Medium-sized cyclophanes. Part 62:[1] Formylation of *anti*-[*n*.2]metacyclophanes — Through-space electronic interactions between two benzene rings

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Abstract: Formylation of *anti*-[*n*.2]metacyclophanes (**1**) (*n* = 2, 3, 4) with dichloromethyl methyl ether in the presence of $TiCl_4$ occurred selectively at *para*-position to the internal methyl substituents of *anti*-[*n*.2]metacyclophanes. Similar reaction of *anti*-5,13-di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophane (**6a**) with dichloromethyl methyl ether in the presence of $TiCl_4$ led to *ipso*-formylation at the *tert*-butyl group to give *anti*-5-*tert*-butyl-13-formyl-8,16-dimethyl[2.2]-metacyclophane (**7a**) as well as the corresponding 2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**10**), *anti*-5-*tert*-butyl-8,16-dimethyl-13-(3-methyl-1-butene-2-yl)[2.2]metacyclophane (**8**), and *anti*-5,13-di-*tert*-butyl-*exo*-1-hydroxy-8,16-dimethyl[2.2]metacyclophane (**9**) depending on the reaction conditions. The higher yield of *ipso*-formylated product is obtained in the presence of $AlCl_3$ $MeNO_2$ in 80% yield along with *anti*-5-*tert*-butyl-8,16-dimethyl-13-(3-methyl-1-butene-2-yl)[2.2]metacyclophane (**13**). Thus, the yield of *ipso*-formylation at the *tert*-butyl group of **6a** was strongly affected by the activity of the formylation catalyst. Interestingly, in the formylation of *anti*-6,14-di-*tert*-butyl-9,17-dimethyl[3.2]metacyclophane (**6b**) under the same reaction conditions, *syn*-6,14-di-*tert*-butyl-7-formyl-9,17-dimethyl[3.2]metacyclophane (**14b**) was obtained in 40% yield arising from the *anti*-*syn*-ring inversion of the formylation intermediate along with *ipso*-formylation product **7b** in 42% yield. In the formylation of *anti*-[4.2]metacyclophane (**6c**) only the mono-*ipso*-formylated product **7c** was obtained in 92% yield. The formation of a two-fold *ipso*-formation product, i.e., *anti*-5,13-diformyl-8,16-dimethyl[2.2]metacyclophane (**3a**), was not observed under the reaction conditions used. The mechanism of the *ipso*-formation as well as the formation of the present novel reaction products **8** and **9** is also discussed.

Key words: cyclophanes, strained molecules, electrophilic aromatic substitution, *ipso*-formylation, σ-complex intermediates, through-space electronic interactions.

Résumé : La formylation des *anti*-[*n*.2]métacyclophanes (**1**) (*n* = 2, 3, 4) à l'aide d'oxyde de méthyle et de dichlorométhyle, en présence de $TiCl_4$, se produit d'une façon sélective en position *para* par rapport aux substituants méthyles internes des *anti*-[*n*.2]métacyclophanes. Une réaction semblable de l'*anti*-5,13-di-*tert*-butyl-8,16-diméthyl[2.2]métacyclophane (**6a**) avec de l'oxyde de méthyle et de dichlorométhyle, en présence de $TiCl_4$, conduit à une formylation en position *ipso* par rapport au groupe *tert*-butyle et, suivant les conditions réactionnelles à la formation de l'*anti*-5-*tert*-butyl-13-formyl-8,16-diméthyl[2.2]métacyclophane (**7a**) ainsi que du 2,7-di-*tert*-butyl-*trans*-10b,10c-diméthyl-10b,10c-dihydropyrène (**10**), de l'*anti*-5-*tert*-butyl-8,16-diméthyl-13-(3-méthylbut-1-én-2-yl)[2.2]métacyclophane (**8**) et de l'*anti*-5,13-di-*tert*-butyl-*exo*-1-hydroxy-8,16-diméthyl[2.2]métacyclophane (**9**). Le rendement le plus élevé de produit formylé en position *ipso* (80%) est obtenu en présence de $AlCl_3$, dans le $MeNO_2$; à ses côtés, il se forme aussi de l'*anti*-5-*tert*-butyl-8,16-diméthyl-13-(3-méthylbut-1-én-2-yl)[2.2]métacyclophane (**13**). Le rendement en formylation en position *ipso* par rapport au groupe *tert*-butyle du produit **6a** est donc fortement affecté par l'activité du catalyseur de formylation. Il est intéressant de noter que la formylation de l'*anti*-6,14-di-*tert*-butyl-9,17-diméthyl[3.2]métacyclophane (**6b**) dans les mêmes conditions expérimentales conduit à la formation, avec un rendement de 40%, du *syn*-6,14-di-*tert*-butyl-7-formyl-9,17-diméthyl[3.2]métacyclophane (**14**b) qui résulte d'une inversion de cycle *anti*-*syn* de l'intermédiaire de formylation; ce produit se forme aux côtés du produit de formylation *ipso* (**7b**) obtenu avec un rendement de 42%. Lors

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de la formylation de l'*anti*-[4.2]métacyclophane (**6c**), on n'obtient que le produit de formylation *ipso* (**7c**) avec un rendement de 92%. Dans les conditions réactionnelles utilisées, on n'a pas observé de formation de double formylation *ipso*, l'*anti*-5,13-diformyl-8,16-diméthyl[2.2]métacyclophane (**3a**). On discute du mécanisme de formation des produits de formylation *ipso* ainsi que de la formation des nouveaux produits **8** et **9**.

Mots clés : cyclophanes, molécules tendues, substitution aromatique électrophile, formylation *ipso*, complexes-σ comme intermédiaires, interactions électroniques à travers l'espace.

[Traduit par la Rédaction]

Introduction

Because of electronic interaction between two benzene rings, the proximity of 8,16-positions, and the considerable strain energy, [2.2]metacyclophane (MCP = metacyclophane) is prone to giving transannular reaction products under the electrophilic, radical, and photolytic reaction conditions together with other transformation products derived from tetrahydropyrene (2,3). These products have usually been rationalized as involving initial dehydrogenation to 4,5,9,10-tetrahydropyrene.

Maquestiau et al. (4) reported formylation of [2.2]MCP with dichloromethyl *n*-butyl ether in the presence of $TiCl_4$ according to the Rieche procedure (5) to give 4-formyl[2.2]MCP, as shown in Scheme 1. This result was different from other electrophilic aromatic substitution of [2.2]MCP; e.g., bromination, iodination, and nitration, which afforded the corresponding 2-substituted 4,5,9,10-tetrahydropyrenes via addition-elimination mechanism (2). The relatively late transition state in the formylation of [2.2]MCP compared with other electrophilic aromatic substitution might be proposed.

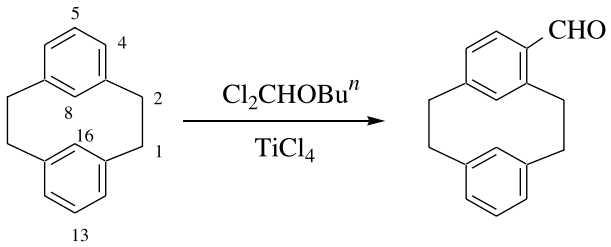
However, there is no report concerning the formylation of internally substituted [2.2]MCPs. We undertook the present work to obtain further information about the chemical behaviour of [2.2]MCPs as well as [3.2]- and [4.2]MCPs, which are less strained than [2.2]MCPs.

Results and discussion

When formylation of *anti*-8,16-dimethyl[2.2]MCP (**1a**) (6) with dichloromethyl methyl ether in the presence of $TiCl_4$ as a catalyst was carried out at 0°C for 1 h, *anti*-5-formyl-8,16-dimethyl[2.2]MCP (**2a**) and *anti*-5,13-diformyl-8,16-dimethyl[2.2]MCP (**3a**) were obtained in 20 and 80% yield, respectively. Treatment of **1a** with dichloromethyl methyl ether at room temperature for 3 h increased the yield of the diformyl compound (**3a**) to 95% (Scheme 2).

Formylation of *anti*-9,17-dimethyl[3.2]- (**1b**) (7) and *anti*-10,18-dimethyl[4.2]MCP (**1c**) (7) at 0°C for 1 h under the same conditions used with **1a**, afforded diformyl derivatives (**3b**) and (**3c**) in 93 and 91% yield, respectively. In the [3.2]- and [4.2]MCP systems the diformylations were both completed within 1 h, which is different from the result that the complete diformylation required at least 3 h in the [2.2]MCP system. The different formylation behaviors of [*n*.2]MCPs can be explained by the stability of the cationic intermediates, which could arise from the through-space electronic interaction with the benzene ring located on the opposite side. Thus, in the case of the [2.2]MCP system, the second electrophilic substitition with dichloromethyl methyl ether

Scheme 1.



can be more strongly suppressed because of deactivation of the second aromatic ring by CH(OMe)Cl group-like nitration of 8,16-dimethyl[2.2]MCP, which only afforded mononitration product even in the drastic nitration conditions (8).

It should be noted that formyl groups of **2a** and **3a** are introduced at positions 5 and 13 of the MCP ring with formylation occurring selectively *para* to the methyl substituents of [2.2]MCP. Similar orientations are observed in the [3.2]- and [4.2]MCP systems. In contrast, treatment of 1,2,3-trimethylbenzene (**4**) with dichloromethyl methyl ether under the same conditions used with **1** afforded a 90% yield of 2,3,4-trimethylbenzaldehyde (**5**). The above results suggest that the orientation of the formylation of **1** is determined by the internal methyl substituents in place of methylene groups of the bridges and quite different from the orientation that can be expected from the result of formylation of 1,2,3-trimethylbenzene (**4**). The deviation of the benzyl carbon atom of methylene groups from the plane of the benzene ring (9) might decrease the degree of stabilization of the σ-complex intermediate by hyperconjugation compared with that of the internal methyl groups.

Attempted formylation of *anti*-5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP (**6a**) (6) with dichloromethyl methyl ether (Table 1) in the presence of $TiCl_4$ at room temperature for 0.5 h gave mono-*ipso*-formylated product *anti*-5-formyl-13-*tert*-butyl-8,16-dimethoxy[2.2]MCP (**7a**) in 25% yield as a major product along with *anti*-5,13-di-*tert*-butyl-*exo*-1-hydroxy-8,16-dimethyl[2.2]MCP (**9**), *anti*-5-*tert*-butyl-8,16-dimethyl-13-(3-methyl-1-butene-2-yl)[2.2]MCP (**8**), and the corresponding 2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**10**), depending on the reaction conditions. Thus, decreasing the reaction temperature from 25°C to 0°C or to –20°C decreases the yield of *ipso*-formylated product **7a** but increases the yield of **8** and **9**. In contrast, prolonging the reaction time to 3 h or increasing the reaction temperature to 40°C leads to a slight increase of the yield of *ipso*-formylated product **7a**. Therefore, the present *ipso*-formylation at the *tert*-butyl group of **6a** was found to be strongly affected by the reaction time and temperature.

Scheme 2.

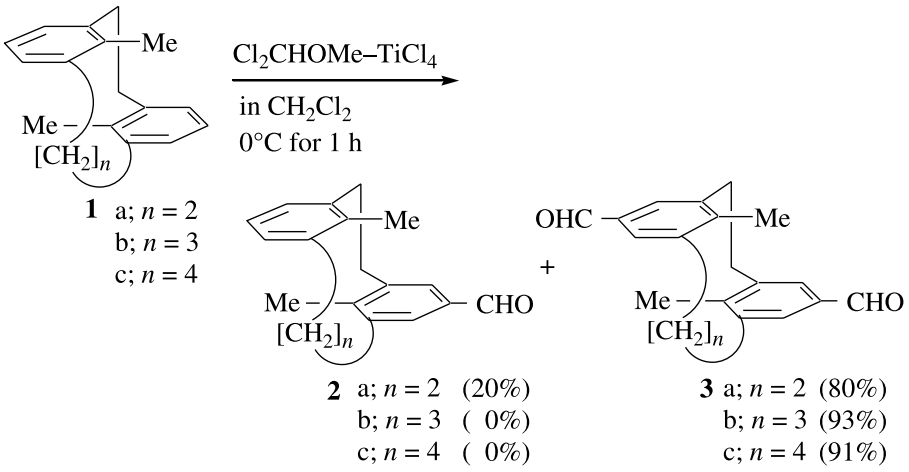


Table 1. Treatment of [2.2]MCP **6a** with dichloromethyl methyl ether in the presence of titanium tetrachloride.

			Products (%)[a]			
Run	Temp (°C)	Time (h)	**6a**	**7a**	**8**	**9**
1[b]	0	0.5	9	15	25	27
2[b]	–20	0.5	6	13	31	27
3[b]	25	0.5	4	25	16	20
4	25	3	3	35	6	15
5	40	0.5	<1	30	<1	<1

[a]Isolated yields are shown.
[b]Small amount of 2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**10**) was obtained.

However, in spite of the prolonged reaction time, di-*ipso*-formylated compound **3a** was not obtained. Furthermore, formation of the corresponding *syn*-8,16-dimethyl[2.2]MCP arising from the *anti*-*syn*-ring inversion like the nitration of *anti*-5,13-di-*tert*-butyl-8,16-dimethoxy[2.2]MCP was also not observed (10).

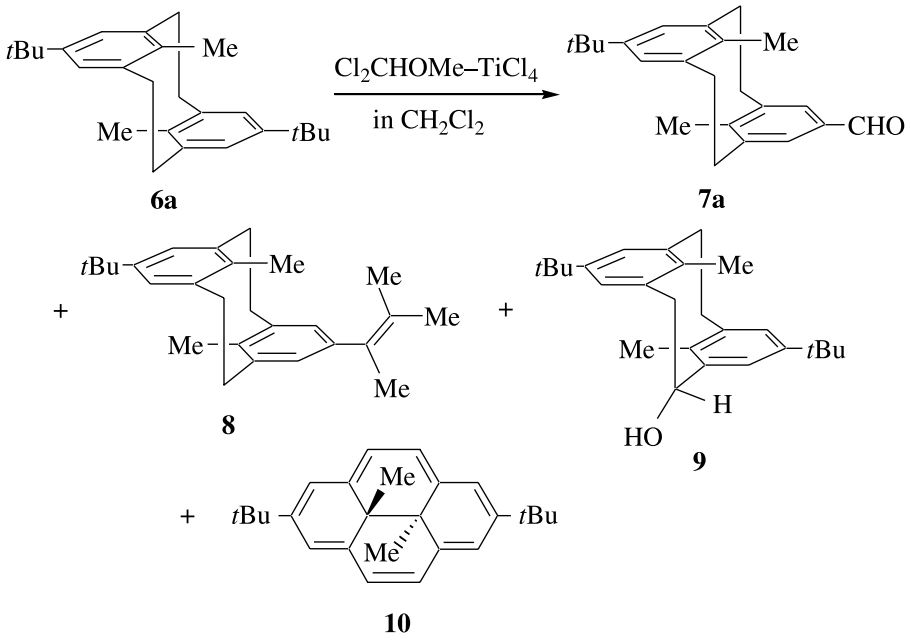
Formylation of *anti*-6,14-di-*tert*-butyl-9,17-dimethyl[3.2]-MCP (**6b**) and *anti*-7,15-di-*tert*-butyl-10,18-dimethyl[4.2]-MCP (**6c**), carried out under the same conditions, afforded *anti*-6-formyl-14-*tert*-butyl-9,17-dimethyl[3.2]MCP (**7b**) in 95% yield but the latter MCP **(6c)** afforded only recovered. From this finding, the order of reactivity of *anti*-[*n*.2]MCPs for formylation is estimated to be [2.2]- > [3.2]- > [4.2]MCP. This finding also suggests that the degree of the stability of the cation intermediate, which may be due to a through-space electronic interaction with the opposing benzene ring, decreases as the size of the polymethylene bridge increases.

On the other hand, Reinhoudt and co-workers (11) reported the high-yield four-fold *ipso*-nitration of *tert*-butylcalix[4]arenes. To the best of our knowledge, none of the *ipso*-formylation reactions have been reported in the normal aromatic systems (12). In the MCP system, a first σ-complex intermediate would be stabilized by a through-space electronic interaction with the opposing benzene ring, thus accelerating the reaction. However, only one *tert*-butyl group is *ipso*-formylated because of deactivation of the second aromatic ring by the CH(OMe)Cl group.

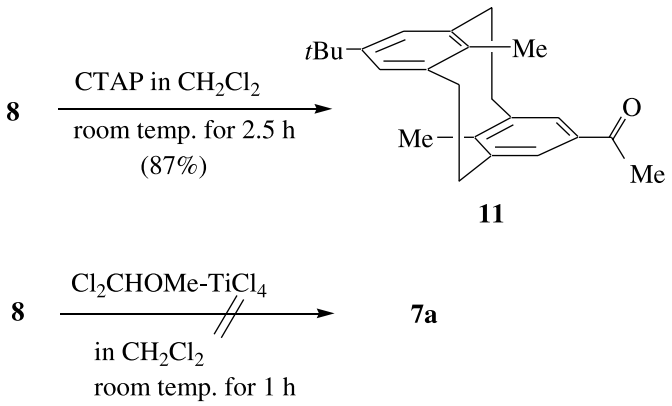
The structures of products **7a** and **8** were determined on the basis of their elemental analyses and spectral data. The IR (NaCl) spectrum of **7a** shows $\upsilon_{C=O}$ at 1670 cm^{-1}, typical of an aromatic aldehyde. The ^1H NMR ($CDCl_3$) spectrum of **7a** shows two methyl protons at 0.49 and 0.64 ppm, a *tert*-butyl proton at 1.30 ppm, two aromatic protons at 7.14 and 7.64 ppm, and a formyl proton at 9.84 ppm, respectively. The ^1H NMR spectrum of **8** shows internal methyl protons as singlets at δ 0.58 and 0.69 and three methyl protons as singlets at δ 1.65, 1.80, and 1.93 (relative intensity 1:1:1). Two aromatic protons are observed at δ 6.89 and 7.12 as singlets that are clearly associated with the protons at C-12 and C-14, and C-4 and C-6, respectively. Structure **8** can also be determined by the fact that there are five nonequivalent methyl groups at 14.38, 14.70, 20.70, 20.75, and 22.16 and two olefinic carbons at 126.25 and 129.86 in ^{13}C NMR spectrum. Furthermore, when **8** was treated with cetyltrimethylpermanganate in methylene dichloride (13), the corresponding oxidation product *anti*-5-acetyl-13-*tert*-butyl-8,16-dimethyl[2.2]MCP (**11**) was obtained in 87% yield (Scheme 4). On the basis of this chemical conversion and spectral data, **8** is assigned the structure *anti*-5-*tert*-butyl-8,16-dimethyl-13-(3-methyl-2-butene-2-yl)[2.2]MCP. It was also found that the formylation of **8** in methylene dichloride under the same reaction conditions did not afford *ipso* substitution product **7a**. Only the recovery of the starting compound **8** resulted. This finding suggests that the intermediate for the formation of **7a** is not **8**.

The structures of products **9** and **10** were also determined on the basis of their elemental analyses and spectral data. The assignment of **10** was carried out by the comparison with physical properties and spectral data of the authentic sample (14). We previously assigned (15) the ^1H NMR signals of *anti*-1-*exo*-5,13-trichloro-8,16-dimethyl[2.2]MCP and have assigned the ^1H NMR signals of **9** in a similar fashion. Thus, the ^1H NMR spectrum of **9** shows two internal methyl resonances as singlets at δ 0.52 and 0.86 and a bridge methine signal as double doublets at δ 5.34 (J = 2.2/4.6 Hz). One of the two methyl protons is in a strongly deshielding region of oxygen atoms of *exo*-OH on the ethylene bridge resulting in a much larger downfield shift (δ 0.86) than that of the other methyl proton (δ 0.52). In contrast, the

Scheme 3.



Scheme 4.



aromatic protons were observed as a multiplet around δ 7.18–7.21 that is almost same as that for the *exo*-Cl arrangement of *anti*-1-*exo*-5,13-trichloro-8,16-dimethyl[2.2]-MCP (δ 7.0–7.3). A deshielded aromatic proton due to the *endo*-OH oxygen atom on the ethylene bridge was not observed. On the basis of the spectral data, compound **9** is assigned the structure *anti*-5,13-di-*tert*-butyl-*exo*-1-hydroxy-8,16-dimethyl[2.2]MCP.

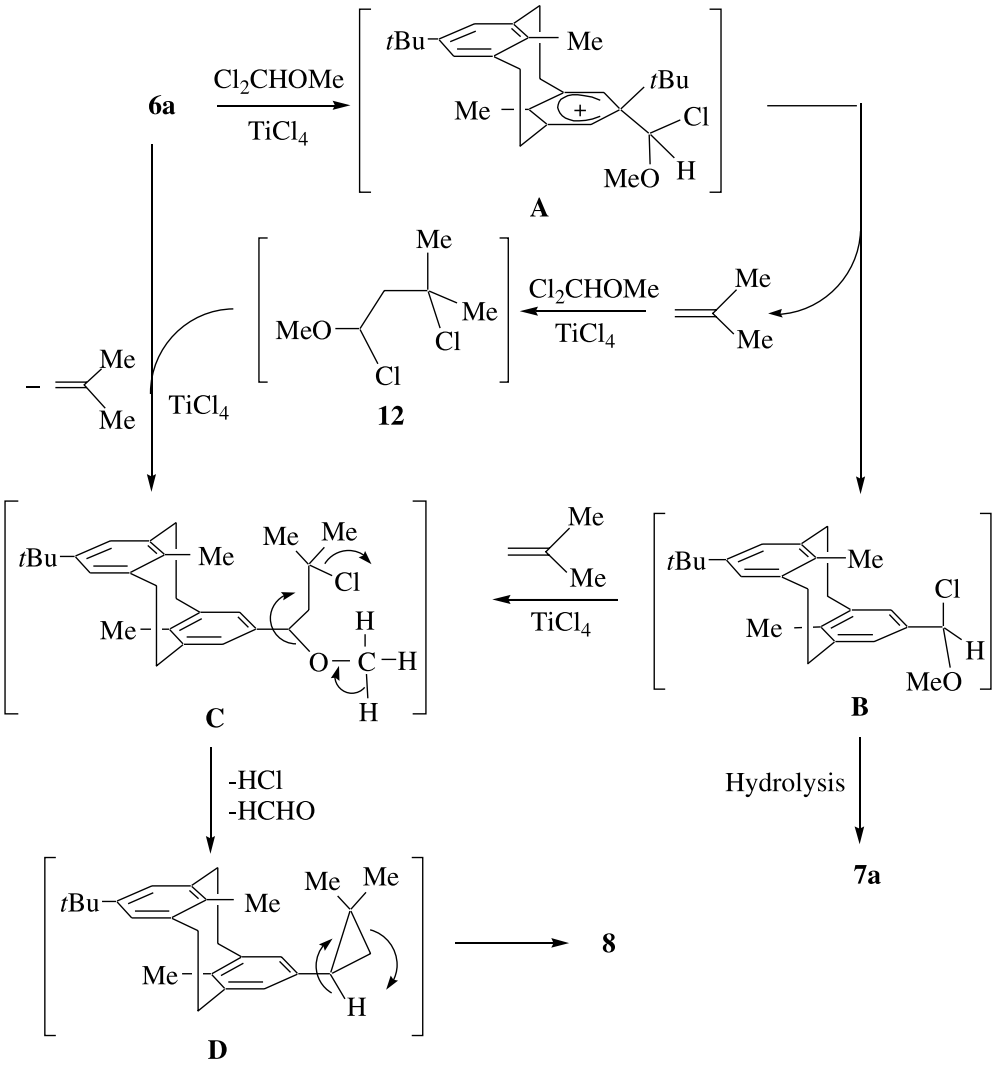
Although the detailed mechanism of formation of **8** is not clear, a reaction pathway for the formation of **8** from **6a** is tentatively proposed in Scheme 5. The *ipso*-electrophilic attack at the *tert*-butyl group could afford the cation intermediate **A,** which could eliminate the isobutene to afford intermediate **B** following hydrolysis by the quenched with water to give *ipso*-formylation product **7a**. On the other hand, Brüggen et al. (16) reported that isobutene reacts with dichloromethyl methyl ether to afford the addition product **12**. In fact, generated isobutene was trapped by the reaction with toluene in the presence of $AlCl_3$ under the Ar gas flow condition to afford *tert*-butyltoluene. Thus, the addition product generated in the present system can react with **6a** on the *ipso*-position at the *tert*-butyl group to afford the intermediate **C** from which the elimination of formaldehyde and HCl form the cyclopropane ring (intermediate **D**) following the ring opening reaction that occurs to afford **8**.

The formation of alcohol **9** during the formylation of **6a** with dichloromethyl methyl ether leads to the first direct introduction of hydroxy group into the methylene group of [2.2]MCP **6a**. However, the detailed mechanism of formation of **9** is not clear in the present stage.

It was also found that dehydration of alcohol **9** with $TiCl_4$ or concd. HCl in benzene at room temperature for 80 h afforded *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **10** in 10% and 32% along with recovery of the starting compound. Therefore, the reaction pathway for the formation of *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **10** in the present formylation reaction via the elimination of H_2O from the alcohol **9** itself to afford the corresponding [2.2]MCP-1-ene can be proposed. From [2.2]MCP-1-ene, **10** might be produced via intermediate [2.2]MCP-1,9-diene, as expected on the basis of earlier reported observations that [2.2]MCP-1,9-dienes gave the tautomerization product 10b,10c-dihydropyrenes (17).

Interestingly, the higher yield of *ipso*-formylated product is obtained in the presence of $AlCl_3$–$MeNO_2$ in 80% yield along with *anti*-5-*tert*-butyl-8,16-dimethyl-13-(3-methyl-1-butene-2-yl)[2.2]MCP (**13a**). Thus, the yield of *ipso*-formylation at the *tert*-butyl group of **6a** was strongly affected by the activity of the formylation catalyst. In contrast, in the formylation of *anti*-6,14-di-*tert*-butyl-9,17-dimethyl-[3.2]MCP (**6b**) under the same reaction conditions, *syn*-6,14-di-*tert*-butyl-7-formyl-9,17-dimethyl[3.2]MCP (**14b**) was obtained in 40% yield arising from the *anti*-*syn*-ring inversion of the formylation intermediate along with *ipso*-formylation product **7b** in 42% yield. In the formylation of *anti*-[4.2]MCP (**6c**) only the mono *ipso*-formylated product **7c** was obtained in 92% yield. The formation of a two-fold *ipso*-formation product, i.e., *anti*-5,13-diformyl-8,16-di-

Scheme 5.



Scheme 6.

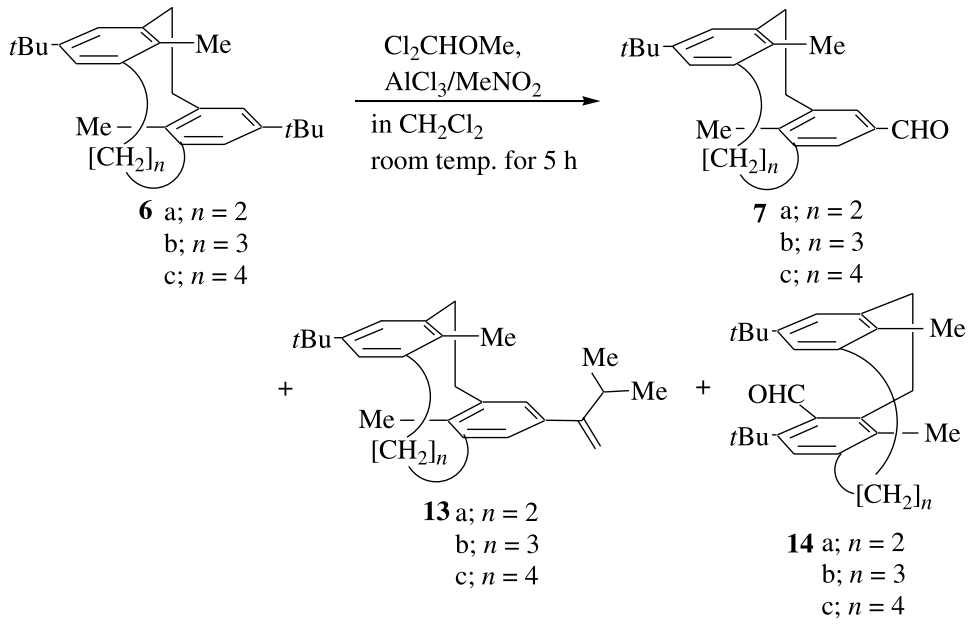
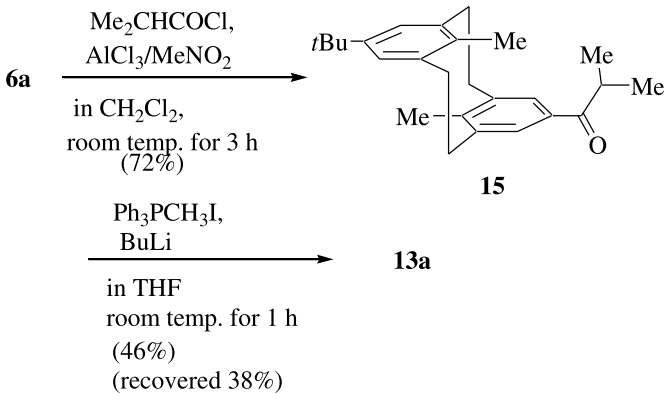


Table 2. Treatment of [*n*.2]MCPs **6a–c** with dichloromethyl methyl ether in the presence of $AlCl_3$ $MeNO_2$.[a]

Run	Substrate	Number of methylene units (*n*)	Products (%)[b,c]		
1	**6a**	2	**7a** (80)[60]	**13a** (20)[15]	**14a** (0)
2	**6b**	3	**7b** (42)[35]	**13b** (0)	**14b** (40)[22]
3	**6c**	4	**7c** (92)[72]	**13c** (0)	**14c** (0)

[a]Conditions: $AlCl_3$ (5 equiv) Cl_2CHOMe (14 equiv).
[b]Relative yields determined by GLC analysis are shown.
[c]Isolated yields are shown in square brackets.

Scheme 7.



methyl[2.2]MCP (**3a**), was not observed under the reaction conditions used (Scheme 6, Table 2).

Previously we reported (7b) that *anti*-**6b** is thermally stable and does not interconvert at 150°C in DMSO solution or at 400°C in the solid state. Although the detailed mechanistic conclusion to rationalize the present observation of *anti*-to-*syn*-conversion is not clear, one might assume similar behavior to that of the nitration or protic acid induced intramolecular condensation of *anti*-8,16-dimethoxy[2.2]MCP to afford the corresponding 17-oxa[2.2.1](1,3,2)cyclophane via *anti*-to-*syn*-ring inversion (9).

The structures of products **13a** and **14b** were determined on the basis of their elemental analyses and spectral data. The ^{1}H NMR spectrum of **13a** shows internal methyl protons as singlets at δ 0.59 and 0.65 and two methyl protons as a doublet at δ 1.11. Two *exo*-methylenes are observed at δ 4.92 and 5.08 as doublets (J = 1.3 Hz). Furthermore, **13a** was alternatively prepared by the *ipso*-acylation of **6a** with isobutanoyl chloride in the presence of $TiCl_4$ followed by Wittig reaction of **15** with methyltriphenylphosphonium iodide in the presence of butyllithium (Scheme 7). On the basis of the spectral data and the comparison of the authentic sample synthesized, **13a** is assigned the structure *anti*-5-*tert*-butyl-8,16-dimethyl-13-(3-methyl-1-butene-2-yl)[2.2]MCP.

The IR (NaCl) spectrum of **14b** shows $\upsilon_{C=O}$ at 1683 cm^{-1}, typical of an aromatic aldehyde. Especially, the mass spectral data for **14b** (M^+ = 390) strongly support the mono formylated product for **6b**. Interestingly, the ^{1}H NMR spectra of **14b** showed the methyl protons at δ 1.73 and 1.96 ppm, respectively, quite a different chemical shift from that of **6a** (δ 0.68 ppm) because of the ring current of the opposite aromatic ring (2,18). The aromatic protons were observed at δ 6.71 and 7.12 ppm (relative intensity 2:1). The former protons are observed at much higher field position than that of *anti*-**6a** (7.04 ppm) because of the face-to-face overlapping between the two benzene rings. These findings strongly support the theory that the structure of **14a** adopts *syn*-conformation. It was also found that one of the ethano-bridge protons has been observed in a deshielded region (δ 3.45–3.50) owing to the formyl group at position seven (the ortho position for the ethano-bridge). Consequently, **14b** is assigned the structure *syn*-6,14-di-*tert*-butyl-7-formyl-9,17-dimethyl[3.2]MCP.

Experimental

All melting points (Yanagimoto MP-S1) were uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Nippon Denshi JEOL FT-270 spectrometer. Chemical shifts are reported as δ values (ppm) relative to internal Me_4Si. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 mass spectrometer at an ionization energy of 70 eV using a direct-inlet system through GLC; *m*/*z* values reported include the parent ion peak. Infrared (IR) spectra were obtained on a Nippon Denshi JIR-AQ2OM spectrophotometer as KBr disks. Elemental analyses were performed by Yanaco MT-5. Gas–liquid chromatograph (GLC) analyses were performed using a Shimadzu gas chromatograph (GC-14A); silicone OV-1, 2 m; programmed temperature rise, 12°C min^{-1}; carrier gas nitrogen, 25 mL min^{-1}.

Materials

The preparation of *anti*-5,13-di-*tert*-butyl-8,16-dimethyl-[2.2]metacyclophane (**6a**), *anti*-6,14-di-*tert*-butyl-9,17-dimethyl[3.2]MCP (**6b**), and *anti*-7,15-di-*tert*-butyl-10,18-dimethyl[4.2]MCP (**6c**) was carried out as previously reported (6,7).

Formylation of dimethyl[2.2]MCP (1) with Cl_2CHOCH_3. Typical procedure

To a solution of *anti*-8,16-dimethyl[2.2]MCP (6) (**1a**) (236 mg, 1.0 mmol) and Cl_2CHOCH_3 (0.56 mL, 6.2 mmol) in CH_2Cl_2 (10 mL) was added a solution of $TiCl_4$ (0.45 mL, 4.1 mmol) in CH_2Cl_2 (4 mL). After the reaction mixture was stirred at 0°C for 1 h, it was poured into a large amount of ice-water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed with water, dried over Na_2SO_4, and evaporated in vacuo to leave a residue that was chromatographed on silica gel ($CHCl_3$ as an eluent) to give **2a** (52.8 mg, 20%) and **3a** (232.4 mg, 80%), respectively.

anti-*5-Formyl-8,16-dimethyl[2.2]MCP (2a)*

Colorless prisms (hexane), mp 182–185°C. IR (KBr) υ_{max}: 3050, 2940, 2860, 2810, 1685 (C=O), 1580, 1375, 1265,

1180, 1110, 780, 745, 720. ^{1}H NMR ($CDCl_3$) δ: 0.52 (s, 3 H), 0.65 (s, 3H), 2.60–3.20 (m, 8H), 6.84–7.23 (m, 3H), 7.64 (s, 2H), 9.85 (s, 1H). MS *m*/*z*: 264 ([M]$^+$). Anal. calcd. for $C_{19}H_{20}O$: C 86.32, H 7.62; found: C 86.33, H 7.65.

anti-*5,13-Diformyl-8,16-dimethyl[2.2]MCP (3a)*

Colorless prisms (hexane), mp 280–282°C. IR (KBr) υ_{max}: 2960, 2825, 2790, 2725, 1670 (C=O), 1585, 1550, 1450, 1375, 1330, 1315, 1260, 1245, 1200, 1190, 1145, 1115, 970, 910, 755, 725, 685. ^{1}H NMR ($CDCl_3$) δ: 0.58 (s, 6H), 2.60–3.30 (m, 8H), 7.64 (s, 4H), 9.86 (s, 2H). MS *m*/*z*: 292 ([M]$^+$). Anal. calcd. for $C_{20}H_{20}O_2$: C 82.16, H 6.89; found: C 82.20, H 6.93.

Formylation of *anti*-9,17-dimethyl[3.2]MCP (**1b**) (7) and *anti*-10,18-dimethyl[4.2]MCP (**1c**) (7) was carried out as a same procedure as described above to afford (**3b**) and (**3c**) in 93 and 91% yield, respectively.

anti-*6,14-Diformyl-9,17-dimethyl[3.2]MCP (3b)*

Colorless prisms (hexane), mp > 300°C. IR (KBr) υ_{max}: 2950, 1680 (C=O), 1590, 1570, 1550, 1445, 1387, 1265, 1255, 1137, 1123, 1111, 1025, 965, 907, 885, 753, 732, 678. ^{1}H NMR ($CDCl_3$) δ: 0.77 (s, 6H), 1.62 (s, 4H), 2.65–3.20 (m, 6H), 7.60 (s, 4H), 9.91 (s, 2H). MS *m*/*z*: 306 ([M]$^+$). Anal. calcd. for $C_{21}H_{22}O_2$: C 82.31, H 7.23; found: C 82.24, H 7.30.

anti-*7,15-Diformyl-10,18-dimethyl[4.2]MCP (3c)*

Colorless prisms (hexane), mp 202–205°C. IR (KBr) υ_{max}: 2950, 2810, 1672 (C=O), 1582, 1560, 1425, 1378, 1258, 1184, 1138, 1103, 1015, 956, 876, 745, 772. ^{1}H NMR ($CDCl_3$) δ: 0.97 (s, 6H), 1.32 (m, 2H), 1.50–1.70 (m, 4H), 2.30–2.47 (m, 2H), 2.79–3.19 (m, 4H), 7.44 (d, *J* = 1.5 Hz, 2H), 7.69 (d, *J* = 1.5 Hz, 2 H), 9.93 (s, 2H). MS *m*/*z*: 320 ([M]$^+$). Anal. calcd. for $C_{22}H_{24}O_2$: C 82.46, H 7.55; found: C 82.62, H 7.71.

Formylation of 1,2,3-trimethylbenzene (4) with Cl_2CHOCH_3

To a solution of 1,2,3-trimethylbenzene (**4**) (240 mg, 2.0 mmol) and Cl_2CHOCH_3 (0.56 mL, 6.2 mmol) in CH_2Cl_2 (10 mL) was added a solution of $TiCl_4$ (0.45 mL, 4.1 mmol) in CH_2Cl_2 (4 mL). After the reaction mixture was stirred at 0°C for 1 h and at room temperature for 3 h, it was treated as described above to give 2,3,4-trimethylbenzaldehyde (**5**) as a pale yellow oil (266.4 mg, 90%); IR (NaCl) υ_{max}: 1670 (C=O). ^{1}H NMR ($CDCl_3$) δ: 2.20 (s, 3H), 2.33 (s, 3H), 2.57 (s, 3H), 7.13 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 9.80 (s, 1H). MS *m*/*z*: 148 ([M]$^+$). Anal. calcd. for $C_{10}H_{12}O$: C 81.04, H 8.16; found: C 81.30, H 8.10.

General procedure for treatment of *anti*-5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP (6a) with Cl_2CHOCH_3 in the presence of $TiCl_4$

To a solution of **6a** (348 mg, 1.0 mmol) and Cl_2CHOCH_3 (0.54 mL, 6.0 mmol) in CH_2Cl_2 (10 mL) was added, dropwise, titanium tetrachloride (0.44 mL, 4.0 mmol) in CH_2Cl_2 (4 mL) at 0°C under an argon. After the reaction mixture was stirred under several reaction conditions, it was poured into ice-water and extracted with CH_2Cl_2 (30 mL × 3). The extracts were washed with water, dried over Na_2SO_4, and concentrated. The residue was chromatographed over silica gel (Wako, C-300; 100 g) with hexane–ether (1:1) as eluent to give **7a**, **8**, **9**, and **10**. The reaction conditions and product yields are compiled in Table 1.

The isobutene, which was generated in the reaction system, was passed through a mixture of toluene (10 mL) containing aluminium chloride (5 mg, 0.037 mmol) with argon gas at room temperature. The reaction mixture was poured into ice-water and extracted with CH_2Cl_2 (10 mL × 3). The extracts were washed with brine, dried over Na_2SO_4, and evaporated in vacuo (30°C 20 torr^{-1}) (1 torr = 133.322 Pa). The residue was analyzed by ^{1}H NMR spectroscopy and gas chromatography from which the formation of *tert*-butyltoluene was qualitatively confirmed.

anti-*5*-tert-*Butyl-13-formyl-8,16 dimethyl[2.2]metacyclophane (7a)*

Pale yellow oil. IR (NaCl) υ_{max}: 1670 (C=O). ^{1}H NMR ($CDCl_3$) δ: 0.49 (s, 3H), 0.64 (s, 3H), 1.30 (s, 9H), 2.70–3.10 (m, 8H), 7.14 (s, 2H), 7.64 (s, 2H), 9.84 (s, 1H). MS *m*/*z*: 320 ([M]$^+$). Anal. calcd. for $C_{23}H_{28}O$ (320.48): C 86.20, H 8.81; found: C 86.45, H 8.65.

2,7-Di*-tert-*butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (10)

Colorless prisms (hexane); mp 203–204°C (lit. (14) value mp 203–204°C).

anti-*5*-tert-*Butyl-8,16-dimethyl-13-(3-methyl-2-butene-2-yl)[2.2]metacyclophane (8)*

Colorless needles (hexane), mp 141–142°C. IR (KBr) υ_{max}: 2990, 2960, 2890, 1465, 1360, 1290, 1280, 1190, 890, 860, 740, 710. ^{1}H NMR ($CDCl_3$) δ: 0.58 (s, 3H, Me-8), 0.69 (s, 3H, Me-16), 1.29 (s, 9H, *t*-Bu), 1.65 (s, 3H, Me), 1.80 (s, 3H, Me), 1.93 (s, 3H, Me), 2.57–2.99 (m, 8H, CH_2), 6.89 (s, 2H, ArH-4,6), 7.12 (s, 2H, ArH-12,14). ^{13}C NMR ($CDCl_3$) δ: 14.38 (q, CH_3-8), 14.70 (q, CH_3-16), 20.70, 20.75, 22.16 (q, CH_3), 31.39 (q, $C(CH_3)_3$), 33.93 (s, $C(CH_3)_3$), 36.46, 36.60 (t, CH_2), 124.10 (d, ArCH), 126.25 (s, β-olefin), 127.10 (d, ArCH), 129.86 (s, α-olefin), 136.17, 136.58, 139.48, 140.41, 140.61, 146.77 (s, ArC). MS *m*/*z*: 360 ([M]$^+$). Anal. calcd. for $C_{27}H_{36}$ (360.59): C 89.94, H 10.06; found: C 89.81, H 10.20.

anti-*5,13-Di*-tert-*butyl-exo-1-hydroxy-8,16-dimethyl-[2.2]metacyclophane (9)*

Colorless needles (hexane), mp 258–259°C. IR (KBr) υ_{max}: 3580 (OH), 2980, 2880, 1475, 1460, 1360, 1280, 1190, 1020, 880, 770. ^{1}H NMR ($CDCl_3$) δ: 0.52 (s, 3H, Me), 0.86 (s, 3H, Me), 1.27 (s, 9H, *t*-Bu), 1.30 (s, 9H, *t*-Bu), 2.01 (broad s, 1H, OH, exchange with D_2O), 2.73–3.13 (m, 6H, CH_2 and C*H*$_2$CH(OH)), 5.34 (dd, 1H, *J* = 2.2/4.6 Hz, C*H*OH), 7.01 (d, 1H, *J*= 2.0 Hz, ArH), 7.18–7.21 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$) δ: 14.03, 14.34 (q, CH_3), 31.30, 31.34 (q, $C(CH_3)_3$), 33.84, 33.89 (s, $C(CH_3)_3$), 35.83, 36.34 (t, CH_2CH_2), 44.56 (t, $CH_2CH(OH)$), 80.66 (d, CH(OH)), 122.73, 124.98, 125.21, 125.80 (d, ArCH), 133.65, 135.22, 136.71, 136.94, 139.66, 140.77, 146.23, 146.34 (s, ArC)). MS *m*/*z*: 364 ([M]$^+$). Anal. calcd. for $C_{26}H_{36}O$ (360.59): C 85.66, H 9.95; found: C 85.35, H 9.78.

Oxidation of 8 with cetyltrimethylpermanganate affording *anti*-5-acetyl-13-*tert*-butyl-8,16-dimethyl-[2.2]MCP (11)

To a solution of **8** (36 mg, 0.1 mmol) in CH_2Cl_2 (1 mL) was added, dropwise, CTAP (40 mg, 0.1 mmol) in CH_2Cl_2 (1 mL) within 1 min at room temperature. After being stirred for 2.5 h, the reaction mixture was filtered over celite and Na_2SO_4. The filtrate was evaporated in vacuo to give **11** (29 mg, 87%) as a colourless solid. Recrystallization from hexane gave the *title compound* **11** as colorless prisms; mp 155–157°C; IR (KBr) υ_{max}: 1665 (C=O). ^{1}H NMR ($CDCl_3$) δ: 0.50 (s, 3H), 0.63 (s, 3H), 1.30 (s, 9H), 2.55 (s, 3H), 2.73–3.04 (m, 8H), 7.13 (s, 2H), 7.73 (s, 2H). MS *m*/*z*: 334 ([M]$^+$). Anal. calcd. for $C_{24}H_{30}O$: C 86.18, H 9.04; found: C 86.65, H 8.98.

Conversion of 9 to 10: Typical procedure

A solution of **9** (182 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) or benzene (5 mL) was stirred at room temperature for several times. The reaction mixture was evaporated in vacuo. The residue was purified through silica gel column by eluting with hexane–ether (1:1) to give **10**. When titanium tetrachloride (379 mg, 0.22 mL, 2.0 mmol) or concd. HCl (1 drop) was used as an additive the reaction mixture was poured into ice-water and extracted with CH_2Cl_2. The extracts were washed with brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified according to the same manner described above.

General procedure for treatment of 6 with Cl_2CHOCH_3 in the presence of $AlCl_3$ $MeNO_2$

To a solution of **6b** (207 mg, 0.572 mmol) and Cl_2CHOCH_3 (0.72 mL, 7.9 mmol) in CH_2Cl_2 (12 mL) was added, dropwise, a solution of $AlCl_3$ (458 mg, 3.4 mmol) in $MeNO_2$ (1.0 mL) at 0°C under argon. After the reaction mixture was stirred at 0°C for 1 h and at room temperature for 5 h it was poured into ice-water and extracted with CH_2Cl_2 (30 mL × 3). The extracts were washed with water, dried over Na_2SO_4, and concentrated to give, as an oil, a mixture of (161 mg, 82%), in the ratio 50:50 (GLC analysis). The residue was chromatographed over silica gel (Wako, C-300; 100 g) with benzene and benzene–$CHCl_3$ (1:1) as eluent to give **7b** (77 mg, 35%) and **14b** (42 mg, 22%) as an oil, respectively.

syn-*6,14-Di*-tert-*butyl-7-formyl-9,17-dimethyl[3.2]metacyclophane (14b)*

Pale yellow oil. IR (NaCl) υ_{max}: 1683 (C=O). ^{1}H NMR ($CDCl_3$) δ: 1.28 (9 H, s), 1.46 (s, 9H), 1.73 (s, 3H), 1.96 (s, 3H), 2.25–2.35 (m, 2H), 2.15–3.20 (m, 7H), 3.45–3.50 (m, 1H), 6.71 (broad s, 2H), 7.12 (s, 1H), 10.09 (s, 1H). MS *m*/*z*: 390 ([M]$^+$). Anal. calcd. for $C_{28}H_{38}O$ (390.61): C 86.10, H 9.81; found: C 86.24, H 9.52.

anti-*14*-tert-*Butyl-6-formyl-9,17-dimethyl[3.2]MCP (7b)*

Pale yellow oil. IR (NaCl) υ_{max}: 1680 (C=O). ^{1}H NMR ($CDCl_3$) δ: 0.64 (s, 3H), 0.78 (s, 3H), 1.30 (s, 9H), 2.00–2.20 (m, 2H), 2.50–3.20 (m, 8H), 7.04 (d, 1H, *J* = 2.0 Hz), 7.08 (d, 1H, *J* = 2.0 Hz), 7.56 (s, 2H), 9.87 (s, 1H). MS *m*/*z*: 334 ([M]$^+$). Anal. calcd. for $C_{24}H_{30}O$ (334.51): C 86.18, H 9.04; found: C 86.40, H 9.25.

Similarly, compounds **7a, 13a**, and **7c** were prepared in the same manner as described above in 60, 15, and 72% yields, respectively.

anti-*5*-tert-*Butyl-8,16-dimethyl-13-(3-methyl-1-butene-2-yl)[2.2]metacyclo-phane (13a)*

Colorless needles (hexane), mp 154–155°C. IR (KBr) υ_{max}: 2970, 2930, 2860, 1615, 1470, 1455, 1350, 1270, 1180, 890, 880, 850. ^{1}H NMR ($CDCl_3$) δ: 0.59 (s, 3H), 0.65 (s, 3H), 1.11 (d, 6H, *J* = 6.6 Hz), 1.29 (s, 9H), 2.70–3.03 (m, 9H, CH_2 and CH), 4.92, 5.08 (d, each 1H, *J* = 1.3 Hz, olefinic proton), 7.12 (s, 4H). MS *m*/*z*: 360 ([M]$^+$, 57), 303 ([M$^+$– *t*-Bu]). Anal. calcd. for $C_{27}H_{36}$ (360.59): C 89.93, H 10.07; found: C 89.65, H 10.01.

anti-*15*-tert-*Butyl-7-formyl-10,18-dimethyl[4.2]MCP (7c)*

Pale yellow prisms (hexane), mp 86–89°C. IR (KBr) υ_{max}: 1693 (C=O). ^{1}H NMR ($CDCl_3$) δ: 0.85 (s, 3H), 0.99 (s, 3H), 1.31 (s, 9H), 1.05–1.20 (m, 4H), 2.16–2.42 (m, 2H), 2.71–3.11 (m, 6H), 6.87 (d, 1H, *J* = 1.8 Hz), 7.15 (d, 1H, *J* = 1.8 Hz), 7.36 (d, 1H, *J* = 1.8 Hz), 7.65 (d, 1H, *J* = 1.8 Hz), 9.91 (s, 1H, CHO). MS *m*/*z*: 348 ([M]$^+$). Anal. calcd. for $C_{25}H_{32}O$ (348.53): C 86.15, H 9.19; found: C 86.37, H 9.25.

Acylation of 6a with isobutanoyl chloride in the presence of $TiCl_4$

To a solution of **6a** (299.1 mg, 0.858 mmol) and isobutanoyl chloride (365.3 mg, 3.43 mmol) in CH_2Cl_2 (6.6 mL) was added, dropwise, a solution of $TiCl_4$ (1.21 mL, 11.03 mmol) in CH_2Cl_2 (1.5 mL) at 0°C under an argon. After the reaction mixture was stirred at 0°C for 1 h and at room temperature for 1 h, it was poured into ice-water and extracted with CH_2Cl_2 (30 mL × 3). The extracts were washed with water, dried over Na_2SO_4, and concentrated. The residue was chromatographed over silica gel (Wako, C-300; 100 g) with $CHCl_3$ as an eluent to give **15** as prisms. Recrystallization from hexane gave *anti*-13-*tert*-butyl-5-isobutanoyl-8,16-dimethyl[2.2]metacyclophane (**15**) (223 mg, 71.8%) as colorless prisms (hexane), mp 114–116°C. IR (KBr) υ_{max}: 1672 (C=O). ^{1}H NMR ($CDCl_3$) δ: 0.52 (s, 3H), 0.63 (s, 3H), 1.30 (s, 9H), 1.20 (d, 6H, *J* = 6.7 Hz), 2.70–3.10 (m, 8H), 3.50–3.60 (m, 1H), 7.13 (s, 2H), 7.75 (s, 2H). MS *m*/*z*: 362 ([M]$^+$). Anal. calcd. for $C_{26}H_{34}O$ (360.59): C 86.13, H 9.45; found: C 86.08, H 9.51.

Wittig reaction of 15 with methyltriphenylphosphonium iodide affording *anti*-5-*tert*-butyl-8,16-dimethyl-13-(3-methyl-1-butene-2-yl)[2.2]MCP (13a)

To a suspension of methyltriphenylphosphonium iodide (121 mg, 0.3 mmol) in dry THF (10 mL) was added, dropwise, 1.6 N butyllithium hexane solution (0.19 mL, 0.30 mmol) within 1 min at room temperature under an argon. After the reaction mixture was stirred for 0.5 h, a solution of **15** (54 mg, 0.15 mmol) in dry THF (1 mL) was added, dropwise, within 1 min. After being stirred for 1 h, the reaction mixture was poured into ice-water and extracted with ether. The extracts were washed with water, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified through silica gel column (Wako, C-300; 100 g) by eluting with hexane to give **13a** (25 mg, 46%) and unchanged **15**

(21 mg, 38%) as colourless solid. Recrystallization from hexane gave **13a** as colorless prisms.

Conclusions

We conclude that the selective *ipso*-formylation reactions of *anti*-di-*tert*-butyl[*n*.2]MCPs **6** led to the first-reported direct introduction of one formyl group because of a through-space electronic interaction with the opposing benzene ring, similar to the electrophilic aromatic substitution of MCPs. The yield of *ipso*-formylation of **6** was controlled by the activity of the catalyst used. Especially, the present *ipso*-formylation with dichloromethyl methyl ether in the presence of $AlCl_3$ $MeNO_2$ provides excellent yields and easy isolation of the products. The presently developed procedure was further applied to the direct removal of a *tert*-butyl group by electrophilic substitution of *anti*-di-*tert*-butyl-8,16-dimethyl[2.2]MCP **6a**, which are prone to give transannular reaction products under the electrophilic reaction conditions. The chemical behaviours of [*n*.2]MCPs for other electrophilic reagents are now under study.

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