determined on the crude hydrogenation mixture by ^1H NMR by measuring the relative intensities of the OMe signals due to the two diastereoisomers, which appear at 3.58 and 3.60 ppm, respectively, in Me_2SO-d_6, and by HPLC analysis, by comparison with authentic samples prepared from L-aspartic acid and L- and D-phenylalanine, respectively. The crude hydrogenation mixtures obtained in entries 2 and 4 were deformylated with methanolic hydrogen chloride to give, on neutralization and crystallization, aspartame (1), over 99.5% pure by HPLC, in 65% and 45% yield, respectively.

Similarly, starting from *N*-carbobenzoxy-L-aspartic anhydride, through the above sequence, N^2-carbobenzoxydehydroaspartame **5b**, mp 162 °C, α^{20}_D +32.6° (*c* 1, MeOH), was obtained. The latter material, on hydrogenation in the presence of (*R*)-prophos as a ligand of rhodium, afforded L,L-**2b** and L,D-**3b** in an over 90:10 ratio. Deprotection of the latter mixture by hydrogenolysis in the same pot with 10% Pd/C affords, on crystallization, aspartame (1), in 75% overall yield from **5b**.

The above results thus show the accessibility of L,L-aspartame (1) through a procedure involving as key step the generation of the L-phenylalanine moiety at the latest stages via asymmetric hydrogenation of N-protected α-L-aspartyl dehydropeptides. The method will be hardly competitive with the synthesis of 1 based on enzymatically produced L-phenylalanine as starting material, but it can be considered a further example of the significance to organic synthesis of the catalytic asymmetric hydrogenation.

Experimental Section

***N*-(*N*-Formyl-α-L-aspartyl)-D,L-2-chlorophenylalanine Methyl Ester (4a).** To a mixture of 230 g (1 mol) of D,L-phenylserine methyl ester hydrochloride in 400 mL of chloroform was added dropwise under stirring at room temperature 100 mL (1.43 mol) of $SOCl_2$. The reaction mixture was kept at room temperature for 12 h and then evaporated to dryness under vacuum at 40 °C. The residue separated from methanol–diethyl ether (1:1) to afford 210 g (85%) of D,L-2-chlorophenylalanine methyl ester hydrochloride, mp 175 °C. Anal. Calcd for $C_{10}H_{13}O_2NCl_2$: C, 47.99; H, 5.23; N, 5.60. Found: C, 47.82; H, 5.20; N, 5.63. A solution of 25 g (0.1 mol) of D,L-2-chlorophenylalanine methyl ester hydrochloride in 200 mL of H_2O was treated at 23 °C with 6.3 g (0.05 mol) of Na_2CO_3 in 400 mL of H_2O. After standing for 10 min the reaction mixture was extracted with ethyl acetate (2 × 50 mL), and the combined organic extracts, once dried over Na_2SO_4, were added dropwise under stirring at 0 °C to a solution of 14.3 g (0.1 mol) of *N*-formyl-L-aspartic anhydride (prepared by treating L-aspartic acid in 99% formic acid with acetic anhydride) in 50 mL of ethyl acetate containing 6 mL of acetic acid. After being stirred 2 h at 0 °C, the reaction mixture was cooled to −10 °C, thus separating 27 g (75%) of *N*-formyl-α-L-aspartyl-D,L-2-chlorophenylalanine methyl ester (**4a**): mp 148 °C; α^{20}_D −36° (*c* 1, MeOH). Anal. Calcd. for $C_{15}H_{17}O_6N_2Cl$: C, 50.49; H, 4.80; N, 7.85. Found: C, 50.42; H, 4.83; N, 7.81.

(*Z*)-*N*-(*N*-Formyl-α-L-aspartyl)-Δ-phenylalanine Methyl Ester (5a). To a stirred solution of 35.8 g (0.1 mol) of **4a** in 75 mL of THF was added portionwise at room temperature during 2 h 10.8 g (0.2 mol) of NaOMe. after 20 min the reaction mixture was diluted with 200 mL of ethyl acetate and treated under stirring with 200 mL of 10% HCl. After 10 min the organic phase was separated, washed with 50 mL of a 20% NaCl solution, dried over Na_2SO_4, and evaporated to dryness. The resiue was crystallized from ethyl acetate to give 24.2 g (75%) of **5a**: mp 155–157 °C; α^{20}_D +20.5° (*c* 1.1, MeOH). Anal. Calcd. for $C_{15}H_{16}O_6N_2$: C, 56.25; H, 5.04; N, 8.75. Found: C, 56.29; H, 5.01; N, 8.69. The methyl ester **6**, mp 142 °C, α^{20}_D +2.3° (*c* 1, MeOH)8 was obtained from methanol from the treatment of **5a** with CH_2N_2.

Aspartame (1). The hydrogenation experiments of **5a** were performed on 6.4 g (0.02 mol) in 10–15% solutions, under the conditions reported in Table I. At the end of the adsorption the reaction mixture was filtered (when required) and evaporated to dryness. The residue was taken up in ca. 40 mL of boiling water, concentrated until cloudy, and kept at 0 °C for 12 h. The precipitate was collected and deformylated by boiling for 30 min with 40 mL of 1 N HCl–methanol (1:6.5). The solution was neutralized with solid Na_2CO_3 and concentrated under vacuum to complete elimination of methanol, thus separating, on cooling to 0 °C, aspartame (1), mp 245–247 °C, α^{20}_D +31° (*c* 1, CH_3COOH), 99.5% by HPLC. The precipitated aspartame (1) from entries 2 and 4 weighs 3.66 (65%) and 2.35 g (45%), respectively.

Registry No. 1, 22839-47-0; **2a**, 33605-76-4; **2b**, 33605-72-0; **3a**, 99792-97-9; **4a**, 99792-96-8; **5a**, 100101-47-1; **5b**, 100101-48-2; **6**, 100020-80-2; D,L-phenylserine methyl ester hydrochloride, 80182-99-6; D,L-β-chlorophenylalanine methyl ester hydrochloride, 100020-81-3; *N*-formyl-L-aspartic anhydride, 33605-73-1; *N*-carbobenzoxy-L-aspartic anhydride, 4515-23-5.

Synthesis of Dihydroxy Thia Crown Ethers and Derivatization to Bicyclic Crown Compounds

Isao Ikeda, Yu-ichi Tsuji, Yohji Nakatsuji, and Mitsuo Okahara*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka, Japan 565

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Crown ethers containing reactive groups are important intermediates for a variety of highly functionalized derivatives.[1] Despite this, thia crown ethers are not well-known[2] in spite of their excellent complexing ability toward transition-metal cations.[3] On the other hand, crown ethers having two or more functional groups are particularly interesting because of their potential application in the synthesis of bicyclic compounds.[4] We have recently reported a facile procedure for synthesizing aza crown ethers with two hydroxyl groups[5] and now describe the synthesis of a new class of thia crown ethers. These new thia crowns have two hydroxyl groups and can be converted into crown ethers having an oxathiane subcyclic unit.

The reaction of oligoethylene glycol diglycidyl ethers[6] (1) with sodium hydrosulfide in water at 60 °C for 3 h gave the dihydroxy thia crown ethers (**2**) in 52–63% yield (Scheme I). Ethanol and *tert*-butyl alcohol were also found to be desirable for this reaction, whereas the desired compounds were not obtained under the same reaction conditions when dioxane was used as solvent.

Although compounds **2** may be promising complexation agents for transition-metal cations,[3] they showed poor complexing ability toward alkali metal cations. However,

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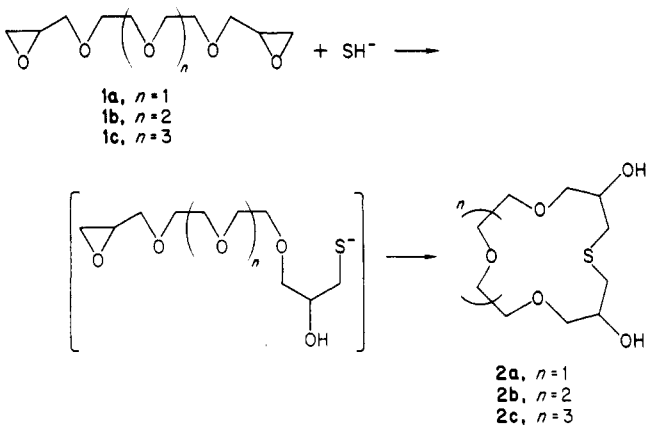
0022-3263/86/1951-1128$01.50/0

Scheme I



their complexing ability is easily improved by further derivatization of the functional groups as follows.

The dihydroxy thia crown ether **2b** was treated with *p*-toluenesulfonyl chloride in the presence of sodium hdyroxide in dioxane at 60 °C according to the previously reported method[7] to give a new type of crown ether (**3b**) having an oxathiane unit in 45% yield. According to the similar procedure, **2c** also gave the corresponding 18-crown-6 derivative **3c** in 55% yield. However, the cyclization reaction of **2a** was not so clean under the same reaction conditions and so its isolation was not attempted. This procedure is a novel route to these bicyclic crown ethers, a kind of substituted crown ethers.

Cation binding by crown ethers is affected by donor atom strength and steric effects as well as other factors. The effect of an alkyl substituent on the 15-crown-5 ring is known to slightly decrease the crown's complexing ability toward Na^+ and K^+.[8] On the other hand, the presence of an electron-donating group on the side arm is known to increase the complexation ability of the crown ether.[9] However, there is little information of the effect of electron-withdrawing group in the substituent on complexation besides benzo crown ethers.[10] Compounds **3** possess an interesting structure because the extent of the electron withdrawing can be changed by oxidizing the sulfur atom in the substituent.

The sulfur atom of compound **3b** was oxidized with 35% hydrogen peroxide solution[11] to give a sulfoxide-type crown ether (**4**) in 61% yield. Compound **4** was further converted to a sulfone-type crown ether (**5**) in 82% yield according to Scheme II.

The complexation data are shown in Table I. The complexing ability of compound **3b** is almost the same as that of unsubstituted 15-crown-5. The increase in oxidation number of sulfur atom of the subcyclic unit decreased the stability constants toward K^+ and Na^+. Since the rigidity of the six-membered ring should prohibit a direct interaction of sulfur, sulfoxide, or sulfone group with the cation, the reduced complexing ability of the crown ether must be due to the decrease in electron density of the oxygen atom of the subcyclic unit.

Experimental Section

IR and ^1H NMR spectra were recorded on a Hitachi 260 spectrometer and a JEOL JNM-PS-100 spectrometer, respectively. Mass spectral data were measured with a Hitachi RMU-6E mass spectrometer at an ionization potential of 70 eV. Oligoethylene glycol diglycidyl ethers (**1**) were prepared by the previously reported procedure.[6]

9,13-Dihydroxy-1,4,7-trioxa-11-thiacyclotetradecane (2a). Both aqueous solutions of diethylene glycol diglycidyl ether (**1a**, $n = 1$) (10.91 g, 0.05 mol) in 100 mL of water and sodium hydrogen sulfide (70% aqueous solution; 4.00 g, 0.05 mol) in 100 mL of water were simultaneously added from separate dropping funnels to water (50 mL) with stirring at 60 °C over a period of 3 h, and the mixture was stirred for an additional 0.5 h. After neutralizing the mixture with dilute HCl, the solution was concentrated. The residue was dissolved in appropriate amounts of dichloromethane and dried over $MgSO_4$. The mixture was filtered and passed through a short column (Kieselgel-60). The eluents were concentrated and distilled in a Kugelrohr apparatus (130 °C (0.01 torr)) to give a slightly yellow viscous oil (7.34 g, 58%); IR (neat) 3410, 2900, 1460, 1410, 1360, 1300, 1260, 1140, 940, 870, 845 cm^{-1}; NMR ($CDCl_3$) δ 2.52–3.12 (m, 4 H), 3.38–4.21 (m, 16 H); MS, *m/e* (relative intensity) 252 (M^+, 2), 234 (24), 133 (13), 127 (15), 191 (42), 87 (88), 73 (99), 45 (100).

Anal. Calcd for $C_{10}H_{20}O_5S$: C, 47.60; H, 7.99; S, 12.71. Found: C, 47.27; H, 8.05; S, 12.72.

12,16-Dihydroxy-1,4,7,10-tetraoxa-14-thiacycloheptadecane (2b): yield 63%; bp 150 °C (0.01 torr) (Kugelrohr); IR (neat) 3450, 2900, 1460, 1420, 1360, 1300, 1250, 1140, 940, 870, 840 cm^{-1}; NMR ($CDCl_3$) δ 2.48–3.10 (m, 4 H), 3.41–4.10 (m, 20 H); MS, *m/e* (relative intensity) 296 (M^+, tr), 278 (34), 260 (5), 234 (8), 145 (19), 133 (25), 101 (31), 87 (100), 73 (62), 59 (45), 45 (82).

Anal. Calcd for $C_{12}H_{24}O_6S$: C, 48.63; H, 8.16; S, 10.82. Found: C, 48.25; H, 8.20; S, 10.53.

15,19-Dihydroxy-1,4,7,10,13-pentaoxa-17-thiacycloeicosane (2c): yield 52%; bp 160 °C (0.01 torr) (Kugelrohr); IR (neat) 3420, 2870, 1450, 1410, 1350, 1300, 1250, 1100, 940, 870, 840 cm^{-1}; NMR ($CDCl_3$) δ 2.59–3.00 (m, 4 H), 3.36–4.12 (m, 24 H); MS, *m/e* (relative intensity) 340 (M^+, tr), 322 (12), 304 (3), 145 (19), 133 (37), 89 (70), 87 (100), 73 (62), 59 (36), 45 (94).

Anal. Calcd for $C_{14}H_{28}O_7S$: C, 49.39; H, 8.29; S, 9.42. Found: C, 49.21; H, 8.30; S, 9.26.

3,6,9,12,18-Pentaoxa-16-thiabicyclo[12.3.1]octadecane (3b). To a stirred suspension of powdered sodium hydroxide (5.05 g, 0.12 mol) in 100 mL of dioxane was added a solution of dihydroxy thia crown ether **2b** (5.93 g, 0.02 mol) and *p*-tolenesulfonyl chloride (3.81 g, 0.02 mol) in 200 mL of dioxane at 60 °C over a 25-h period, and the mixture was further stirred for another 15 h at that temperature. Insoluble matters were removed by filtration. The solution was concentrated and distilled in a Kugelrohr apparatus (120 °C (0.01 torr)) to give a slightly yellow viscous liquid (2.48 g, 45%): IR (neat) 2900, 1460, 1420, 1360, 1310, 1260, 1130, 940, 870 cm^{-1}; NMR ($CDCl_3$) δ 2.06–2.88 (m, 4 H), 3.29–4.48 (m, 18 H); MS, *m/e* (relative intensity) 278 (M^+, 35), 260 (5), 234 (5), 145 (16), 133 (25), 101 (24), 89 (52), 87 (65), 73 (75), 45 (100).

Anal. Calcd for $C_{12}H_{22}O_5S$: C, 51.78; H, 7.97; S, 11.52. Found: C, 51.54; H, 8.03; S, 11.29.

3,6,9,12,15,21-Hexaoxa-19-thiabicyclo[15.3.1]heneicosane (3c). The synthesis of **3c** was carried out by the similar cyclization procedure used in the synthesis of **3b** except that potassium hydroxide was used as the base instead of sodium hydroxide: yield 55%; bp 140 °C (0.01 torr) (Kugelrohr); IR (neat) 2900, 1460, 1420, 1360, 1305, 1260, 1130, 945, 880 cm^{-1}; NMR ($CDCl_3$) δ 2.09–2.98 (m, 4 H), 3.36–4.30 (m, 22 H); MS, *m/e* (relative intensity) 322 (M^+, 15), 304 (4), 145 (10), 133 (25), 101 (17), 89 (55), 87 (52), 73 (65), 45 (100).

Anal. Calcd for $C_{14}H_{26}O_6S$: C, 52.15; H, 8.13; S, 9.95. Found: C, 51.84; H, 8.11; S, 9.86.

3,6,9,12,18-Pentaoxa-16-thiabicyclo[12.3.1]octadecane 16-Oxide (4). To a stirred mixture of compound **3** (2.21 g, 0.0079 mol) and water (2.0 g) was added 35% hydrogen peroxide solution[11] (0.77 g, 0.008 mol) by portions at 10–20 °C, and the mixture was stirred for 10 h. The excess hydrogen peroxide was decom-

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Scheme II

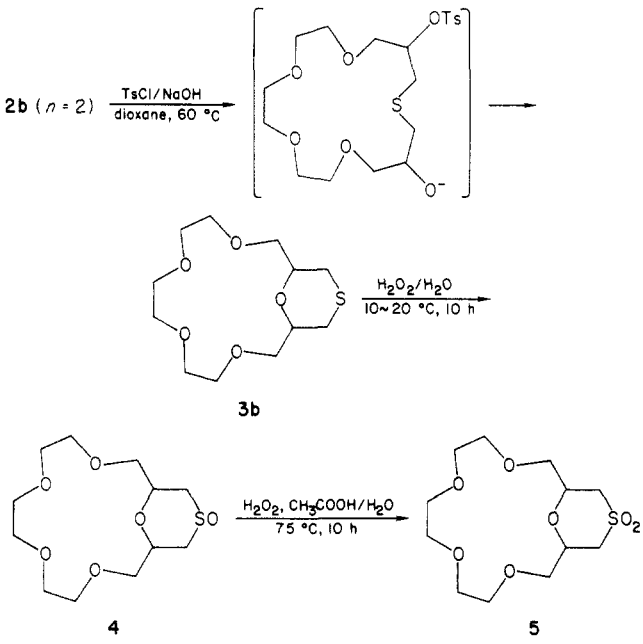

Table I. Stability Constants for Crown Ethers toward Na^+ and K^+ by Potentiometric Titration[a]

compd	log $K'(Na^+)$	log $K'(K^+)$
2a	<1	<1
2b	<1	<1
2c	1.95	2.48
3b	3.38	3.41
4	2.84	3.03
5	2.59	2.78
15-crown-5	3.31[b]	3.34[b]

[a] Reference 12, measured in MeOH at 25 °C. [b] Reference 13.

posed by sodium thiosulfate. Water (50 mL) was added to the mixture, and the mixture was extracted with dichloromethane (200 mL × 3). The dichloromethane solution was concentrated and distilled in a Kugelrohr apparatus (140 °C (0.1 torr)) to give a slightly yellow viscous oil (1.42 g, 61%): IR (neat) 2900, 1460, 1410, 1360, 1300, 1260, 1130, 1050, 950, 880 cm^{-1}; NMR ($CDCl_3$) δ 2.32-3.25 (m, 4 H), 3.25-4.76 (m, 18 H); MS, *m/e* (relative intensity) 294 (M^+, 5), 238 (8), 189 (19), 145 (15), 133 (22), 101 (43), 89 (39), 73 (34), 57 (51), 45 (100), 41 (91).

Anal. Calcd for $C_{12}H_{22}O_6S$: C, 48.96; H, 7.53; S, 10.89. Found: C, 48.71; H, 7.70; S, 10.64.

3,6,9,12,18-Pentaoxa-16-thiabicyclo[12.3.1]octadecane 16,16-Dioxide (5). To a mixture of compound **4** (1.14 g, 0.0039 mol) and acetic acid (0.96 g, 0.016 mol) was added 35% hydrogen peroxide solution (1.55 g, 0.016 mol) by portions at 75 °C and the mixture was stirred for 10 h. Water (50 mL) was added to the mixture, and the mixture was extracted with dichloromethane (200 mL × 3). The organic layer was concentrated and distilled in a Kugelrohr apparatus (160 °C (0.01 torr)) to give a slightly yellow waxy solid (0.99 g, 82%): IR (neat) 2900, 1460, 1350, 1300, 1250, 1125, 1020, 940, 860 cm^{-1}; NMR ($CDCl_3$) δ 2.74-3.36 (m, 4 H), 3.36-4.78 (m, 18 H); MS, *m/e* (relative intensity) 311 (M^+ + 1, tr), 310 (M^+, tr), 267 (1), 223 (5), 189 (19), 133 (9), 101 (35), 89 (30), 87 (32), 73 (33), 59 (32), 57 (47), 45 (75), 41 (100).

Anal. Calcd for $C_{12}H_{22}O_7S$: C, 46.44; H, 7.14; S, 10.33. Found: C, 46.57; H, 7.21; S, 10.09.

Registry No. **1a**, 4206-61-5; **1b**, 1954-28-5; **1c**, 17626-93-6; **2a**, 100228-56-6; **2a**·Na^+, 100205-45-6; **2a**·K^+, 100205-46-7; **2b**, 100205-57-0; **2b**·Na^+, 100205-47-8; **2b**·K^+, 100205-48-9; **2c**, 100205-58-1; **2c**·Na^+, 100205-49-0; **2c**·K^+, 100205-50-3; **3b**, 100205-59-2; **3b**·Na^+, 100205-51-4; **3b**·K^+, 100205-52-5; **3c**, 100205-60-5; **4**, 100205-61-6; **4**·Na^+, 100205-53-6; **4**·K^+, 100205-54-7; **5**, 100205-62-7; **5**·Na^+, 100205-55-8; **5**·K^+, 100205-56-9.

On the Relation between Ring Size and Geometry of 2-Bromo-2-cycloalkenyl Acetates Formed from Dibromobicyclo[*n*.1.0]alkanes by Silver Acetate Catalyzed Reactions. Use of ^3J(C-H) Couplings To Assign the Geometry of Trisubstituted Olefins

Satoru Ito, Herman Ziffer,* and Ad Bax

Laboratory of Chemical Physics, National Institute of Arthritis, Diabetes, and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, Maryland 20205

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As part of a study[1] of the chiroptical properties of medium-ring cycloalkenyl *p*-bromobenzoates, several cis- and trans-2-substituted 2-cycloalkenyl acetates were required. Reese and Shaw[2] have shown that (*Z*)-2-bromo-2-cyclooctenol and (*Z*)-2-bromo-2-cyclononenol can be conveniently prepared by silver perchlorate promoted solvolyses of the corresponding dibromobicyclo[*n*.1.0]alkanes in aqueous acetone. In order to obtain directly the desired acetates, we modified the Reese and Shaw procedure by reacting the dibromobicyclo[*n*.1.0]alkane with silver acetate in acetonitrile containing a small quantity of acetic acid (see Scheme I). We were surprised to find that compounds **1**, **2**, and **3** obtained under our conditions were not the anticipated *Z* isomers but instead the *E* stereoisomers. The reaction of silver acetate in acetonitrile containing acetic acid with higher homologues of dibromobicyclo[*n*.1.0]alkanes yielded 2-bromo-2-cycloalkenyl acetates in which the size of the ring appeared to influence the geometry about the double bond. The geometry of the double bond in two new compounds has been assigned from data on ^3J(C-H) coupling constants obtained from a new 2D NMR pulse sequence developed by Bax and Freeman.[3]

Results

A series of *gem*-dibromobicyclo[*n*.1.0]alkanes was prepared by the reaction of dibromocarbene with cis- and trans-olefins.[4] Treatment with silver acetate in acetonitrile containing acetic acid afforded 2-bromo-2-cycloalkenyl acetates. Proton NMR spectra (220 MHz) of the crude reaction mixtures established the formation of a single 2-bromo-2-cycloalkenyl acetate; the presence of as little as 5% of the other isomer would have been observable. A comparison of the chemical shifts and splitting patterns of the olefinic proton in the purified acetates (**1a**, **2a**, and **3a**) shows them to be very similar. Enzymic hydrolysis[5] converted the esters into the corresponding alcohols (**1b**, **2b**, and **3b**); the geometries of the latter were assigned as *E* by a comparison of proton NMR data with data in the literature.[2,6] The chemical shifts of the methine protons of the allylic acetates **4a**, **5a**, and **6a** and the splitting pattern of the olefinic proton differed from those observed for **1a**, **2a** and **3a** (see Table I). Since compounds **5a** and **6a** were new, it was necessary to assign unambiguously the geometry about the double bond. Compound **4a** was likewise new, but NMR data for **4b** had previously been reported.[2,6] However, for the reasons given below, the

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