Cl in methanol-water (1 : 1) mixed solvent at room temperature to afford the desired **3a**. This condition was previously employed for the chemoselective reduction of nitro group on aromatic rings with various labile functionalities.[7] In this study, we found that Fe/NH_4Cl in methanol-water (1 : 1) condition was also very effective for the mild reduction of azido group on diazine heterocycles. In an essentially identical fashion, methoxydiazines **1**[8] and **2**[9] were transformed smoothly into the corresponding aminomethoxydiazines **3**[10] and **4**[3] in excellent yields, respectively. The results are summarized in Scheme 1. Due to easy access of starting materials, good yield and simple one-pot procedure, these synthetic approaches can be compared favorably with other methods.

Experimental section

The typical procedure is as follows; To a solution 2,2,6,6-tetramethylpiperidine (1.5 mL, 8.9 mmol) in THF (20 mL) was added *n*-butyllithium (5.4 mL, 1.6 M in hexane, 8.6 mmol) at −78 ℃ under a nitrogen atmosphere. The resulting mixture was stirred for 30 min at −78 ℃, and then canulated to THF solution (10 mL) of 4,6-dimethoxypyrimidine **1a** (1 g, 7.1 mmol) at −78 ℃. After being stirred for 15 min at −78 ℃, tosyl azide (1.8 g, 9.1 mmol) was added to the resulting solution. The mixture was warmed to room temperature and the solvent was removed under reduced pressure. The resulting residue was dissolved in methanol-water (1 : 1) mixed solvent, and then treated successively with Fe (2 g, 35.8 mmol) and NH_4Cl (1.9 g, 35.5 mmol). After the mixture was stirred for 12h at room temperature, usual workup followed chromatography on silica gel (chloroform/methanol) gave **3a** as white crystals in 87% yield.

5-amino-4,6-dimethoxypyrimidine (3a). white powder; mp 93-95 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 3.44 (br s, NH_2), 4.01 (s, OCH_3), 7.98 (s, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.6, 114.6, 145.6, 157.8; EI-MS (m/z, relative intensity) 155 (M^+, 100%), 154 (39), 140 (27), 126 (26), 112 (35), 108 (21), 97 (12), 85 (34), 72 (14); IR ν_{max} (KBr) cm^{-1} 3440, 3309.

5-amino-2,4-dimethoxypyrimidine (3b). white powder; mp 84-86 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 3.17 (br s, NH_2), 3.92 (s, OCH_3), 4.03 (s, OCH_3), 7.71 (s, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.7, 55.1, 124.2, 141.2, 159.1, 161.5; EI-MS (m/z, relative intensity) 155 (M^+, 100%), 154 (39), 140 (28), 126 (42), 125 (48), 85 (23), 83 (30), 70 (24), 57 (25); IR ν_{max} (KBr) cm^{-1} 3407, 3325.

4-amino-3-methoxypyridazine (4a). white powder; mp 126-128 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 4.15 (s, OCH_3), 4.51 (br s, NH_2), 6.54 (d, J=5.24 Hz, C_5-H), 8.41 (d, J=5.24 Hz, C_6-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 108.1, 136.5, 148.2, 156.3; EI-MS (m/z, relative intensity): 125 (M^+, 100%), 124 (42), 96 (47), 69 (28), 68 (39); IR ν_{max} (KBr) cm^{-1} 3466, 3309.

4-amino-3,6-dimethoxypyridazine (4b). white powder; mp 177-179 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, OCH_3), 4.07 (s, OCH_3), 4.42 (br s, NH_2), 6.07 (s, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.8, 55.1, 97.5, 138.8, 153.9, 163.7; EI-MS (m/z, relative intensity) 155 (M^+, 100%), 154 (82), 126 (17), 95 (21), 68 (40), 67 (20); IR ν_{max} (KBr) cm^{-1} 3423, 3326.

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Calix[4]arene : An Efficient Synthesis of 5-*tert*-Butyl-11-methyl-17,23-diphenyl-25,26,27,28-tetrahydroxycalix[4]arene

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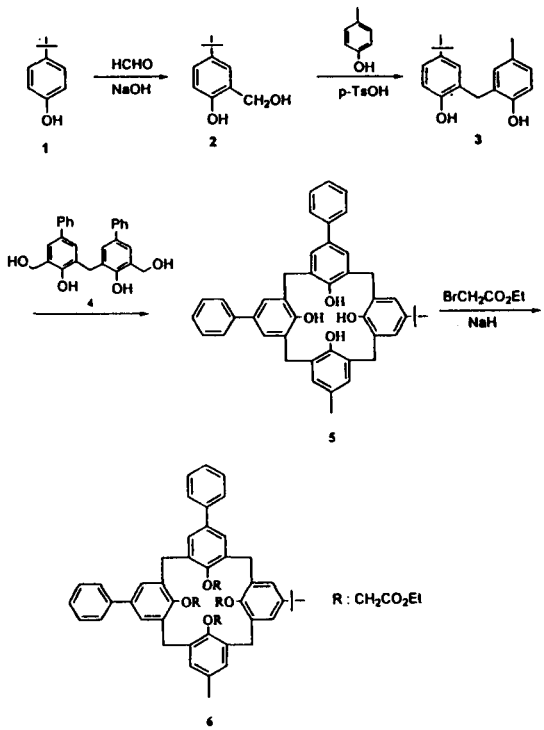
Calixarenes are synthetic macrocycles available in a variety of ring sizes and interesting both as complexation hosts for ions and molecules and as frameworks for elaborating more complex structure and have received a great deal of attention in recent years.[1~3]

One of the main features of naturally occurring host molecules is their capacity for enantioselective recognition. Various attempts have therefore been made to obtain chiral host molecules based on calixarenes. The most simple method to convert calixarene into chiral derivatives is the introduction of chiral substituent at the lower[4,5] or upper[6,7] rim of calixarene skeleton. More interest has been focused on the possibility of synthesizing "inherently" chiral calix[4]arenes, which are built up of nonchiral subunits and consequently owe their chirality to the fact that the calixarene molecule



Scheme 1.

is not planar. The attempts for asymmetric molecules of this type involved the synthesis of calix[4]arenes with three (in AABC pattern) or four different *p*-substituted phenol units[8~10] or the introduction of *m*-substituted phenol units.[11~15] The same asymmetric pattern can be achieved by O-alkylation or O-acylation at the lower[16~19] rim of calixarene. Calix[4]arene **5**, which has three different substituents in AABC pattern at the upper rim of calix, has no symmetry element and is chiral. The synthesis of compound **5** was reported by Böhmer and coworkers[8] using a five-step reaction procedure. However, the experimental details and characterizations were not described. As shown on the following scheme, this short paper deals with the improved synthesis of chiral calix[4]arene **5** by a three-step reaction.

Böhmer and coworkers[8] prepared the compound **3** by the four-step reaction starting from bromination of *p-tert*-butylphenol followed by hydroxymethylation, condensation with *p*-cresol and then debromination. In this study **3** was prepared by two-step reaction. Following the published procedure[20] the mixture of *p-tert*-butylphenol, 35% formaldehyde and NaOH was stirred 5 days at 40 ℃ to afford the compound **2** in 60% yield. If the same reaction was carried using a larger amount of formaldehyde and base, both the ortho positions of phenol were hydroxymethylated.[21] When a mixture of compound **2**, *p*-cresol and *p*-toluenesulfonic acid in benzene was refluxed for 20 h dimer **3** was afforded in 92% yield. The equimolar solution of dimers **3** (BC) and **4** (AA) in dry dioxane was added dropwise to the refluxing solution of $TiCl_4$ in dioxane. After reflux 53 h under nitrogen, the resulting reaction mixture was treated with the usual procedure[19] to afford calix[4]arene **5** in 22% isolated yield. The calix[4]arene **5** shows temperature dependent ^1H NMR spectrum.[22] The two broad resonance peaks from the $ArCH_2Ar$ protons at room temperature split into eight sets of doublet at 0 ℃. At even lower temperature (−55 ℃) the OH protons also appear as four singlets. ^{13}C NMR spectrum of **5** has 29 peaks (32 expected) from aromatic carbons and one peak each from methyl and *t*-butyl carbons. The $ArCH_2Ar$ carbons show four peaks at around 32 ppm. Both of the ^1H and ^{13}C NMR spectra support the cone conformation and chirality of **5**. However, ^1H NMR spectrum indicates that the conformational interconversion cone to cone of calix[4]arene **5** is rapid at room temperature. For chiral calix[4]arene this rapid equilibrium is equivalent to racemization. Therefore, stable enantiomer will not be obtainable, unless this interconversion is completely hindered. To obtain stable enantiomer it is necessary to fix the calix[4]arene conformation by the introduction of suitable residue on the phenolic hydroxy groups and ethyl bromoacetate is one of the most frequently studied reagent which leads to tetraester derivatives in the cone conformation.[23] When the calix[4]arene **5** was reacted with excess ethyl bromoacetate in THF in the presence of NaH, 62% of compound **6** in the cone conformation was isolated by column chromatography. The conformation of **6** can be unambiguously deduced from the ^1H and ^{13}C NMR spectra. In ^1H NMR spectrum, the resonance peak from $ArCH_2Ar$ protons appears as 8 sets of doublet at room temperature, and 4 singlets from the OCH_2CO protons. The methyl and methylene protons of OCH_2CH_3 groups appear as 3 sets of triplet and quartet in 1 : 2 : 1 ratio respectively. The ^{13}C NMR spectrum of compound **6** has 4 peaks from carbonyl carbons, 28 peaks from aromatic carbons, 4 peaks from OCH_2 CO carbons and 4 peaks from the $ArCH_2Ar$ carbons at around 32 ppm. These spectral patterns support the structure of **6** which is chiral and fixed in cone conformation. We tried to isolate pure enantiomer of **6** by HPLC using the chiral column, however the suitable separation conditions was not found yet.

In this work we have demonstrated that asymmetrically substituted calix[4]arene is readily available by '2+2' fragment condensation between AA type phenol dimer and BC type dimer, which were prepared by the single-step and two-step reactions, respectively.

Experimental

Melting points of all compounds were taken in sealed and evacuated capillary tubes on Syblon thermolyne apparatus with polarizing microscope and were not corrected. IR spectra were determined on a Nicolet Impact 400 FT-IR spectrometer as KBr pellet. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini 300 (300 and 75 MHz) (OCRC) and Bruker AMX 500 instrument (Seoul National University). Chemical shifts are recorded as δ values in parts per million relative to TMS (δ 0.0) as an internal standard. Mass spectra were recorded on Hewlett-Packard 5890-JMS AX505WA GC-Mass Spectrometer. TLC analyses were carried out on silica gel plates (absorbent thickness 250 μm). Flash chromatography was carried out with E. Merck silica gel (230-400 mesh ASTM). Elution rate was 2 in/min. Elemental analyses were carried out at OCRC.

5-Tert-butyl-2-hydroxybenzyl alcohol 2 was prepared in 60% yield by the published procedure[20]; mp 90-91 ℃ (lit[20] 91-92 ℃).

3-(3-Hydroxymethyl-5-phenylsalicyl)-5-phenyl-2-hydroxybenzyl alcohol 3 was prepared following the published procedure[21]: mp 128-129 ℃ (lit[21]. 127-128 ℃).

2-(5-Methylsalicyl)-4-tert-butylphenol 4. A mixture of compound **2** (10.8 g, 60 mmol), *p*-cresol (32.4 g, 5 mole equivalent to compound **2**) and *p*-toluenesulfonic acid (40 mg) in benzene (250 mL) was refluxed for 20 hr. After removing the excess *p*-cresol by steam distillation, the residue was extracted with chloroform. The organic layer was washed with water, dried and evaporated to afford viscous oily residue, which was triturated with hexane. The resulting solid was collected by filtration and purified by recrystallization from chloroform and hexane to give 14.9 g (92%) of colorless solid: mp 147 ℃; IR (KBr) 3260 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 9.18, (s, 2, OH), 7.30-6.72 (m, 6, ArH), 3.89 (s, 2, CH_2), 2.26 (s, 3, CH_3), 1.30 (s, 9, *t*Bu); ^{13}C NMR ($CDCl_3$) δ 150.59, 150.52, 144.26, 131.35, 130.77, 128.50, 127.70, 126.82, 126.27, 124.99, 115.88, 115.51 (Ar), 33.86 ($\underline{C}(CH_3)_3$), 31.33 ($C(\underline{C}H_3)_3$), 31.11 ($ArCH_2Ar$), 20.27 (CH_3); Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.95; H, 8.22. Found: C, 80.14; H, 8.07.

5-Tert-butyl-11-methyl-17,23-diphenyl-25,26,27,28-tetrahydroxycalix[4]arene 5. In a 1 L three neck flask equipped with condenser, dropping funnel and stirrer, a mixture of 150 mL of dry dioxane and 1.7 mL (15.5 mmol) of $TiCl_4$ was refluxed under nitrogen. A solution 3.7 mmole (1.00 g) of dimer **4** and 3.7 mmol (1.30 g) of bishydroxymethyl dimer **3** in 200 mL of dry dioxane was added during 6 h. After refluxing was continued for 53 h, the solvent was evaporated *in vacuo*. The residue was dissolved in chloroform, and after addition of 20 g of silica gel, the solvent was evaporated again. The silica gel was extracted for 2 days with hexane in a Soxhlet apparatus. After removal of solvent, the residue was recrystallized from chloroform and hexane to afford 525 mg (22%) of the desired calix[4]arene as crystalline solid: mp 336 ℃; IR (KBr) 3155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.33 (s, 4, OH), 7.48-6.87 (m, 18, ArH), 4.28 (br. m, 4, CH_2), 3.69 (br. m, 4, CH_2), 2.13 (s, 3, CH_3), 1.25 (s, 9, *t*Bu); ^{13}C NMR ($CDCl_3$) δ 149.00, 148.57, 146.81, 146.48, 144.95, 141.13, 141.01, 135,73, 135.57, 131.64, 129.88, 129.65, 129.03, 128.94, 128.78, 128.73, 128.56, 128.51, 128.39, 128.14, 128.01, 127.94, 127.89, 127.71, 127.44, 127.10, 126.92, 126.84, 126.07 (Ar), 33.88 ($\underline{C}(CH_3)_3$), 32.14, 32.04, 31.90, 31.78 ($ArCH_2Ar$), 31.27 (CH_3)$_3$), 20.32 (CH_3); FAB mass: m/e 646 (Calcd. M^+ 646); Anal. Calcd. for $C_{45}H_{42}O_4$: C, 83.55; H, 6.56. Found: C, 83.71; H, 6.50.

5-Tert-butyl-11-methyl-17,23-diphenyl-25,26,27,28-tetrakis(ethoxycabonyl)methoxy-calix[4]arene 6. To heated suspension of compound **5** (500 mg, 0.78 mmol) and NaH (400 mg 60% oil dispersion, 16 mmol) in dry THF (100 mL) a solution of ethyl bromoacetate (2.5 mL, 22.5 mmol) in dry THF (15 mL) was added dropwise under nitrogen and then the reaction mixture was refluxed for 24 h. After removal of THF *in vacuo*, small amount of ethanol was added to destroy the excess NaH and then organic material was extracted with chloroform. The organic layer was washed with water, dried and evaporated to afford oily residue, which was purified by flash chromatographic separation (eluent was 1 : 4 mixture of acetone and hexane) to afford 475 mg (62%) of the product as crystalline solid. mp 71 ℃; IR (KBr) 1750 and 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.56-6.24 (m, 18, ArH), 5.02 (d, 1, CH_2, J=13.5 Hz), 4.97 (d, 1, CH_2, J=13.5 Hz), 4.90 (d, 1, CH_2, J=14.1 Hz), 4.87 (d, 1, CH_2, J=14.1 Hz), 4.75 (s, 2, OCH_2CO), 4.74 (s, 2, OCH_2CO), 4.65 (s, 2, OCH_2CO), 4.63 (s, 2, OCH_2CO), 4.27 (q, 2, CH_2, J=7 Hz), 4.26 (q, 4, CH_2, J=7 Hz), 4.21 (q, 2, CH_2, J=7 Hz), 3.38 (d, 1, CH_2, J=13.5 Hz), 3.30 (d, 1, CH_2, J=14.1 Hz), 3.26 (d, 1, CH_2, J=14.1 Hz), 3.20 (d, 1, CH_2, J=13.5Hz), 1.57 (s, 3, CH_3), 1.33 (t, 3, CH_3, J=7 Hz), 1.32 (t, 6, CH_3, J=7 Hz), 1.30 (t, 3, CH_3, J=7 Hz), 1.18 (s, 9, *t*Bu); ^{13}C NMR ($CDCl_3$) δ 170.94, 170.90, 170.28, 170.24 (C=O) 156.21, 155.24, 154.41, 153.22, 145.77, 141.10, 140.97, 135,93, 135.77, 135.66, 135.42, 134.58, 134.44, 134.08, 133.27, 133.19, 132.34, 128.88, 128.69, 128.48, 127.61, 127.44, 127.33, 126.99, 126.71, 126.66, 126.09, 126.04 (Ar), 71.60, 71.52, 71.39, 70.83 ($CO\underline{C}H_2$), 60.53, 60.46, 60.22, 60.20 (CH_2), 33.74 ($\underline{C}(CH_3)_3$), 31.78, 31.52, 31.50, 31.33 ($ArCH_2Ar$), 31.22 ($\underline{C}H_3)_3$), 20.14 (CH_3), 13.97, 13.95, 13.90 (CH_3); FAB mass: m/e 990 (Calcd. M^+ 990); Anal. Calcd. for $C_{61}H_{66}O_{12}$: C, 73.91; H, 6.72. Found: C, 74.05; H, 6.70.

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Structure of Unique N,N-Dimethylformamide Solvate of Cobalt(II) Chloride

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Cobalt(II) complexes adopt two major geometries, distorted octahedral and tetrahedral arrangements. The obvious structures of the two geometries were exemplified by the following well known equilibrium (eq. 1).[1]

$$[Co(OH_2)_6]^{2+} + 4Cl^- \rightleftarrows [CoCl_4]^{2-} + 6H_2O \quad (1)$$

The local geometry of the d^7 electronic configuration (Co^{II}) has been found to depend on ligand polarizability as well as ligand size.[2,3]

N,N-Dimethylformamide (DMF) is an excellent ionizing solvent for various classes of compounds due to its convenient liquid state from −61° to 153 ℃. In addition, DMF has good electrochemical stability, which makes it a popular solvent for polarography and electroreduction of organic and inorganic compounds.[4] DMF adducts as good intermediates for further reaction have been interesting topic.[5] DMF has two possible donor sites, N or O, but all the DMF metal compounds were elucidated as metal-oxygen bond by X-ray crystal studies.[6] In particular, attention has been paid to the ionization equilibria and stability of cobalt(II) chloride in DMF. In the presence of chloride ions, DMF molecules of $[Co(DMF)_6]^{2+}$ were successively replaced by chloride ions to form the following various coordination complexes (eq. 2-5).[7] $[Co(DMF)Cl_3]^-$ and $[Co(DMF)_5Cl]^+$ species were found to be the electroactive components on nickel electrode in DMF.[7] Furthermore, based on the visible absorption spectra and molar conductance, Grzybkowski *et al.* suggested that cobalt(II) chloride predominantly undergoes a disproportionation to yield of $[Co(DMF)_6]^{2+}\cdot 2[Co(DMF)Cl_3]^-$ in DMF solution at room temperature.[8]

$$[Co(DMF)_6]^{2+} + Cl^- \rightleftarrows [Co(DMF)_5Cl]^+ + DMF \quad (2)$$

$$[Co(DMF)_5Cl]^+ + Cl^- \rightleftarrows [Co(DMF)_2Cl_2] + 3DMF \quad (3)$$

$$[Co(DMF)_2Cl_2] + Cl^- \rightleftarrows [Co(DMF)Cl_3]^- + DMF \quad (4)$$

$$[Co(DMF)Cl_3]^+ + Cl^- \rightleftarrows [CoCl_4]^{2-} + DMF \quad (5)$$

The formation of the cobalt solvate molecule is very sensitive to the chemical condition, and thus is controversial. In order to elucidate the isolated species in the solid state, X-ray structure of DMF adduct of cobalt(II) chloride is herein established.

Experimental

Materials and Instrumentation. Cobalt(II) chloride ($CoCl_2\cdot 6H_2O$) and N,N-dimethylformamide (DMF) were purchased from Junsei. Elemental analysis (C, H, N) was carried out at the Korea Basic Science Center. Infrared spectra were obtained in 5000-400 cm^{-1} range on a Perkin Elmer 16F PC FTIR spectrometer with samples prepared as KBr pellets.

Preparation of $[Co(DMF)_6]^{2+}\cdot 2[Co(DMF)Cl_3]^-$. $CoCl_2\cdot 6H_2O$ (2.38 g, 1.0 mmol) was dissolved in 20 mL of DMF. Excess ethylether was added into the solution, and left at −10 ℃ to obtain blue crystals suitable for X-ray crystallography in 76% yield. Anal. found (Calcd. for $C_{24}H_{56}N_8O_8Cl_6Co_3$): C, 29.40 (29.59); H, 5.68 (5.79); N, 11.45 (11.50). IR (KBr, cm^{-1}): 1665 (sh), 1650 (br, s), 1498 (m), 1438 (m), 1382 (s), 1254 (m), 1114 (s), 1062 (w), 686 (s).

X-ray Crystal Analysis. The crystal was wedged in a Lindemann capillary with mother liquor. The X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated Mo Kα (λ=0.71073 Å) at ambient temperature. Unit cell dimension was based on 25 well-centered reflections by using a least-square procedure. During the data collection, three standard reflections monitored every hour did not show any significant intensity variation. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical psi-scan method. The structure was solved by Patterson method (SHELXS-86), and was refined by full-matrix least squares techniques (SHELXL-93).[9] All non-hydrogen atoms were refined anisotropically. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1. Final atomic coordinates and isotropic thermal parameters are given in Table 2.