

Synthesis of Calix[4]arenes in AAAB or AABB Type Substitution at Upper Rim

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Seven calix[4]arenes, having two different substituents in AAAB or AABB pattern at the upper rim of calix were synthesized by fragmentation condensation reaction of *p*-substituted phenol trimer (AAA) with 2,6-bishydroxymethylated 4-substituted phenol (B) or that of dimer (AA) with 2,2'-bishydroxymethylated dimer (BB). An equimolar mixture of the coupling components (trimer and monomer or dimer and dimer) was refluxed in dioxane in the presence of TiCl₄ to afford calix[4]arene 6 and 7 in 15-38% yield. The structure of calix[4]arenes was confirmed by elemental analysis and the ¹H/¹³C NMR spectroscopy.

Introduction

Calixarenes are macrocyclic compounds available in a variety of ring sizes and are of interest both as complexation hosts for ions and molecules and as frameworks for elaborating more complex structures.¹⁻³ The preparation of calix[4]arenes containing more than two different functional groups at the upper rim of calix has attracted our attention^{4,5} and that of several research groups⁶⁻¹² because of the possibility of easily obtaining new host molecules. These calix[4]arenes also can be used as a starting material for the introduction of chirality. The stepwise routes giving to differently substituted calix[4]arenes were developed by No and Gutsche¹³ and Böhmer and coworkers,^{7,14} but the methods are relatively long and tedious, producing low overall yields. Since Reinhoudt and coworkers¹¹ reported that the difference in reactivity of phenyl rings of the diametrically dimethoxylated calix[4]arene can be utilized for the selective functionalization of calix[4]arene at upper rim, various calix[4]arenes which have two different substituents in ABAB or AAAB type at upper rim were synthesized using the reactivity difference between *O*-alkylated (or acylated) benzene ring and unsubstituted phenol ring of partially *O*-substituted calix[4]arene.^{2,3}

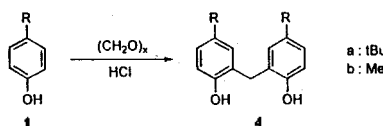
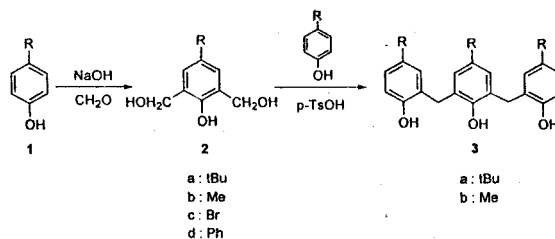
The synthesis of calixarenes having two to four different phenolic units was reported by Böhmer using the '2+2' or '3+1' coupling procedure.^{6,7,15} Although in principle versatile, the fragmentation condensation procedure to yield calix[4]arene is plagued by serious synthetic problem; trimers were prepared by a six-step reaction starting from the bromination of *p*-substituted phenol followed by repetition of bromomethylation and condensation with another *p*-substituted phenol and the overall yield was low. Here we describe a three-step (or two-step) method for the preparation of calix[4]arenes with two different substituents in AAAB or AABB pattern at the upper rim.

Results and Discussion

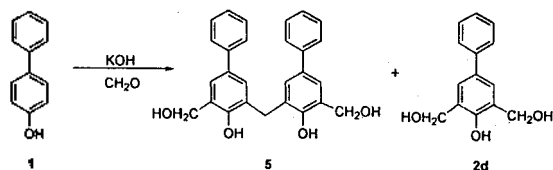
The target calix[4]arenes were synthesized by fragmentation condensation reaction of *p*-substituted phenol trimer (AAA) with 2,6-bishydroxymethylated *p*-substituted phenol (B) or that of dimer (AA) with bishydroxymethylated dimer

(BB). In the synthesis of coupling component, we concerned about the speed and simplicity, *i.e.*, they should be synthesized by one- or two-step reaction with reasonable yield. And we also concerned about further functional group introduction at upper rim of calix directly or after removal of *t*-butyl groups. Therefore, bromine, *t*-butyl, methyl and phenyl groups are selected as para-substituents.

As shown on Scheme 1, 2,6-bis(hydroxymethyl)-4-substituted phenol 2a and 2c were synthesized by the published procedures^{16,17} with minor modification in isolation and purification of products. A mixture of *p*-substituted phenol, formaldehyde and NaOH was heated for 5 days under nitrogen atmosphere to produce crude product which was purified by recrystallization or flash chromatography.¹⁸ 2,6-Bishydroxymethyl-4-phenylphenol 2d was prepared in 35% yield as second major product in the preparation of compound 5¹⁹ (see Scheme 2). Compounds 2a and 2b were treated with excess *p*-*tert*-butylphenol and *p*-cresol respectively in the presence of catalytic amount of *p*-toluenesulfonic acid in benzene, unreacted excess phenol and solvent were removed by steam distillation. The crude product was purified to afford the corresponding trimers 3a and 3b in 95 and 91% yield respectively. Compound 3b was also prepared by the treatment of *p*-cresol with paraformaldehyde in xylene in the presence of conc HCl for 20h at 60 °C, unreacted *p*-cresol



Scheme 1.



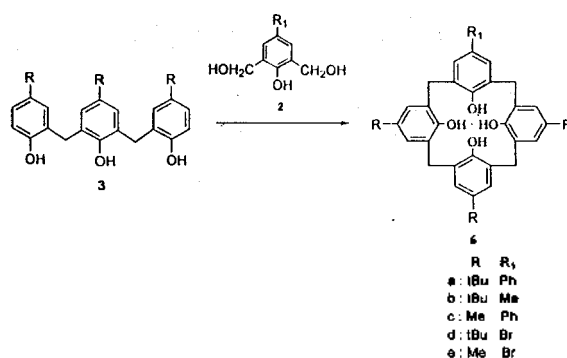
Scheme 2.

and solvent were removed by steam distillation. The residue was triturated with chloroform to afford compound **3b** in 57% yield as chloroform insoluble solid. In this preparation the *p*-cresol dimer **4b**²⁰ was also isolated in 30% yield by the flash chromatography of the residue obtained after trimer **3b** was isolated. When the reaction was carried out at lower temperature (45–50 °C) the yield of **4b** was increased to 65% (based on the starting amount of *p*-cresol) and pure **4b** was isolated by vacuum distillation. Compound **4a** was prepared in 92% (based on the consumed 2*p*-*tert*-butylphenol) yield by acid-catalyzed condensation of *p*-*tert*-butylphenol and para-formaldehyde using the similar method as **4b**.

Bishydroxymethylated *p*-phenylphenol dimer **5** was prepared using the published procedure.¹⁹ After the mixture of *p*-phenylphenol, 35% formaldehyde and KOH was stirred for 4 days at 40 °C, the resulting paste was acidified with dil. HCl to produce crude product, which was boiled with chloroform. The chloroform insoluble material was collected and recrystallized from methanol to afford **5** in 55% yield. In this preparation bishydroxymethylated monomer **2d** was also isolated in 35% yield.

Using these monomers, dimers and trimers as coupling components, seven calix[4]arenes were synthesized by '3+1' or '2+2' fragmentation condensation reaction as shown on Scheme 3. An equimolar mixture of trimer (AAA) and bishydroxymethylated phenol (B) or dimer (AA) and bishydroxymethylated phenol dimer (BB) in dry dioxane was added dropwise to the refluxing solution of TiCl₄ in dioxane. After reflux under nitrogen, the dark red solution was evaporated *in vacuo*, the residue was dissolved in chloroform, and after addition of silica gel, the resultant mixture was evaporated again. The silica gel was extracted with hexane in a Soxhlet apparatus. After removal of solvent, the residue was purified to give the desired calix[4]arene **6** and **7** in 15–38% yield. The preparation of calix[4]arene **7a** was already reported by our laboratory,¹⁹ however, in this study **5** was used in the condensation reaction instead of bisbromomethylated *p*-phenylphenol dimer. Thus, the overall step was reduced by one step (the bromination of **5**) and overall yield was also improved.

The structure of calix[4]arenes was confirmed by elemental analysis and the ¹H and ¹³C NMR spectroscopy, which support the proposed macrocyclic structure. ¹H NMR spectra show two broad resonance peaks at around 4.2 and 3.5 ppm from protons of bridge methylene groups which support the symmetry of calix[4]arene **6** and **7**. ¹³C NMR spectra, showing the expected number of peaks (18 peaks for **6a** and **6c**, 14 peaks for **6b** and **6d** and 16 peaks for **7a** and **7b**) from aromatic carbons and two peaks at about 32 ppm from the ArCH₂Ar bridge methylene carbons, was also compatible with the proposed structure (see Table 1).



Scheme 3.

Table 1. Number of ¹³C NMR spectral peaks of the calix[4]arenes **6** and **7**

Compound	Aromatics	ArCH ₂ Ar	C(CH ₃) ₃	C(CH ₃) ₃	CH ₃
6a	18	1	2	2	—
6b	14	2	2	2	1
6c	18	2	—	—	1
6d	14	2	2	2	—
6e	a	2	a	2	—
7a	16	2	1	1	—
7b	16	2	—	—	1

¹³C NMR spectrum of calix[4]arene **6e** was not able to obtain with good quality due to limited solubility of this compound in various deuterated solvents.

In conclusion, calix[4]arenes having two different substituents in AAAB and AABB patterns at upper rim were synthesized by the relatively simple convergent method. These calix[4]arenes can be used as a starting material for the synthesis of chiral calix[4]arenes by the elimination of symmetry and also used for further functional group introduction.

Experimental

Melting points of all compounds were taken in sealed and evacuated capillary tubes on a 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 ¹³C 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. Elemental analyses were carried out at OCRC. TLC analyses were carried out on silica gel plates (absorbent thickness 250 μ m). Flash chromatography was carried out with E. Merck silica gel (230-400 mesh ASTM). Elution rate were 2 in/min. 2,6-Bishydroxymethyl-4-methylphenol **2b** was purchased from Aldrich and used without further purification. 2,6-Bis(hydroxymethyl)-4-*tert*-butylphenol **2a**,^{16,17} 2,6-bis(hydroxymethyl)-4-phenylphenol **2d**,¹⁹ 2-(5-*tert*-butylsalicyl)-4-*tert*-butylphenol **4a**¹⁹ and 3-(3-hydroxymethyl-5-phenylsalicyl)-5-phenyl-2-hydroxybenzyl alcohol **5**¹⁹ were prepared following published procedures.

2,6-Bishydroxymethyl-4-bromophenol 2c. After the mixture of *p*-bromophenol (10.0 g, 57.8 mmole), NaOH (2.3 g dissolved in 32 mL of water) and 35% formaldehyde (9.2 mL) was heated for 5 d at 50 °C under nitrogen atmosphere, the resulting paste was poured into 100 mL of 1% HCl solution, stirred for 2 h and the precipitate was collected by filtration. After the crude product was decolorized by short column chromatography, a total of 10.5 g (78%) of the desired product was isolated by a recrystallization from acetone and hexane as a colorless crystalline solid: mp 178-179 °C; IR (KBr) 3410, 3310 cm^{-1} ; ¹H NMR (acetone-*d*₆) 7.50 (s, 2, ArH), 4.92 (s, 4, CH₂), 2.91 (s, 3, OH); Anal. Calcd. for C₈H₈BrO₃: C, 41.22; H, 3.90; Br, 34.28. Found: C, 41.16; H, 3.82; Br, 34.19.

2-[3-(5-*Tert*-butylsalicyl)-5-*tert*-butylsalicyl]-4-*tert*-butylphenol 3a. A mixture of compound **2a** (16.5 g, 78.8 mmole), *p*-*tert*-butylphenol (120 g, 5 mole equivalent per hydroxymethyl group of **2a**) and *p*-toluenesulfonic acid (100 mg) in benzene (200 mL) was refluxed for 24 h. After removing the excess *p*-*tert*-butylphenol 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 35.4 g (95%) of colorless solid: mp 229-230 °C; IR (KBr) 3240 cm^{-1} ; ¹H NMR (acetone-*d*₆) δ 8.47 (br. s, 1, OH), 7.11 (d, 2, ArH, *J*=2.5 Hz), 6.96 (s, 2, ArH), 6.85 (d, 1, ArH, *J*=2.5 Hz), 6.83 (d, 1, ArH, *J*=2.5 Hz), 6.83 (d, 1, ArH, *J*=2.5 Hz), 6.55 (d, 2, ArH, *J*=8.4 Hz), 3.75 (s, 4, CH₂), 2.67 (br. s, 2, OH), 1.03 (s, 18, *t*Bu), 1.02 (s, 9, *t*Bu); Anal. Calcd. for C₃₂H₄₂O₃: C, 80.95; H, 8.94. Found: C, 81.01; H, 8.91.

2-[3-(5-Methylsalicyl)-5-methylsalicyl]-4-methylphenol 3b. Method A: A mixture of 2,6-bishydroxymethyl *p*-cresol **2b** (5.04 g, 30 mmole), *p*-cresol (20 g, 3 mole equivalent per hydroxymethyl group) and *p*-toluenesulfonic acid (100 mg) in benzene (100 mL) was refluxed for 24 h. After removing the excess *p*-cresol by steam distillation, the residue was collected by filtration, dried and recrystallized from acetone and hexane to give 9.45 g (91%) of colorless solid: mp 217-218 °C (lit²⁰ 215 °C); IR (KBr) 3147 cm^{-1} ; ¹H NMR (acetone-*d*₆) δ 8.51 (br. s, 1, OH), 7.05-6.78 (m, 8, ArH), 3.90 (s, 4, CH₂), 2.96 (br. s, 2, OH), 2.20 (s, 6, CH₃), 2.17 (s, 3, CH₃); ¹³C NMR (acetone-*d*₆) δ 152.77, 150.25, 132.10, 130.02, 129.26, 129.86, 128.63, 128.58, 128.12, 115.95, (Ar), 30.62 (CH₂), 20.12, 20.03 (CH₃). Method B: A mixture of *p*-cresol (21.6

g 200 mmole), paraformaldehyde (2.60 g) and conc HCl (8 mL) in xylene (130 mL) was heated for 20 h at 60 °C. After removal of excess *p*-cresol by steam distillation, the residue was triturated with chloroform (20 mL). Chloroform insoluble material was collected by filtration, washed with cold chloroform and hexane to afford 10.8 g of trimer as a colorless solid. An additional 2.4 g of the desired product was obtained from the flash chromatographic separation (eluent was 3 : 1 mixture of hexane and acetone) of the viscous oily residue obtained by evaporation of chloroform. Total yield was 57%. In this preparation, dimer was also obtained in 30% yield from the flash chromatographic separation.

2-(5-Methylsalicyl)-4-methylphenol 4b. was prepared following the published procedure²⁰ as follows. A mixture of *p*-cresol (50.0 g 463 mmole), paraformaldehyde (6.50 g) and conc HCl (8 mL) in xylene (250 mL) was heated for 20 h at 50 °C. After removal of excess *p*-cresol by steam distillation, the residue was triturated with chloroform (20 mL). After chloroform insoluble material was collected by filtration (trimer; 7.6 g, 14%), chloroform solution was washed with water and dried. A total 34.3 g (65%) of the desired product was obtained by vac. distillation of the viscous oily residue resulted from the evaporation of chloroform: mp 127-128 °C (lit²⁰ 126 °C); IR (KBr) 3260 cm^{-1} ; ¹H NMR (CDCl₃) δ 7.52 (s, 2, OH), 7.12-6.72 (m, 6, ArH), 3.88 (s, 2, CH₂), 2.29 (s, 6, CH₃); ¹³C NMR (CDCl₃) δ 150.37, 131.39, 130.86, 129.61, 126.94, 115.91 (Ar), 30.82 (CH₂), 20.25 (CH₃).

Preparation of calix[4]arene 6

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 mmole) of TiCl₄ was refluxed under nitrogen. A solution of trimer or dimer (3.5 mmole) and bishydroxymethyl monomer or dimer (3.5 mmole) 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 d with hexane in a Soxhlet apparatus. After removal of solvent, the residue was purified to give the desired calix[4]arenes as a colorless crystalline solid.

5,11,17-Tri-*tert*-butyl-23-phenyl-25,26,27,28-tetrahydroxycalix[4]arene 6a. was obtained in 35% yield by the trituration of residue with hexane: mp 340-341 °C; IR (KBr) 3160 cm^{-1} ; ¹H NMR (CDCl₃) δ 10.36, (s, 4, OH), 7.40-7.38 (m, 4, ArH), 7.26 (s, 4, ArH), 7.10 (s, 3, ArH), 7.05 (s, 2, ArH), 4.31 (br. m, 4, CH₂), 3.56 (br. m, 4, CH₂), 1.23 (s, 18, *t*Bu), 1.20 (s, 9, *t*Bu); ¹³C NMR (CDCl₃) δ 148.96, 146.84, 146.56, 144.81, 144.76, 141.15, 135.43, 128.88, 128.74, 128.17, 127.97, 127.70, 127.37, 127.00, 126.79, 126.26, 126.02, 125.91 (Ar), 33.84, 33.75 (C(CH₃)₃), 32.26 (ArCH₂Ar), 31.23, 31.14 (C(CH₃)₃); Anal. Calcd for C₄₆H₅₂O₄: C, 82.58; H, 7.85. Found: C, 82.71, H, 7.79.

5,11,17-Tri-*tert*-butyl-23-methyl-25,26,27,28-tetrahydroxycalix[4]arene 6b. was obtained in 38% yield by the trituration of residue with hexane: mp >360 °C (slightly decompose at 345 °C); IR (KBr) 3140 cm^{-1} ; ¹H NMR (CDCl₃) δ 10.26, (s, 4, OH), 7.08 (d, 2, ArH, *J*=2.3 Hz), 7.03 (m, 4, ArH), 6.85 (s, 2, ArH), 4.14 (br, 4, CH₂), 3.48 (br, 4, CH₂), 1.62 (s, 3, CH₃), 1.22 (s, 18, *t*Bu), 1.19 (s, 9, *t*Bu); ¹³C NMR

(CDCl₃) δ 146.91, 146.76, 146.43, 144.66, 144.60, 131.27, 129.63, 128.40, 128.05, 127.81, 127.49, 126.14, 125.96, 125.73 (Ar), 33.80, 33.74 (C(CH₃)₃), 32.24, 31.99 (ArCH₂Ar), 31.20, 31.12 (C(CH₃)₃) 20.32 (CH₃); Anal. Calcd. for C₄₁H₅₀O₄: C, 81.13; H, 8.32. Found: C, 81.25; H, 8.26.

5,11,17-Trimethyl-23-phenyl-25,26,27,28-tetrahydroxycalix[4]arene 6c. was obtained in 26% yield by recrystallization of the residue from acetone and hexane: mp 349 °C (slightly decompose at 346 °C); IR (KBr) 3150 cm⁻¹; ¹H NMR (CDCl₃) δ 10.20, (s, 4, OH), 7.45-6.85 (m, 13, ArH), 4.22 (br. m, 4, CH₂), 3.48 (br. m, 4, CH₂), 2.15 (s, 3, CH₃), 2.14 (s, 6, CH₃); ¹³C NMR (CDCl₃) δ 148.84, 146.73, 146.55, 141.19, 135.40, 131.50, 131.34, 129.68, 129.63, 129.56, 128.78, 128.73, 128.29, 128.14, 127.96, 127.89, 127.09, 126.84 (Ar), 31.72, 31.48 (ArCH₂Ar), 20.24 (CH₃); Anal. Calcd. for C₃₇H₃₄O₄: C, 81.88; H, 6.33. Found: C, 81.98; H, 6.24.

5-Bromo-11,17,23-Tri-tert-butyl-25,26,27,28-tetrahydroxycalix[4]arene 6d. was obtained in 22% yield by the trituration of residue with hexane: mp >360 °C; IR (KBr) 3150 cm⁻¹; ¹H NMR (CDCl₃) δ 10.23, (s, 4, OH), 7.27 (s, 2, ArH), 7.16 (s, 2, ArH), 7.11 (d, 2, ArH, *J*=2.4 Hz), 7.02 (d, 2, ArH, *J*=2.4 Hz), 4.22 (br. m, 4, CH₂), 3.48 (br. m, 4, CH₂), 1.24 (s, 18, *t*Bu), 1.20 (s, 9, *t*Bu); ¹³C NMR (CDCl₃) δ 148.57, 148.74, 146.37, 145.02, 144.89, 131.59, 130.73, 128.22, 127.59, 126.69, 126.45, 126.01, 125.78, 113.80 (Ar), 33.86, 33.79 (C(CH₃)₃), 32.18, 31.81 (ArCH₂Ar), 31.20, 31.13 (C(CH₃)₃); Anal. Calcd. for C₄₀H₄₇BrO₄: C, 71.51; H, 7.07; Br, 11.89. Found: C, 71.42; H, 6.99; Br, 11.80.

5-Bromo-11,17,23-Trimethyl-25,26,27,28-tetrahydroxycalix[4]arene 6e. was obtained in 20% yield by the trituration of residue with hexane: mp >360 °C; IR (KBr) 3160 cm⁻¹; ¹H NMR (CDCl₃) δ 10.09, (s, 4, OH), 7.15 (s, 2, ArH), 6.88-6.82 m, 6, ArH), 4.17 (br. m, 4, CH₂), 3.43 (br. m, 4, CH₂), 2.16 (s, 6, CH₃), 2.15 (s, 3, CH₃); ¹³C NMR (CDCl₃) δ 32.18, 31.81 (ArCH₂Ar), 31.20, 31.13 (C(CH₃)₃); Anal. Calcd. for C₃₁H₂₉BrO₄: C, 68.25; H, 5.37; Br, 14.65. Found: C, 68.37; H, 5.42; Br, 14.77.

5,11-Diphenyl-17,23-di-tert-butyl-25,26,27,28-tetrahydroxycalix[4]arene 7a. was obtained in 24% yield by the recrystallization from chloroform and hexane: mp 332-333 °C (lit¹⁹ 332-333 °C); IR (KBr) 3160 cm⁻¹; ¹H NMR (CDCl₃) δ 10.33, (s, 4, OH), 7.35 (m, 10, ArH), 7.27 (s, 4, ArH) 7.07 (s, 4, ArH), 4.31 (br, 4, CH₂), 3.59 (br, 4, CH₂), 1.21 (s, 18, *t*Bu); ¹³C NMR (CDCl₃) δ 148.75, 146.41, 144.82, 140.83, 135.47, 129.06, 128.65, 128.44, 128.00, 127.98, 127.78, 127.14, 126.93, 126.78, 126.15, 125.85 (Ar), 34.06 (C(CH₃)₃), 32.44, 32.37 (ArCH₂Ar), 31.46 (C(CH₃)₃); Anal. Calcd. for C₄₆H₄₈O₄: C, 83.69; H, 7.02. Found: C, 84.03; H, 7.04.

5,11-Dimethyl-17,23-diphenyl-25,26,27,28-tetrahydroxycalix[4]arene 7b. was obtained in 15% yield by trituration of the residue with hexane: mp 352-353 °C; IR (KBr) 3160 cm⁻¹; ¹H NMR (CDCl₃) δ 10.27, (s, 4, OH), 7.45-7.26 (m, 14, ArH), 6.88 (d, 4, ArH, *J*=6.0 Hz), 4.29 (br, 4, CH₂), 3.57 (br, 4, CH₂), 2.15 (s, 6, CH₃); ¹³C NMR (CDCl₃) δ 148.75, 146.64, 141.11, 135.65, 131.55, 129.71, 129.67, 128.90, 128.72,

128.52, 128.25, 128.08, 127.97, 127.91, 127.11, 126.87 (Ar), 32.00, 31.49 (ArCH₂Ar), 20.23 (CH₃); Anal. Calcd. for C₄₂H₃₆O₄: C, 83.41; H, 6.01. Found: C, 83.27; H, 6.10.

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