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Metacyclophanes and Related Compounds. 12. Reaction of 8,16-Dimethyl[2.2]metacyclophane with Iodine Monochloride[1]

Masashi Tashiro,* Takehiko Yamato, and Kazumasa Kobayashi

Research Institute of Industrial Science and Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University 86 6-1 Kasuga-kohen, Kasuga-shi, Fukuoka 816, Japan

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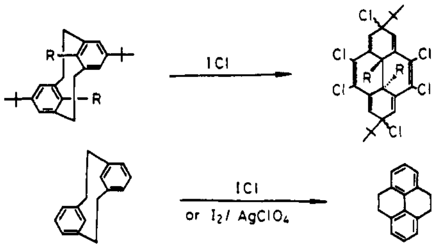
Reaction of 8,16-dimethyl[2.2]metacyclophane (1) with iodine in the presence of HIO_4 and H_2SO_4 afforded 5-iodo-8,16-dimethyl- (**2a**) and 5,13-diiodo-8,16-dimethyl[2.2]metacyclophane (**2b**) in 10% and 67% yields, respectively. However, treatment of 1 with iodine monochloride, which is a well-known powerful iodinating reagent, gave mainly 5-monochloro- and 5,8-dichloro[2.2]metacyclophane derivatives. It was also found that reaction of 1 with a large excess of ICl afforded 1,5,13-trichloro-8,16-dimethyl[2.2]metacyclophane in 90% yield, and 1 gave 5,13-dichloro-8,16-dimethyl[2.2]metacyclophan-1-ene by treatment with KO-*t*-Bu in *t*-BuOH.

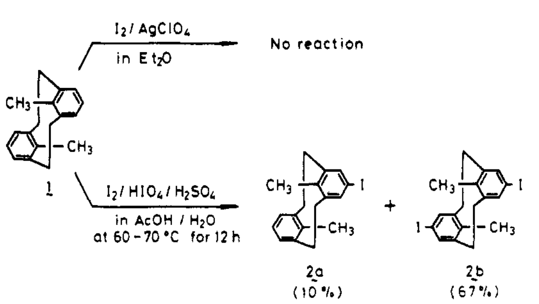
It has been reported that reaction of 8,16-dimethyl-5,13-di-*tert*-butyl[2.2]metacyclophane (MCP) with excess iodine monochloride afforded the corresponding hexachlorotetrahydropyrene.[2] Recently, Sato et al. reported that reaction of [2.2]MCP itself with iodine monochloride or with iodine and silver perchlorate afforded tetrahydropyrene.[3]



However, there is no information on the reaction of 8,16-dialkyl[2.2]MCPs with iodine monochloride, which is a powerful iodinating reagent for aromatic compounds,[4] or with iodine in the presence of acidic catalysts.[5] We here report on the chemical behavior of 8,16-dimethyl[2.2]MCP with these iodinating reagents.

Results and Discussion

Treatment of 8,16-dimethyl[2.2]MCP (1) with iodine in the presence of silver perchlorate according to Sato's procedure[3] resulted only in recovery of starting compound 1 in almost quantitative yield. However, reaction of 1 with iodine in the presence of HIO_4 and H_2SO_4 afforded **2a** and **2b**.

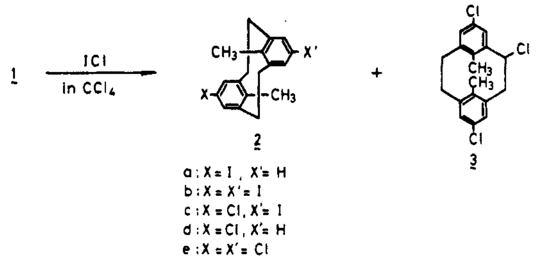


On the other hand, reaction of 1 with iodine monochloride gave several compounds 2 as well as 3, the products depending on the ratio of the reactants as shown in Table I.

Table I. Reaction of 8,16-Dimethyl[2.2]MCP (1) with Iodine Monochloride[a]

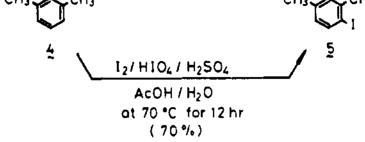
run	ICl/1, mol/mol	product[b] (%)
1[c]	1	**2a** (6), **2d** (29), **2e** (3)
2[d]	2	**2a** (12), **2b** (+),[e] **2c** (4), **2d** (64), **2e** (16)
3	5	**2c** (30), **2e** (69)
4	15	**3** (90)[f]

[a] Reaction was carried out at 20 °C for 2 h. [b] Yields were determined by mean of GC. [c] Compound 1 was recovered in 55% yield. [d] Compound 1 was recovered in 2% yield. [e] Plus sign means less than 1% yield. [f] Isolated yield is 67%.



As shown in Table I, the reaction with an equimolar amount of ICl afforded a mixture of **2a**, **2d**, and **2e**. Surprisingly, the principal product of the reaction was the monochlorinated compound **2d**; one of the expected products, **2a**, was obtained in only 6% yield, and no **2b** was formed. The yields of the chlorinated products **2d** and **2e** increased with increasing ratios of ICl. When the excess of ICl was increased further, chlorination occurred not only on the aromatic rings but also on the aliphatic carbon to give 3 in good yield. The structures of **2a–e** were assigned on the basis of elemental analyses and spectral data. It should be noted that the halogen atoms of **2a–e** are at positions 5 and 13 of the MCP ring, halogenation occurring selectively para to the methyl substituents of MCP. The structure of 3 is discussed below.

Treatment of 1,2,3-trimethylbenzene (4) with ICl under the same conditions used with 1 afforded a 90% yield of 2,3,4-trimethyliodobenzene (5), which was also obtained in 70% yield by treatment of 4 with iodine in the presence of HIO_4/H_2SO_4. In contrast, reaction of 1 with ICl af-



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(1) Part 11. Tashiro, M.; Yamato, T. *J. Org. Chem.*, submitted for publication.

(2) Tashiro, M.; Yamato, T., submitted for publication.

(3) Sato, T.; Wakabayashi, M.; Okamura, Y. *Bull Chem. Soc. Jpn.* **1967**, *40*, 2363.

(4) (a) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1957**, *79*, 1412. (b) Andrews, L. J.; Keefer, R. M. *Ibid.* **1957**, *79*, 5169.

(5) Suzuki, H.; Nakamura, K.; Goto, R. *Bull. Chem. Soc. Jpn.* **1968**, *39*, 128.

0022-3263/84/1949-3380$01.50/0

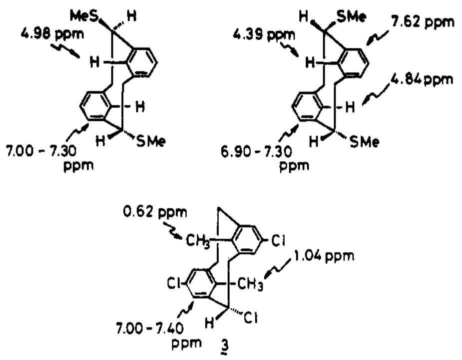
Table II. Reaction of 5,13-Diiodo-8,16-dimethyl[2.2]MCP (2b) with ICl[a]

$$\mathbf{2b} \xrightarrow[\mathrm{CCl_4}]{\mathrm{ICl}} \mathbf{2c}, \mathbf{2e}, \mathbf{3}$$

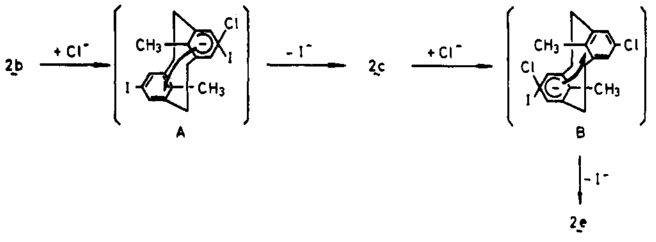
run	ICl/**2b**, mol/mol	product[b] (%)
1[c]	1	**2c** (6), **2e** (6)
2[d]	5	**2c** (6), **2e** (32)
3	15	**3** (70)

[a] Reaction temperature, 20 °C; time, 2 h. [b] Yields were determined by GC. [c] Compound **2b** was recovered in 88% yield. [d] Compound **2e** was recovered in 60% yield.

Chart I

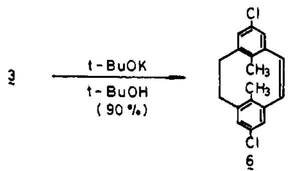


forded the chlorinated compounds **2c**, **2d**, and **2e**. The data of Table I suggest that iodides **2a** and **2b** might be formed initially and then be converted into the corresponding chlorides by an iodine–chlorine exchange reaction, which has not been observed in usual aromatic iodinations with ICl. Accordingly, we carried out the reaction of **2b** with ICl under similar conditions, with the results shown in Table II. As we surmised, chlorinated compounds **2c**, **2e**, and **3** were formed from **2b**. This finding is the first example of a chlorine exchange reaction of an aromatic iodo compound with ICl. Although a detailed mechanism has not been worked out, we suggest that a spatial interaction of the two benzene rings of MCP may promote the exchange, which is observed in the MCP system but not in simple aromatic compounds.



The Cl^- anion generated from ICl attacks **2b** to form an intermediate A, which should be stablized by interaction with the opposing benzene ring, whose π-electron density is reduced by the iodine or chlorine atoms. In the MCP system a Meisenheimer complex would be stablized by the opposing benzene ring, thus accelerating the reaction.

Structure of 3. When **3** was treated with KO-*t*-Bu in *tert*-butyl alcohol, the corresponding cyclophanene **6** was obtained in good yield. Boekelheide et al.[6] assigned the ¹H NMR signals of bis(mercaptomethyl)[2.2]MCP as indicated in Chart I, and we have assigned the ¹H NMR signals of **3** in similar fashion.



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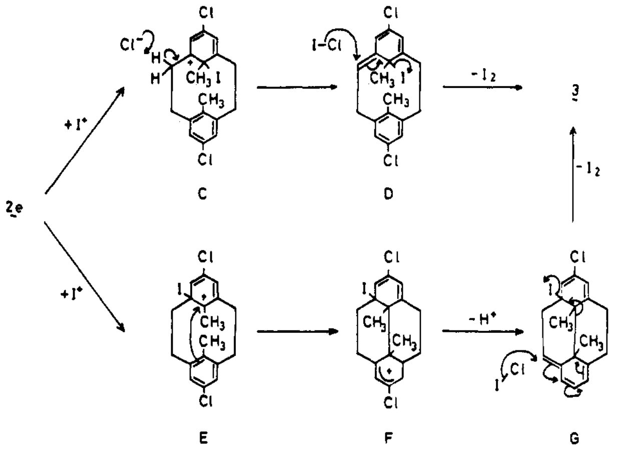
Scheme I



On the basis of the chemical conversion and spectral data, **3** is assigned the structure 1-*exo*-3,15-trichloro-8,16-dimethyl[2.2]MCP. Although the detailed mechanism of formation of **3** is not clear, one might assume the reaction pathway shown in Scheme I.

The iodo cation attacks the ipso positions of **2e** to form intermediates C and E, from which **3** might be produced directly or indirectly.

The preparation of metacyclophan-1-ene **6** from **1** through **3** appears to be a useful route to cyclophanenes, and studies of the scope and limitations of the route are in progress.

Experimental Section

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

Analytical Procedure. Analyses were carried out by GLC using a JGC-20KEP Nippon Denshi gas chromatograph, silicone OV-1 30%, 0.75 m, column temperature 220 °C, carrier gas nitrogen, 50 mL min^{-1}.

Iodination of 1 with Iodine in the Presence of HIO_4/H_2SO_4. A mixture of 136.8 mg (0.58 mmol) of **1**, 114 mg (0.58 mmol) of HIO_4-2 H_2O, 295 (1.16 mmol) of I_2, 10 mL of AcOH, 1 mL of H_2O, 0.2 mL of concentrated H_2SO_4 was warmed at 65–70 °C for 12 h, was then cooled to room temperature, and extracted with dichloromethane. The extract was washed with sodium thiosulfate solution and water, dried over sodium sulfate, and evaporated in vacuo to leave a residue that was purified by column chromatography (silica gel) with benzene as eluant to afford a mixture of **2a** and **2b**. This was recrystallized from hexane to give 20 mg (10%) of **2a** and 190 mg (67.1%) of **2b**.

2a: colorless prisms (hexane); mp 190–192 °C; IR (KBr) 3040, 2930, 1540, 1360, 1240, 880 cm^{-1}; ¹H NMR ($CDCl_3$) δ 0.52 (3 H, s), 0.72 (3 H, s), 2.60–3.00 (8 H, m), 6.82–7.10 (5 H, m); mass spectrum, *m/e* 362 (M^+). Anal. Calcd for $C_{18}H_{19}I$: C, 59.68; H, 5.29. Found: C, 59.79; H, 5.40.

2b: colorless prisms (hexane); mp 285–286 °C dec; IR (KBr) 2950, 2910, 1540, 1440, 1315, 1170, 880, 840, 800, 720 cm^{-1}; ¹H NMR ($CDCl_3$) δ 0.66 (6 H, s), 2.48–3.04 (8 H, m), 7.36 (4 H, s); mass spectrum, *m/e* 488 (M^+). Anal. Calcd for $C_{18}H_{18}I_2$: C, 44.29; H, 3.72. Found: C, 43.68; H, 3.72.

Reaction of 1 with Iodine Monochloride. To a solution of 342 mg (1.45 mmol) of **1** in 250 mL of carbon tetrachloride was

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(6) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1973**, *96*, 1547.

added a solution of 471 mg (2.90 mmol) of iodine monochloride in 30 mL of carbon tetrachloride at 20 °C. After the reaction mixture was stirred for 2 h, it was poured into a large amount of ice–water and extracted with dichloromethane. The extract was washed with sodium thiosulfate solution and water, dried over sodium sulfate, and evaporated in vacuo to leave the mixture of **2a–e** and recovered **1** (the yields were determined by GLC analysis).

Compounds **2d** and **2e** were prepared by chlorination of **1** with sulfuryl chloride. Compound **2e** was obtained in small amount by preparative GLC.

2c: colorless prisms; ^{1}H NMR ($CDCl_3$) δ 0.68 (6 H, s), 2.6–2.9 (8 H, m), 7.06 (4 H, s); mass spectrum, *m/e* 396, 398 (M^+).

Compound **3** was obtained in 67% yield by recrystallization of the reaction mixture of run 4 from hexane. **3**: colorless prisms (hexane); mp 255–256 °C; IR (KBr) 3040, 2950, 1565, 1440, 1420, 1375, 1175, 890, 860, 830, 825, 800, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.62 (3 H, s), 1.04 (3 H, s), 2.60–3.04 (4 H, m), 3.18 (1 H, dd, *J* = 15 Hz, 5.5 Hz), 3.4 (1 H, dd, *J* = 15 Hz, 5.5 Hz), 5.40 (1 H, dd, *J* = 5.5 Hz, 2.5 Hz), 7.00–7.40 (4 H, m); mass spectrum, *m/e* 338, 340, 342, 344 (M^+). Anal. Calcd for $C_{18}H_{17}Cl_3$: C, 63.64; H, 5.04. Found: C, 63.69; H, 5.10.

Chlorination of 1 with Sulfuryl Chloride. To a solution of 273.6 mg (1.16 mmol) of **1** and 4 mL of sulfuryl chloride in 120 mL of carbon tetrachloride was added 1 mL of boron trifluoride–ether complex at room temperature. After the reaction mixture was refluxed for 12 h, it was cooled, poured into a large amount of ice–water, and extracted with dichloromethane. The extract was dried over sodium sulfate and evaporated in vacuo to give a mixture of **2d** and **2e** in 12% and 88% yields, respectively. (The yields were determined by GLC analyses.) The mixture was recrystallized from hexane to afford 31 mg (10%) of **2d** and 250 mg (70%) of **2e**.

2d: colorless prisms (MeOH); mp 201–202 °C; IR (KBr) 3040, 2930, 1560, 1370, 1250, 1010, 960, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.52 (3 H, s), 0.69 (3 H, s), 2.52–3.01 (8 H, m), 6.74–7.10 (5 H, m); mass spectrum, *m/e* 270, 272 (M^+). Anal. Calcd for $C_{18}H_{19}Cl$: C, 79.84; H, 7.07. Found: C, 79.10; H, 7.01.

2e: colorless prisms (hexane); mp 244–245 °C; IR (KBr) 3040, 2930, 1570, 1360, 1210, 1010, 950, 940 cm^{-1}; NMR ($CDCl_3$) δ 0.66 (6 H, s), 2.52–3.01 (8 H, m), 7.05 (4 H, s); mass spectrum, *m/e* 304, 306, 308 (M^+). Anal. Calcd for $C_{18}H_{18}Cl_2$: C, 70.83; H, 5.94. Found: C, 70.40; H, 5.81.

Reaction of 4 with Iodine Monochloride. To a solution of 1.20 g (10 mmol) of **4** in 50 mL of carbon tetrachloride was added a solution of 1.95 g (12 mmol) of iodine monochloride in 10 mL of carbon tetrachloride at 20 °C. After the reaction mixture was stirred for 6 h, it was poured into a large amount of ice, extracted with sodium thiosulfate solution and water, dried over sodium sulfate, and evaporated in vacuo to leave a residue that was distilled under reduced pressure to give 2.21 g (90%) of **5**.

5: colorless liquid; bp 80–82 °C (2 mm) [lit.[7] bp 144–145 °C (20 mm)].

Iodination of 4 with Iodine in the Presence of HIO_4/H_2SO_4. A mixture of 6.01 g (50 mmol) of **4**, 2.31 g (9.1 mmol) of $HIO_4 \cdot 2H_2O$, 5.1 g (20 mmol) of iodine, 25 mL of AcOH, 3 mL of H_2O, and 1 mL of concentrated H_2SO_4 was warmed at 65–70 °C for 12 h, was then cooled to room temperature, and extracted with dichloromethane. The extract was washed with sodium thiosulfate solution and water, dried over sodium sulfate, and evaporated in vacuo to leave a residue that was distilled under reduced pressure to give 8.61 g (70%) of **5**.

Reaction of 2b with Iodine Monochloride. Typical Procedure. To a solution of 96 mg (0.2 mmol) of **2b** in 40 mL of carbon tetrachloride was added a solution of 62.4 mg (1 mmol) of iodine monochloride in 4 mL of carbon tetrachloride at 20 °C. After the reaction mixture was stirred for 2 h, it was poured into a large amount of ice–water, extracted with sodium thiosulfate solution and water, dried over sodium sulfate, and evaporated in vacuo to leave a mixture of **2c** and **2e** and recovered **2b** in 60%, 32%, and 60% yields, respectively (the yields were determined by GLC analyses).

Reaction of 3 with *t*-BuOK. A solution of 100 mg (0.294 mmol) of **3** and 250 mg (2.23 mmol) of potassium *tert*-butoxide in 30 mL of *tert*-butyl alcohol was refluxed for 12 h under a nitrogen atmosphere. After the reaction mixture was cooled to room temperature, it was extracted with dichloromethane. The extract was washed with water, dried over sodium sulfate, and evaporated in vacuo to leave a residue, which on column chromatography (silica gel) with hexane as eluent afforded 80 mg (89.6%) of **6**: colorless prisms (MeOH); mp 223–224 °C; IR (KBr) 3040, 2920, 1555, 1430, 1175, 890, 850, 830, 775, 750, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (6 H, s), 2.40–2.90 (4 H, m), 6.53 (2 H, s), 6.81 (2 H, d, *J* = 2.5 Hz), 6.94 (2 H, d, *J* = 2.5 Hz); mass spectrum, *m/e* 302, 304, 306 (M^+). Anal. Calcd for $C_{18}H_{16}Cl_2$: C, 71.30; H, 5.32. Found: C, 71.06; H, 5.37.

Registry No. **1**, 51689-61-3; **2a**, 91239-66-6; **2b**, 91239-67-7; **2c**, 91239-68-8; **2d**, 91239-69-9; **2e**, 91239-70-2; **3**, 91239-71-3; **4**, 526-73-8; **5**, 41381-33-3; ICl, 7790-99-0; sulfuryl chloride, 7791-25-5.

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[7] Suzuki, H.; Sugiyama, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 586.

Poly(isothianaphthene)

F. Wudl,* M. Kobayashi, and A. J. Heeger

Institute for Polymers and Organic Solids, Department of Physics, University of California, Santa Barbara, California 93106

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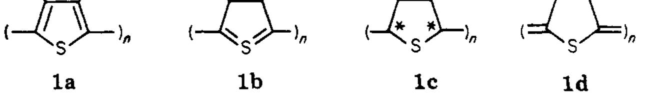
The title polymer was prepared by several different approaches. Electrochemical polymerization of isothianaphthene is strongly electrolyte dependent; nonnucleophilic anions produce poly(dihydroisothianaphthene), whereas nucleophilic anions (Br^-, Cl^-) allow formation of the title compound. The latter, either in a Brønsted acid ($HSO_4 \cdot nH_2O$) doped form or chloride doped form is a better conductor than polythiophene by ca. 1 order of magnitude and about as good a conductor as poly(3-methylthiophene).

Within the rapidly expanding field of polymeric conductors,[1] the poly(heterocycles) have received attention because they are easily prepared in film form and are considerably more stable to atmospheric exposure than poly(acetylene) or poly(phenylene).[2] As an extension of our recent entry into the study of poly(thiophene),[3] we sought to prepare poly(isothianaphthene), a polymer of a

Scheme I[a]



1a 1b 1c 1d

[a] * = +, −, ·.

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(1) Proceedings of the International Conference on the Physics and Chemistry of Polymeric Conductors, *J. Phys. Colloq.* (*Orsay, Fr.*) **1983**, *C-3*.

(2) For use in stabilizing a semiconductor surface, see: Noufi, R.; Frank, A. J.; Nozik, A. J. *J. Am. Chem. Soc.* **1981**, *103*, 184 and references therein.

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