ergy is −266.30544 au, and the dipole moment is 2.664 Debyes. The MP2 analytic second derivative of the energy with respect to nuclear displacements confirmed the C_2 structure to be a minimum. Infrared vibrational frequencies and absorption intensities are given in Table I.

The most intense band of the spectrum is computed to be at 1721 cm^{-1}. MP2 frequencies are typically calculated to be ~3–5% higher than actually observed.[3] Hence we predict that this band should actually appear near 1650 cm^{-1}. While the parent system is unknown, this computed frequency is in good agreement with the observed unusual band in several simple derivatives. Crandall and coworkers have reported that tetramethyl-1 has an absorption band at 1629 cm^{-1} and mono-*tert*-butyl-1 an absorption band at 1615 cm^{-1}. Examination of the normal mode and potential energy distribution of the 1721-cm^{-1} band reveals this is primarily due to the antisymmetric stretch of the two C*–C bonds (C* is the central carbon). Isotopic substitution with tri-^{13}C shifts the computed band to 1663 cm^{-1}, with di-^{18}O to 1717 cm^{-1} and with d_4 to 1687 cm^{-1}. Smaller contributions from the C*–O stretching motions and hydrogen bending motions are also present in this mode. For methyloxirane and *trans*-dimethyloxirane which have a single oxirane ring, MP2/6-31G* calculations[4] predict modes at 1588 and 1577 cm^{-1}, respectively, with dominant C*–C stretching contributions along with hydrogen bending. The corresponding experimental bands in these two cases were found to be at ~1500 cm^{-1}. The presence of two C*–C bonds in the present case causes the antisymmetric C*–C stretch to appear at a higher frequency than the C*–C stretching frequency of a single oxirane group.

Acknowledgment. We thank the National Science Foundation for support through an instrument grant (CHE 8808018) and Intergraph Corp. of Huntsville, AL, for the provision of computing systems and software.

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Medium-Sized Cyclophanes. 16.[1] Bromination of 8,16-Dihydroxy[2.2]metacyclophanes

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

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

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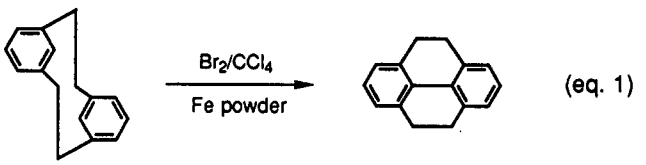
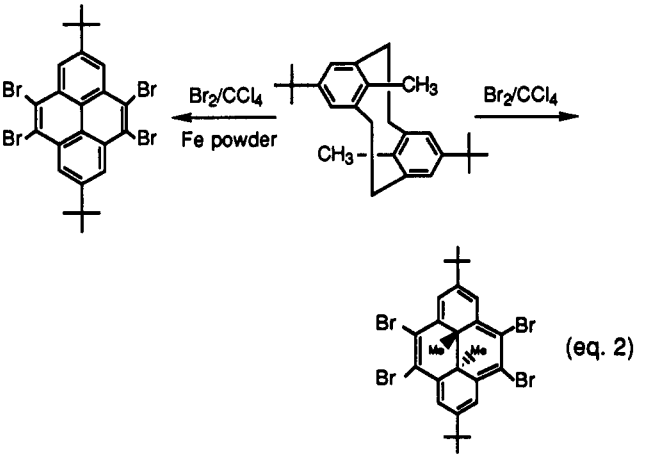
Introduction

Due to electronic interaction between the two benzene rings, the proximity of 8,16-positions, and considerable strain energy, [2.2]metacyclophane (MCP = metacyclophane) is prone to undergo transannular reactions.[2-6] These have usually been rationalized as involving initial dehydrogenation to 4,5,9,10-tetrahydropyrene. Sato and his co-workers[7] have reported that the reaction of 8,16-unsubstituted [2.2]MCP with bromine in the presence of iron powder affords the corresponding tetrahydropyrene via the addition–elimination mechanism (eq 1). Subsequently, we reported[8] that bromination of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP in the presence or absence of iron powder as a catalyst afforded 2,7-di-*tert*-butyl-4,5,9,10-tetrabromo-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene and 2,7-di-*tert*-butyl-4,5,9,10-tetrabromopyrene, respectively (eq 2). The results suggested a useful route to *trans*-10b,10c-dialkyl-10b,10c-dihydropyrenes.



(eq. 1)



(eq. 2)

Although *trans*-10b,10c-dihydropyrenes where the substituents at the 10b and 10c positions are hydrogen or alkyl groups have been prepared by Boekelheide and his coworkers,[9,10] attempts at introducing other functional groups into the internal positions were unsuccessful. Thus, we undertook the present work in order to evaluate the possibility of the novel reaction mentioned above for the preparation of *trans*-10b,10c-dihydroxy-10b,10c-dihydropyrenes.

Results and Discussion

When 5,13-di-*tert*-butyl-8,16-dihydroxy[2.2]MCP (**1b**)[11] was treated with excess bromine in carbon tetrachloride at room temperature for 1 h, none of the expected product **2** was detected (Scheme I). However, a novel product **3** was obtained as colorless prisms in quantitative yield. The

† Saga University.
‡ Kyushu University.

(1) Medium-Sized Cyclophanes. Part 15: Yamato, T.; Matsumoto, J.; Tokuhisa, K.; Shigekuni, M.; Suehiro, K.; Tashiro, M. *J. Org. Chem.* **1992**, *57*, 396.
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Scheme I

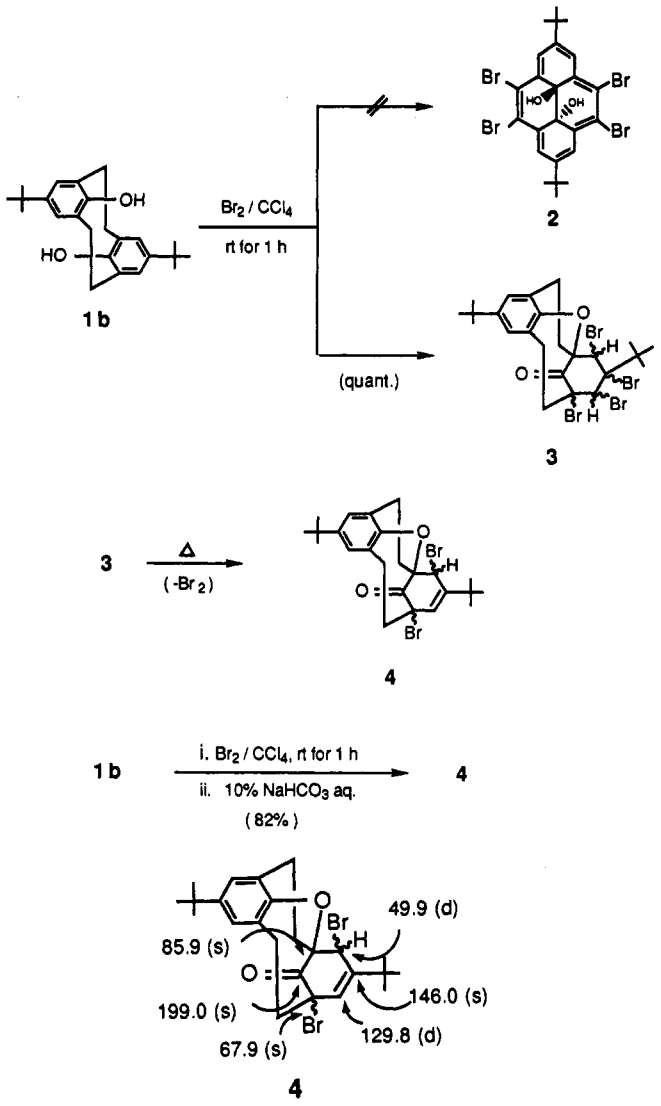
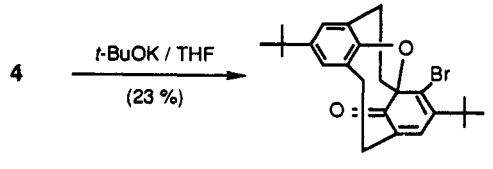


Figure 1.

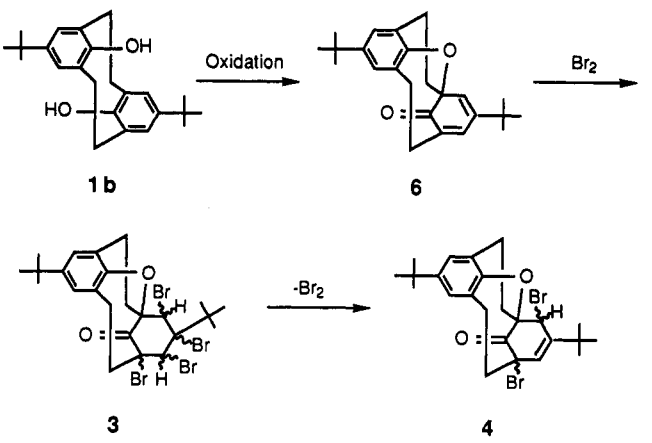
structure of **3** was deduced from its spectral data. Also, its UV (λmax: 280 nm) data are different from those of *trans*-10b,10c-dialkyl-10b,10c-dihydropyrenes which are deeply colored compounds. The stereochemistry of **3** is pending definition. The tetrabromo spiro compound **3** was too labile to purify by recrystallization, and column chromatography using silica gel or alumina afforded a dibromo spiro compound **4**. It was also observed that treatment of **3** with aqueous 10% $NaHCO_3$ gave compound **4** in 82% yield. The IR (KBr) spectrum of **4** shows $\nu_{C=O}$ at 1740 cm^{-1}, typical of a saturated cyclic carbonyl compound. The ^1H NMR ($CDCl_3$) spectrum of **4** shows a methine proton at 4.82 ppm and an olefinic proton at 6.10 ppm as a doublet (J = 2 Hz), respectively. The observed ^{13}C NMR spectrum of **4** is assigned in Figure 1.

When **4** was treated with *t*-BuOK in THF, the corresponding HBr elimination product **5** was obtained in 23% yield (eq 3). On the basis of this chemical conversion and



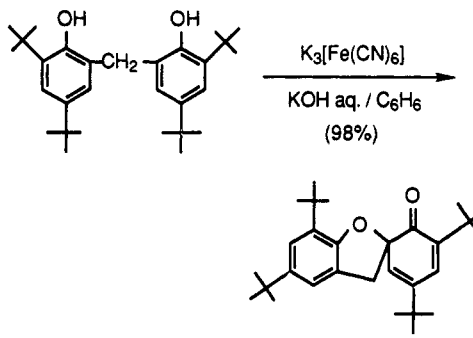
(eq. 3)

Scheme II



spectral data, **4** is assigned the structure 5,6′-di-*tert*-butyl-3,8′-ethanospiro[3,6-dibromocyclohex-4-en-2-one-1,2′-chroman].

It has been reported[12] that an intramolecular O–C coupling reaction occurs during the oxidation of 3,3′,5,5′-tetra-*tert*-butyl-2,2′-dihydroxydiphenylmethane by $K_3[Fe(CN)_6]$ to give the corresponding spiro derivative (eq 4).



(eq. 4)

A similar intramolecular O–C coupling reaction during the bromination of **1b** might occur to give an intermediate like spiro compound **6**, with further bromination to yield **3**. Thus, we attempted preparation and isolation of intermediate **6** by oxidation of **1b** with $K_3[Fe(CN)_6]$, according to the method previously cited.[12] The expected compound **6** was obtained as pale yellow prisms in 98% yield. Bromination of **6** under the same conditions initially employed afforded **3** in quantitative yield. As before, further treatment of this product with 10% $NaHCO_3$ again gave **4** in almost quantitative yield. These results confirm that compounds **6** and **3** are likely intermediates in the formation of **4** from bromination of **1b** (Scheme II).

Attempted bromination of 8,16-dihydroxy[2.2]MCP (**1a**)[11] with excess bromine in carbon tetrachloride, carried out under the same reaction conditions as **1b**, led to a tetrabromo spiro compound **8** in 70% yield. However, the possible hexabromo spiro intermediate **7** was too labile to isolate (Scheme III). In contrast, compound **1a** when treated with bromine in acetic acid afforded the corresponding 5,13-dibromo-8,16-dihydroxy[2.2]MCP (**1c**) in 58% yield. Although the detailed mechanistic conclusion to rationalize these observations is not clear, one might assume Br_2/CCl_4 converts **1a** to a spiro skeleton via intramolecular O–C coupling reaction of a phenoxy radical intermediate like oxidation with $K_3[Fe(CN)_6]$,[12] but Br_2/HOAc easily generates Br^+, which can only serve as an electrophile in this process. Bromination of **1c**, or the dibromo spiro compound **9**, which was prepared by oxi-

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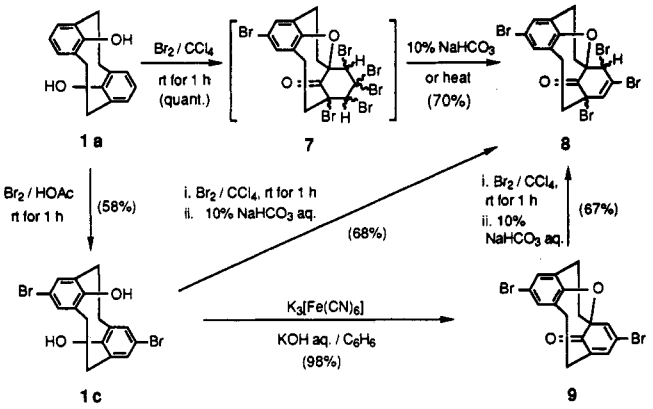
Scheme III



dation of **1c** with $K_3[Fe(CN)_6]$, afforded **8** in 68% and 67% yields, respectively (Scheme III).

However, attempted bromination of the spiro compound **10**, which is prepared by oxidation of 8,16-dihydroxy-[2.2]MCP (**1a**) with $K_3[Fe(CN)_6]$, with excess bromine in carbon tetrachloride failed. The starting compound **10** was quantitatively recovered. These results strongly suggest that compounds **1c** and **9** could be intermediates for the formation of **8** during the bromination of **1a**, but not compound **10**.

Conclusion

Bromination of 8,16-dihydroxy[2.2]MCPs **1** with bromine in carbon tetrachloride afforded the novel brominated cyclophanes having the spiro skeleton via the intramolecular O–C coupling reaction. Similar spiro compounds were formed by oxidation of **1** with $K_3[Fe(CN)_6]$ in alkaline solution.

Experimental Section

All melting points are uncorrected. NMR spectra were recorded at 270 MHz on a Nippon Denshi JEOL FT-270 NMR spectrometer 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-01SA-2 spectrometer at 75 eV using a direct inlet system.

Materials. Preparation of 8,16-dihydroxy[2.2]MCP (**1a**) and 5,13-di-*tert*-butyl-8,16-dihydroxy[2.2]MCP (**1b**) were previously described.[11]

Bromination of 8,16-Dihydroxy[2.2]metacyclophane (1) with Bromine in Carbon Tetrachloride. Typical Procedure. To a solution of 50 mg (0.14 mmol) of **1b** in 30 mL of carbon tetrachloride was added a solution of 180 mg (0.06 mL, 1.1 mmol) of bromine in 10 mL of carbon tetrachloride at room temperature. After the reaction mixture was stirred for 1 h, it was poured into water (10 mL). The organic layer was extracted with CH_2Cl_2 (10 mL). The extract was washed with 10% aqueous sodium thiosulfate (5 mL) and water (5 mL), dried (Na_2SO_4), and evaporated in vacuo to leave a residue, which was washed and filtered with a small amount of hexane to give **3** in almost quantitative yield.

5,6′-Di-*tert*-butyl-3,8′-ethanospiro[3,4,5,6-tetrabromocyclohexan-2-one-1,2′-chroman] (3): colorless prisms; mp 238–240 °C; IR (KBr) 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (9 H, s), 1.33 (9 H, s), 2.16–3.60 (6 H, m), 4.95 (1 H, d, J = 2 Hz), 5.20–5.27 (2 H, m), 6.10 (1 H, d, J = 2 Hz), 6.99 (1 H, d, J = 4 Hz), 7.25 (1 H, d, J = 4 Hz); MS m/e 662, 664, 666, 668, 670 (M^+).

Compound **3** was too labile to purify by recrystallization and column chromatography using silica gel or alumina. In hexane solution compound **3** gradually changed to **4**. When this mixture was treated with refluxing hexane for 10 min, compound **3** was completely converted to **4**. Recrystallization from a mixture of hexane–benzene (1:1) to give 54 mg (76%) of **4**.

5,6′-Di-*tert*-butyl-3,8′-ethanospiro[3,6-dibromocyclohex-4-en-2-one-1,2′-chroman] (4): colorless prisms (hexane–benzene (1:1)); mp >228 °C dec; IR (KBr) 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (9 H, s), 1.28 (9 H, s), 2.0–3.3 (8 H, m), 4.82 (1 H, d, J = 2 Hz), 6.10 (1 H, d, J = 2 Hz), 6.85 (1 H, d, J = 2.5 Hz), 6.98 (1 H, d, J = 2.5 Hz); ^{13}C NMR ($CDCl_3$) δ 24.81 (t), 27.79 (t), 28.90 (t), 29.72 (q), 34.52 (s), 35.67 (s), 46.69 (t), 49.90 (d), 67.86 (s), 85.94 (s), 122.74 (d), 123.56 (d), 129.76 (d), 130.29 (s), 131.28 (s), 146.02 (s), 148.25 (s), 151.11 (s), 198.97 (s); UV ($CHCl_3$) λ_{max} (log ϵ) 260 (4.24), 310 (3.72), 358 (2.64) nm; MS m/e 508, 510, 512 (M^+). Anal. Calcd for $C_{24}H_{30}O_2Br_2$: C, 56.48; H, 5.92. Found: C, 56.37; H, 5.86.

Bromination of 1 with Bromine in Carbon Tetrachloride and Treatment of 10% Aqueous Sodium Bicarbonate. Typical Procedure. To a solution of 150 mg (0.42 mmol) of **1b** in 40 mL of carbon tetrachloride was added a solution of 550 mg (0.18 mL, 3.4 mmol) of bromine in 10 mL of carbon tetrachloride at rt. After the reaction mixture was stirred for 1 h, it was poured into water (10 mL). The organic layer was extracted with CH_2Cl_2. The extract was washed with 10% aqueous sodium thiosulfate, 10% aqueous sodium bicarbonate, and water (each 5 mL), dried (Na_2SO_4), and evaporated in vacuo to leave a residue, which was recrystallized from a mixture of hexane–benzene (1:1) to give 175 mg (82%) of **4**.

Compound **1a** was reacted with bromine in the same manner described above to give **8** in 70% yield.

3,5,6,6′-Tetrabromo-3,8′-ethanospiro[cyclohex-4-en-2-one-1,2′-chroman] (8): colorless prisms (carbon tetrachloride); mp 216–217 °C; IR (KBr) 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.80–3.40 (8 H, m), 4.90 (1 H, d, J = 1 Hz), 6.52 (1 H, d, J = 1 Hz), 7.08 (1 H, d, J = 2 Hz), 7.18 (1 H, d, J = 2 Hz); MS m/e 552, 554, 556, 558, 560 (M^+). Anal. Calcd for $C_{16}H_{12}O_2Br_4$: C, 34.57; H, 2.18. Found: C, 34.30; H, 2.25.

Reaction of 4 with *t*-BuOK To Give 5. To a solution of 50 mg (0.1 mmol) of **4** in 20 mL of tetrahydrofuran was added 30 mg (0.25 mmol) of *t*-BuOK at room temperature. After the reaction mixture was stirred for 1 h, it was poured into water (20 mL). The organic layer was extracted with CH_2Cl_2 (50 mL). The extract was washed with water (20 mL), dried (Na_2SO_4), and evaporated in vacuo to leave a residue, which was recrystallized from hexane to give 10 mg (23%) of **5**: colorless prisms (hexane); mp 196–199 °C; IR (KBr) 1720, 1700 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (9 H, s), 1.25 (9 H, s), 2.0–3.5 (8 H, m), 5.70 (1 H, d, J = 2 Hz), 6.90 (1 H, d, J = 2.5 Hz), 6.99 (1 H, d, J = 2.5 Hz); MS m/e 428, 430 (M^+). Anal. Calcd for $C_{24}H_{29}O_2Br$: C, 67.13; H, 6.81. Found: C, 67.33; H, 6.45.

Oxidation of 1 with $K_3[Fe(CN)_6]$. Typical Procedure. To a solution of 511 mg (1.45 mmol) of **1b** in 10 mL of benzene was gradually added at room temperature a solution of 2.40 g of $K_3[Fe(CN)_6]$ and 1.74 g of KOH in 50 mL of water over a period of 15 min. After the reaction mixture was stirred at rt for 30 min, the organic layer was separated, washed with water, dried (Na_2SO_4), and evaporated in vacuo to leave a residue which was triturated with a small amount of hexane and filtered to give 500 mg (98%) of **6**.

5,6′-Di-*tert*-butyl-3,8′-ethanospiro[cyclohexa-3,5-dien-2-one-1,2′-chroman] (6): pale yellow prisms (hexane–benzene (2:1)), mp >280 °C dec; IR (KBr) 1725 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) at 25 °C δ 1.20 (18 H, broad s), 2.56 (8 H, broad s), 6.40 (4 H, broad s); ^1H NMR ($CDCl_3$) at −50 °C δ 1.10 (9 H, s), 1.24 (9 H, s), 1.9–3.4 (8 H, m), 5.70 (1 H, d, J = 2 Hz), 6.22 (1 H, d, J = 2 Hz), 6.92 (1 H, d, J = 2 Hz), 7.02 (1 H, d, J = 2 Hz); UV (cyclohexane) λ_{max} (log ϵ) 280 (3.31), 355 (2.39), 370 (2.32) nm; MS m/e 350 (M^+). Anal. Calcd for $C_{24}H_{32}O_2$: C, 82.24; H, 8.63. Found: C, 82.27; H, 8.57.

Compounds **1c** and **1a** were reacted with $K_3[Fe(CN)_6]$ in the same manner for **1b** to give **9** and **10** in 98% and 35% yields, respectively.

5,6′-Dibromo-3,8′-ethanospiro[cyclohexa-3,5-dien-2-one-1,2′-chroman] (9): pale yellow prisms (hexane–benzene (2:1)); mp >230 °C dec; IR (KBr) 1730 (C=O); ^1H NMR ($CDCl_3$) 2.1–2.9 (8 H, broad s), 6.3–6.9 (4 H, broad s); MS m/e 394, 396, 398 (M^+). Anal. Calcd for $C_{16}H_{12}O_2Br_2$: C, 48.52; H, 3.05. Found: C, 48.57; H, 3.23.

3,8′-Ethanospiro[cyclohexa-3,5-dien-2-one-1,2′-chroman] (10): pale yellow prisms (hexane); mp 96–98 °C; IR (KBr) 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.56 (8 H, broad s), 6.54 (6 H, broad s); MS m/e 238 (M^+). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.63; H, 6.01.

Bromination of 1a with Bromine in Acetic Acid. To a solution of 100 mg (0.42 mmol) of **1a** in 30 mL of acetic acid was added a solution of 160 mg (1.0 mmol) of bromine in 10 mL of acetic acid at rt. After the reaction mixture was stirred for 1 h, it was poured into water (10 mL). The organic layer was extracted with CH_2Cl_2. The extract was washed with 10% aqueous sodium thiosulfate, 10% aqueous sodium bicarbonate, and water (each 5 mL), dried (Na_2SO_4), and evaporated in vacuo to leave a residue, which was recrystallized from carbon tetrachloride to give 96 mg (58%) of **1c**: pale yellow prisms (carbon tetrachloride); mp >265 °C dec; IR (KBr) 3580 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.52–2.96 (8 H, m), 3.70 (2 H, s, exchanged by D_2O), 7.16 (4 H, s); MS *m/e* 396, 398, 400 (M^+). Anal. Calcd for $C_{16}H_{14}O_2Br_2$: C, 48.27; H, 3.54. Found: C, 47.86; H, 3.51.

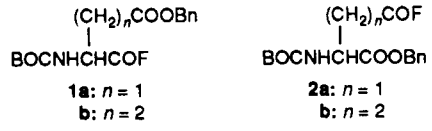
Protected β- and γ-Aspartic and -Glutamic Acid Fluorides

Louis A. Carpino* and El-Sayed M. E. Mansour

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

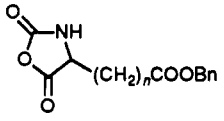
Received June 18, 1992

The preparation of synthetically useful FMOC-, BOC-, and Z-substituted α-amino acid fluorides, including those bearing a variety of protected side chains, has recently been described.[1,2] In the case of aspartic and glutamic acids the isomeric ω-acid fluorides could also prove to be of significant synthetic utility. The published collection of BOC-substituted α-amino amino acid fluorides included the β- and γ-benzyl ester, α-acid fluorides.[1b] More recently, in the pursuit of new routes to asparagine and glutamine derivatives, we had occasion to prepare the analogous β- and γ-acid fluorides and were surprised to find that the properties (mp, optical rotation) of these two compounds fit precisely the data previously recorded for the isomeric α-fluorides. Closer examination revealed that due to a labeling error the compounds listed earlier as **1a,b** are in fact the non-α-fluorides **2a,b**.



1a: *n* = 1 **b**: *n* = 2 **2a**: *n* = 1 **b**: *n* = 2

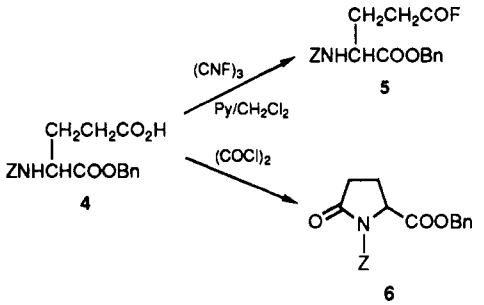
In the present note we describe the authentic α-acid fluorides **1a,b**. Both syntheses were accompanied by the formation of traces of the corresponding Leuch's anhydrides **3** (NCAs). Contamination by such NCAs is limited



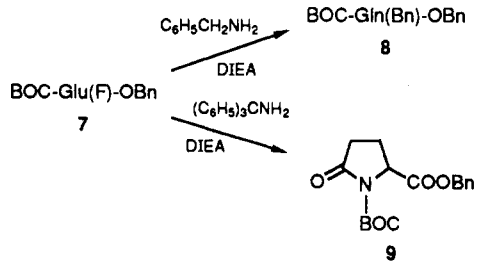
3a,b

to amino acids bearing α-BOC protection, no such reaction having yet been observed for the analogous FMOC- and Z-α-acid fluorides. Z-Amino acid chlorides differ from the fluorides in that the former are readily converted to NCAs on standing or heating.[3]

The FMOC- and Z-substituted β- and γ-acid fluorides are also described in the present note (Table I). In the case of α-FMOC-glutamic acid α-benzyl ester, γ-acid fluoride the reaction with cyanuric fluoride was carried out at room temperature as is normal for FMOC α-fluorides and a trace of the corresponding pyroglutamic acid ester accompanied the acid fluoride. No pyroglutamate was observed in the case of the α-BOC or α-Z analogs probably because these reactions were carried out at low temperatures (−30 to −20 °C) as is normal for the more acid-sensitive systems. Repetition of the FMOC synthesis at low temperature also avoided this side reaction. The preparations described here represent additional examples of the relative stability of amino acid fluorides vis-a-vis the corresponding chlorides. As in the NCA synthesis described earlier, an acid chloride intermediate is involved in some routes to pyroglutamates (e.g., **4** to **6**).[4,5]



The β- and γ-acid fluorides described in this note were initially examined as intermediates for the synthesis of the *N*-trityl derivatives of Asn and Gln. Although simple amines reacted readily, e.g., **7** on treatment with benzyl amine to give **8**, the highly hindered[6] tritylamine gave none



of the glutamine derivative. Instead only the pyroglutamic acid ester **9** was obtained. In the meantime simple routes to the *N*-trityl derivatives of both Asn and Glu have been reported.[7] Both of these compounds have now been converted to the corresponding FMOC-protected α-acid fluorides which proved to be soluble, highly reactive, stable acylating agents for solution and solid-phase peptide synthesis.

Once all four isomers of the fluorides of BOC-substituted aspartic acid and glutamic acid esters became available it could be seen by comparison of their ^1H NMR spectra that the α-acid fluorides can be distinguished from their β- and γ-isomers by virture of differences in the methylene protons α to the acid fluoride and ester carbonyl functions. Thus for **1b** the methylene group α to the carbonyl ester function appears as a clean triplet whereas for **2b** this

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