prepared by mixing 5 mL methanol and 5 mL of aqueous 10% KI/7.2% HCl. The reaction mixture was allowed to sit in the dark for 30 min. Upon completion, the reaction mixture was titrated to end point with ~0.01 M $Na_2S_2O_3$. The results were corrected for a blank titration. The percentage of active oxygen for the hemiperketals was found to be 95 ± 2%.

^{17}O NMR Spectroscopy. The ^{17}O NMR spectra were recorded on a Varian VXR-400 spectrometer equipped with a 10-mm broad-band probe. All spectra were acquired at natural abundance at 25 °C in methylene chloride. The concentration of the compounds employed in these experiments was 0.2 M. The signals were referenced to external deionized water at 25 °C. The instrumental settings were spectral width 35 kHz, 2K data points, 90° pulse angle (40-μs pulse width) 150-μs acquisition delay, 29-ms acquisition time. Typically 40 000–100 000 scans were required. The spectra were recorded with sample spinning and without lock. The signal-to-noise ratio was improved by applying a 25–50 Hz exponential broadening factor to the FID prior to Fourier transformation. The data point resolution was improved to ±0.1 ppm by zero filling to 8K data points. The reproducibility of the chemical shift data is estimated to be better than ±2.0 ppm.

Acknowledgment is made to the National Science Foundation (CHE-9017230) for support of this research. NMR instrumentation was obtained, in part, by a NSF Equipment Grant (CHE8409599).

Registry No. **1a**, 133610-01-2; **1b**, 137363-38-3; **1c**, 133610-04-5; *trans*-**1d**, 133610-50-1; *cis*-**1d**, 133610-05-6; **1e**, 137363-39-4; **2a**, 137363-40-7; **2b**, 137363-41-8; **2c**, 137363-42-9; *trans*-**2d**, 137363-43-0; *cis*-**2d**, 137363-44-1; **2e**, 25243-43-0.

Medium-Sized Cyclophanes. 15. Bromination and Lewis Acid Catalyzed Isomerization of 8,16-Diethyl[2.2]metacyclophane[1]

Takehiko Yamato,*,† Jun-ichi Matsumoto,† Kiwamu Tokuhisa,† Mitsuaki Shigekuni,† Kazuaki Suehiro,† and Masashi Tashiro‡

Department of Industrial Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi, Saga 840, Japan, and Research Institute of Advanced Material Study, Kyushu University, 6-1, Kasuga-kohen, Kasuga-shi, Fukuoka 816, Japan

Received May 31, 1991

Introduction

Sato and his co-workers[2] have reported that bromination of 8,16-unsubstituted [2.2]metacyclophane (MCP = metacyclophane) with bromine in the presence of Fe powder afforded the corresponding tetrahydropyrene via an addition–elimination mechanism.[3-8]

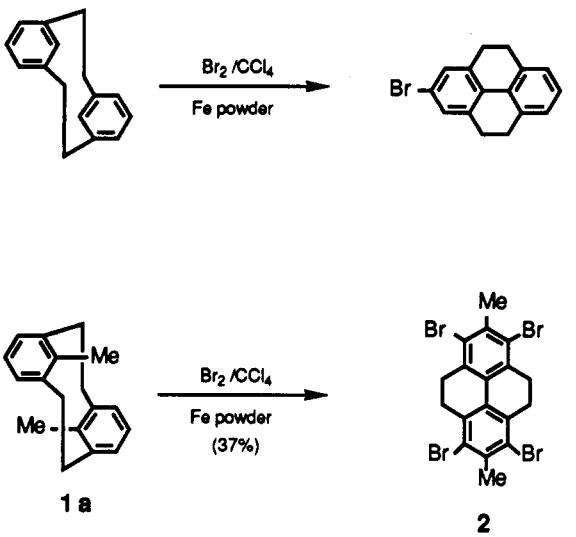
Recently, we reported[9] that in similar bromination reactions of 8,16-dimethyl[2.2]MCP (**1a**), the isomerization and transannular cyclization product, 2,7-dimethyl-1,3,6,8-tetrabromo-4,5,9,10-tetrahydropyrene (**2**), was obtained due to the release of the strain in the molecule. This novel isomerization and transannular cyclization reaction might be attributed to the methyl groups at the 8,16-positions, which increase the strain in the molecule in comparison with the 8,16-unsubstituted [2.2]MCPs.

Therefore, we decided to investigate the substituent effects at 8,16-positions on the bromination of [2.2]MCPs.

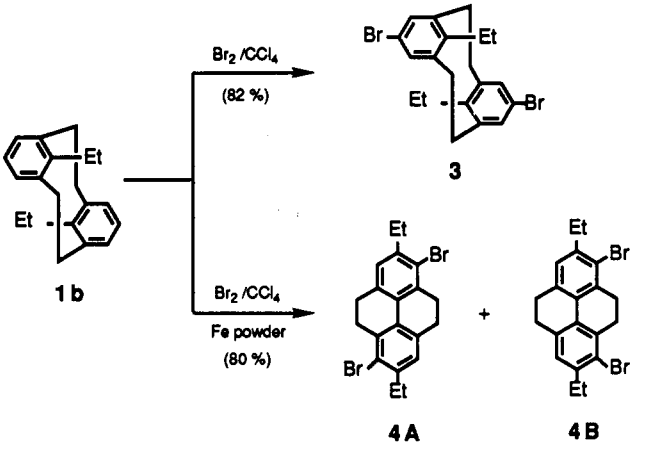
The reaction of 8,16-diethyl[2.2]MCP (**1b**) with bromine and its treatment with Lewis acids in CCl_4 are reported in this paper.

† Saga University.
‡ Kyushu University.

Scheme I



Scheme II



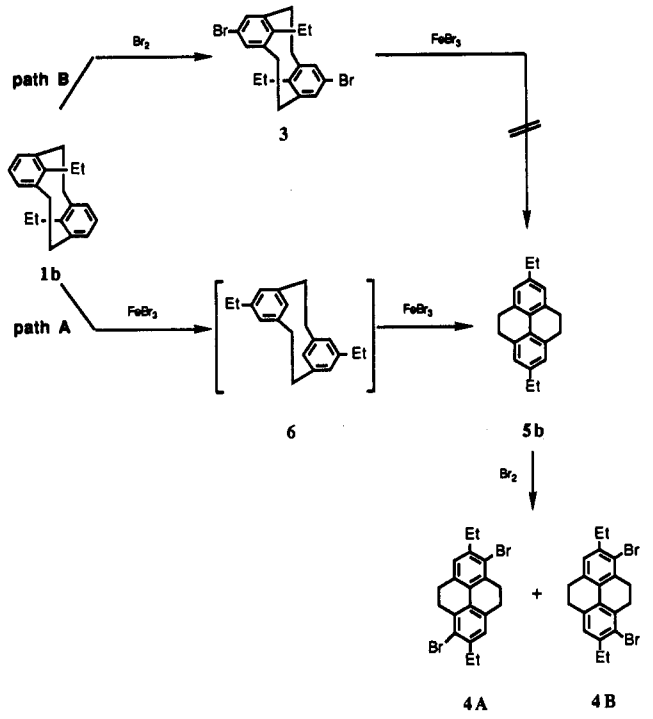
Results and Discussion

Bromination of 8,16-diethyl[2.2]MCP (**1b**) with 6 equiv of bromine at room temperature for 5 min led to 5,13-dibromo-8,16-diethyl[2.2]MCP (**3**) in 82% yield analogous to the bromination of 8,16-dimethyl[2.2]MCP (**1a**). On the other hand, bromination in the presence of Fe powder for 2 h under the same reaction conditions as described above afforded a mixture of 1,6-dibromo-2,7-diethyl- (**4A**) and 1,8-dibromo-2,7-diethyl-4,5,9,10-dihydropyrene (**4B**) in 80% yield (Scheme II). The structure of **4A** and **4B** was assigned by spectral data and elemental analysis. It seems that compound **4** might be formed by isomerization and transannular cyclization of **1b** catalyzed by $FeBr_3$, which should be produced from bromine and Fe powder present during the bromination.

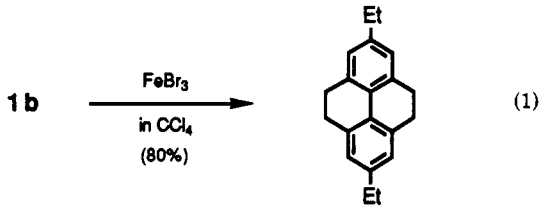
(1) Medium-Sized Cyclophanes. 14. Yamato, T.; Matsumoto, J.; Takahiro, A.; Tokuhisa, K.; Tashiro, M. *J. Chem. Res., Synop.* **1991**, 276.
(2) Sato, T.; Wakabayashi, M.; Okamura, Y. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2363.
(3) Allinger, N. L.; Goldon, B. J.; Hu, S. E.; Ford, R. A. *J. Org. Chem.* **1967**, *32*, 2772.
(4) Sato, T.; Nishiyama, K. *J. Chem. Soc., Chem. Commun.* **1972**, 163.
(5) Sato, T.; Nishiyama, K. *J. Org. Chem.* **1972**, *37*, 3254.
(6) Sato, T.; Takemura, T. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1195.
(7) Yamagishi, T.; Torizuka, K.; Sato, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1140.
(8) Sato, T.; Akabori, S.; Muto, S.; Hata, K. *Tetrahedron* **1968**, *24*, 5567.
(9) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1981**, *46*, 1543.

0022-3263/92/1957-0395$03.00/0

Scheme III



In fact, when 8,16-diethyl[2.2]MCP (**1b**) was treated with $FeBr_3$ in a carbon tetrachloride solution at room temperature for 3 h, the expected product, 2,7-diethyl-4,5,9,10-tetrahydropyrene (**5b**) was obtained in 80% yield (eq 1).



(1)

However, attempted isomerization of **1b** with other Lewis acids, such as $TiCl_4$ or $FeCl_3$, performed under the same reaction conditions failed. The starting compound **1b** was recovered in quantitative yield. Furthermore, reaction of 5,13-dibromo-8,16-diethyl[2.2]MCP (**3**) with $FeBr_3$ resulted only in recovery of the starting compound.

These results strongly suggest that the reaction pathway for bromination of **1b** with bromine in the presence of Fe powder proceeds via path **A** as shown in Scheme III.

It was also found that when 8,16-dimethyl[2.2]MCP (**1a**) was treated with $FeBr_3$ under the same conditions as the diethyl derivative (**1b**), the starting compound was recovered in almost quantitative yield.

It is concluded that the above isomerization reaction is strongly affected by the bulkiness of the substituents in the 8,16-positions which increase the strain in the molecule. The preparation of 2,7-diethyl-4,5,9,10-tetrahydropyrene (**5b**) from **1b** appears to be a useful route to 2,7-dialkyl-4,5,9,10-tetrahydropyrenes, 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 recorded at 270 MHz. Mass spectra were obtained at 75 eV using a direct inlet system.

Preparation of 5,13-Dibromo-8,16-diethyl[2.2]metacyclophane (3). A solution of 153.2 mg (0.58 mmol) of **1b**[10] in 50 mL of CCl_4 was stirred at rt as a solution of 0.56 g (3.48 mmol) of Br_2 in 10 mL of CCl_4 was added. After 5 min, the reaction mixture was poured into a large amount of ice-water. The organic layer was extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried over Na_2SO_4 and evaporated in vacuo to leave a residue, which was recrystallized from hexane to afford 200 mg (82%) of **3**: colorless prisms (hexane); mp 292–293 °C; IR (KBr) 3040, 2940, 1550, 1440, 1420, 1390, 1360, 1320, 1180, 1040, 955, 860, 820, 750 cm^{-1}; NMR ($CDCl_3$) δ 0.36 (6 H, t, J = 7 Hz), 1.14 (4 H, q, J = 7 Hz), 2.56–3.04 (8 H, m), 7.16 (4 H, s); MS (m/e) 420, 422, 424 (M^+). Anal. Calcd for $C_{20}H_{22}Br_2$: C, 56.90; H, 5.25. Found: C, 56.71; H, 5.22.

Preparation of 1,6-Dibromo-2,7-diethyl- (4A) and 1,8-Dibromo-2,7-diethyl-4,5,9,10-dihydropyrene (4B). A solution of 153.2 mg (0.58 mmol) of **1b** in 50 mL of CCl_4 was stirred at rt as a solution of 0.56 g (3.48 mmol) of Br_2 in 10 mL of CCl_4 was added. After 2 h, the reaction mixture was poured into a large amount of ice-water. The organic layer was extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried over Na_2SO_4 and evaporated in vacuo to leave a residue, which was chromatographed on silica gel, using a hexane as an eluent to afford 195 mg (80%) of a mixture of **4A** and **4B**, and the ratio of **4A** and **4B** was determined to be 60:40 by its NMR spectrum. This mixture was recrystallized from methanol to give small amounts of **4A** or **4B** as colorless prisms: mp 157–160 °C; IR (KBr) 3040, 2930, 1550, 1360, 1230, 1150, 900, 850 cm^{-1}; NMR ($CDCl_3$) δ 1.14 (6 H, t, J = 7.5 Hz), 2.68–2.92 (8 H, m), 2.85 (4 H, q, J = 7.5 Hz), 7.27 (2 H, s); MS (m/e) 418, 420, 422 (M^+). Anal. Calcd for $C_{20}H_{20}Br_2$: C, 56.93; H, 4.50. Found: C, 57.17; H, 4.80.

Preparation of 2,7-Diethyl-4,5,9,10-tetrahydropyrene (5b). A mixture of 96.9 mg (0.4 mmol) of **1b** in 50 mL of CCl_4 was stirred at rt as 1.18 g (4 mmol) of $FeBr_3$ was added. After 3 h, the reaction mixture was poured into a large amount of ice-water. The organic layer was extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried over Na_2SO_4 and evaporated in vacuo, and the residue was chromatographed on silica gel with hexane as an eluent. Recrystallization from methanol gave 84 mg (80%) of 2,7-diethyl-4,5,9,10-tetrahydropyrene (**5b**): colorless prisms (methanol); mp 96–97 °C; IR (KBr) 3040, 2940, 1530, 1350, 1225, 1110, 910, 840 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (6 H, t, J = 7.5 Hz), 2.68 (4 H, q, J = 7.5 Hz), 2.82 (8 H, s), 7.00 (4 H, s); MS (m/e) 262 (M^+). Anal. Calcd for $C_{20}H_{20}$: C, 91.55; H, 8.45. Found: C, 91.40, H, 8.30.

Reaction of 1b with $TiCl_4$ and $FeCl_3$. To a mixture of 96.9 mg (0.4 mmol) of **1b** in 50 mL of CCl_4 was added 4 mmol of $TiCl_4$ or $FeCl_3$ with stirring at rt. After 12 h, the reaction mixture was treated as described above to give starting material **1b** in quantitative yield.

Registry No. **1b**, 76447-47-7; **3**, 137363-46-3; **4A**, 137363-45-2; **4B**, 137363-47-4; **5b**, 76447-48-8.

(10) Yamato, T.; Arimura, T.; Tashiro, M. *J. Chem. Soc., Perkin Trans 2* **1987**, 1.

Asymmetric Diels–Alder Reactions of Carboxylic Ester Dienophiles Promoted by Chiral Lewis Acids

Paul N. Devine and Taeboem Oh*

Department of Chemistry, State University of New York, Binghamton, New York 13902-6000

Received June 20, 1991

The Diels–Alder reaction has proven to be a powerful stratagem in organic synthesis.[1] An area which has received considerable interest in recent years is the control of absolute stereochemistry.[2] One successful method

(1) For a review of Diels–Alder reactions see: (a) Desmoni, G.; Tacconi, G.; Pollini, G. P. *Natural Product Synthesis Through Pericyclic Reactions*; ACS Monograph 180; American Chemical Society: Washington, DC, 1984; Chapter 5. (b) Hamer, J. *1,4-Cycloaddition Reactions*; Academic: New York, 1967.

0022-3263/92/1957-0396$03.00/0