Metacyclophanes and Related Compounds. 4. Halogenations of 8,16-Dialkyl-*anti*-5,13-di-*tert*-butyl[2.2]-metacyclophan-1-enes and 2,7-Di-*tert*-butyl-*trans*-10b,10c-dialkyl-10b,10c-dihydropyrenes[1,2]

Masashi Tashiro* and Takehiko Yamato

Contribution from the Research Institute of Industrial Science, Kyushu University, Sakamoto, Kasuga, Kasuga-shi, Fukuoka 816, Japan. *Received September 21, 1981*

Abstract: 8,16-Dialkyl-*anti*-5,13-di-*tert*-butyl[2.2]metacyclophan-1-enes (**13**) and 2,7-di-*tert*-butyl-*trans*-10b,10c-dialkyl-10b,10c-dihydropyrenes (**20a–c**) were prepared from the corresponding alkylbenzenes in several steps. The bromination of **13** and **20** with bromine in a carbon tetrachloride solution afforded 2,7-di-*tert*-butyl-4,5,9,10-tetrabromo-*trans*-10b,10c-dialkyl-10b,10c-dihydropyrenes (**2**). Treatment of **20** with iodine in a boiling benzene solution gave the dealkylated compound, 2,7-di-*tert*-butylpyrene (**28**). Such dealkylation was also observed in the bromination of **20** with bromine in the presence of Fe powder. However, without Fe powder, the bromination of **20** did not give any products. It was also found that the chlorination of **13a** and **20a** with iodine chloride or chlorine afforded the further chlorinated 2,7-di-*tert*-butyl-2,4,5,9,10-hexachloro-*trans*-10b,10c-dimethyl-2,7,10b,10c-tetrahydropyrene (**30**). The reaction pathways of the halogenation of the titled compounds are also discussed.

Although [2.2]metacyclophan-1-enes[3-5] and *trans*-10b,10c-dialkyl-10b,10c-dihydropyrenes[6-12] have been prepared by Boekelheide and his co-workers, their preparative routes from easily available compounds seem to be too long for practical purposes. Therefore, chemical information about these compounds is very much limited.

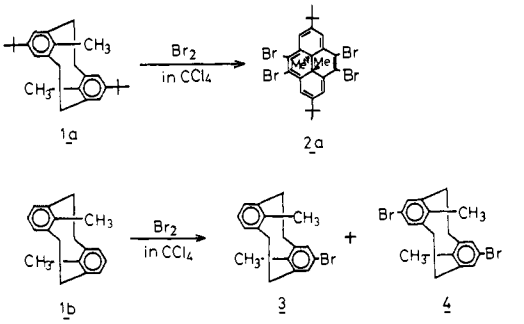
In previous work, we found that[13] bromination of 8,16-dimethyl-*anti*-5,13-di-*tert*-butyl[2.2]metacyclophane (**1a**) afforded the novel product, 2,7-di-*tert*-butyl-4,5,9,10-tetrabromo-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**2a**), even though bromination of 8,16-dimethyl-*anti*-[2.2]metacyclophane (**1b**) gave a mixture of the normal products, **3** and **4** (Scheme I).

We undertook the present work in order to obtain information about the chemical behavior of the titled compounds in their halogenation reactions.

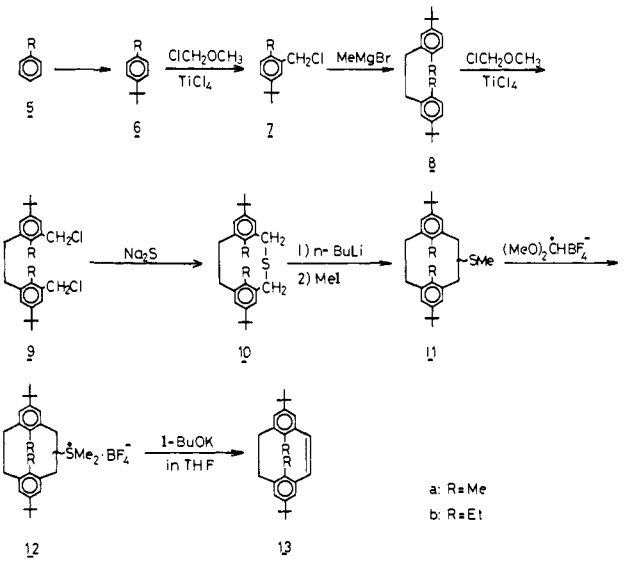
Results and Discussion

Preparation of 8,16-Dialkyl-*anti*-5,13-di-*tert*-butyl[2.2]metacyclophan-1-enes (13). These compounds (**13**) were prepared from the corresponding alkylbenzenes (**5**) in eight steps as shown in Scheme II. The preparations of **8**[14] and **9a**[15] were described in previous papers. The chloromethylation of **8b** was carried out according to the reported method[15] and gave the expected **9b**. The described compounds (**13**) were obtained from compound **9** in four steps by following the methods reported by Boekelheide and his co-workers.[11,12]

Scheme I



Scheme II

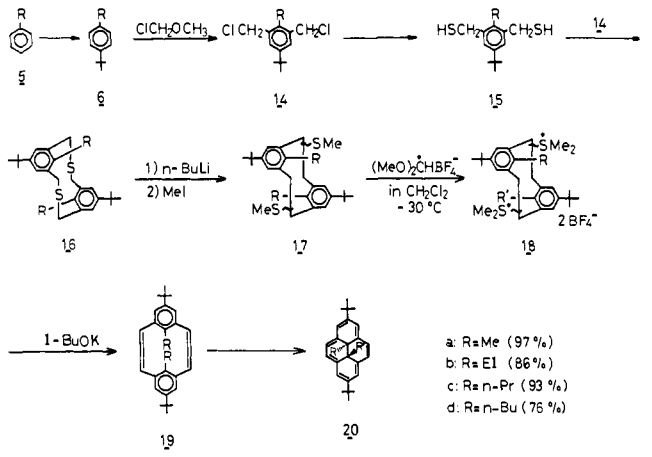


Preparation of 2,7-Di-*tert*-butyl-*trans*-10b,10c-dialkyl-10b,10c-dihydropyrenes (20). These compounds (**20**) were easily prepared from *anti*-dithia[3.3]metacyclophanes (**16**), which[13] were obtained from the corresponding **5** in four steps (Scheme III). The compounds **19a–d** are very labile and change spontaneously to the corresponding **20a–c**. Although **20a** could be recrystallized from hexane, the compounds **20b–d** were labile in a boiling hexane

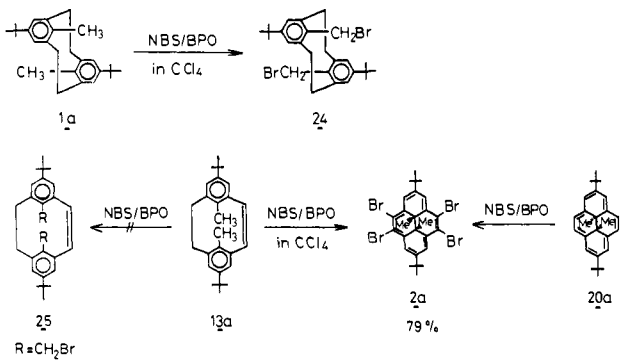
(1) Part 2: Tashiro, M.; Yamato, T. *Org. Prep. Proced. Int.*, submitted for publication.
(2) Part of this work was published as a preliminary communication: Tashiro, M.; Yamato, T. *Chem. Lett.* **1980**, 1127.
(3) Blaschke, H.; Ramey, C. E.; Golden, I.; Boekelheide, V. *J. Am. Chem. Soc.* **1970**, *92*, 3675.
(4) Ramey, C. E.; Boekelheide, V. *J. Am. Chem. Soc.* **1970**, *92*, 3681.
(5) Hess, B. A.; Bailey, A. S.; Boekelheide, V. *J. Am. Chem. Soc.* **1967**, *89*, 2746.
(6) Boekelheide, V.; Phillips, J. B. *Proc. Natl. Acad. Sci. U.S.A* **1964**, *51*, 550.
(7) Boekelheide, V.; Phillips, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 1095.
(8) Phillips, J. B.; Molyneux, R. J.; Sturm, E.; Boekelheide, V. *J. Am. Chem. Soc.* **1967**, *89*, 1704.
(9) Boekelheide, V.; Miyasaka, T. *J. Am. Chem. Soc.* **1967**, *89*, 1709.
(10) Boekelheide, V.; Mylton, T. A. *J. Am. Chem. Soc.* **1970**, *92*, 3669.
(11) Mitchell, R. M.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547.
(12) Mitchell, R. M.; Otsubo, T.; Boekelheide, V. *Tetrahedron Lett.* **1975**, 219.
(13) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1981**, *46*, 1543.
(14) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1978**, *43*, 1413.
(15) Tashiro, M.; Yamato, T. *Synthesis* **1978**, 435.

0002-7863/82/1504-3701$01.25/0

Scheme III

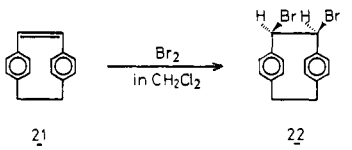


Scheme IV

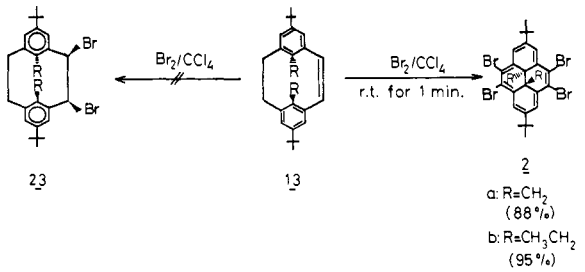


solution and could only be purified by column chromatography on silica gel.

Bromination. As mentioned above, the bromination of **1a** with bromine in a carbon tetrachloride solution afforded **2a** in good yields.[13] This finding suggests that **13a** might be a possible intermediate in the formation of **2a** in the bromination of **1a**. On the other hand, it was reported that[16] bromination of [2.2]paracyclophan-1-ene (**21**) with bromine afforded the corresponding *cis*-dibromide **22**.

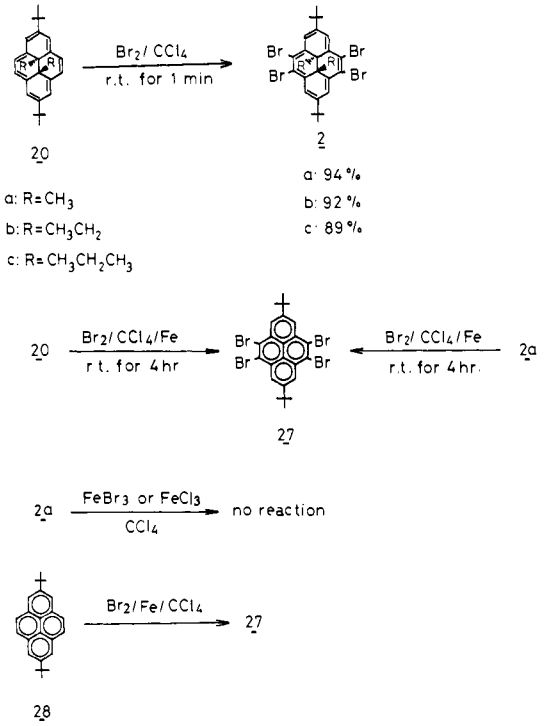


Therefore, the bromination of **13a** with bromine in a carbon tetrachloride solution was carried out at room temperature for 1 min to give the corresponding **2** in good yield, but not the dibromide **23**.



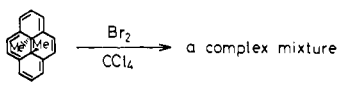
It has been reported that[13] bromination of **1a** with *N*-bromosuccinimide (NBS) in the presence of benzoyl peroxide (BPO) afforded the dibromide **24** (Scheme IV). However, similar reaction of **13a** gave **2a** in 79% yield, but not the expected compound (**25**).

Scheme V



It was also found that the bromination of **20a** with NBS under similar conditions afforded **2a**.

Phillips et al.[8] reported that the bromination of *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**26**) in a carbon tetrachloride solution afforded a complex mixture of polybromo derivatives. Recently, Mitchell et al.[17] reinvestigated this reaction and obtained the same result, even at −78 °C.



However, the bromination of **20a–20c** with bromine in a carbon tetrachloride solution afforded the corresponding tetrabromides, **2a–c**, in good yields (Scheme V).

It was also found that the bromination of **20a–c** with bromine in the presence of Fe powder gave surprisingly the dealkylated compound, 2,7-di-*tert*-butyl-4,5,9,10-tetrabromopyrene (**27**), in good yields. This compound (**27**) was also obtained by treatment of **2a** with bromine in the presence of Fe powder and by bromination of 2,7-di-*tert*-butylpyrene (**28**), but neither $FeBr_3$ nor $FeCl_3$ in carbon tetrachloride solution reacted with **2a**.

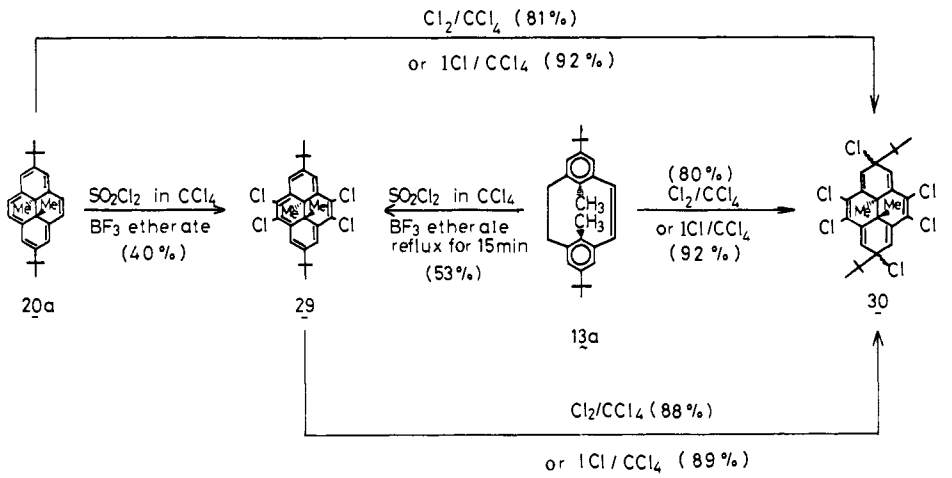
Chlorination. The chlorination of both **13a** and **20a** was carried out with sulfuryl chloride in the presence of boron trifluoride etherate in a carbon tetrachloride solution. The presence of the catalyst is necessary for this reaction to occur (Scheme VI). Furthermore, the chlorination of **13a** and **20a** with chlorine or ICl in a carbon tetrachloride solution afforded the further chlorinated **30**, which was also obtained by similar chlorination of **29**. This result suggests that **29** is an intermediate in the formation of **30** in the chlorination of **13a** and **20a**. Unfortunately, the configuration of **30** is still obscure. The chemistry of this compound (**30**) is being investigated now.

It was also found that **30** was formed when **2a** was treated with ICl in a carbon tetrachloride solution. In this case, a halogen exchange reaction as well as the 1,8 addition of chlorine to **29** occurred (Scheme VII).

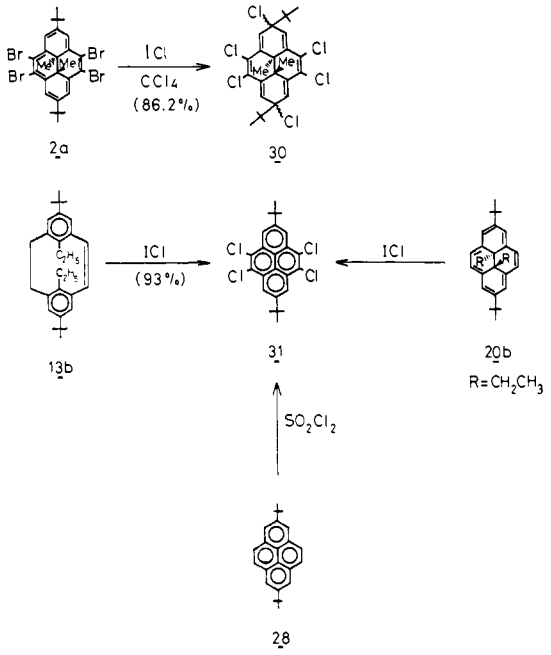
(16) Cram, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 3512.

(17) Mitchell, R. M.; Lai, Y. H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733.

Scheme VI

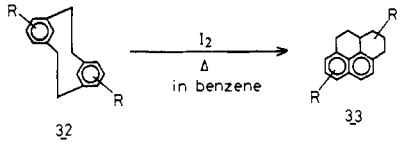


Scheme VII

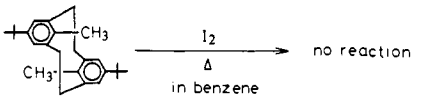


The chlorination of both **13b** and **20b** with ICl in carbon tetrachloride gave dealkylated **31**, which was also obtained by the chlorination of **28** with sulfuryl chloride.

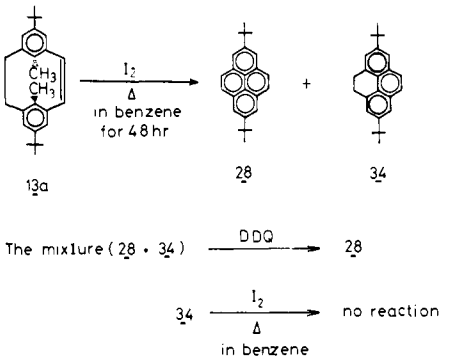
Reaction with Iodine. Sato and Nishiyama reported that[18,19] when some [2.2]metacyclophanes (**32**) were treated with iodine in a boiling benzene solution, the rearranged products (**33**) were obtained.



However, **1a** did not give any products in a similar reaction.[13]



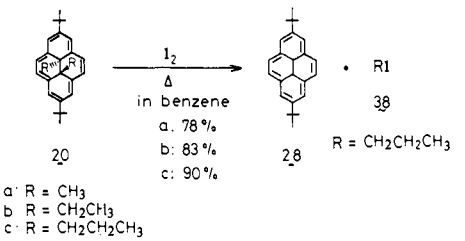
Scheme VIII



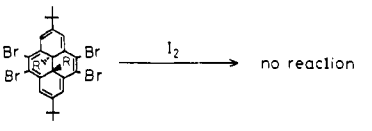
On the other hand, treatment of **13a** with iodine in boiling benzene afforded a mixture of **28** and the 4,5-dihydropyrene derivative **34** with a total yield of 78% (Scheme VIII). The molar ratio of **28**:**34** was 60:40, estimated from an ^1H NMR spectrum of the mixture.

Oxidation with DDQ of the mixture obtained afforded pure **28**. However, after isolation from the mixture, **34** did not give any products upon treatment with iodine in similar conditions, and it was recovered in almost quantitative yield. This finding suggests that **34** is not an intermediate in the formation of **28** in the reaction of **13a** with iodine. Although a similar oxidative dealkylation was reported by Ramey and Boekelheide,[4] the mechanism was not explained.

When **20a–c** were treated with iodine in boiling benzene for 48 h, 2,7-di-*tert*-butylpyrene (**28**) was produced in good yield in

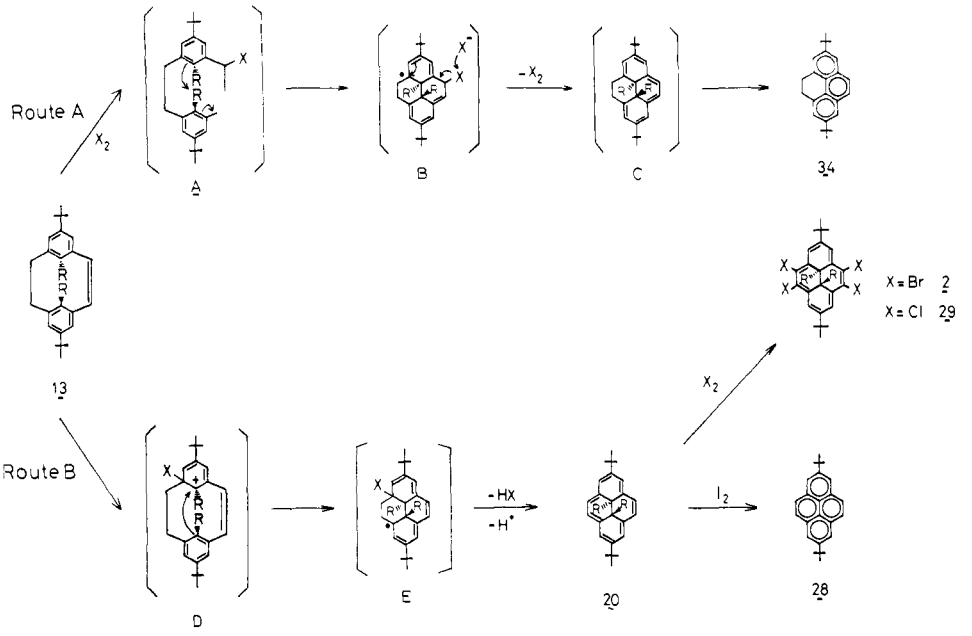


all cases. In the case of **20c**, propyl iodide (**38**) was obtained as well. However, similar treatment of **2a** with iodine did not give any products, and **2a** was recovered in quantitative yield.

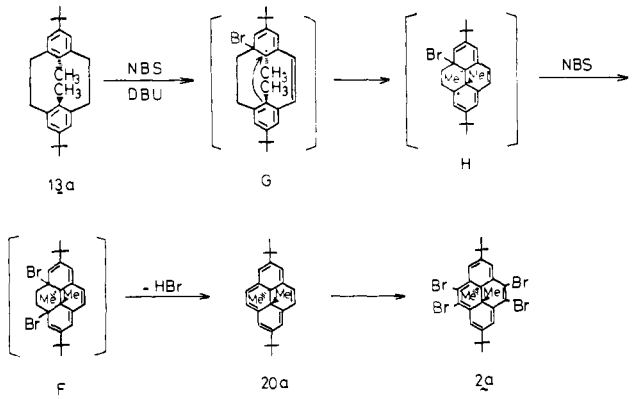


(18) Sato, T.; Nishiyama, K. *J. Chem. Soc., Chem. Commun.* **1972**, 163.
(19) Sato, T.; Nishiyama, K. *J. Org. Chem.* **1972**, *37*, 3254.

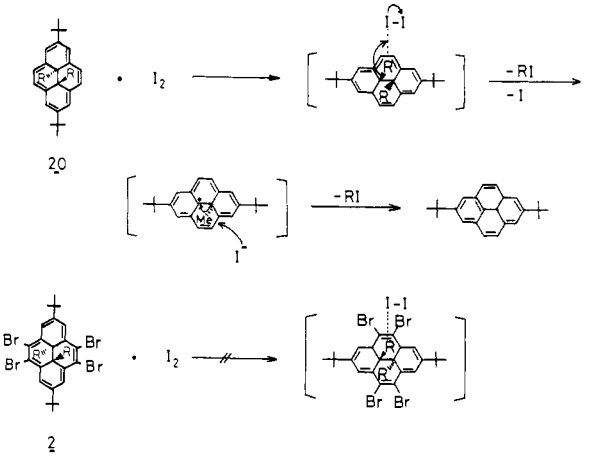
Scheme IX



Scheme X

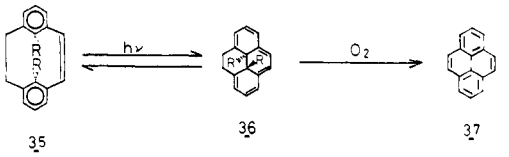


Scheme XI



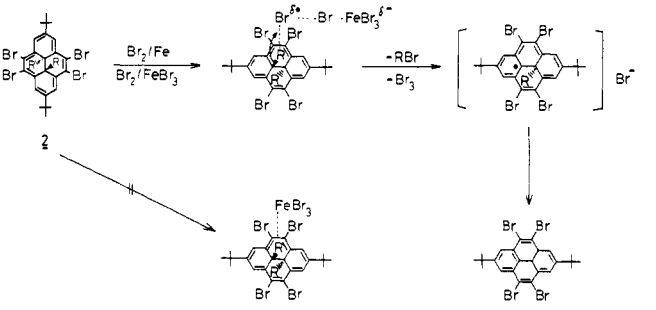
As mentioned above, treatment of **13a** with iodine in a boiling benzene solution afforded **28** and **34**, and the later compound did not react to form **28** under similar conditions. This finding means that there are two separate reaction pathways that yield **28** and **34**, as shown in Scheme IX. Dihydropyrene derivatives (**20**) could be an intermediate in the formation of **28**. Indeed, when **20** was treated with iodine in a boiling benzene solution, dealkylation gave **28** as described above.

Although intermediate C could not be isolated here, Ramey and Boekelheide obtained the same type of product (**36**) in the photoreaction of **35**. They also isolated compound **37** by the



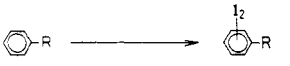
oxidation of **36** as described above. Therefore, reaction route A seems to be reasonable. Bromination and chlorination of **13** might proceed only via reaction route B, since **34** was not formed. The experimental results described above strongly suggest that compounds **20** are clearly intermediates for the formation of **2** and **29** in the bromination and chlorination of **13**, respectively. The fact that the bromination of **13a** with NBS, as well as with bromine itself, gave **2a** but not **25** might suggest that the bromine produced radically from NBS attached to the ipso position and afforded intermediate G, which was followed by a second bromination and dehydrobromination to form compound **20** (Scheme X).

Scheme XII



It has been reported that these are transannular reactions of the metacyclophane series in the electrophilic substitution and radical reaction mechanisms.[20,21] These reaction mechanisms are consistent with our proposed reaction pathways.

It is well-known that iodine reacts with aromatic compounds to give a charge-transfer complex (CT complexes). However,



(20) Sato, T.; Akabori, S.; Muto, S.; Hata, K. *Tetrahedron Lett.* **1968**, *24*, 5557.

(21) Nishiyama, K.; Hata, K.; Sato, T. *Tetrahedron Lett.* **1975**, *31*, 239.

bromine does not generally form such CT complexes. Although the mechanism of dealkylation of 10b,10c-dialkyl-10b,10c-dialky-10b,10c-dihydropyrenes is not clear, we tentatively proposed the reaction pathways illustrated in Schemes XI and XII.

Experimental Section

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

Preparation of 5,5′-Di-*tert*-butyl-3,3′-bis(chloromethyl)-2,2′-diethyldiphenylethane (9b). To a solution containing 5,5′-di-*tert*-butyl-2,2′-diethyldiphenylethane (**8b**,[14] 22.3 g, 68 mmol), chloromethyl methyl ether (16.3 g, 204 mmol), and carbon disulfide (40 mL) at 5 °C was added titanium chloride (8.8 mL). After the reaction mixture was stirred at 15 °C for 30 min, the reaction was quenched with ice water (150 mL) and the mixture extracted with ether. The etheral solution was dried over sodium sulfate and evaporated in vacuo to afford the crude product, which on recrystallization from hexane gave 18 g (62.5%) of **9b**: colorless prisms (hexane); mp 145–6 °C; IR (KBr) 3040, 2950, 1460, 1150 cm^{-1}; NMR ($CDCl_3$) δ 1.18 (6 H, t, J = 8 Hz), 1.22 (18 H, s), 2.65 (4 H, q, J = 8 Hz), 2.86 (4 H, s), 4.40 (4 H, s), 6.82–7.10 (4 H, m). Anal. Calcd for $C_{28}H_{40}Cl_2$: C, 75.15; H, 9.01. Found: C, 75.01; H, 8.92.

Preparation of 9,17-Dimethyl-2-thia[3.2]metacyclophane (10a). A solution of 21.4 g (89.3 mmol) of $Na_2S{\cdot}9H_2O$ in 60 mL of water was added dropwise from a Hershberg funnel with stirring under nitrogen to a solution of 8.38 g (20 mmol) of **9a**[15] in 2.0 L of absolute ethanol. When addition was complete (1 h), the mixture was refluxed for 36 h with stirring. Then the reaction mixture was concentrated and the residue extracted with 500 mL of dichloromethane. The dichloromethane extract was concentrated and the residue chromatographed on active Al_2O_3 with a 1:1 benzene–hexane mixture as the eluant. The crystals isolated from the elute were recrystallized from hexane and gave 5.18 g (68.2%) of **10a**: colorless prisms (hexane); mp 233–234 °C; IR (KBr) 3040, 2950, 1475, 1350, 875 cm^{-1}; NMR ($CDCl_3$) δ 0.84 (6 H, s), 1.29 (18 H, s), 2.60, 2.96 (4 H, A_2B_2 pattern), 3.68, 3.86 (4 H, AB pattern, J = 16 Hz), 7.08 (4 H, s); mass spectrum, m/e 380 (M^+). Anal. Calcd for $C_{26}H_{36}S$: C, 82.04; H, 9.53. Found: C, 81.82; H, 9.52.

Compound **10b** was obtained in 73.5% yield by the same method: colorless prisms (hexane); mp 254–256 °C; IR (KBr) 3040, 2950, 1600, 1480, 1445, 1360, 1280, 1220, 1050, 880, 850, 770 cm^{-1}; NMR ($CDCl_3$) δ 0.50 (6 H, t, J = 8 Hz), 1.31 (18 H, s), 1.55 (4 H, q, J = 8 Hz), 2.62–2.97 (4 H, m), 3.83 (4 H, s), 7.10–7.20 (4 H, m); mass spectrum, m/e 408 (M^+). Anal. Calcd for $C_{28}H_{40}S$: C, 82.19; H, 9.87. Found: C, 82.11; H, 9.81.

Wittig Rearrangement of 10a To Give 11a. To a stirred solution of 1.52 g (4 mmol) of **10a** in 15 mL of dry tetrahydrofuran under nitrogen was added 3 mL of a 15% hexane solution of *n*-butyllithium (7 mmol), with ice cooling. After the reaction solution was stirred for 10 min at room temperature, 0.63 mL (10 mmol) of methyl iodide was added. The reaction mixture was worked up by addition of H_2O and CH_2Cl_2. The dichloromethane extract was washed with water, drived over Na_2SO_4, and concentrated. The products were purified by filtration through silica gel with hexane–benzene 1:1 to give 1.51 g (95.6%) of **11a**: colorless crystals; mp 125–135 °C; IR (KBr) 3040, 2980, 1600, 1485, 1460, 1425, 1280, 1100, 1020, 890, 840 cm^{-1}; NMR ($CDCl_3$) δ 0.58–0.60 (6 H, Me), 1.28–1.32 (18 H, *t*-Bu), 2.14 (3 H, SCH_3), 2.54–3.28 (6 H, CH_2CHS-CH_3 and CH_2CH_2), 4.00–4.17 (1 H, CHSMe), 7.18–7.81 (4 H, A H). Anal. Calcd for $C_{27}H_{38}S$: C, 82.17; H, 9.71. Found: C, 82.40; H, 9.84.

Compound **11b** was prepared in 97.6% yield by the same method: colorless crystals; mp 105–115 °C; IR (KBr) 3040, 2960, 1600, 1480, 1460, 1360, 1275, 1180, 1060, 890, 855, 750, 680 cm^{-1}; NMR ($CDCl_3$) δ 0.24–0.40 (6 H, CH_2CH_3), 0.98–1.16 (4 H, CH_2CH_3), 1.28–1.34 (18 H, *t*-Bu), 2.17 (3 H, SMe), 2.52–3.24 (6 H, CH_2CHSMe and CH_2CH_2), 4.04–4.22 (1 H, CH_2CHSMe), 7.10–7.78 (4 H, A H). Anal. Calcd for $C_{29}H_{42}S$: C, 82.40; H, 10.02. Found: C, 82.34; H, 10.06.

Preparation of Sulfonium Salt (12a). A solution of 1.51 g (3.83 mmol) of a mixture of isomers **11a** in 10 mL of dichloromethane was added with stirring to a suspension of 2.1 g of dimethoxycarbonium tetrafluoroborate in 5 mL of dichloromethane that was held at −30 °C under nitrogen. The mixture was allowed to warm to room temperature and was stirred an additional 4 h. Then, 40 mL of ethyl acetate was added, the mixture was stirred, and the solvent was decanted. Fresh ethyl acetate (20 mL) was added to the oily residue and the solution was stirred for 2 h more. The resulting crystalline precipitate was collected and dried, giving 1.2 g (60.6%) of **12a**: colorless crystals; mp 267–268 °C dec; IR (KBr) 3040, 2960, 1600, 1480, 1460, 1435, 1360, 1280, 1185, 1050, 885, 790, 720 cm^{-1}; NMR (Me_2SO-d_6 δ 0.60–0.63 (6 H, Me), 1.25–1.28 (18 H, *t*-Bu), 2.60–3.08 (6 H, CH_2CH-$S^+<$ and CH_2CH_2), 3.32 (6 H, $^+SMe_2$), 4.56–4.72 (1 H, $-CH-S^+<$), 7.20–7.35 (4 H, Ar H).

Sulfonium salt **12b** was obtained in 65% yield by the same method: colorless crystals; mp 265–267 °C; IR (KBr) 3040, 2960, 1585, 1470, 1445, 1420, 1355, 1265, 1040, 920, 880, 860 cm^{-1}; NMR (Me_2SO-d_6) δ 0.20–0.40 (6 H, CH_2CH_3), 1.00–1.23 (4 H, CH_2CH_2), 3.38 (6 H, $^+SMe_2$), 4.68–4.88 (1 H, $-CH-S^+<$), 7.16–7.31 (4 H, Ar H).

Hofmann Elimination of 12a To Give 5,13-Di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophan-1-ene (13a). To a solution of 474 mg (4.23 mmol) of potassium *tert*-butoxide in 25 mL of tetrahydrofuran was added with stirring 1.2 g (2.42 mmol) of **12a**. After the mixture was stirred at room temperature under nitrogen for 4 h, benzene was added and the mixture was acidified by the addition of dilute aqueous hydrochloric acid. The organic layer was separated, washed with water, dried, and concentrated. The residue was recrystallized from methyl alcohol to give 740 mg (88.4%) of **13a**: pale yellow needles (MeOH); mp 210–211 °C; IR (KBr) 3040, 2940, 1580, 1460, 1385, 1335, 1275, 1180, 875, 850, 780, 750, 700 cm^{-1}; NMR ($CDCl_3$) δ 0.71 (6 H, s), 1.28 (18 H, s), 2.50, 2.87 (4 H, A_2B_2 pattern, J = 8 Hz), 6.57 (2 H, s), 6.82 (2 H, d, J = 2 Hz), 6.96 (2 H, d, J = 2 Hz); mass spectrum, m/e 346 (M^+). Anal. Calcd for $C_{26}H_{34}$: C, 90.11; H, 9.89. Found: C, 89.89; H, 9.74.

Compound **13b** was obtained in 63.2% yield in the same manner: pale brown prisms (MeOH); mp 220–221 °C; IR (KBr) 3040, 2940, 1575, 1460, 1440, 1355, 1275, 1180, 880, 850, 780, 710 cm^{-1}; NMR ($CDCl_3$) δ 0.32–0.64 (6 H, m), 1.27 (18 H, s), 1.45–1.65 (4 H, m), 2.44–2.92 (4 H, m), 6.53 (2 H, s), 6.77 (2 H, d, J = 2 Hz), 6.92 (2 H, d, J = 2 Hz); mass spectrum m/e 374 (M^+). Anal. Calcd for $C_{28}H_{38}$: C, 89.78; H, 10.23. Found: C, 89.50; H, 10.26.

Wittig Rearrangement of 16 To Give 17. The following experimental procedure was applied in all cases. To a stirred solution of 6 mmol of **16**[13] in 30 mL of dry tetrahydrofuran under nitrogen was added 9 mL of a 15% hexane solution of *n*-butyllithium (14.4 mmol) with ice cooling. After the solution was stirred for 10 min at room temperature, 1.89 mL (30 mmol) of methyl iodide was added to the reaction mixture. The reaction mixture was worked up by addition of H_2O and CH_2Cl_2. After the dichloromethane extract was washed with water, dried, and concentrated, the products were purified by chromatography on silica gel.

17a: colorless crystals; mp 259–263 °C; IR (KBr) 3040, 2960, 1590, 1480, 1450, 1360, 1270, 1260, 1235, 1090, 1025, 880, 825, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.6–1.0 (6 H, CH_3), 1.29–1.35 (18 H, $C(CH_3)_3$], 2.15 (6 H, s, SCH_3), 2.65–2.83 (2 H, CH_2), 3.10–3.32 (2H, CH_2), 4.00–4.17 (2 H, CH), 7.20–7.90 (4 H, Ar H). Anal. Calcd for $C_{28}H_{40}S_2$: C, 76.30; H, 9.15. Found: C, 76.04; H, 9.21.

17b: colorless crystals; mp 185–195 °C; IR (KBr) 3040, 2960, 1590, 1470, 1450, 1360, 1265, 1230, 1200, 1050, 995, 890, 840, 740 cm^{-1}; NMR ($CDCl_3$) δ 0.24–0.43 (6 H, CH_2CH_3), 0190–1.30 (4 H, CH_2CH_3), 1.30–1.36 [18 H, $C(CH_3)_3$], 2.17 (6 H, s, SCH_3), 2.65–2.83 (2 H, CH_2), 3.07–3.27 (2 H, CH_2), 4.07–4.25 (2 H, CH), 7.15–7.87 (4 H, Ar H). Anal. Calcd for $C_{30}H_{44}S_2$: C, 76.86; H, 9.46. Found: C, 77.02; H, 9.80.

17c: colorless crystals; mp 165–200 °C; IR (KBr) 3040, 2960, 1590, 1470, 1450, 1360, 1270, 1235, 1080, 980, 880, 830, 735 cm^{-1}; NMR ($CDCl_3$) δ 0.37–0.53 (6 H, $CH_2CH_2CH_3$), 0.60–1.16 (8 H, $CH_2CH_2CH_3$), 1.30–1.36 [18 H, $C(CH_3)_3$], 2.16 (6 H, s, SCH_3), 2.66–2.78 (2 H, CH_2), 3.06–3.25 (2 H, CH_2), 4.08–4.25 (2 H, CH), 7.14–7.86 (4 H, Ar H). Anal. Calcd for $C_{32}H_{48}S_2$: C, 77.35; H, 9.74. Found: C, 77.40; H, 9.75.

17d: colorless crystals; mp 235–242 °C; IR (KBr) 3030, 2940, 2900, 1585, 1460, 1445, 1350, 1265, 1230, 985, 880, 830, 735 cm^{-1}; NMR ($CDCl_3$) δ 0.57–1.12 (18 H, $CH_2CH_2CH_2CH_3$), 1.30 (18 H, s, *t*-Bu), 2.13 (6 H, s, SMe), 2.62–2.73 (2 H, CH_2), 3.04–3.20 (2 H, CH_2), 4.00–4.16 (2 H, CH), 7.10 (2 H, d, J = 2.5 Hz), 7.70 (2 H, d, J = 2.5 Hz). Anal. Calcd for $C_{34}H_{52}S_2$: C, 77.80; H, 9.99. Found: C, 77.42; H, 10.06.

Preparation of Sulfonium Salt (18). Typical Procedure. A solution of 2.78 g (5.85 mmol) of the mixture of isomers **17a** in 20 mL of dichloromethane was added with stirring to a suspension of 6.5 g (40 mmol) of dimethoxycarbonium tetrafluoroborate in 10 mL of dichloromethane held at −30 °C under nitrogen. The mixture was allowed to warm to room temperature and was stirred for an additional 4 h. Then to the reaction mixture was added 40 mL of ethylacetate, the mixture was stirred, and the solvent was decanted. Fresh ethyl acetate (20 mL) was added to the oily residue and the solution was stirred for 2 h more. The resulting crystalline precipitate was collected and dried, giving 3.56 g (94.4%) of **18a**: colorless crystals; mp 245–248 °C; IR (KBr) 3040, 2960, 1600, 1480, 1430, 1050, 890, 815, 800, 715 cm^{-1}; NMR (Me_2SO-d_6) δ 0.62–0.88 (6 H, CH_3), 1.30 (18 H, *t*-Bu), 2.96 (6 H, s, $^+SMe_2$), 3.08–3.50 (4 H, CH_2), 3.39 (6 H, s, $^+SMe_2$), 7.43–7.64 (4 H, Ar H).

Compounds **18b**, **18c**, and **18d** were also obtained in this manner from **17b**, **17c**, and **17d**, respectively. **18b**: colorless crystals; mp >300 °C; IR (KBr) 3040, 2960, 1600, 1480, 1430, 1360, 1275, 1180, 1040, 885,

865, 800, 740 cm^{-1}; NMR (Me_2SO-d_6) δ 0.20–0.48 (6 H, CH_2CH_3), 1.11–1.24 (4 H, CH_2CH_3), 1.33–1.35 (18 H, *t*-Bu), 2.93 (6 H, s, $^+SMe_2$), 3.08–3.50 (4 H, CH_2), 3.33 (6 H, s, $^+SMe_2$), 4.68–4.95 (2 H, CHS^+Me_2), 7.28–7.58 (4 H, ArH).

18c: colorless crystals; mp >300 °C; IR (KBr) 3040, 2960, 1600, 1480, 1430, 1360, 1280, 1040, 930, 820, 730 cm^{-1}; NMR (Me_2SO-d_6) δ 0.40–0.80 (10 H, $CH_2CH_2CH_3$), 0.96–1.30 (4 H, $CH_2CH_2CH_3$), 1.35 (18 H, *t*-Bu), 2.92 (6 H, $^+SMe_2$), 3.07–3.46 (4 H, CH_2), 3.32 (6 H, $^+SMe_2$), 4.64–4.92 (2 H, CHS^+Me_2), 7.28–7.59 (4 H, Ar H).

18d: colorless crystals; mp 283–285 °C dec; IR (KBr) 3020, 2950, 2850, 1590, 1460, 1420, 1360, 1040, 875, 815, 720 cm^{-1}; NMR (Me_2SO-d_6) δ 0.20–1.17 (18 H, $CH_2CH_2CH_2CH_3$), 1.31–1.33 (18 H, *t*-Bu), 2.92 (6 H, s, $^+SMe_2$), 3.07–3.43 (4 H, CH_2), 3.38 (6 H, s, $^+SMe_2$), 4.63–4.84 (2 H, CHS^+Me_2), 8.04–9.58 (4 H, Ar H).

Hofmann Elimination of 18 To Give 20. Typical Procedure. To a solution of 2.13 g (19.04 mmol) of potassium *tert*-butoxide in 100 mL of tetrahydrofuran was added with stirring 3.50 g (5.44 mmol) of **18a**. After the reaction mixture was stirred at room temperature under nitrogen for 4 h, benzene was added and the mixture was acidified by the addition of dilute aqueous hydrochloric acid. The organic layer was separated, washed with water, dried, and concentrated. The residue was chromatographed on silica gel with petroleum ether as the eluant. The deep green crystals isolated from the elute were recrystallized from hexane to give 1.81 g (96.8%) of **20a**: dark green needles (hexane); mp 203–204 °C; IR (KBr) 3040, 2960, 1600, 1450, 1380, 1360, 1345, 1230, 875 cm^{-1}; NMR ($CDCl_3$) δ −4.06 (6 H, s), 1.70 (18 H, s), 8.20 (4 H, s), 8.52 (4 H, s); mass spectrum, *m/e* 344 (M^+). Anal. Calcd for $C_{26}H_{32}$: C, 90.14; H, 9.35. Found: C, 90.64; H, 9.36.

Compounds **20b**, **20c**, and **20d** were also obtained in this manner. **20b**: dark brown prisms; mp 155–157 °C; IR (KBr) 3040, 2960, 1590, 1450, 1360, 1220, 950, 880, 780 cm^{-1}; NMR ($CDCl_3$) δ 3.66 (4 H, q, *J* = 7.5 Hz), 1.74 (6 H, t, *J* = 7.5 Hz), 1.66 (18 H, s), 8.39 (4 H, s), 8.52 (4 H, s); mass spectrum *m/e* 372 (M^+).

20c: dark brown prisms; mp 155–157 °C; IR (KBr) 3040, 2960, 1590, 1450, 1350, 1220, 1110, 1020, 875, 780, 695 cm^{-1}; NMR ($CDCl_3$) δ −3.81∼−3.64 (4 H, m), −1.74∼−1.34 (4 H, m), −0.56 (6 H, t, *J* = 7.5 Hz), 1.66 (18 H, s), 8.36 (4 H, s), 8.50 (4 H, s); mass spectrum, *m/e* 400 (M^+). Anal. Calcd for $C_{30}H_{40}$: C, 89.94; H, 10.06. Found: C, 89.87; H, 9.97.

20d: deep brown prisms; mp 136–137 °C; IR (KBr) 3020, 2940, 1585, 1445, 1345, 1220, 1090, 870, 780, 690 cm^{-1}; NMR ($CDCl_3$) δ −3.78∼−3.62 (4 H, m), −1.74∼−1.41 (4 H, m), −0.42∼−0.13 (4 H, m), 0.0 (6 H, t, *J* = 7 Hz), 1.65 (18 H, s), 8.36 (4 H, s), 8.50 (4 H, s); mass spectrum, *m/e* 428 (M^+). Anal. Calcd for $C_{32}H_{44}$: C, 89.65; H, 10.35. Found: C, 89.45; H, 10.39.

Bromination of 13 with Bromine. Typical Procedure. To a solution of 200 mg (0.578 mmol) of **13a** in 100 mL of carbon tetrachloride was added 0.56 g (3.48 mmol) of bromine in 20 mL of carbon tetrachloride with stirring at room temperature. After 1 min, the reaction mixture was poured into a large amount of ice water. The organic layer was extracted with dichloromethane. The dichloromethane solution was dried over Na_2SO_4 and evaporated in vacuo, and the residue was chromatographed on a silica gel with hexane as the eluant. The deep green crystals isolated from the elute were recrystallized from hexane and gave 335 mg (87.8%) of **2a**: green prisms (hexane); mp 228–230 °C; IR (KBr) 3040, 2960, 1575, 1460, 1360, 1330, 1220, 1120, 965, 900, 860, 780 cm^{-1}; NMR ($CDCl_3$) δ −3.50 (6 H, s), 1.71 (18 H, s), 8.96 (4 H, s); mass spectrum, *m/e* 660 (M^+). Anal. Calcd for $C_{26}H_{28}Br_4$: C, 47.30; H, 4.28. Found: C, 47.75; H, 4.39.

Compound **2b** was also obtained in this manner in 95.1% yield: deep brown prisms (hexane); mp 165–166 °C; IR (KBr) 3040, 2960, 1570, 1450, 1350, 1300, 1250, 1200, 1120, 985, 870, 820, 785 cm^{-1}; NMR (CDCl) δ −3.08 (4 H, q, *J* = 7.5 Hz), −1.53 (6 H, t, *J* = 7.5 Hz), 1.66 (18 H, s), 9.00 (4 H, s); mass spectrum, *m/e* 688 (M^+). Anal. Calcd for $C_{28}H_{32}Br_4$: C, 48.65; H, 4.69. Found: C, 48.76; H, 4.63.

Reaction of 13a with *N*-Bromosuccinimide. A mixture of 200 mg (0.58 mmol) of **13a**, 1.02 g (5.72 mmol) of *N*-bromosuccinimide, and 80 mg of benzoyl peroxide in 200 mL of carbon tetrachloride was refluxed for 1 h. After the reaction mixture cooled, it was treated with 10% sodium hydroxide solution and water, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel with hexane as the eluant. The deep green crystals isolated from the elute were recrystallized from hexane to give 300 mg (78.6%) of **2a**.

Reaction of 20a with *N*-Bromosuccinimide. A mixture of 100 mg (0.29 mmol) of **20a**, 214 mg (1.2 mmol) of *N*-bromosuccinimide, and 15 mg of benzoyl peroxide in 300 mL of carbon tetrachloride was refluxed for 1 h. The reaction mixture was treated as described above to give 131 mg (69%) of **2a**.

Bromination of 20 with Bromine. (A) In the Absence of Iron Powder. Typical Procedure. To a solution of 100 mg (0.29 mmol) of **20a** in 50 mL of carbon tetrachloride was added a solution of 0.28 g (1.74 mmol) of bromine in 10 mL of carbon tetrachloride with stirring at room temperature. After 1 min, the reaction mixture was poured into a large amount of ice water. The organic layer was extracted with dichloromethane. The dichloromethane solution was dried over Na_2SO_4 and evaporated in vacuo, and the residue was chromatographed on silica gel with hexane as the eluant. The deep green crystals isolated from the elute were recrystallized from hexane to give 180 mg (94%) of **2a**.

Compounds **2b** and **2c** were also obtained in this manner.

2c: deep brown prisms; mp 188–189 °C; IR (KBr) 3040, 2960, 1575, 1460, 1330, 1200, 1120, 980, 870, 735, 715 cm^{-1}; NMR ($CDCl_3$) δ −3.26∼−3.08 (4 H, m), −1.55∼−1.16 (4 H, m), −0.40 (6 H, t, *J* = 7.5 Hz), 1.67 (18 H, s), 8.96 (4 H, s); mass spectrum, *m/e* 716 (M^+). Anal. Calcd for $C_{30}H_{36}Br_4$: C, 50.31; H, 5.07. Found: C, 50.29; H, 5.04.

(B) In the Presence of Iron Powder. Typical Procedure. To a solution of 100 mg (0.29 mmol) of **20a** and 100 mg of iron powder in 50 mL of carbon tetrachloride was added a solution of 0.28 g (1.74 mmol) of bromine in 10 mL of carbon tetrachloride with stirring at room temperature. After 4 h, the reaction mixture was poured into a large amount of ice water. The organic layer was extracted with dichloromethane. The dichloromethane extract was dried over Na_2SO_4 and evaporated in vacuo, and the residue was chromatographed on silica gel with hexane as the eluant. The colorless crystals isolated from the elute were recrystallized from hexane to give 180 mg (99%) of **27**. Compound **27** was also obtained from **20b** and **20c** in this manner.

Reaction of 2a with $FeBr_3$. To a solution of 100 mg (0.29 mmol) of **2a** in 50 mL of carbon tetrachloride was added 100 mg (0.338 mmol) of $FeBr_3$ with stirring at room temperature. After 4 h, the reaction mixture was poured into a large amount of ice water. The organic layer was extracted with dichloromethane. The dichloromethane solution was dried over Na_2SO_4 and evaporated in vacuo, and the residue was chromatographed on silica gel with hexane as the eluant. The colorless crystals isolated from the elute were recrystallized from hexane to give 97 mg of starting material **2a**.

Reaction of 2a with $FeCl_3$. To a solution of 200 mg (0.29 mmol) of **2a** in 50 mL of carbon tetrachloride was added 100 mg (0.598 mmol) of $FeCl_3$ with stirring at room temperature. After 4 h, the reaction mixture was treated as described above to give 86 mg of starting material **2a**.

Bromination of 28 with Bromine. To a solution of 50 mg (0.159 mmol) of **28** and a small amount of iron powder in 25 mL of carbon tetrachloride was added a solution of 0.14 g (0.875 mmol) of bromine in 5 mL of carbon tetrachloride with stirring at room temperature. After 4 h, the reaction mixture was treated as described above to give 79 mg (79%) of **27**.

Chlorination with Sulfuryl Chloride. Typical Procedure. To a solution of 100 mg (0.289 mmol) of **13a**, and 1.0 mL of sulfuryl chloride in 30 mL of carbon tetrachloride was added a small amount of boron trifluoride etherate at room temperature. The reaction mixture was refluxed for 15 min. After the reaction mixture cooled, it was poured into a large amount of ice water. The organic layer was extracted with dichloromethane. The dichloromethane solution was dried over Na_2SO_4 and evaporated in vacuo, and the residue was chromatographed on silica gel with hexane as the eluant. The deep green crystals isolated from the elute were recrystallized from hexane to give 73.9 mg (53.1%) of **29**: deep green plates (hexane); mp 235–237 °C; IR (KBr) 3040, 2960, 1580, 1460, 1365, 1340, 1240, 980, 920, 875, 680 cm^{-1}; NMR ($CDCl_3$) δ −3.44 (6 H, s), 1.71 (18 H, s), 8.88 (14 H, s); mass spectrum, *m/e* 482 (14), 484 (7) (M^+). Anal. Calcd for $C_{26}H_{28}Cl_4$: C, 64.75; H, 5.85. Found: C, 64.71; H, 5.82. Compound **29** was also obtained in 40% yield from **20a** in this manner.

Chlorination with Chlorine. Typical Procedure. Through a solution of 200 mg (0.58 mmol) of **13a** in 80 mL of carbon tetrachloride was passed chlorine with stirring at room temperature for 15 min. The reaction mixture was concentrated under reduced pressure to leave a residue that after solidification by addition of a small amount of hexane gave 252.4 mg (80%) of **30**: colorless needles (benzene); mp 222–226 °C dec; IR (KBr) 3040, 2960, 1540, 1470, 1450, 1220, 1160, 1095, 995, 940, 900, 875, 740 cm^{-1}; NMR ($CDCl_3$) δ 1.12 (6 H, s), 1.16 (18 H, s), 6.77 (4 H, s); mass spectrum, *m/e* 487 ($M^+ - C_4H_9$). Anal. Calcd for $C_{28}H_{34}Cl_6$: C, 56.45; H, 5.10. Found: C, 56.50; H, 4.95. Compound **30** was also obtained from **20a** and **29** in this manner.

Chlorination with Iodine Monochloride. Typical Procedure. To a solution of 200 mg (0.58 mmol) of **13a** in 80 mL of carbon tetrachloride was added a solution of 1.41 g (8.7 mmol) of iodine monochloride in 20 mL of carbon tetrachloride with stirring at room temperature. After 4 h, the reaction mixture was concentrated under reduced pressure and left a residue that after solidification by addition of a small amount of hexane gave 290 mg (91.9%) of **30**. Compound **30** was also obtained from **20a** and **29** in this manner.

Compound **31** was obtained from **13b** in the same manner: colorless prisms (hexane); mp 280–282 °C; IR (KBr) 3040, 2980, 1600, 1560, 1465, 1455, 1360, 1245, 1060, 990, 870, 720, 665 cm^{-1}; NMR ($CDCl_3$) δ 1.60 (18 H, s), 8.71 (4 H, s); mass spectrum, *m/e* 452 (M^+). Anal. Calcd for $C_{24}H_{22}Cl_4$: C, 63.74; H, 4.90. Found: C, 63.50; H, 4.88.

Reaction with Iodine. Typical Procedure. A solution of 100 mg (0.289 mmol) of **13a** and 441 mg (1.74 mmol) of iodine in 30 mL benzene was refluxed for 48 h. The reaction mixture was washed with 10% sodium thiosulfate solution and then with water. The benzene solution was dried over Na_2SO_4 and evaporated in vacuo. The residue was chromatographed on silica gel with hexane–benzene 1:1 as eluant. Colorless crystals (79.3 mg, 87.1%) were isolated from the eluate, and the ratio of **28** to **34** was determined to be 60:40 by its NMR spectrum. Similar reactions of **20a–c** afforded **28** in good yield. In the case of **20c**, the reaction mixture was analyzed by GC to detect formation of **38**.

Reaction of the Mixture (28 + 34) with DDQ. A solution of 79.3 mg of the mixture of **28** and **34** and 50 mg of DDQ in 50 mL of toluene was refluxed for 4 h. After the reaction mixture was cooled and concentrated, the residue was extracted and chromatographed on silica gel with hexane:benzene 1:1 as the eluant to give 70 mg (77%) of **28** as colorless prisms. **28**: pale yellow prisms (hexane); mp 210–212 °C; IR (KBr) 3040, 2960, 1600, 1440, 1355, 1220, 920, 875, 800, 715 cm^{-1}; NMR ($CDCl_3$) δ 1.48 (18 H, s), 7.87 (4 H, s), 8.14 (4 H, s); mass spectrum, *m/e* 314 (M^+). Anal. Calcd for $C_{24}H_{26}$: C, 91.67; H, 8.33. Found: C, 91.67; H, 8.41.

Reaction of the Mixture (28 + 34) with Iodine. A solution of 100 mg of the mixture of **28** and **34** and 441 mg (1.74 mmol) of iodine in 30 mL of benzene was refluxed for 48 h. The reaction mixture was treated as described above to give 95 mg (**28** and **34**) of colorless crystals, whose ratio was not exchanged. The GC analysis of the reaction mixture of **20c** with iodine showed the formation of *n*-propyl iodide (**38**). Although **2a** was treated with iodine under the same conditions as described above, no product formed.

Registry No. 2a, 76447-51-3; **2b**, 76466-35-8; **2c**, 76626-78-3; **8b**, 65276-10-0; **9a**, 67691-33-2; **9b**, 81688-07-5; **10a**, 81688-08-6; **10b**, 81688-09-7; **11a**, isomer 1, 81688-10-0; **11a**, isomer 2, 81738-73-0; **11b**, isomer 1, 81688-11-1; **11b**, isomer 2, 81738-74-1; **12a**, isomer 1, 81688-13-3; **12a**, isomer 2, 81738-76-3; **12b**, isomer 1, 81688-15-5; **12b**, isomer 2, 81738-78-5; **13a**, 81688-16-6; **13b**, 81688-17-7; **16a**, 76447-66-0; **16b**, 76447-68-2; **16c**, 76447-69-3; **16d**, 76447-70-6; **17a**, 76446-96-3; **17b**, 76446-97-4; **17c**, 76446-98-5; **17d**, 76466-30-3; **18a**, 81688-84-8; **18b**, 81688-86-0; **18c**, 81688-88-2; **18d**, 81688-90-6; **20a**, 76626-75-0; **20b**, 76626-76-1; **20c**, 76626-77-2; **20d**, 81555-09-1; **27**, 76466-34-7; **28**, 24300-91-2; **29**, 76626-79-4; **30**, 81688-18-8; **31**, 81688-19-9; **34**, 69618-61-7; chloromethyl methyl ether, 107-30-2.

Metacyclophanes and Related Compounds. 7. Preparation and Reduction of [2.2]Metacyclophanequinone[1]

Masashi Tashiro,*[2] Keizo Koya,[2b] and Takehiko Yamato[2]

Contribution from the Research Institute of Industrial Science, and the Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Sakamoto, Kasuga, Kasuga-shi, Fukuoka 816, Japan. *Received October 19, 1981*

Abstract: Two preparative methods for [2.2]metacyclophanequinone (**7a**) from 8,16-dimethoxy-5,13-di-*tert*-butyl[2.2]-metacyclophane (**5**) are described. The partially hydrogenated compound 5,8-dihydroxy[2]-(2,6)-benzoquionono[2]metacyclophane (**18**) was prepared from **7a**. It was found that compound **18** is colorless as a solid but is colored in solution. Some discussions of the above phenomena are also included in this paper.

Although many [2.2]paracyclophanequinones[3–9] and [3.3]-metacyclophanequinone[10] have been prepared, [2.2]metacyclophanequinones have not yet been synthesized.

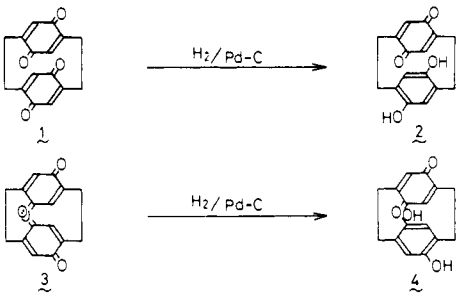
We have previously reported that[11] 8,16-dimethoxy-5,13-di-*tert*-butyl[2.2]metacyclophane (**5**) was easily prepared from anisole in only six steps. This compound (**5**) seems to be a suitable starting material for the preparation of [2.2]metacyclophanequinone.

Staab and Rebafka[6,7] reported that the partial hydrogenation of [2.2]paracyclophanequinones **1** and **3** afforded the interesting intramolecular quinhydrones **2** and **4** as black and dark violet crystals, respectively.

We undertook the present work in order to prepare the title compound and to obtain some information about its chemical nature.

Results and Discussion

When **5** was treated with BBr_3 in benzene at room temperature for 24 h, a mixture of **6a** and **6b** (1:1) was obtained with a total yield of 70%. The separation of **6a** and **6b** could be carried out by fractional recrystallization of the mixture with hexane. However, **6a** was exclusively obtained by the prolonged reaction (155 h) in 86% yield.



Oxidation of **6a** with $Tl(OCOCF_3)_3$[12–14] in CF_3COOH afforded the desired [2.2]metacyclophanequinone (**7a**) in 53% yield. Similar oxidation of **6b** gave 5-*tert*-butyl-8-methoxy[2]-(2,6)-benzoquinono[2]metacyclophane (**7b**) in 70% yield (Scheme I, route A). Another preparative route (route B) of **7a** from **6a** is shown in Scheme II.

We have previously reported that[15] the $AlCl_3$–CH_3NO_2 catalyzed trans-*tert*-butylation of 8,16-dimethyl-5,13-di-*tert*-butyl-[2.2]metacyclophane (**8**) in benzene afforded 8,16-dimethyl-[2.2]metacyclophane (**9c**) together with *tert*-butylbenzene (**10**).

(1) (a) A part of this paper was published as a preliminary communication: Tashiro, M.; Yamato, T. *Chem. Lett.* **1979**, 595. (b) Part 4: Tashiro, M.; Yamato, T. *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) (a) Research Institute of Industrial Sciences. (b) Department of Molecular Science and Technology.
(3) Cram, D. J.; Day, A. C. *J. Org. Chem.* **1966**, *31*, 1227.
(4) Rebafka, W.; Staab, H. A. *Angew. Chem.* **1973**, *85*, 831.
(5) Rebafka, W.; Staab, H. A. *Angew. Chem.* **1974**, *86*, 234.
(6) Staab, H. A.; Rebafka, W. *Chem. Ber.* **1977**, *110*, 3333.
(7) Staab, H. A.; Rebafka, W. *Chem. Ber.* **1977**, *110*, 3351.
(8) Vogler, H.; Ege, G.; Staab, H. A. *Tetrahedron* **1975**, *31*, 2441.
(9) Staab, H. A.; Herz, C. P.; Henke, H. W. *Tetrahedron Lett.* **1974**, 4393.
(10) Staab, H. A.; Herz, C. P.; Döhling, A. *Tetrahedron Lett.* **1979**, 791.
(11) Tashiro, M.; Yamato, T. *Chem. Lett.* **1979**, 595.
(12) McKillop, A.; Fowler, J. S.; Zelesko, M. J.; Hunt, J. D. *Tetrahedron Lett.* **1969**, 2423.
(13) McKillop, A.; Swann, B. P.; Taylor, E. C. *Tetrahedron* **1970**, *26*, 4031.
(14) Shinmyozu, T.; Inazu, T.; Yoshino, T. *Chem. Lett.* **1978**, 1319.
(15) Tashiro, M.; Yamato, T. *Synthesis* **1978**, 435.

0002-7863/82/1504-3707$01.25/0