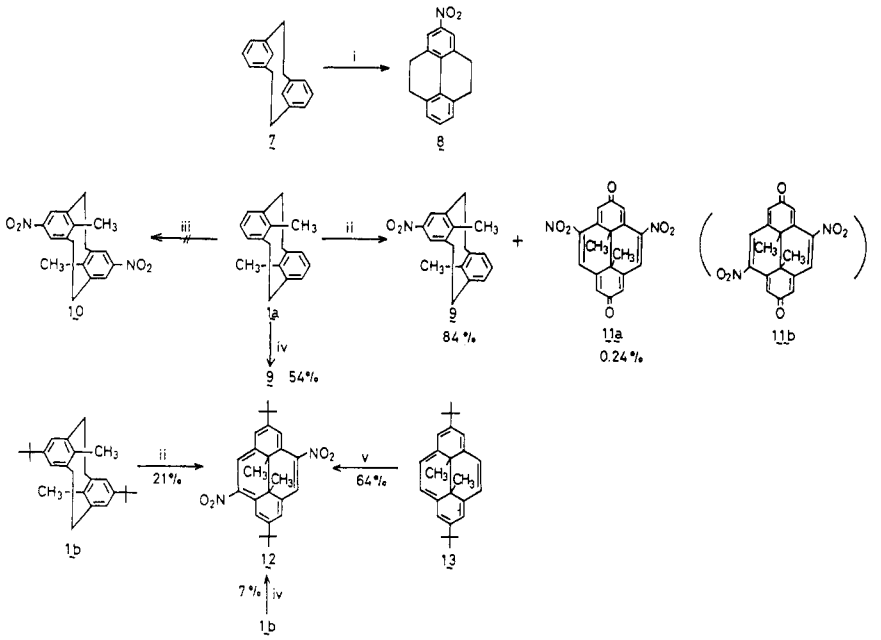
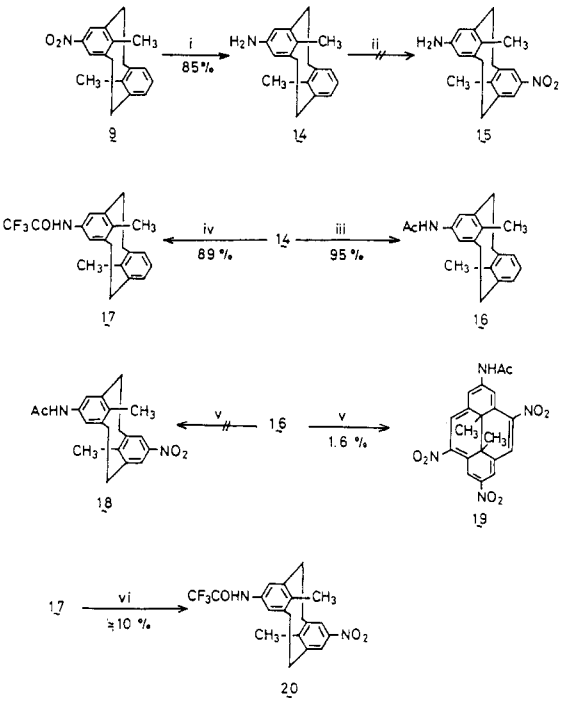
Scheme II[a]



[a] (i) HNO_3; (ii) fuming HNO_3/AcOH/room temperature (rt), 1 h; (iii) HNO_3/H_2SO_4, 80 °C, 2.5 h; (iv) $Cu(NO_3)_2/Ac_2O$, rt, 12 h; (v) $Cu(NO_3)_2/Ac_2O$, 0–2 °C, 2 h.

Scheme III[a]

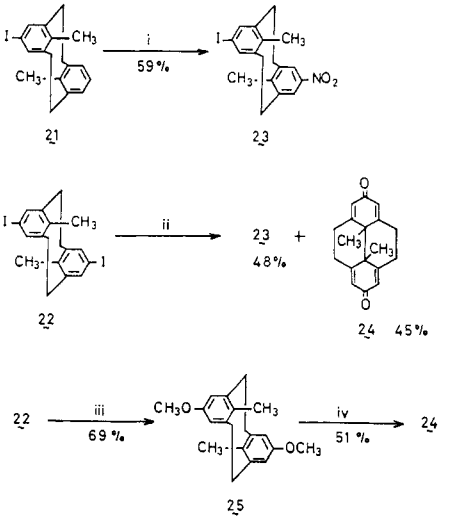


[a] (i) 10% Pd–C/H_2/benzene, rt, 3 h; (ii) fuming HNO_3/AcOH/rt, 1 h; (iii) Ac_2O/benzene, reflux 2 h; (iv) $(CF_3CO)_2O$/benzene, reflux 2 h; (v) fuming HNO_3/AcOH/rt, 3 min; (vi) 70% HNO_3/AcOH/rt, 5 min.

hydroPRN (**19**) was obtained in low yield with a large amount of resinous materials. However, the expected 5-[(trifluoroacetyl)amino]-8,16-dimethyl-5-nitro[2.2]MCP (**20**) was obtained in about 10% yield in the reaction of **17** together with a large amount of resinous materials.

Nitrations of 8,16-dimethyl-5-iodo- (**21**)[6] and 8,16-dimethyl-5,13-diiodo[2.2]MCP (**22**)[6] with fuming HNO_3 were

Scheme IV[a]



[a] (i) fuming HNO_3/AcOH/rt, 30 min; (ii) fuming HNO_3/AcOH/rt, 1 h; (iii) CH_3ONa/CH_3OH/DMF, 100 °C, N_2; (iv) $FeCl_3/CHCl_3$.

carried out under the conditions shown in Scheme IV. The former reaction afforded 8,16-dimethyl-5-iodo-13-nitro[2.2]MCP (**23**) in 59% yield. However, the latter nitration afforded **23** and 2,7-dioxo-10b,10c-dimethyl-2,4,5,7,9,10,10b,10c-octahydroPRN (**24**) in 48% and 45% yields. Compound **24** was also obtained by oxidation of 5,13-dimethoxy-8,16-dimethyl[2.2]MCP (**25**)[7] with $FeCl_3$ in $CHCl_3$ according to the literature.[8]

Although the detailed mechanism of formation of **24** from **22** is still obscure, the following reaction pathway might be proposed (Scheme V).

Nitronium ion may attack the ipso position of **22** to form intermediate A, followed by attack by the ONO_2^- ion and hydrolysis to give **24**.

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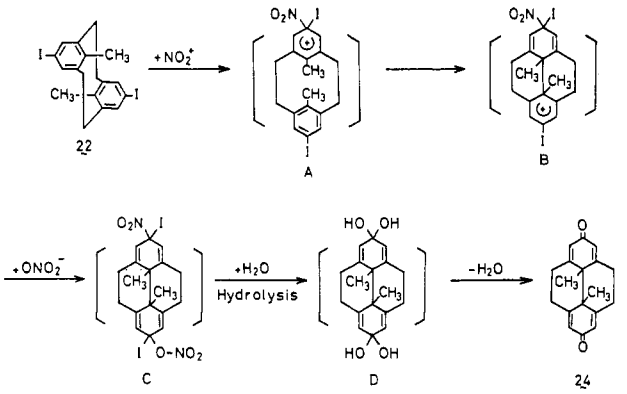
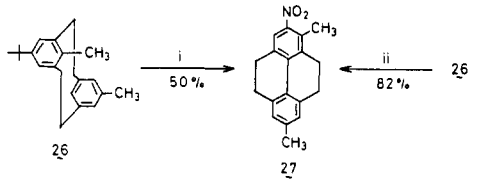
Scheme V

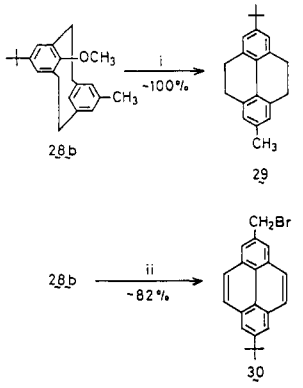


Scheme VI[a]



[a] (i) fuming HNO_3/AcOH, rt, 1 h; (ii) $Cu(NO_3)_2$/AcOH, rt, 1 h.

Scheme VII[a]



[a] (i) I_2/benzene, reflux, 6 h; (ii) NBS/benzoyl peroxide/CCl_4.

Nitration of 8-Substituted-[2.2]MCPs. The nitration of 5-*tert*-butyl-8,13-dimethyl[2.2]MCP (**26**) with fuming HNO_3 or $Cu(NO_3)_2$ surprisingly afforded 1,7-dimethyl-2-nitrotetrahydroPRN (**27**) in 50% or 82% yield (Scheme VI). The reaction pathway for the formation of **27** will be discussed later.

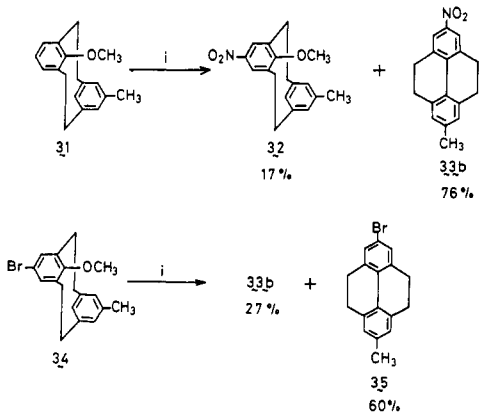
It was previously reported that[8] when 8-methoxy[2.2]-MCP **28b** was treated with I_2 in boiling benzene, the corresponding 4,5,9,10-tetrahydroPRN **29** was formed and that[1] bromination of **28b** with NBS afforded 2-*tert*-butyl-7-(bromomethyl)-4,5,9,10-terahydroPRN (**30**).

This result suggests that the methoxy group at the internal position of [2.2]MCPs seems to have different reactivity from the other groups (Scheme VII).

Indeed, when 8-methoxy-13-methyl[2.2]MCP (**31**) was treated with fuming HNO_3 at room temperature, the expected 8-methoxy-13-methyl-5-nitro[2.2]MCP (**32**) and unexpected 2-methyl-7-nitro-4,5,9,10-tetrahydroPRN (**33b**) were obtained in 17% and 76% yields. Similar nitration of 5-bromo-8-methoxy-13-methyl[2.2]MCP (**34**) afforded 2-bromo-7-methyl-4,5,9,10-tetrahydroPRN (**35**) and **33b** in 60% and 27% yields (Scheme VIII).

Nitration of 5-*tert*-butyl-8-methoxy-13-substituted-[2.2]MCPs **28a–g** was also carried out under various conditions in order to obtain information about the effect of

Scheme VIII[a]



[a] (i) Fuming HNO_3, rt, 1 h.

Scheme IX

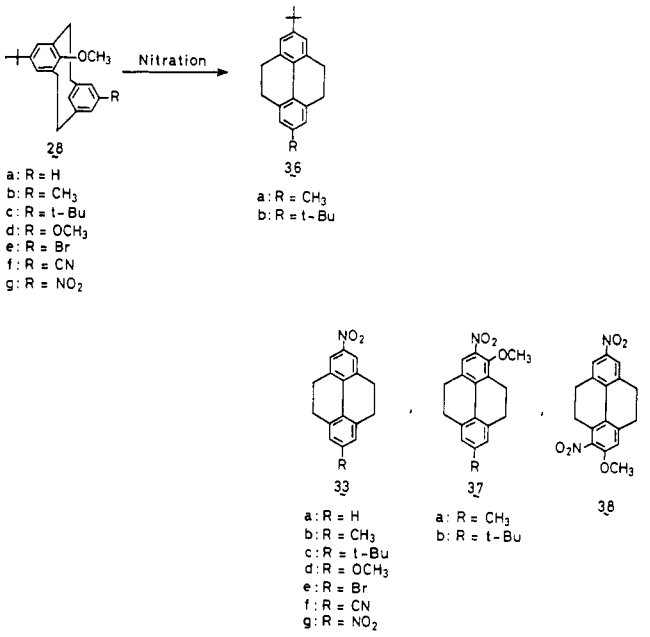


Table I. Nitration of 5-*tert*-Butyl-8-methoxy-13-substituted-[2.2]metacyclophanes 28a–g at Room Temperature for 1 h[a]

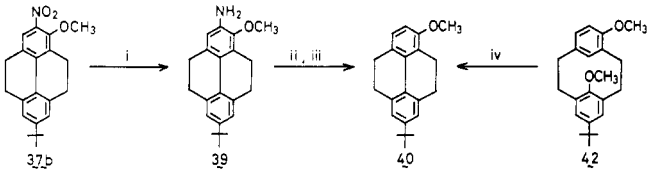
run	substr	reagent	product[b] (yield, %)
1	**28a**	fuming HNO_3	**33a** (40)
2	**28b**	fuming HNO_3	**33b** (81)
3	**28b**	$Cu(NO_3)_2$	**33b** (35), **37a** (62)
4	**28c**	fuming HNO_3	**33c** (82)
5	**28c**	63% HNO_3	**33c** (50), **36b** (30)
6	**28c**	$Cu(NO_3)_2$	**33c** (30), **37b** (60)
7	**28d**	fuming HNO_3	**38** (90)
8	**28e**	fuming HNO_3	no reaction
9	**28f**	fuming HNO_3	no reaction
10	**28g**	fuming HNO_3	no reaction
11	**28e**	HNO_3/H_2SO_4	**33e** (60)
12	**28f**	HNO_3/H_2SO_4	**33f** (90)
13	**28g**	HNO_3/SO_4	**33g** (95)

[a] The detailed reaction conditions are shown in the Experimental Section. [b] Isolated yields are shown.

substituents at the 13 position of [2.2]MCP. The results are summarized in Table I and in Scheme IX.

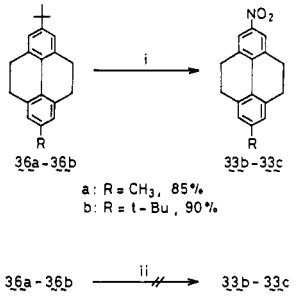
As shown in Table I, nitration of **28a–c** and **28d** with fuming HNO_3 afforded the corresponding 2-substituted-7-nitro-4,5,9,10-tetrahydroPRNs **33a–c** and 2-methoxy-1,7-dinitro-4,5,9,10-tetrahydroPRN (**38**) in good yield, respectively. The nitration of **28e–g** required the mixed acid

Scheme X[a]



[a] (i) Pd–C/H_2; (ii) $NaNO_2$/HCl; (iii) H_3PO_2; (iv) I_2/benzene, reflux.

Scheme XI[a]



[a] (i) fuming HNO_3; (ii) 63% HNO_3.

to obtain the corresponding 2-substituted-7-nitro-4,5,9,10-tetrahydroPRNs **33e–g** in good yield.

It was also found that reaction of **28b** and **28c** with $Cu(NO_3)_2$ afforded, besides the corresponding **33b** and **33c**, 1-methoxy-7-methyl-2-nitro-4,5,9,10-tetrahydroPRN (**37a**) and 7-*tert*-butyl-1-methoxy-2-nitro-4,5,9,10-tetrahydroPRN (**37b**). Compound **37b** was converted to **40**, which was prepared by treatment of **42** with I_2 in boiling benzene in order to confirm the structure of **37b** (Scheme X).

It should be noted that although reaction of **28c** with fuming HNO_3 afforded 2-*tert*-butyl-7-nitro-4,5,9,10-tetrahydroPRN (**33c**) in 82% yield, the reaction with 63% HNO_3 afforded 2,7-di-*tert*-butyl-4,5,9,10-terahydroPRN (**36b**) and **33c** in 30% and 50% yield. This result suggested that **36b** might be an intermediate for the formation of **33c** in the nitration of **28c** with fuming HNO_3. Indeed, when **36a** and **36b** were treated with fuming HNO_3, the corresponding **33b** and **33c** were obtained in 85% and 90% yield, respectively. However, **36a,b** did not give any product in the reaction with 63% HNO_3 (Scheme XI).

Reaction Pathways. As described above, the nitration of MCPs except **1a** under various conditions afforded mainly the hydropyrene derivatives. Although detailed reaction mechanisms for the formation of the hydropyrenes from MCPs are not still clear, the reaction pathways might be proposed according to Schemes XII and XIII.

Attack of nitronium ion might occur at the ipso position 5, and then the products might be formed through the intermediates shown in Scheme XII.

On the other hand, formation of **27** and **37a,b** might be well elucidated by proton-induced isomerizations as shown in Scheme XIII.

Experimental Section

Materials. Preparations of [2.2]MCPs **1a**,[3] **1b**,[3] **21**,[6] **22**,[6] **28a**,[8] **28b**,[8] **28c**,[8] **28e**,[8] **28f**,[8] and **31**[1] were previously described. The others (**26**, **28d**, **28g**, **34**, and **42**) were prepared according to the routes shown in Schemes XIV–XVI.

Preparation of Dithia[3.3]metacyclophanes. Typical Procedure. A solution of 12.25 g (50 mmol) of 2,6-bis(chloromethyl)-4-*tert*-butyltoluene (**43a**)[9] and 9.2 g (50 mmol) of 3,5-bis(mercaptomethyl)toluene (**44a**) in 200 mL of benzene was added dropwise over period of 24 h from a Henshborg funnel with stirring under nitrogen to a solution of 6.6 g of potassium hydroxide in 4 L of absolute ethanol. After the addition, the reaction mixture was concentrated and the residue was extracted with 500 mL of dichloromethane. The dichloromethane extract was concentrated and the residue was chromatographed over Al_2O_3, using a mixture of hexane/benzene (1:1) as an eluent to give 12.46 g (70%) of 17-*tert*-butyl-6,9-dimethyl-2,11-dithia[3.3]metacyclophane (**45a**): colorless oil; IR (KBr) 3050, 2950, 1600, 1475, 1450, 1360, 1220, 870, 740, 700, 675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (9 H, s), 2.15 (3 H, s), 2.20 (3 H, s), 3.44, 3.68 (4 H, AB pattern, J_{AB} = 16 Hz), 3.76, 3.99 (4 H, AB pattern, J_{AB} = 16 Hz), 5.40 (1 H, br s), 6.60 (2 H, br s), 6.95 (2 H, s); MS *m/e* 356 (M^+). Anal. Calcd for $C_{22}H_{28}S_2$: C, 74.10; H, 7.92. Found: C, 74.40; H, 8.00.

Compounds **45b** and **45c** were prepared by reaction of **43b** with **44a** and by reaction of **43c**[9] with **44b**[11] according to the method described above.

6-Bromo-2,11-dithia-17-methyl-9-methoxy[3.3]metacyclophane (45b): yield 67.4%; colorless prisms (hexane/benzene 1:1), mp 222–223 °C; IR (KBr) 3040, 2950, 1600, 1460, 1425, 1410, 1255, 1235, 1200, 1170, 1005, 860, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.24 (3 H, s), 3.41 (2 H, d, *J* = 14.5 Hz), 3.66 (3 H, s), 3.67 (2 H, d, *J* = 14.5 Hz), 3.74 (2 H, d, *J* = 14.5 Hz), 4.19 (2 H, d, *J* = 14.5 Hz), 6.80 (3 H, br s), 7.07 (2 H, s); MS, *m/e* 394, 396 (M^+). Anal. Calcd for $C_{18}H_{19}OS_2Br$: C, 54.68; H, 4.84. Found: C, 54.90; H, 4.87.

6-*tert*-Butyl-2,11-dithia-9-methoxy-17-nitro[3.3]metacyclophane (45c): 67%; colorless prisms (hexane), mp 263–265 °C; IR (KBr) 3050, 2960, 1520, 1480, 1390, 1345, 1315, 1200, 1100, 1010, 880, 730, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (9 H, s), 3.50 (2 H, d, *J* = 14 Hz), 3.71 (3 H, s), 3.74 (2 H, d, *J* = 14 Hz), 3.85 (2 H, d, *J* = 14 Hz), 4.26 (2 H, d, *J* = 14 Hz), 6.93 (2 H, s), 7.41 (1 H, s), 7.77 (2 H, s); MS, *m/e* 403 (M^+). Anal. Calcd for $C_{21}H_{25}O_3S_2N$: C, 62.50; H, 6.24; N, 3.47. Found: C, 63.02; H, 6.27; N, 3.61.

6-*tert*-Butyl-9,14-dimethoxy-2,11-dithia[3.3]metacyclophane (49) was obtained in 76.5% yield in the same manner[3] from 2,4-bis(chloromethyl)anisole (**47**) and 4-*tert*-butyl-2,6-bis(mercaptomethyl)anisole (**48**)[9] as colorless prisms (hexane), mp 124–125 °C: IR (KBr) 2960, 1600, 1500, 1480, 1430, 1410, 1360, 1260, 1200, 1170, 1120, 1040, 1000, 890, 820, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (9 H, s), 3.17–4.36 (8 H, m), 3.68 (6 H, s), 6.28–6.98 (5 H, m); MS, *m/e* 388 (M^+). Anal. Calcd for $C_{22}H_{28}S_2O_2$: C, 68.00; H, 7.26. Found: C, 68.00; H, 7.31.

Preparation of 2,6-Bis(bromomethyl)-4-bromoanisole (43b). A solution of 2.1 g (9.8 mmol) of 2,6-dimethyl-4-bromoanisole in 6 mL of 1,2-dibromoethane was heated to reflux. To this solution was added a solution of 1.3 mL of bromine in 1.3 mL of 1,2-dibromoethane under tungsten lamp irradiation.

After the solution was refluxed for 1 h, it was cooled to room temperature and concentrated under reduced pressure. The residue was extracted with dichloromethane and washed with 10% sodium hydroxide solution and water and dried over sodium sulfate. The dichloromethane extract was evaporated in vacuo to leave a residue that was recrystallized from hexane to give 2.3 g (64%) of **43b** as colorless prisms (hexane): mp 82–83 °C; IR (KBr) 3045, 2950, 2820, 1455, 1420, 1235, 1205, 1165, 1080, 990, 870, 780, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.95 (3 H, s), 4.43 (4 H, s), 7.44 (2 H, s); MS, *m/e* 369, 371, 373, 375 (M^+). Anal. Calcd for $C_9H_9OBr_3$: C, 28.99; H, 2.43. Found: C, 29.10; H, 2.54.

Preparation of Dithia[3.3]metacyclophane 2,2,11,11-Tetraoxides. The oxidation of 2,11-dithia[2.2]MCPs was carried out according to the reported manner.[3]

17-*tert*-Butyl-6,9-dimethyl-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxide (46a): 98.3%; colorless prisms, mp >300 °C; IR (KBr) 3050, 2950, 1600, 1440, 1410, 1300, 1260, 1175, 1110, 890, 870, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (9 H, s), 1.95 (3 H, s), 2.28 (3 H, s), 4.14 (4 H, s), 4.31 (2 H, d, *J* = 15 Hz), 4.63 (2 H, d, *J* = 15 Hz), 5.72 (1 H, s), 7.21 (2 H, s), 7.53 (2 H, s); MS, *m/e* 420 (M^+). Anal. Calcd for $C_{22}H_{28}S_2O_4$: C, 62.82; H, 6.71. Found: C, 62.59; H, 6.56.

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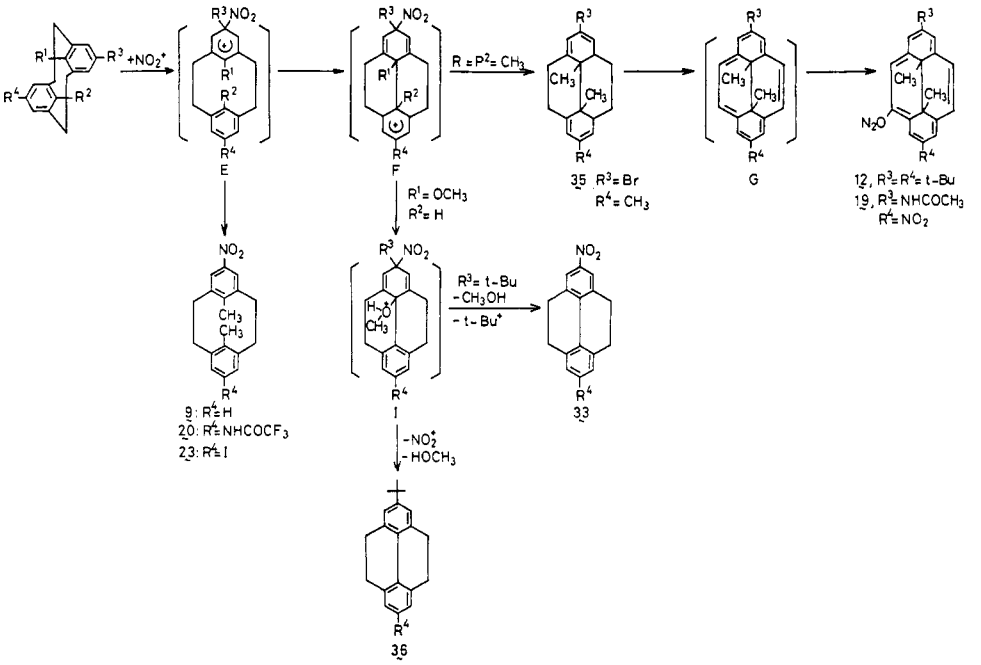
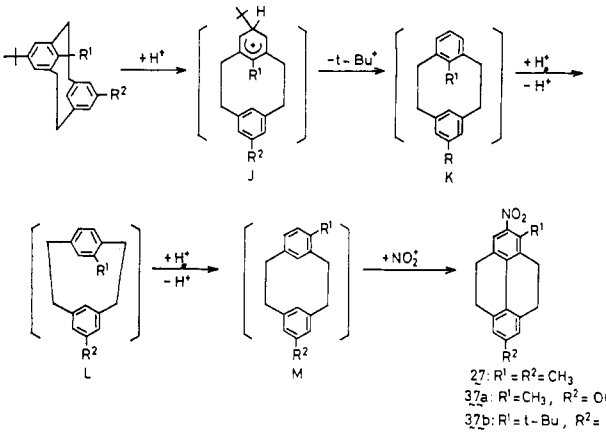
(13) Reich, V. S.; Rose, G. G.; Wilson, W. *J. Chem. Soc.* **1947**, 1234.

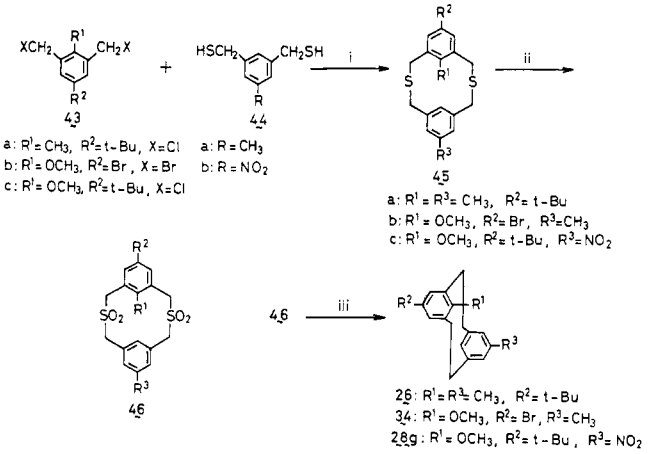
Scheme XII



Scheme XIII



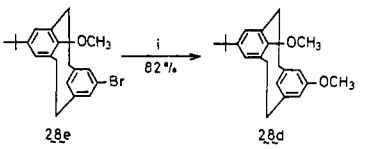
Scheme XIV[a]



[a] (i) KOH/EtOH, high dilution conditions; (ii) *m*-chloroperbenzoic acid; (iii) 500 °C/1 mmHg.

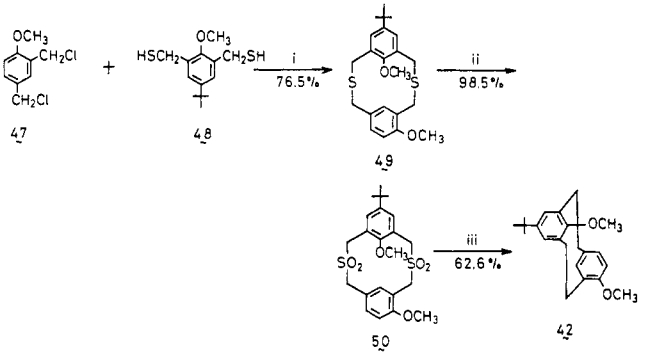
6-Bromo-17-methyl-9-methoxy-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxide (46b): 94.9%; colorless prisms, mp >300 °C; IR (KBr) 3020, 2930, 1600, 1455, 1400, 1385, 1320, 1295, 1275, 1210, 1180, 1115, 995, 900, 875, 710 cm^{-1}; ^1H NMR

Scheme XV[a]



[a] (i) $CH_3ONa/CH_3OH/DMF$.

Scheme XVI[a]



[a] (i) KOH/EtOH, high dilution conditions; (ii) *m*-CPBA; (iii) 500 °C/1 mmHg.

($CDCl_3$) δ 2.20 (3 H, s), 3.75 (3 H, s), 4.18 (2 H, d, J = 12 Hz), 4.22 (2 H, d, J = 12 Hz), 4.57 (2 H, d, J = 14.5 Hz), 4.86 (2 H, d, J = 14.5 Hz), 7.02 (2 H, s), 7.34 (2 H, br s); MS, m/e 458, 460 (M^+). Anal. Calcd for $C_{18}H_{19}O_5S_2Br$: C, 47.06; H, 4.17. Found: C, 47.20; H, 4.05.

6-*tert*-Butyl-9-methoxy-17-nitro-2,11-dithia[2.2]metacyclophane 2,2,11,11-tetraoxide (46c): 98.3%; colorless prisms, mp >300 °C; IR (KBr) 3050, 2950, 2910, 1530, 1480, 1350, 1320, 1310, 1275, 1260, 1205, 1175, 1115, 995, 900, 895, 850, 760, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (9 H, s), 3.80 (3 H, s), 4.06 (2 H, d, J = 14.5 Hz), 4.34 (2 H, d, J = 14.5 Hz), 4.67 (2 H, d, J = 14.5 Hz), 4.93 (2 H, d, J = 14.5 Hz), 7.30 (2 H, s), 7.90 (1 H, s), 8.08 (2 H, s); MS, m/e 467 (M^+). Anal. Calcd for $C_{21}H_{25}O_7NS_2$: C, 53.94; H, 5.39; N, 3.00. Found: C, 53.38; H, 5.28; N, 2.99.

50: 98.5%; colorless prisms, mp >300 °C; IR (KBr) 2910, 1510, 1490, 1310, 1270, 1200, 1170, 1110, 1000, 890, 860, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (9 H, s), 3.72 (3 H, s), 3.76 (3 H, s), 3.80–4.93

(8 H, m), 6.40–7.40 (5 H, m); MS, *m/e* 452 (M^+). Anal. Calcd for $C_{22}H_{28}S_2O_6$: C, 58.38; H, 6.24. Found: C, 58.31; H, 6.28.

Preparation of [2.2]Metacyclophanes. According to the reported method,[3] the title compounds **26**, **28g**, **34**, and **42** were prepared by pyrolysis of the corresponding dithia[3.3]metacyclophane 2,2,11,11-tetraoxides **45a–c** and **50** at 500 °C under reduced pressure (1 mmHg).

5-*tert*-Butyl-8,13-dimethyl[2.2]metacyclophane (26): 60%; colorless prisms (methanol), mp 50–52 °C; IR (KBr) 3020, 2950, 2860, 1595, 1480, 1460, 1360, 1180, 880, 845, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.52 (3 H, s), 1.34 (9 H, s), 2.00–3.03 (8 H, m), 2.24 (3 H, s), 3.52 (1 H, br s), 6.85 (2 H, br s), 7.00 (2 H, s); MS, *m/e* 292 (M^+). Anal. Calcd for $C_{22}H_{28}$: C, 90.35; H, 9.65. Found: C, 90.38; H, 9.38.

5-Bromo-13-methyl-8-methoxy[2.2]metacyclophane (34): 88.1%; colorless prisms (methanol), mp 122–123 °C; IR (KBr) 3040, 2940, 1595, 1460, 1415, 1250, 1210, 1180, 1160, 1025, 1015, 840, 820, 720, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.09–2.20 (2 H, m), 2.29 (3 H, s), 2.48–2.60 (2 H, m), 2.68–2.78 (2 H, m), 2.94–3.00 (3 H, m), 3.00 (3 H, s), 4.05 (1 H, br s), 6.85 (2 H, br s), 7.17 (2 H, s); MS, *m/e* 330, 332 (M^+). Anal. Calcd for $C_{18}H_{19}OBr$: C, 65.26; H, 5.78. Found: C, 64.99; H, 5.88.

5-*tert*-Butyl-13-nitro-8-methoxy[2.2]metacyclophane (28q): 75.8%; pale yellow prisms (methanol), mp 131–132 °C; IR (KBr) 3040, 2950, 1520, 1470, 1455, 1340, 1330, 1290, 1200, 1180, 1100, 1085, 1010, 900, 760, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (9 H, s), 2.14–3.16 (8 H, m), 2.98 (3 H, s), 4.21 (1 H, s), 7.11 (2 H, s), 7.94 (2 H, d, J = 1.2 Hz); MS, *m/e* 339 (M^+). Anal. Calcd for $C_{21}H_{25}O_3N$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.53; H, 7.46; N, 4.51.

5-*tert*-Butyl-8,12-dimethoxy[2.2]metacyclophane (42): 62.6%; colorless oil; IR (KBr) 3040, 2970, 2940, 1600, 1500, 1480, 1460, 1440, 1360, 1290, 1240, 1220, 1200, 1040, 1020, 865, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (9 H, s), 1.52–3.60 (8 H, m), 3.00 (3 H, s), 3.78 (3 H, s), 3.91 (1 H, d, J = 2.5 Hz), 6.62 (1 H, d, J = 8 Hz), 6.98 (1 H, dd, J = 2.5 Hz, J = 8 Hz), 7.03 (2 H, s); MS, *m/e* 324 (M^+). Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.59; H, 8.51.

Preparation of 8,13-Dimethoxy-5-*tert*-butyl[2.2]metacyclophane (28d). To 24 mL of methanol was added 730 mg (31.7 mmol) of sodium, and then a mixture of 240 mg of CuI and 673 mg (1.88 mmol) of **28e** in 3 mL of DMF was added. After the reaction mixture was refluxed for 26 h, it was poured into a large amount of ice water and extracted with dichloromethane. The dichloromethane solution was dried over $MgSO_4$ and evaporated in vacuo to leave the colorless solid, which was recrystallized from methanol to give 500 mg (82.1%) of **28d** as colorless prisms, mp 93–95 °C: IR (KBr) 3040, 2950, 1580, 1480, 1450, 1420, 1290, 1205, 1180, 1160, 1140, 1100, 1060, 1020, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (9 H, s), 2.07–3.00 (8 H, m), 3.04 (3 H, s), 3.66 (1 H, s), 3.79 (3 H, s), 6.61 (2 H, s), 7.04 (2 H, s); MS, *m/e* 324 (M^+). Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.35; H, 8.84.

Nitration of 8,16-Dimethyl[2.2]metacyclophane (1a). To a solution of 2 g (8.5 mmol) of **1a** in 500 mL of AcOH was added gradually at room temperature over period of 1 h a solution of 30 mL of fuming HNO_3 in 100 mL of AcOH. After the reaction mixture was stirred for 1 h at the same temperature, it was poured into a large amount of ice water. The organic layer was extracted with dichloromethane, and then the extract was washed with water, dried with $MgSO_4$ and evaporated in vacuo. The residue was then chromatographed on silica gel by using a mixture of hexane and dichloromethane (1:1) or dichloromethane as an eluent to give 2.06 g (86%) of 8,16-dimethyl-5-nitro[2.2]metacyclophane (**9**) from the mixed solvent fraction and 13 mg (0.24%) of 4,10-dinitro-2,7-dioxo-10b,10c-dimethyl-10b,10c-dihydropyrene (**11a**) from the dichloromethane fraction, respectively. **9**: pale yellow prisms (toluene), mp 258–261 °C; IR (KBr) 3060, 2975, 2950, 2930, 2860, 1580, 1570, 1495, 1450, 1375, 1370, 1330, 1280, 1185, 1140, 1085, 900, 795, 775, 750, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.59 (3 H, s), 0.65 (3 H, s), 2.60–3.18 (8 H, m), 6.84–7.20 (3 H, m), 7.99 (2 H, s); MS, *m/e* 281 (M^+). Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.80; H, 6.79; N, 5.20.

11a: greenish prisms (toluene), mp 300 °C dec; IR (KBr) 1665, 1645, 1620, 1530, 1360, 1270, 1020, 910, 835, 820, 740, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00 (3 H, s), 2.08 (3 H, s), 6.32 (2 H, s), 6.40 (2 H, d, J = 10 Hz), 6.68 (2 H, d, J = 10 Hz); MS, *m/e* 352 (M^+). Anal. Calcd for $C_{18}H_{12}N_2O_6$: C, 61.36; H, 3.43; N, 7.95. Found: C, 61.25; H, 3.59; N, 7.97.

Reaction of 1a with $Cu(NO_3)_2$. To a solution of **1a** in 100 mL of Ac_2O was added 150 mg of $Cu(NO_3)_2$ gradually at 0 °C. After the reaction was stirred at room temperature for 12 h, it was treated and worked up as described above to give 64.5 mg (54%) of **9**.

Nitration of 5,13-Di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophane (1b) with Fuming HNO_3. To a solution of 100 mg (0.29 mmol) of **1b** in 150 mL of AcOH was gradually added a solution of 1.8 mL of fuming HNO_3 and 4 mL of AcOH at room temperature. After the reaction mixture was stirred for 1 h, it was poured into a large amount of ice water. The organic layer was washed with water, dried with $MgSO_4$, and evaporated in vacuo to leave a residue that was thin layer chromatographed on silica gel by using benzene as an eluent to give 26 mg (21%) of 2,7-di-*tert*-butyl-4,9-dinitro-10b,10c-dimethyl-10b,10c-dihydropyrene (**12**) as brown prisms (hexane), mp 234.5–236 °C, lit.[5] mp 222–224 °C.

Reaction of 1b with $Cu(NO_3)_2$. To a solution of 100 mg (0.29 mmol) of **1b** in 100 mL of Ac_2O was added 150 mg of $Cu(NO_3)_2$ at 0 °C. After the reaction mixture was stirred at 0 °C for 10 min and stirred at room temperature for 8 min, it was treated and worked up as described above to give 9.1 mg (0.021 mmol) of **12**.

Preparation of 5-Amino-8,16-dimethyl[2.2]metacyclophane (14) by Reduction of 9. After hydrogen gas was introduced into a solution of 1.08 g (5.07 mmol) of **9** in 10 mL of benzene in the presence of 100 mg of 10% Pd/C with stirring for 3 h at room temperature, the Pd/C was filtered off. The filtrate was evaporated in vacuo to leave the residue, which was recrystallized from cyclohexane to give 0.9 g (93%) of **14** as colorless prisms, mp 215–218 °C: IR (KBr) 3430, 3350, 3060, 2975, 2940, 2860, 1610, 1590, 1460, 1335, 1185, 855, 780, 740, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.49 (3 H, s), 0.83 (3 H, s), 1.20–2.00 (2 H, br s, disappeared with D_2O), 2.40–3.00 (8 H, m), 6.48 (2 H, s), 6.66–7.07 (3 H, m); MS, *m/e* 251 (M^+). Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57. Found: C, 86.16; H, 8.52; N, 5.52.

Preparation of 5-(Acetylamino)-8,16-dimethyl[2.2]metacyclophane (16). After a solution of 500 mg (1.99 mmol) of **14** and 0.19 mmol of Ac_2O in 20 mL of benzene was refluxed for 2 h, it was cooled to room temperature. The precipitate formed during the reaction was collected by filtration and recrystallized with ethanol to give 571 mg (95%) of **16** as colorless needles, mp 257–259 °C: IR (KBr) 3300, 2925, 1655, 1585, 1530, 1460, 1398, 1180, 865, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.54 (3 H, s), 0.70 (3 H, s), 2.56–3.03 (8 H, m), 6.68–7.34 (6 H, m, 1 H disappeared with D_2O); MS, *m/e* 293 (M^+). Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 82.12; H, 7.91; N, 4.77.

Preparation of 5-[(Trifluoroacetyl)amino]-8,16-dimethyl[2.2]metacyclophane (17). After a solution of 500 mg of **14** and 418 mg (1.99 mmol) of trifluoroacetic anhydride in 20 mL of benzene was stirred at room temperature for 1 h, it was poured into a large amount of ice water. The organic layer was extracted with dichloromethane. The extract was dried with $MgSO_4$ and evaporated in vacuo to leave a residue, which was recrystallized with cyclohexane to give **17** as colorless prisms, mp 171–171.5 °C: IR (KBr) 3400, 3375, 3250, 2950, 2940, 2860, 1710, 1690, 1590, 1540, 1460, 1330, 1290, 1210, 1180, 1110, 730, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.57 (3 H, s), 0.69 (3 H, s), 2.60–3.08 (8 H, m), 6.72–7.14 (3 H, m), 7.30 (2 H, s), 7.70 (1 H, br s, disappeared with D_2O); MS, *m/e* 347 (M^+). Anal. Calcd for $C_{20}H_{20}NOF_3$: C, 69.15; H, 5.80; N, 4.03. Found: C, 69.39; H, 5.66; N, 4.52.

Nitration of 16. To a solution of 100 mg (0.34 mmol) of **16** in 15 mL of AcOH was gradually added a solution of fuming HNO_3 in 2 mL of AcOH at room temperature. After the reaction mixture was stirred for 3 min, it was poured into a large amount of ice water. The organic layer was extracted with dichloromethane. The extract was washed with water, dried with $MgSO_4$, and evaporated in vacuo to leave a residue that was thin layer chromatographed on silica gel by using dichloromethane as eluent to give 2.2 mg (1.6%) of 2-(acetylamino)-4,7,9-trinitro-10b,10c-dimethyl-10b,10c-dihydropyrene (**19**) as deep green prisms (benzene), mp 264–267 °C: IR (KBr) 3320, 1720, 1645, 1540, 1450, 1325, 1290, 1240, 1200, 1140, 1080, 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ –3.80 (3 H, s), –3.15 (3 H, s), 2.52 (3 H, s), 7.37 (2 H, s), 8.66 (1 H, br

s), 9.59 (2 H, s), 9.65 (2 H, s); MS, m/e 424 (M^+). Anal. Calcd for $C_{20}H_{16}N_4O_7$: C, 56.61; H, 3.80; N, 13.20. Found: C, 58.05; H, 3.92; N, 12.05.

Nitration of 17. To a solution of 100 mg (0.29 mmol) of **17** in 50 mL of AcOH was added a solution of 0.9 mL of 70% HNO_3 in 2 mL of AcOH at room temperature. After the reaction mixture was stirred for 5 min, it was treated and worked up as described above to give 11 mg (10%) of 8,16-dimethyl-5-[(trifluoroacetyl)amino]-13-nitro[2.2]metacyclophane (**20**) as yellow needles (CCl_4), mp 274–277 °C dec; IR (KBr) 3360, 2975, 2940, 2870, 1718, 1695, 1595, 1500, 1340, 1325, 1300, 1210, 1195, 1180, 1160, 900, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.59 (3 H, s), 0.78 (3 H, s), 2.66–3.20 (8 H, m), 7.35 (2 H, s), 7.72 (1 H, br s), 7.99 (2 H, s); MS, m/e 392 (M^+). Anal. Calcd for $C_{20}H_{19}N_2O_3F_3$: C, 61.22; H, 4.88; N, 7.14. Found: C, 60.45; H, 4.78; N, 7.67.

Nitration of 5-Iodo-8,16-dimethyl[2.2]metacyclophane (21). To a solution of 50 mg of **21** in 50 mL of AcOH was added a mixed solution of 0.9 mL of fuming HNO_3 and 2 mL of AcOH at room temperature. After the reaction mixture was stirred for 30 min, it was poured into a large amount of ice water. The organic layer was extracted with dichloromethane. The extract was washed with water, dried with $MgSO_4$ and evaporated in vacuo to leave a residue that was thin layer chromatographed on silica gel by using benzene as eluent to give 33.1 mg (59%) of 5-iodo-8,16-dimethyl-13-nitro[2.2]metacyclophane (**23**) as pale yellow needles (benzene), mp 278–281 °C dec; IR (KBr) 3090, 2975, 2940, 2875, 1510, 1450, 1340, 1322, 1182, 1158, 910, 818, 732 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.54 (3 H, s), 0.79 (3 H, s), 2.54–3.16 (8 H, m), 7.42 (2 H, s), 7.96 (2 H, s); MS, m/e 407 (M^+). Anal. Calcd for $C_{18}H_{18}NO_2I$: C, 53.09; H, 4.45; N, 3.44. Found: C, 53.63; H, 4.59; N, 3.63.

Nitration of 5,13-Diiodo-8,16-dimethyl[2.2]metacyclophane (22). To a solution of 150 mg (0.31 mmol) of **23** in a mixed solvent of 30 mL of dichloromethane and 20 mL of AcOH was added at room temperature a mixed solution of 1 mL of fuming HNO_3 and 2 mL of AcOH. After the reaction mixture was stirred for 1 h, it was treated and worked up as described above to give 60.3 mg (48%) of **23** and 37.1 mg (45%) of 2,7-dioxo-10b,10c-dimethyl-2,7,10b,10c-tetrahydropyrene (**24**) as pale yellow needles (CCl_4), mp 283–285 °C dec, lit. mp 265 °C dec.

Preparation of 5,13-Dimethoxy-8,16-dimethyl[2.2]metacyclophane (25). To 10 mL of methanol were added 283 mg of Na and then a suspension of 150 mg of **22** in 10 mL of DMF and 10 mg of CuI. After the mixture was heated at 100 °C for 24 h under N_2, it was poured into 100 mL of water and the precipitate formed was washed with dichloromethane. The dichloromethane solution was washed with water, dried with $MgSO_4$, and evaporated in vacuo to leave a residue that was recrystallized from hexane to give 5,13-dimethoxyl-8,16-dimethyl[2.2]metacyclophane (**25**) as colorless prisms, mp 213–215 °C, lit. mp 212.5–213 °C.

Nitration of 8,13-Dimethyl-5-*tert*-butyl[2.2]metacyclophane (26). To a solution of 146 mg (0.5 mmol) of **26** in 150 mL of AcOH was added gradually at room temperature a solution of 2.7 mL of fuming HNO_3 and 6 mL of AcOH. After the reaction mixture was stirred for 1 h, it was poured into a large amount of ice water. The organic layer was washed with water, dried with $MgSO_4$, and evaporated in vacuo to leave a residue that was column chromatographed on silica gel by using a mixture of hexane and benzene (1:1) to give 69.8 mg (50%) of 1,7-dimethyl-2-nitro-4,5,9,10-tetrahydropyrene (**27**) as yellow prisms (methanol), mp 104–105 °C: IR (KBr) 3020, 2950, 1605, 1575, 1510, 1420, 1335, 1285, 1240, 1205, 940, 880, 860, 840, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.36 (3 H, s), 2.44 (3 H, s), 2.80–3.10 (8 H, m), 6.95 (2 H, s), 7.56 (2 H, s); MS, m/e 279 (M^+). Anal. Calcd for $C_{18}H_{17}O_2N$: C, 77.39; H, 6.13; N, 5.01. Found: C, 77.53; H, 6.22; N, 5.16.

Reaction of 26 with $Cu(NO_3)_2$. To a solution of 100 mg (0.342 mmol) of **26** in 100 mL of Ac_2O was gradually added 100 mg of $Cu(NO_3)_2$ at 0 °C. After the reaction mixture was stirred at room temperature for 1 h, it was treated and worked up as described above to give 78 mg (81.8%) of **27**.

Nitration of 8-Methoxy-13-methyl[2.2]metacyclophane (31). To a solution of 126 mg (0.5 mmol) of **31** in 150 mL of AcOH was added gradually at room temperature a solution of 2.7 mL of fuming HNO_3 and 6 mL of AcOH. After the reaction mixture was stirred for 1 h, it was poured into a large amount of ice water. The organic layer was washed with water, dried with $MgSO_4$, and evaporated in vacuo to leave a residue that was column chromatographed on silica gel by using a mixture of hexane and benzene (1:1) to give 120 mg (75.5%) of **33b** and 25 mg (17%) of 5-nitro-13-methyl-8-methoxy[2.2]metacyclophane (**32**), respectively.

32: pale yellow prisms (methanol), mp 195–197 °C; IR (KBr) 3010, 2930, 1570, 1500, 1460, 1330, 1295, 1260, 1220, 1175, 1080, 1020, 900, 860, 750, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10–3.10 (8 H, m), 3.12 (3 H, s), 4.09 (1 H, s), 6.89 (2 H, s), 7.97 (2 H, s); MS, m/e 297 (M^+). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.69; H, 6.44; N, 4.71. Found: C, 72.59; H, 6.65; N, 4.81.

33b: pale yellow prisms (hexane/benzene, 5:1), mp 161–162 °C; IR (KBr) 3010, 2940, 1605, 1580, 1505, 1460, 1420, 1330, 1175, 1085, 885, 850, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.36 (3 H, s), 2.80–3.00 (8 H, m), 6.96 (2 H, s), 7.94 (2 H, s); MS, m/e 265 (M^+). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.60; H, 5.78; N, 5.42.

Nitration of 5-Bromo-8-methoxy-13-methyl[2.2]metacyclophane (34). To a solution of 82.8 mg (0.25 mmol) of **34** in 75 mL of AcOH was added gradually at room temperature a solution of 1.35 mL of fuming HNO_3. The mixture was stirred for 1 h and then treated as described above to give 45 mg (59.1%) of 2-bromo-7-methyl-4,5,9,10-tetrahydropyrene (**35**) and 18 mg (27%) of **33b**.

35: colorless prisms (methanol), mp 157–159 °C; IR (KBr) 3100, 2950, 2900, 1610, 1580, 1450, 1430, 1230, 1040, 860, 810, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.32 (3 H, s), 2.82 (8 H, s), 6.89 (2 H, s), 7.70 (2 H, s); MS, m/e 298, 300 (M^+). Anal. Calcd for $C_{17}H_{15}Br$: C, 68.22; H, 5.05. Found: C, 67.93; H, 4.84.

Nitration of 5-*tert*-Butyl-8-methoxy-13-substituted-[2.2]metacyclophanes 28a–g. Nitration with HNO_3. General Procedure. To a solution of 0.5 mmol of **28** in 150 mL of AcOH was added gradually at room temperature a solution of 2.7 mL of fuming HNO_3 or 63% HNO_3 and 6 mL of AcOH. After the reaction mixture was stirred for 1 h, it was poured into a large amount of ice water. The organic layer was washed with water, dried with $MgSO_4$, and evaporated in vacuo to leave a residue that was column chromatographed on silica gel by using hexane and a mixture of hexane and benzene (1:1) as eluent to give the products in the yields shown in Table I.

Nitration with $Cu(NO_3)_2$. To a solution of 100 mg of **28** in 100 mL of Ac_2O was gradually added 100 mg of $Cu(NO_3)_2$ at 0 °C. After the reaction mixture was stirred at room temperature for 1 h, it was treated and worked up as described above to give the products.

2-*tert*-Butyl-7-methyl-4,5,9,10-tetrahydropyrene (36a): colorless prisms (methanol), mp 116–117 °C (lit.[9] mp 116–117 °C).

2,7-Di-*tert*-butyl-4,5,9,10-tetrahydropyrene (36b): colorless prisms (methanol), mp 234–235 °C (lit.[10] mp 223–224 °C).

2-Nitro-4,5,9,10-tetrahydropyrene (33a): pale yellow prisms (ethanol), mp 109–110 °C (lit. mp 110–111 °C).

2-Nitro-7-methyl-4,5,9,10-tetrahydropyrene (33b).

7-*tert*-Butyl-2-nitro-4,5,9,10-tetrahydropyrene (33c): pale yellow prisms (methanol), mp 154–155 °C; IR (KBr) 3010, 2940, 1580, 1500, 1420, 1325, 1075, 890, 870, 765, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (9 H, s), 2.86–3.04 (8 H, m), 7.15 (2 H, s), 7.94 (2 H, s); MS, m/e 307 (M^+). Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.16; H, 6.87; N, 4.56. Found: C, 78.13; H, 6.79; N, 4.50.

2,6-Dinitro-7-methoxy-4,5,9,10-tetrahydropyrene (38): pale yellow prisms (hexane/benzene, 1:3), mp >300 °C; IR (KBr) 3100, 2950, 2900, 1600, 1590, 1525, 1515, 1460, 1440, 1370, 1330, 1290, 1230, 1220, 1200, 1180, 1100, 920, 900, 825, 780, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.15–2.50 (8 H, m), 3.19 (3 H, s), 6.15 (1 H, s), 7.61 (1 H, d, J = 2 Hz), 7.72 (1 H, d, J = 2 Hz); MS, m/e 326 (M^+). Anal. Calcd for $C_{17}H_{14}O_5N_2$: C, 62.57; H, 4.32; N, 8.59. Found: C, 62.79; H, 4.41; N, 8.65.

2-Nitro-1-methoxy-7-methyl-4,5,9,10-tetrahydropyrene (37a): pale yellow needles (methanol), mp 134–135 °C; IR (KBr) 3010, 2940, 1600, 1575, 1505, 1440, 1335, 1290, 1220, 1100, 990, 880, 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (3 H, s), 2.77–3.00 (8 H, m), 3.88 (3 H, s), 6.94 (2 H, s), 7.61 (1 H, s); MS, m/e 295 (M^+). Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.18; H, 5.71; N, 4.97.

7-*tert*-Butyl-2-nitro-1-methoxy-4,5,9,10-tetrahydropyrene (37b): pale yellow prisms (methanol), mp 157–161 °C; IR (KBr)

3010, 2940, 1500, 1470, 1330, 1020, 860, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (9 H, s), 2.45 (3 H, s), 2.83–3.00 (2 H, s), 7.14 (2 H, s), 7.55 (2 H, s); MS, *m/e* 321 (M^+). Anal. Calcd for $C_{21}H_{23}NO_3$: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.32; H, 7.24; N, 4.63.

Nitration with Mixed Acid. To a solution of 0.5 mmol of **28e–g** in 150 mL of AcOH was added gradually at room temperature a solution of 2.2 mL of fuming HNO_3 and 1 mL of concentrated sulfuric acid. After the reaction mixture was stirred for 1 h, it was poured into a large amount of ice water. The organic layer was washed with water, dried over $MgSO_4$, and evaporated in vacuo to leave a residue that was recrystallized to give **33d–f**.

2-Nitro-7-bromo-4,5,9,10-tetrahydropyrene (33e): yellow prisms (hexane/benzene, 1:2), mp 248–250 °C; IR (KBr) 2940, 1605, 1575, 1510, 1440, 1420, 1340, 1310, 1250, 1225, 1080, 985, 910, 890, 855, 810, 870, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.80–3.05 (8 H, m), 7.30 (2 H, s), 7.96 (2 H, s); MS, *m/e* 329, 331 (M^+). Anal. Calcd for $C_{16}H_{12}BrO_2N$: C, 58.20; H, 3.66; N, 4.24. Found: C, 58.31; H, 3.74; N, 4.39.

2-Nitro-7-cyano-4,5,9,10-tetrahydropyrene (33f): pale brown prisms (benzene), mp >300 °C; IR (KBr) 3060, 2940, 2210, 1580, 1505, 1440, 1430, 1335, 1085, 920, 900, 775, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.92–3.08 (8 H, m), 7.43 (2 H, s), 8.00 (2 H, s); MS, *m/e* 276 (M^+). Anal. Calcd for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.68; H, 4.52; N, 10.12.

2,7-Dinitro-4,5,9,10-tetrahydropyrene (33q): yellow prisms (hexane/benzene, 1:3), mp >300 °C; IR (KBr) 3100, 2950, 1590, 1445, 1425, 1335, 1100, 920, 900, 765, 745, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.05 (8 H, s), 8.02 (4 H, s); MS, *m/e* 296 (M^+). Anal. Calcd for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; N, 9.46. Found: C, 64.84; H, 4.16; N, 9.53.

Nitration of 2-Methyl-7-*tert*-butyl-4,5,9,10-tetrahydropyrene (36a) with Fuming HNO_3. To a solution of 138 mg (0.5 mmol) of **36a** in 150 mL of AcOH was added gradually a solution of 2.7 mL of fuming HNO_3 and 6 mL of AcOH. After the reaction mixture was stirred at room temperature for 1 h, it was treated and worked up as described above to give 112.6 mg (85%) of **33b**.

Nitration of 36a with 63% HNO_3. To a solution of 138 mg (0.5 mmol) of **36a** in 150 mL of AcOH was added gradually a solution of 2.7 mL of 63% HNO_3 and 6 mL of AcOH. After the reaction mixture was stirred at room temperature for 1 h, it was treated and worked up as described above to give 136 mg of starting compound (**36a**).

Nitration of 2,7-Di-*tert*-butyl-4,5,9,10-tetrahydropyrene (36b) with Fuming HNO_3. To a solution of 153 mg (0.5 mmol) of **38a** in 150 mL of AcOH was added gradually a solution of 2.7 mL of fuming HNO_3 and 6 mL of AcOH. After the reaction mixture was stirred at room temperature for 1 h, it was treated and worked up as described above to give 138.3 mg (90%) of **33c**.

Nitration of 36b with 63% of HNO_3. To a solution of 153 mg (0.5 mmol) of **36b** in 150 mL of AcOH was added gradually a solution of 2.7 mL of 63% HNO_3 and 6 mL of AcOH. After the reaction mixture was stirred at room temperature for 1 h, it was treated and worked up as described above to give 150 mg of starting compound (**36b**).

Preparation of 1-Methoxy-2-amino-7-*tert*-butyl-4,5,9,10-tetrahydropyrene (39) by Reduction of 37b. After hydrogen gas was introduced into a solution of 150 mg (0.445 mmol) of **37b** in 20 mL of ethanol in the presence of 40 mg of 10% Pd/C under stirring for 3 h at room temperature, the Pd/C was filtered off. The filtrate was evaporated in vacuo to leave the residue, which was recrystallized from hexane to give 130 mg (95%) of **39** as pale yellow prisms, mp 84–87 °C: IR (KBr) 3200, 3010, 2940, 1580, 1460, 1430, 1410, 1325, 1210, 980, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (9 H, s), 2.60–3.20 (8 H, m), 3.74 (3 H, s), 6.48 (1 H, s), 7.07 (2 H, s); MS, *m/e* 307 (M^+). Anal. Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found: C, 81.75; H, 8.26; N, 4.51.

Preparation of 1-Methoxy-7-butyl-4,5,9,10-tetrahydropyrene (40) by Deamination of 39. To a solution of 100 mg (0.325 mmol) of **39** in 2 mL of concentrated hydrochloric acid was added gradually at 10–13 °C a solution of 61 mg (0.78 mmol) of sodium nitrite in 1 mL of water. The reaction mixture was stirred for 15–20 min at 5–10 °C and poured rapidly into 2 mL of ice-cold 30% hydrophosphorous acid solution and then allowed to stand at room temperature for 12 h. The reaction mixture was extracted with dichloromethane. The dichloromethane extract was washed with water, dried over $MgSO_4$, and evaporated in vacuo to leave a residue, which was column chromatographed on silica gel by using a mixture of hexane and benzene (1:1) to give 30 mg (31.6%) of **40** as a colorless oil: IR (Nujol) 2940, 1610, 1480, 1380, 1360, 1100, 1025, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (9 H, s), 2.80–3.00 (8 H, m), 3.83 (3 H, s), 6.69 (1 H, d, J = 8.1 Hz), 6.99 (1 H, d, J = 8.1 Hz), 7.10 (2 H, s); MS, *m/e* 292 (M^+). Anal. Calcd for $C_{21}H_{24}O$: C, 86.25; H, 8.27. Found: C, 86.48; H, 8.31.

Reaction of 8,11-Dimethoxy-5-*tert*-butyl[2.2]metacyclophane (42) with Iodine To Give 40. A solution of 336 mg (1.04 mmol) of **42** and 524 mg (2.08 mmol) of iodine in 6 mL of benzene was stirred for 12 h at 60 °C. The reaction mixture was washed with 10% sodium thiosulfate solution and then with water. The benzene solution was dried over $MgSO_4$ and evaporated in vacuo to leave the residue, which was column chromatographed on silica gel by using hexane as eluent to give 241 mg (79.3%) of **40**.

Oxidation of 8,16-Dimethyl-5,13-dimethoxy[2.2]metacyclophane (25) with $FeCl_3$. After a mixture of 50 mg (0.17 mmol) of **25** and 1.75 mg of $FeCl_3$ in 5 mL of $CHCl_3$ was stirred at room temperature for 3 h, the formed precipitate was filtered. To the filtrate was added 3 mL of 3 N HCl, and the extract was washed with water, dried over Mg_2SO_4, and evaporated in vacuo to leave a residue that was recrystallized from 23 mg (51%) of **24**.

Formation, Structures, and Reactions of Selected α′-Lithioallyl Amides

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Lithiations of the selected allyl amides **6**, **10**, **14**, and **17** give the α′-lithioallyl amides **7**, **11**, **15**, and **18**. The structures of **7**, **11**, and **18** are characterized by their NMR spectra. Electrophilic substitutions of these reagents are usually regioselective at the γ′-position, but there are exceptions. In situ lithiation–electrophilic substitutions are effective for **10** and **17** with LiTMP–$(CH_3)_3SiCl$, *n*-BuLi–$C_6H_5CH_2Cl$, and *n*-BuLi–$Cl(CH_2)_4Cl$. Hydrogen–deuterium isotope effects are consistent with diastereoselective removal of a pseudoequatorial proton from **17**. The lithiations are suggested to occur in an amide–organolithium complex and most readily in systems that can achieve a *Z* conformation.

Allyl organolithium reagents bearing a terminal nitrogen have proven to be of synthetic value, and the chemistry of such species is of continuing interest.[1,2] A number of tertiary allyl amide analogues have been found to undergo

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