Synthesis of 5-*tert*-butyl-8,12,14-trimethyl- and 5-*tert*-butyl-8,12,14,16-tetramethyl[2.2]metacyclophane and their treatment with Lewis acids in benzene

Tomoe Shimizu, Katsuhiko Hida and Takehiko Yamato*

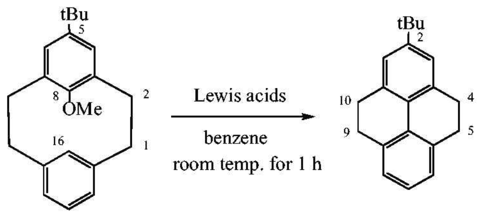
Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi 1, Saga-shi, Saga 840-8502, Japan

Treatment of 5-*tert*-butyl-8,12,14,16-tetramethyl[2.2]MCP with $AlCl_3$-$MeNO_2$ in benzene led to trans-*tert*-butylation to afford 8,12,14,16-tetramethyl[2.2]MCP in good yield along with *tert*-butylbenzene. On the other hand, the same treatment of 5-*tert*-butyl-8,12,14-trimethyl[2.2]MCP led to transannular cyclisation reaction and isomerisation reaction to afford the corresponding strainless 2-*tert*-butyl-3a,6,8-trimethyl-3,3a,4,5,9,10-hexahydropyrene in good yield.

Keywords: cyclophanes, trans-*tert*-butylation, Lewis acid, isomerisation reaction, strain, pentahydropyrene

[2.2]Metacyclophanes ([2.2]MCP) are distinguished by their abnormal physical and chemical properties. Several qualitative explanations have been given for the origin of the abnormality: π-electron repulsion between the benzene rings,[1–7] hyperconjugation with the bridging C–C bonds,[8] nonplanarity of the benzene rings,[9] and transannular π–π interaction between the benzene rings.[10] Boschi and Schmidt[10] suggested from the ionisation energies and transannular π–π resonance integrals of [2.2]MCP that transannular π–π interaction may take place between C-8 and C-16. Later on, Sato and Takemura[11] confirmed the transannular π–π interaction of [2.2]MCPs by comparison of the charge-transfer bands of a cyclophane molecule with those of the corresponding acyclic models. [2.2]MCP showed only a moderate increase reflecting decreased overlap between the two aryl groups, compared with the large enhancement in the π-basicity in the lower membered paracyclophanes. However, only the charge transfer bands of 8,16-unsubstituted [2.2]MCP and its alkyl derivatives were investigated.

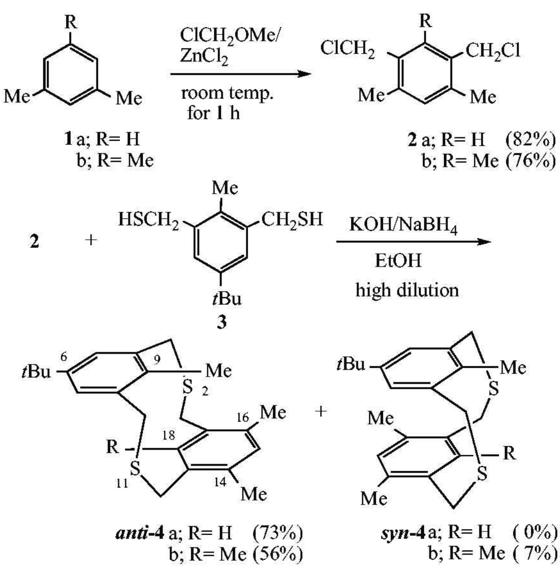
Owing to electronic interaction between the two benzene rings, the proximity of 8,16-positions, and the considerable strain energy, [2.2]MCP is prone to give transannular reaction products under electrophilic reaction conditions.[1,12] In fact, we have reported[13] the Lewis acid-induced transannular cyclisation reaction of 5-*tert*-butyl-8-methoxy[2.2]MCP to give 2-*tert*-butyl-4,5,9,10-tetrahydropyrene with remarkable ease and with high selectivity (Scheme 1). This novel transannular reaction might be attributed to the presence of methoxy group at 8-position, which increase the π-electron density of the benzene ring. These reactions are quite different from those of 8,16-unsubstituted [2.2]MCPs, which give 1,2,3,3a,4,5-hexahydropyrene and might be attributed to the presence of the methoxy group at a position 8, which would increase the difference of the π-electron densities among the two benzene rings. Thus there is substantial interest in investigating the effects of substituents at the positions 8 and 16 on the treatment of [2.2]MCPs with Lewis acids. We report here on the preparation of 5-*tert*-butyl-8,12,14-trimethyl- and 5-*tert*-butyl-8,12,14,16-tetramethyl[2.2]MCP using the sulfur method and their treatment with Lewis acids in benzene.



Scheme 1

Results and discussion

The preparative route of 9,14,16-trimethyl- and 9,14,16,18-tetramethyl-5-*tert*-butyl-2,11-dithia[3.3]MCPs **4a** and **4b** is shown in Scheme 2. 1,5-Bis(chloromethyl)-2,4-dimethylbenzene **2a** and 1,3-bis(chloromethyl)-2,4,6-trimethylbenzene **2b** were prepared by chloromethylation of *m*-xylene **1a** and 1,3,5-trimethylbenzene **1b** with chloromethyl methyl ether in the presence of $ZnCl_2$ as following to the reported procedure.[14–18] The preparation of 4-*tert*-butyl-2,6-bis(sulfanylmethyl)toluene **3** has already been described.[19,20] The cyclisation of bis(chloromethyl)benzenes **2** and 4-*tert*-butyl-2,6-bis(sulfanylmethyl)toluene **3** was carried out under highly diluted conditions in 10% ethanolic KOH in the presence of a small amount of $NaBH_4$, giving the desired 2,11-dithia[3.3]MPCPs **4a** and **4b** in 73 and 63% yields, respectively.[20–24] The ^1H NMR spectrum of **4b** shows six kinds of methyl protons, each as a singlet. By careful column chromatography (silica gel, Wako C-300), two conformers, ***anti*-4b** and ***syn*-4b**, are separated. They are thermally stable and do not interconvert at 150 °C in DMSO solution and at 400 °C in the solid state.



Scheme 2

* Correspondent. E-mail: yamatot@cc.saga-u.ac.jp

The structures of **4** have been elucidated by elemental analyses and spectral data. For instance, the mass spectral data for *anti*-**4b** (M^+ = 384) strongly supports cyclic dimeric structure. The ^{1}H NMR spectrum (in $CDCl_3$) of *anti*-**4b** exhibits two sets of doublets at δ 3.59, 3.69 ppm (J = 14.5 Hz) and δ 3.62, 3.80 ppm (J = 13.5 Hz) for the CH_2SCH_2 methylene protons and two singlets for the internal methyl groups at an upfield shift δ = 1.08 and 1.33 ppm from toluene (δ = 2.31 ppm) due to the ring current of the opposing aromatic ring.[20,22,25–30] With increasing temperature in DMSO-d_6, the doublets do not coalesce below 150 °C, respectively, and the energy barriers of flipping are both above 25 kcal mol^{-1}. These observations strongly suggest that the compound *anti*-**4b** adopts rigid *anti*-conformation. In contrast, the internal methyl protons of *syn*-**4b** is observed at δ 2.46 and 2.47 ppm. Further, the aryl hydrogens at 15-proton and 5,7-positions can clearly be seen to be shielded at δ 6.29 and 6.88 ppm by the adjacent ring, a common consequence of a face-to-face benzene ring[26–35] Also the *tert*-butyl protons was observed at higher field, δ 1.18 ppm compared to that of the *anti*-**4b** at δ 1.35 ppm due to the strong shielding effect of the benzene ring. These observations strongly suggest that the compound *syn*-**4b** adopts a *syn*-conformation. Similarly, the assignment of structures for the *anti* conformer of *anti*-**4a** was readily apparent from their ^{1}H NMR spectra. The internal aromatic proton at the 18-position was observed at a higher field, δ 5.29 ppm and two sets of doublets at δ 3.40, 3.63 ppm (J = 15.0 Hz) and δ 3.80, 3.98 ppm (J = 13.7 Hz) for the CH_2SCH_2 methylene protons. These observations strongly support the rigid *anti*-[3.3]MCP structure *anti*-**4a**. However, the internal methyl protons appeared at δ 2.12 ppm different from those observed in 9,18-dimethyl-2,11-dithia[3.3]MCP *anti*-**4b** (δ 1.08 and 1.33 ppm). No ring current effects of the opposing benzene were observed. These findings might be attributable to the different structure between *anti*-**4a** and *anti*-**4b**.

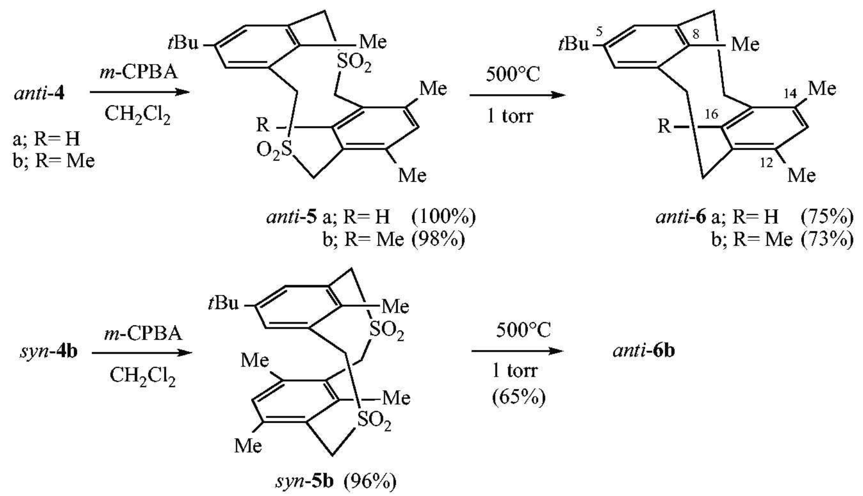
Oxidation of *anti*-**4a**, *anti*-**4b** and *syn*-**4b** with *m*-chloroperbenzoic acid in methylene dichloride afforded the corresponding bissulfone *anti*-**5a**, *anti*-**5b** and *syn*-**5b** in quantitative yield. Pyrolysis of *anti*-**5a** and *anti*-**5b** under reduced pressure (1 torr) at 500 °C was carried out according to the reported method[20–24] to afford the corresponding desired [2.2]MCPs *anti*-**6a** and *anti*-**6b** in 75 and 73% yields, respectively. Interestingly, a similar result was obtained in the case of pyrolysis of *syn*-**5b** to afford *syn*-**6b** carried out under the same reaction conditions. *syn*-*anti*-isomerisation was observed under the reaction conditions used (Scheme 3). These findings strongly suggest that the ring inversion to the thermodynamically more stable *anti*-conformation is possible in the *syn*-9,14,16,18-tetramethyldithia[3.3]MCP tetraoxide *syn*-**5b**.

The structures of **6a** and **6b** were established on the basis of the base peak molecular ions in their mass spectra, and they were assigned the *anti*-stereochemistry *anti*-**6** on the basis of their ^{1}H NMR, since the 8-methyl protons of **6a** and **6b** appears at around δ 0.48–0.52 ppm,[1,20–26] attributable to be shielded by the opposite ring. The similar upper field shift of the internal aromatic proton at 16-position of *anti*-**6a** was observed at δ 3.63 ppm. These observations strongly suggest that compounds **6a** and **6b** both adopt rigid *anti*-conformations.

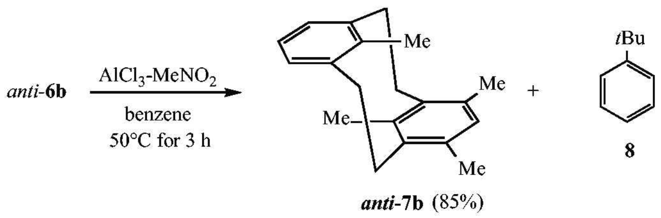
The Lewis acids catalysed trans-*tert*-butylation of *anti*-**6b** in benzene was carried out under various conditions. The $AlCl_3$–$MeNO_2$-catalysed trans-*tert*-butylation reaction of *anti*-**6b** at 50 °C for 3 h afforded the desired 8,12,14,16-tetramethyl[2.2]MCP *anti*-**7b** in 85% yield along with *tert*-butylbenzene **8** (Scheme 4), but titanium tetrachloride was needed in much larger amounts and with longer reaction times than $AlCl_3$-$MeNO_2$. However, no trans-*tert*-butylation of *anti*-**6b** was observed with $SnCl_4$ as the catalyst.

On the other hand, treatment of 5-*tert*-butyl-8,12,14-trimethyl[2.2]MCP *anti*-**6a** with $AlCl_3$–$MeNO_2$ in benzene under the conditions of 50 °C for 3 h led to transannular cyclisation reaction and isomerisation reaction to afford the corresponding strainless 2-*tert*-butyl-3a,6,8-trimethyl-3,3a,4,5,9,10-hexahydropyrene **9** in 85% yield (Scheme 5). It was also found that there was no formation of *tert*-butylbenzene **8** under the reaction conditions used. This result suggests that the present transannular cyclisation reaction and isomerisation reaction might be much faster than trans-*tert*-butylation. Indeed, treatment of compound **9** with $AlCl_3$–$MeNO_2$ in benzene under the same reaction conditions did not afford the trans-*tert*-butylated product and *tert*-butylbenzene **8**. Only the recovery of the starting compound **9** resulted. Thus, a different reaction was observed in the treatment of 8-methyl[2.2]MCPs depending on the substituent at 16-position.

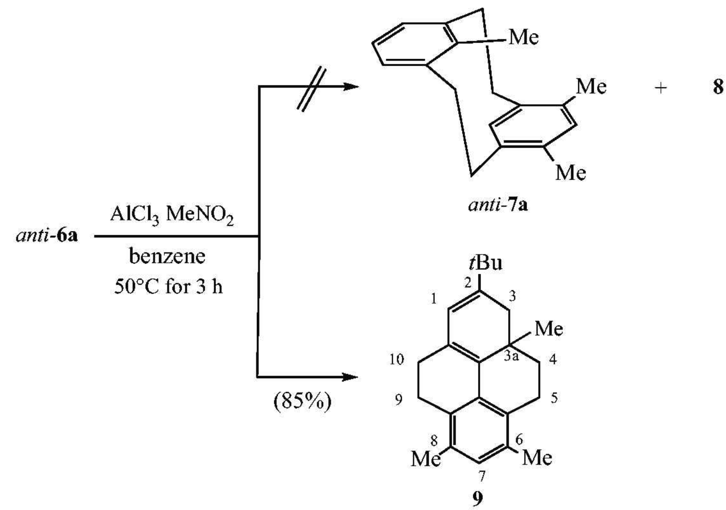
It is concluded that the above present transannular cyclisation reaction and isomerisation reaction of 8,12,14-trimethyl[2.2]MCP *anti*-**6a** to form 2-*tert*-butyl-3a,6,8-trimethyl-3,3a,4,5,9,10-hexahydropyrene **9** is strongly affected



Scheme 3



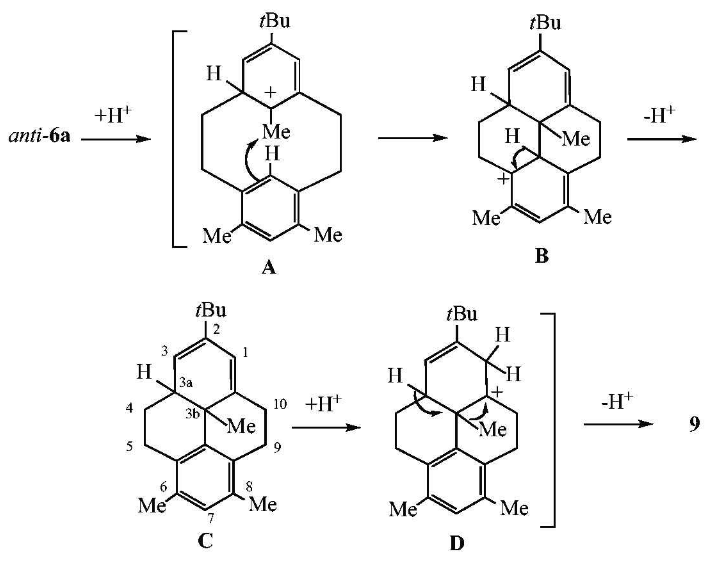
Scheme 4



Scheme 5

by the bulkiness of the methyl group in the 8-position which increases the strain in a molecule like the methoxy group, but prevents the reversal of the steps between intermediates **C** and **D** in Scheme 6. This result is quite different from the Lewis acid-induced transannular reaction of 8-methoxy[2.2]MCPs to give 4,5,9,10-tetrahydropyrene in which the good leaving-group ability of the methoxy group, particularly when complexed by the Lewis acids, may be important.[13]

A mechanism for the formation of **9** from *anti*-**6a** is proposed in Scheme 6. Cram *et al.* reported[36–38] the $AlCl_3$-catalysed isomerisation of [2.2]paracyclophane to the less strained [2.2]metaparacyclophane along with transannular isomerisation products, 1,2,2a,3,4,5-hexahydropyrene and [2.2]MCP. In the case of *anti*-8-methyl[2.2]MCP *anti*-**6a**, the protonation of the *ipso*-position of ethylene bridge on the benzene ring at the 3-position could afford the cation



Scheme 6

intermediate **A**, from which inter-annular bond formation at 8 and 16-positions occurs to form intermediate **B**. The aromatisation transformed **B** to **C** and further protonation might generate the intermediate **D**, from which the 1,2-methyl shift leads to compound **9**.

From the elemental analyses and parent ion peak in the mass spectrum, the product was inferred to be isomeric with the starting material. Detailed structure information was obtained from the ^{1}H NMR spectrum and the ^{13}C NMR spectrum. Although the methylene protons exhibited a complex pattern between δ 1.6 and 2.8 ppm, the olefinic proton resonance at 1-position and the aromatic proton resonance at 7-position showed a singlet at δ 5.66 and 6.80 ppm, respectively. On the basis of the ^{1}H NMR spectrum two isomeric structures 2-*tert*-butyl-3a,6,8-trimethyl-3,3a,4,5,9,10-hexahydropyrene **9** and 2-*tert*-butyl-3b,6,8-trimethyl-3a,3b,4,5,9,10-hexahydropyrene (intermediate **C** in Scheme 6) are possible. As mentioned above, the only one olefinic proton resonance was observed at δ 5.66 ppm. Thus isomer **9** might be a more favourable structure for the present isomerisation product than the structure **C** having two kinds of olefinic protons at 1- and 3-positions. ^{13}C NMR spectrum showed two quaternary carbons at δ 32.01 and 35.04 ppm for *tert*-butyl carbon and C-3a carbon, respectively. From the DEPT NMR technique it was found that four kinds of methyl carbons and five kinds of methylene carbons do exist in the compound.

Conclusions

5-*tert*-Butyl-8,12,14-trimethyl- and 5-*tert*-butyl-8,12,14,16-tetramethyl[2.2]MCP are prepared using the sulfur method. Treatment of 5-*tert*-butyl-8,12,14,16-tetramethyl[2.2]MCP with $AlCl_3$–$MeNO_2$ in benzene led to trans-*tert*-butylation which afforded 8,12,14,16-tetramethyl[2.2]MCP in good yield along with *tert*-butylbenzene. On the other hand the same treatment of 5-*tert*-butyl-8,12,14-trimethyl[2.2]MCP led to transannular cyclisation reaction and isomerisation reaction to afford the corresponding strainless 2-*tert*-butyl-3a,6,8-trimethyl-3,3a,4,5,9,10-hexahydropyrene in good yield. The present study indicates that the substituents effect at the 16-position of the opposite benzene ring does exist in the reaction of [2.2]MCPs with Lewis acids. Further studies on the mechanism for the cycloisomerisation of *anti*-**6a** are in progress.

Experiment

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with Me_4Si as an internal reference. IR spectra were measured as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh performance mass spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed by Yanaco MT-5.

Materials

Preparation of 4-*tert*-butyl-2,6-bis(sulfanylmethyl)toluene **3**[21–23] was as previously described.

Preparation of 1,3-bis(chloromethyl)-2,4,6-trimethylbenzene (**2b**)

To a solution of 1,3,5-trimethylbenzene **1b** (60.0 g, 0.5 mol) and chloromethyl methyl ether (150 mL) was added zinc chloride (40 g, 0.29 mol) at room temperature. After the reaction mixture was stirred for 10 min, it was poured into ice-water (300 mL) and extracted with CH_2Cl_2 (200 mL × 3). The CH_2Cl_2 extract was washed with water (200 mL), saturated aqueous NaCl (100 mL × 2), and dried (Na_2SO_4) and evaporated *in vacuo* to leave a colourless solid. Recrystallisation from hexane gave *compound* **2b** as colourless prisms (82.5 g, 76%), m.p. 102–104 °C (lit.[25] 102–103 °C).

Similarly, 1,5-bis(chloromethyl)-2,4-dimethylbenzene (**2a**) was prepared in 82% yield as colourless prisms (hexane), m.p. 99 °C (lit.[15] 99 °C) by chloromethyation of *m*-xylene (**1a**) under the same reaction conditions as described above.

Preparation of 6-tert-butyl-9,14,16,18-tetramethyl-2,11-dithia[3.3]metacyclophane (**4b**): A solution of 1,3-bis(chloromethyl)-2,4,6-trimethylbenzene **2b** (4.34 g, 20 mmol) and **3** (4.77 g, 20 mmol) in benzene (100 mL) was added dropwise over a period of 12 h from a Hershberg funnel with stirring under nitrogen to a solution of potassium hydroxide (4.0 g, 71 mmol) and sodium borohydride (1 g) in ethanol (4 l). After the addition, the reaction mixture was concentrated and the residue was extracted with CH_2Cl_2 (200 mL × 2). The CH_2Cl_2 extract was concentrated to leave the residue. The residue was chromatographed on silica gel (Wako C-300, 400 g) with hexane–ethylacetate, 1:1 v/v and 1:5 as eluents) to give *anti*-**4b** (4.3 g, 56%) and *syn*-**4b** (0.54 g, 7%) as a colourless solid.

*anti-6-*tert*-Butyl-9,14,16,18-tetramethyl-2,11-dithia[3.3]metacyclophane* (*anti*-**4b**): Colourless prisms (hexane), m.p. 171–172 °C; δ_H ($CDCl_3$) 1.08 (3H, s, CH_3), 1.33 (3H, s, CH_3), 1.35 (9H, s, *t*Bu), 2.40 (6H, s, CH_3), 3.59 (2H, d, *J* = 14.5 Hz, CH_2), 3.62 (2H, d, *J* = 13.5 Hz, CH_2), 3.69 (2H, d, *J* = 14.5 Hz, CH_2), 3.80 (2H, d *J* = 13.5 Hz, CH_2), 6.78 (1H, s, Ar*H*) and 7.38 (2H, s, Ar*H*); *m/z* 384 (M^+) (Found: C, 74.69; H, 8.62. $C_{24}H_{32}S_2$ (384.64) requires C, 74.94; H, 8.39%).

*syn-6-*tert*-Butyl-9,14,16,18-tetramethyl-2,11-dithia[3.3]metacyclophane* (*syn*-**4b**): Colourless prisms (hexane), m.p.171–172 °C; δ_H ($CDCl_3$) 1.18 (9H, s, *t*Bu), 2.19 (6H, s, CH_3), 2.46 (3H, s, CH_3), 2.47 (3H, s, CH_3), 3.79 (2H, d, *J* = 15.1 Hz, CH_2), 3.88 (2H, d, *J* = 15.1 Hz, CH_2), 3.94 (2H, d, *J* = 15.1 Hz, CH_2), 4.09 (2H, d, *J* = 15.1 Hz, CH_2), 6.29 (1H, s, Ar*H*) and 6.88 (2H, s, Ar*H*); *m/z* 384 (M^+) (Found: C, 74.85; H, 8.42. $C_{24}H_{32}S_2$ (384.64) requires C, 74.94; H, 8.39%).

Cyclisation reactions of **2a** and **3** was carried out using the same procedure as described above to afford *anti*-**4a** in 73% yield.

*anti-6-*tert*-Butyl-9,14,16-trimethyl-2,11-dithia[3.3]metacyclophane* (*anti*-**4a**): Colourless prisms, m.p.81–82 °C; δ_H ($CDCl_3$) 1.24 (9H, s, *t*Bu), 2.12 (3H, s, CH_3), 2.17 (6H, s, CH_3), 3.40 (2H, d, *J* = 15.0 Hz, CH_2), 3.63 (2H, d, *J* = 15.0 Hz, CH_2), 3.80 (2H, d, *J* = 13.7 Hz, CH_2), 3.98 (2H, d *J* = 13.7 Hz, CH_2), 5.29 (1H, broad s, Ar*H*) 6.67 (1H, s, Ar*H*) and 7.11 (2H, s, Ar*H*); δ_C ($CDCl_3$) 15.02, 18.76, 31.19, 32.83, 34.07, 35.47, 126.75, 128.96, 131.41, 133.48, 133.91, 134.84, 134.88 and 148.10; *m/z* 370 (M^+) (Found: C, 74.69; H, 8.62. $C_{23}H_{30}S_2$ (370.62) requires C, 74.54; H, 8.16%).

Preparation of 9-methyl-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxides (**5**); *typical procedure*

To a solution of *anti*-**4b** (3.20 g, 8.3 mmol) in $CHCl_3$ (150 mL) was added *m*-chloroperbenzoic acid (3.96 g, 19.5 mmol, 85% purity) at 0 °C while stirring with a magnetic stirrer. After the solution was stirred for 24 h at room temperature, the solvent was evaporated *in vacuo* to leave the residue which was washed with 10% $NaHCO_3$ (100 mL), water (50 mL) and ethanol to afford *anti*-6-*tert*-butyl-9,14,16,18-tetramethyl-2,11-dithia[3.3]metacyclophane-2,2,11,11-tetraoxide (*anti*-**5b**) as colourless prisms (3.65 g, 98%), m.p. >300 °C; δ_H ($CDCl_3$) 1.20 (3H, s, CH_3), 1.27 (3H, s, CH_3), 1.35 (9H, s, *t*Bu), 2.53 (6H, s, CH_3), 4.16 (2H, d, *J* = 14.8 Hz, CH_2), 4.45 (2H, d, *J* = 14.8 Hz, CH_2), 4.49 (2H, d *J* = 14.2 Hz, CH_2), 4.61 (2H, d, *J* = 14.2 Hz, CH_2), 7.02 (1H, s, Ar*H*) and 7.78 (2H, s, Ar*H*); δ_C ($CDCl_3$) 14.43, 15.87, 21.10, 30.95, 34.52, 58.92, 63.56, 123.88, 125.55, 125.88, 129.04, 131.36, 136.48, 140.70, 143.52 and 148.55; *m/z* 320 (M^+–$2SO_2$) (Found: C, 64.39; H, 7.26. $C_{24}H_{32}S_2O_4$ (448.64) requires C, 64.25; H, 7.19%).

Oxidation of *syn*-**4b** and *anti*-**4a** with *m*-CPBA was carried out using the same procedure as described above to afford *syn*-**5b** and *anti*-**5a** in 96 and 100% yields, respectively.

*syn-6-*tert*-Butyl-9,14,16,18-tetramethyl-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxide* (*syn*-**5b**): Colourless prisms, m.p. 217–220 °C (decomp.); δ_H ($CDCl_3$) 1.14 (9H, s, *t*Bu), 2.38 (6H, s, CH_3), 2.39 (3H, s, CH_3), 2.43 (3H, s, CH_3), 4.26 (2H, d, *J* = 14.4 Hz, CH_2), 4.32 (2H, d, *J* = 14.4 Hz, CH_2), 4.65 (2H, d, *J* = 15.0 Hz, CH_2), 4.65 (2H, d, *J* = 15.0 Hz, CH_2), 6.64 (1H, s, Ar*H*) and 7.57 (2H, s, Ar*H*; *m/z* 320 (M^+–$2SO_2$) (Found: C, 64.27; H, 7.16. $C_{24}H_{32}S_2O_4$ (448.64) requires C, 64.25; H, 7.19%).

*anti-6-*tert*-Butyl-9,14,16-trimethyl-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxide* (*anti*-**5a**): Colourless prisms, m.p. >250 °C (decomp.); δ_H ($CDCl_3$) 1.34 (9H, s, *t*Bu), 2.11 (3H, s, CH_3), 2.33 (6H, s, CH_3), 4.15 (2H, d, *J* = 15.2 Hz, CH_2), 4.24 (2H, d, *J* = 15.2 Hz, CH_2), 4.40 (2H, d, *J* = 14.4 Hz, CH_2), 4.70 (2H, d, *J* = 14.4 Hz, CH_2) 5.08 (1H, s, Ar*H*), 6.91 (1H, s, Ar*H*) and 7.60 (2H, s, Ar*H*); δ_C ($CDCl_3$) 16.46, 19.86, 31.09, 34.54, 58.92, 62.55, 124.51, 128.45, 129.58, 133.12, 137.13, 139.98 and 150.89; *m/z* 306 (M^+–$2SO_2$) (Found: C, 63.53; H, 6.85. $C_{23}H_{30}S_2O_4$ (434.61) requires C, 63.56; H, 6.96%).

Pyrolysis of disulfones **5** *to give 5-methyl[2.2]metacyclophanes* (**6**); *typical procedure*: Pyrolysis of disulfones *anti*-**5b** was carried out in an apparatus consisting of a horizontal tube (15 mm in diameter) passing through two adjacent tube furnaces, each of which was 20 cm long. The first furnace provided a temperature that would induce sublimation of the sulfone; the second was used at a higher temperature (500 °C) that would assure pyrolysis. A vacuum pump was connected at the exit from the second furnace. Disulfone *anti*-**5b** (1 g, 2.23 mmol) was pyrolysed at 500 °C under reduced pressure (1 torr) in the above apparatus as follows. The sample of disulfone was placed in the first furnace and small glass beads were packed into the second furnace. The product which sublimed was collected and chromatographed on silica gel (Wako C-300, 100 g) (hexane as eluent) to give a colourless solid. Recrystallisation from methanol gave *anti*-5-*tert*-butyl-8,12,14,16-tetramethyl[2.2]metacyclophane (*anti*-**6b**) as colourless prisms (522 mg, 73%), m.p. 134–137 °C; δ_H ($CDCl_3$) 0.51 (3H, s, CH_3), 0.52 (3H, s, CH_3), 1.29 (9H, s, *t*Bu), 2.33 (6H, s, CH_3), 2.47–2.57 (2H, m, CH_2), 2.66–2.78 (2H, m, CH_2), 2.83–2.89 (2H, m, CH_2), 3.12–3.22 (2H, m, CH_2), 6.57 (1H, s, Ar*H*) and 7.12 (2H, s, Ar*H*); *m/z* 320 (M^+) (Found: C, 90.05; H, 10.17. $C_{24}H_{32}$ (320.52) requires C, 89.94; H, 10.06%).

Pyrolysis of *syn*-**5b** and *anti*-**5a** was carried out using the same procedure as described above to afford *anti*-**6b** and *anti*-**6a** in 65 and 75% yields, respectively.

*anti-5-*tert-*Butyl-8,12,14-trimethyl[2.2]metacyclophane* (*anti*-**6a**): Colourless prisms (hexane), m.p. 66–67 °C; δ_H ($CDCl_3$) 0.48 (3H, s, CH_3), 1.36 (9H, s, *t*Bu), 1.80–1.92 (2H, m, CH_2), 2.30 (6H, s, CH_3), 2.50–2.60 (2H, m, CH_2), 2.82–2.90 (2H, m, CH_2), 3.22–3.30 (2H, m, CH_2), 3.63 (1H, s, Ar*H*), 6.93 (1H, s, Ar*H*) and 7.05 (2H, s, Ar*H*); δ_C ($CDCl_3$) 14.13, 18.78, 31.65, 34.16, 35.04, 37.79, 122.75, 129.78, 132.74, 133.14, 135.18, 139.53, 139.73 and 149.81; *m/z* 306 (M^+) (Found: C, 89.68; H, 10.15. $C_{23}H_{30}$ (306.5) required C, 90.13; H, 9.87).

*$AlCl_3$–$MeNO_2$ catalysed trans-*tert-*butylation of anti-*6b *in benzene*: To a solution of compound *anti*-**6b** (218 mg, 0.68 mmol) in benzene (15 mL) was added a solution of $AlCl_3$ (27.6 mg, 0.204 mmol) in $MeNO_2$ (0.05 mL). After the reaction mixture had been stirred for 3 h at 50 °C, it was poured into ice-water and extracted with ether (30 mL × 2). The ether extract was dried (Na_2SO_4) and concentrated under reduced pressure to leave the residue. The residue was chromatographed on silica gel (Wako C-300, 200 g) (hexane as eluent) to give *anti*-**7b** (153 mg, 85%) as a colourless solid, respectively. The formation of *tert*-butylbenzene **8** was confirmed by GLC.

8,12,14,16-Tetramethyl[2.2]metacyclophane (*anti*-**7b**): Colourless prisms (from MeOH), m.p. 104–107 °C; δ_H ($CDCl_3$) 0.51 (3H, s, CH_3), 0.54 (3H, s, CH_3), 2.34 (6H, s, CH_3), 2.46–2.60 (2H, m, CH_2), 2.68–2.80 (2H, m, CH_2), 2.83–2.90 (2H, m, CH_2), 3.14–3.23 (2H, m, CH_2), 6.60 (1H, s, Ar*H*), 6.87 (1H, t, J = 7.3 Hz, Ar*H*) and 7.12 (2H, d, J = 7.3 Hz, Ar*H*); δ_C ($CDCl_3$) 14.40, 15.96, 19.14, 31.92, 124.44, 126.99, 133.05, 133.10, 136.96, 142.23 and 142.30; *m/z* 264 (M^+) (Found: C, 90.75; H, 9.17. $C_{20}H_{24}$ (264.41) requires C, 90.85; H, 9.15%).

*Treatment of anti-*6a *with $AlCl_3$-$MeNO_2$ in benzene*

To a solution of compound *anti*-**6a** (104 mg, 0.34 mmol) in benzene (7.5 mL) was added a solution of $AlCl_3$ (13.6 mg, 0.102 mmol) in $MeNO_2$ (0.02 mL). After the reaction mixture had been stirred for 3 h at 50 °C, it was poured into ice-water and extracted with ether (15 mL × 2). The ether extract was dried (Na_2SO_4) and concentrated under reduced pressure to leave the residue. The residue was chromatographed on silica gel (Wako C-300, 200 g) (hexane as eluent) to give 2-*tert*-butyl-3a,6,8-trimethyl-3,3d,4,5,9,10-hexahydropyrene **9** (89 mg, 85%) as a colourless solid, respectively. No formation of *tert*-butylbenzene **8** was detected by GLC.

*2-*tert-*Butyl-3a,6,8-trimethyl-3,3a,4,5,9,10-hexahydropyrene* (**9**): Pale yellow prisms, m.p. 73–74 °C; δ_H ($CDCl_3$) 0.92 (3H, s, CH_3), 1.11 (9H, s, *t*Bu), 1.60–1.74 (1H, m, CH_2), 1.78–1.86 (1H, m, CH_2), 2.14 (2H, s, CH_2), 2.19 (3H, s, CH_3), 2.20 (3H, s, CH_3), 2.28–2.48 (2H, m, CH_2), 2.60–2.80 (4H, m, CH_2), 5.66 (1H, s, *CH*) and 6.80 (1H, s, Ar*H*); δ_C ($CDCl_3$) 19.34, 19.91, 23.36, 24.17, 27.26, 28.14, 33.01, 35.04, 36.80, 40.54, 119.52, 126.58, 129.60, 129.79, 130.06, 130.40, 130.91, 131.88, 133, 37 and 146,31; *m/z* 306 (M^+) (Found: C, 90.02; H, 9.66. $C_{23}H_{30}$ (306.5) requires C, 90.13; H, 9.87%).

Received 19 March 2009; accepted 5 June 2009
Paper 09/0502 doi: 10.3184/030823409X465222
Published online: 14 July 2009

References

1 P.M. Keehn and S.M. Rosenfield (eds) Cyclophanes, Academic Press: New York, Vols 1&2, 1983.
2 F. Vögtle, *Cyclophane-chemistry*, Wiley, Chichester, 1993.
3 L.L. Ingraham, *J. Chem. Phys.*, 1957, **27**, 1228.
4 N.L. Allinger, M.A. Da Rooge and R.B. Hermann, *J. Am. Chem. Soc.*, 1961, **83**, 1974.
5 T. Sato, T. Takemura and M. Kainosho, *J. Chem. Soc., Chem. Commun.*, 1974, 97.
6 T. Sato, H. Matsui and R. Komaki, *J. Chem. Soc., Perkin Trans. 1*, 1976, 2053.
7 T. Takemura and T. Sato, *Can. J. Chem.*, 1976, **54**, 3412.
8 R. Gleiter, *Tetrahedron Lett.*, 1969, 4453.
9 D.J. Cram, N.L. Allinger and H. Steinberg, *J. Am. Chem. Soc.*, 1954, **76**, 6132.
10 R. Boschi and W. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 402.
11 T. Sato and T. Takemura, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1195.
12 M. Tashiro, T. Yamato, K. Kobayashi and T. Arimura, *J. Org. Chem.*, 1987, **52**, 3196.
13 T. Yamato, K. Maeda, H. Kamaimura, K. Noda and M. Tashiro, *J. Chem. Res.(S)*, 1995, 310; *(M)*, 1995, 1865.
14 J.V. Braun and J. Neeles, *Ber. Dtsch. Chem. Ges.*, 1934, **67**, 1094.
15 W.TH. Nauta and J.W. Dienske, *Rec. Trav. Chim.*, 1936, **55**, 1000.
16 T. Sato, S. Akabori, S. Muto and K. Hata, *Tetrahedron*, 1968, **24**, 5557.
17 T. Sato and K. Nishiyama, *J. Org. Chem.*, 1972, **37**, 3254.
18 T. Sato and T. Takemura, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1195.
19 M. Tashiro and T. Yamato, *Org. Prep. Proced. Int.*, 1981, **13**, 1.
20 M. Tashiro and T. Yamato, *J. Org. Chem.*, 1981, **46**, 1543.
21 M. Tashiro, K. Koya and T. Yamato, *J. Am. Chem. Soc.*, 1982, **104**, 3707.
22 M. Tashiro and T. Yamato, *J. Org. Chem.*, 1985, **50**, 2939.
23 T. Yamato, T. Arimura and M. Tashiro, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1.
24 M. Tashiro, A. Tsuge, T. Sawada, T. Makishima, S. Horie, T. Arimura, S. Mataka and T. Yamato, *J. Org. Chem.*, 1990, **55**, 2404.
25 M. Tashiro and T. Yamato, *J. Org. Chem.*, 1983, **48**, 1461.
26 B.H. Smith, *Bridged aromatic compounds*, Academic Press, New York. 1964.
27 F. Vögtle and P. Neumann, *Angew. Chem.*, 1972, **84**, 75.
28 F. Vögtle and P. Neumann, *Angew. Chem. Int. Ed. Engl.*, 1972, **11**, 73.
29 F. Vögtle and P. Neumann, *Synthesis*, 1973, 85.
30 F. Vögtle and G. Höhner, *Top. Curr. Chem.*, 1978, **74**, 1.
31 P.M. Keehn and S.M. Rosenfield, *Cyclophanes*, Academic Press, New York. Vol. 1, 1983.
32 R.H. Mitchell and V. Boekelheide, *Tetrahedron Lett.*, 1970, 1197.
33 R.H. Mitchell and V. Boekelheide, *J. Chem. Soc., Chem. Commun.*, 1970, 1555.
34 W. Anker, G.W. Bushnell and R.H. Mitchell, *Can. J. Chem.*, 1979, **57**, 3080.
35 R.H. Mitchell, R.J. Carruther, L. Mazuch and T.W. Dingle, *J. Am. Chem. Soc.*, 1982, **104**, 2544.
36 R.H. Mitchell and V. Boekelheide, *J. Am. Chem. Soc.*, 1974, **96**, 1547.
37 D.T. Hefelfinger and D.J. Cram, *J. Am. Chem. Soc.*, 1970, **92**, 1073.
38 D.T. Hefelfinger and D.J. Cram, *J. Am. Chem. Soc.*, 1971, **93**, 4767.
39 D.J. Cram, D.L. Helgeson, D. Lock and L.A. Singer, *J. Am. Chem., Soc.*, 1966, **88**, 1324.