Calixarenes. 7. *p*-Phenylcalix[4]arene

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p-Phenylcalix[4]arene (**11**), in the cone conformation, is a basket-shaped compound containing a large cavity and, therefore, is of interest for studies of host–guest complexation. Its unequivocal synthesis has been achieved by the stepwise method of Hayes and Hunter, by starting with 2-bromo-4-phenylphenol and adding methylene and *p*-phenylphenol groups sequentially until a linear tetramer (**9**) is attained. Removal of the bromine followed by acid-catalyzed cyclization yields the calixarene **11**, along with two other materials that are presumed to be the isomeric macrocyclic compounds **12** and **13**. *p*-Phenylcalix[4]arene synthesized in this fashion is different from the compound reported by Zinke from the condensation of *p*-phenylphenol and formaldehyde in the presence of base, and it appears that **11** is not a major product, and perhaps not even a minor product, of that reaction mixture.

Calixarenes are [1_n]metacyclophanes comprising cyclic arrays of phenolic residues attached by methylene groups at the positions ortho to the hydroxyl groups. In the cone conformation they have molecular shapes roughly comparable to those of the cycloamyloses.[1] A class of calixarenes that is of particular interest with respect to our goal of using these compounds as enzyme models contains phenyl groups at the *p*-position, as illustrated in Figure 1. Not only do the phenyl groups increase the size of the calixarene cavity by a considerable amount but they also provide potential sites at the 4′-positions for the addition of functional groups. A synthesis of *p*-phenylcalix[4]arene was reported many years ago by Zinke and co-workers[2-4] by means of a one-flask, three-step process in which *p*-phenylphenol is treated with aqueous formaldehyde and sodium hydroxide at 50 °C for 45 h, acidified, heated at 130 °C, suspended in linseed oil, and heated at 220 °C. The product, obtained in unspecified yield, was described[4] as fine, white needles which were insoluble in cold chloroform but recrystallizable from toluene, browning at 330–360 °C, becoming deeply colored at 520–540 °C, but not melting. More recently, one-flask syntheses using a one-step process[5] have been reported by this laboratory[6] and another,[7] the products in these cases being materials of less well-defined crystalline structure which melted between 340 and 390 °C and were tacitly assumed to be cyclic tetramers. In view of our recent work on the product mixture obtained from the condensation of *p-tert*-butylphenol and formaldehyde,[1] however, this assumption must be questioned. The purpose of the present work, therefore, was to carry out an unequivocal synthesis of *p*-phenylcalix[4]arene (**11**) to determine whether or not this material is present in the products obtained either by the three-step or the one-step, one-flask processes.

Recognizing the tenuous basis of Zinke's proofs of structure for the alleged cyclic tetramers, Hayes and Hunter[8] devised what they termed a "rational synthesis" for the *p*-methylcalix[4]arene. This method, which has recently been used in our laboratory for the synthesis of *p-tert*-butylcalix[4]arene[1] and which has been extensively employed and improved in Kämmerer's laboratory,[9] provides the basis for the synthesis of **11**. *p*-Phenylphenol (**1**) was converted in 90% yield to 2-bromo-4-phenylphenol (**2**), and this was treated with aqueous formaldehyde and 6 molar equiv of KOH to afford a 49% yield of 2-bromo-4-phenyl-6-(hydroxymethyl)phenol (**3**), separable from starting material by flash chromatography[10] (Scheme I). Acid-catalyzed condensation of **3** with a 40 molar equiv excess of *p*-phenylphenol produced a mixture from which the unreacted *p*-phenylphenol was removed by fractional crystallization followed by flash chromatography to yield 71% of **4** as a colorless solid. In a similar fashion, hydroxymethylations and acid-catalyzed arylations yielded **5** from **4** (48% yield), **6** from **5** (65% yield), **7** from **6** (73% yield), **8** from **7** (81% yield), and **9** from **8** (46% yield). Debromination of **9** in the presence of Raney nickel and hydrogen afforded a 70% yield of **10** as a colorless, sharp-melting powder which was subjected to high-dilution, acid-catalyzed cyclization under the conditions described by Kämmerer.[9] Howvever, in contrast to the *p-tert*-butyl analogue,[1] cyclization did not yield only one major product but a mixture of three substances which were separated by chromatography. One of these, obtained in 13% yield, melted at 407–409 °C and possessed the characteristics of a calix[4]arene. It had an elemental analysis compatible with a $C_{52}H_{40}O_4$ compound, an osmometric molecular weight of 733 (calcd for **11**, 728), a ^{13}C NMR spectrum showing eight aromatic carbon resonances and one methylene resonance as expected for **11**, an IR absorption at 3180 cm^{-1} characteristic of a strongly intramolecularly hydrogen-bonded compound, and a ^1H NMR spectrum showing a temperature-dependent resonance envelope for the CH_2 hydrogen, viz., a singlet at temperatures above 60 °C, a well-resolved pair of doublets at temperatures below 0 °C, and a coalescence temperature of ca. 36–44 °C in $CDCl_3$ or bromobenzene-d_5 solution and of ca. 0 °C in pyridine-d_5 solution.[11,12] The sharp melting

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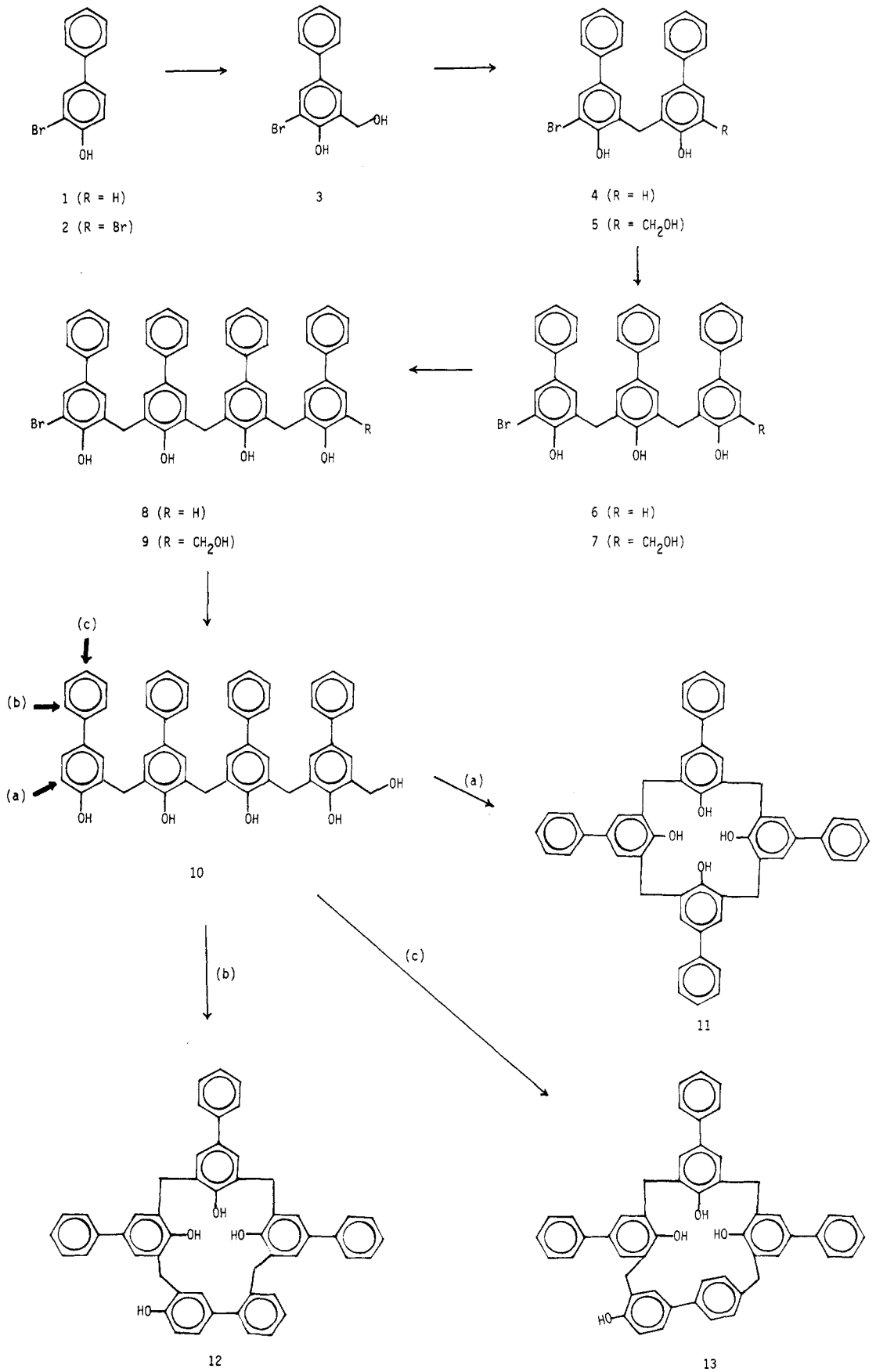
0022-3263/82/1947-2708$01.25/0

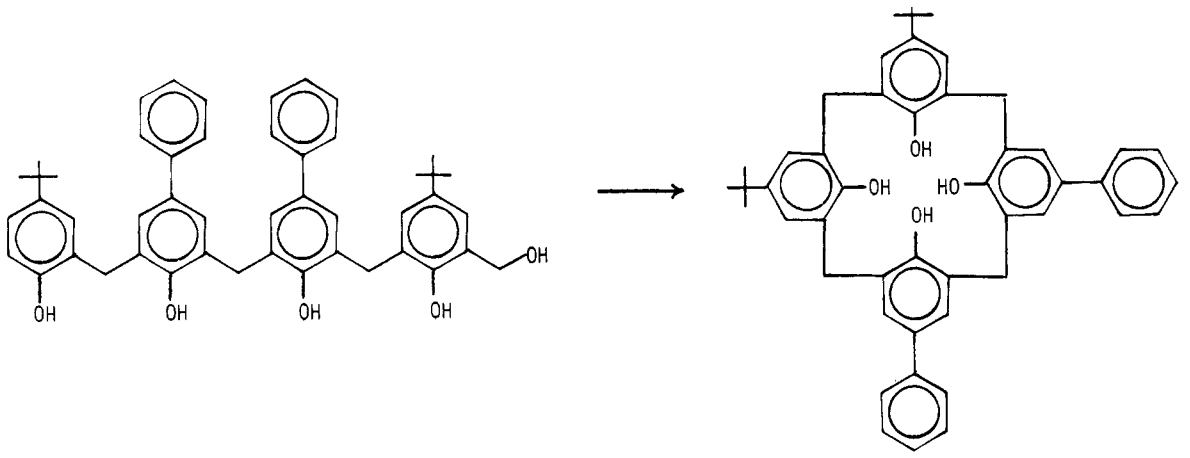
Scheme I



point of this material and its moderate solubility in cold chloroform indicate that it is different from the product reported by Zinke.[4] Many experiments have been carried out in our laboratory with *p*-phenylphenol and formaldehyde by using the original Zinke procedure,[2-4] the Zinke procedure as modified by Cornforth in which Dowtherm is substituted for linseed oil,[13] and the one-step

(12) We are indebted to Mr. Lorenz J. Bauer for providing these spectral data.

Scheme II



14 15

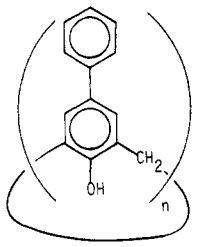


Figure 1. *p*-Phenylcalixarene structure.

procedure.[5] In no case has a compound identical with **11** yet been isolated,[14] and there is little, if any, evidence that it is even a minor component of the reaction mixture. The major isolable product appears to be the cyclic hexamer, as will be discussed in a subsequent communication.

Two other materials in addition to **11** were obtained by the action of HCl in acetic acid on **10**. It is postulated that these are products of cyclization into the 2′- and 4′-positions of the *p*-phenyl ring of compound **10**, as represented by pathways b and c. One of the compounds, obtained in 28% yield, has a melting point of 256–258 °C, an elemental analysis compatible with a $C_{52}H_{40}O_4$ formula, an osmometric molecular weight of 767 which is somewhat higher than the 728 value calculated for a cyclic tetramer, its strongest signal in the mass spectrum at *m/e* 728, a ^1H NMR spectrum showing four singlets for CH_2 resonances and a resonance characteristic of a hydrogen ortho to a phenolic OH group, and an IR spectrum showing absorptions at 3520 and 3290 cm^{-1} for the OH stretching modes and at 878 cm^{-1} for a 1,2,3,5-tetrasubstituted benzene, 820 cm^{-1} for a 1,2,4-trisubstituted benzene, 725 cm^{-1} for a 1,2-disubstituted benzene, and 760 and 690 cm^{-1} for a monosubstituted benzene. A space-filling molecular model of **12** indicates that three of the OH groups can form a cyclic array that can intramolecularly hydrogen bond fairly effectively but that the fourth OH is constrained to remain separated from the other three. The appearance of two OH stretching bands is in accord with such a structure, as are the data cited above.

The structure of the third cyclization product, obtained in 31% yield, is on less certain ground. It melts at 193–195 °C, has an elemental analysis compatible with a $C_{52}H_{40}O_4$ formula, an osmometric molecular weight of 726, the strongest signal in the mass spectrum at *m/e* 728, a ^1H NMR spectrum showing the CH_2 resonances as a multiplet, and an IR spectrum showing only one absorption at 3400 cm^{-1} for the OH stretching mode and strong absorptions at 875 cm^{-1} for a 1,2,3,5-tetrasubstituted benzene and at 755 and 690 cm^{-1} for a monosubstituted benzene. However, a band of only moderate intensity is observed at 795 cm^{-1}, characteristic of a 1,4-disubstituted benzene. A comparison of the ratios of the intensities of absorptions at 875 and 755 cm^{-1} (i.e., 1,2,3,5-tetrasubstituted benzene/monosubstituted benzene) shows that the ratio is lower for **12** and **13** than for **11**, indicating that **11** has more monosubstituted benzene rings than either of the two other products of cyclization. A space-filling molecular model of **13** indicates that three of the OH groups can assume a linear array in which intramolecular hydrogen bonding appears to be somewhat less effective than in **11** or **12**, accounting for the OH stretching band appearing at a higher frequency.

The mass spectra of **11**–**13** are very similar in appearance. In all three cases the most intense signal arises from the parent ion at *m/e* 728, and there are signals, inter alia, at *m/e* 710 (M – H_2O), 546 (trimer), and 364 (dimer or the dication of the tetramer). The spectrum of **11** shows no signals at *m/e* higher than 730, but the spectra of **12** and **13** have a collection of very weak signals up to *m/e* 800 with the strongest (i.e., 2–5% the intensity of the parent peak signal) at *m/e* 800, 784, 770, and 742. Since the signal at *m/e* 728 is so strong, it is believed that these higher *m/e* signals arise from impurities in **12** and **13** rather than from the major component. These higher molecular weight species might be acetyl and/or acetoxy derivatives of **11**, **12**, or **13**, although there is no indication in the IR spectra for the presence of carbonyl functions.

The acid-catalyzed cyclization of the *p-tert*-butyl analogue of **10** provides the corresponding calixarene in high yield,[1] as does the cyclization of **14** to **15**[15] (Scheme II). The phenyl groups in **14** have no influence on the outcome of the cyclization, indicating that the formation of three products from **10** must be due to the presence of the *p*-phenyl group at the terminus into which the cyclization if occurring. This provides additional, though tangential, evidence in favor of structures **12** and **13**.

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Experimental Section[16]

2-Bromo-4-phenylphenol (2). To a solution of 76.3 g (0.52 mol) of *p*-phenylphenol in 800 mL of $CHCl_3$ warmed to 60 °C was added 26.3 mL (0.52 mol) of bromine in 30 mL of $CHCl_3$. Heating was continued overnight, and the mixture was then cooled to room temperature. The dark brown solution was washed several times with water, and the resulting pale yellow solution was dried over anhydrous $MgSO_4$. After partial evaporation of the $CHCl_3$, petroleum ether (bp 35–60 °C) was added, causing the precipitation of 101 g (90%) of **2** as white needles: mp 95–96 °C; IR (KBr) 3200 (br, OH stretching), 825 cm^{-1} (1,2,4-trisubstituted Ar); ^1H NMR (acetone-d_6) δ 7.68–6.92 (m, 8, Ar H), 3.38 (br, 1, OH); R_f ($CHCl_3$/pentane, 13:7) 0.47.

Anal. Calcd for $C_{12}H_9BrO$: C, 57.83; H, 3.61. Found: C, 57.80; H, 3.50.

2-Bromo-4-phenyl-6-(hydroxymethyl)phenol (3). A mixture of 12.45 g (0.05 mol) of **2** and 100 mL of 37% formaldehyde (1.2 mol) cooled in an ice bath was treated with 16.83 g (0.30 mol) of KOH and then stirred at 40 °C for 3 days. The reaction mixture was diluted with cold water and acidified with dilute HCl, and the resulting oily compound was extracted into ether. The ether solution was washed twice with dilute HCl and three times with water, dried over anhydrous $MgSO_4$, and evaporated to leave a very viscous residue which was subjected to flash chromatography (5:1 hexane/acetone as the eluent). Evaporation of the eluate followed by recrystallization from $CHCl_3$/petroleum ether (bp 35–60 °C) gave 6.81 g (49%) of **3** as colorless needles: mp 84–85 °C; IR (KBr) 3500 and 3140 (OH stretching), 875 cm^{-1} (1,2,3,5-tetrasubstituted Ar); ^1H NMR (acetone-d_6) δ 7.63–7.20 (m, 7, Ar H), 4.85 (s, 2, CH_2OH), 3.00 (br, 2, OH); R_f ($CHCl_3$/pentane, 4:1) 0.11.

Anal. Calcd for $C_{13}H_{11}BrO_2$: C, 55.94; H, 3.97. Found: C, 56.01; H, 3.91.

2-(3-Bromo-5-phenylsalicyl)-4-phenylphenol (4). A solution of 4.00 g (15.6 mmol) of **3** and 100 g (684 mmol) of *p*-phenylphenol in 400 mL of xylene was heated to 120 °C, treated with 25 mL of concentrated HCl added over a period of 4 h, and refluxed for 20 h. The mixture solidified upon cooling to room temperature and was dissolved by adding a small amount of ether. The ether–xylene solution was washed with water until free of HCl, dried over anhydrous $MgSO_4$, and then slowly evaorated to yield six batches of fractional crystallizate. The first two fractions were pure *p*-phenylphenol (1), fractions 3–5 were mixtures of **1** and **4**, and the last fraction was a mixture of several compounds, including a small amount of **4**. Fractions 3–5 were combined and subjected to flash chromatography (6:1 hexane/acetone as the eluent) to yield material which, after recrystallization from $CHCl_3$/petroleum ether (bp 35–60 °C) consisted of 4.38 g (71%) of a colorless powder: mp 136–137 °C; IR (KBr) 3360 (br, OH stretching), 875 (1,2,3,5-tetrasubstituted Ar), 820 cm^{-1} (1,2,4-trisubstituted Ar); ^1H NMR (acetone-d_6) δ 7.53–6.85 (m, 15, Ar H), 4.12 (s, 2, CH_2), 3.36 (br, 2, OH); R_f (petroleum ether/acetone, 3:1) 0.40.

Anal. Calcd for $C_{25}H_{19}BrO_2$: C, 69.61; H, 4.44. Found: C, 69.51; H, 4.43.

3-(3-Bromo-5-phenylsalicyl)-5-phenyl-2-hydroxybenzyl Alcohol (5). To a mixture of 1.23 g (4.8 mmol) of **4** and 40 mL of 37% formaldehyde cooled and stirred in an ice bath was added 2.07 g (40 mmol) of KOH, causing the solution to become clear. Stirring at 35 °C was continued for 6 days, after which time the reaction mixture was added to cold water and acidified with 10% HCl, and the white precipitate was collected by filtration. This was washed, dried overnight under suction, flash chromatographed (8:3 hexane/acetone as the eluent), and recrystallized from $CHCl_3$/hexane to give 0.63 g (48%) of a colorless powder: mp 139–140 °C; IR (KBr) 3360 (br, OH stretching), 875 cm^{-1} (1,2,3,5-tetrasubstituted Ar); ^1H NMR (acetone-d_6) δ 7.54–7.20 (m, 14, Ar H), 4.90 (s, 2, CH_2OH), 4.75 (s, 3, OH), 4.12 (s, 2, CH_2); R_f (petroleum ether/acetone, 3:1) 0.29.

Anal. Calcd for $C_{26}H_{21}BrO_3$: C, 67.69; H, 4.59. Found: C, 67.31; H, 4.55.

2-[3-(3-Bromo-5-phenylsalicyl)-5-phenylsalicyl]-4-phenylphenol (6). A mixture of 1.28 g (2.8 mmol) of **5** and 16.2 g (111 mmol) of *p*-phenylphenol in 100 mL of xylene was heated to 130 °C. When the solid started to melt, 10 mL of concentrated HCl was added dropwise over a period of 6 h. Refluxing was continued 20 h, and the mixture was then worked up as described above for **4** to yield 1.10 g (65%) of **6** as a colorless powder after recrystallization from $CHCl_3$/petroleum ether (bp 35–60 °C): mp 152–153 °C; IR (KBr) 3200 (br, OH stretching), 875 (1,2,3,5-tetrasubstituted Ar), 820 cm^{-1} (1,2,4-trisubstituted Ar); ^1H NMR (acetone-d_6) δ 7.54–6.85 (m, 22, Ar H), 4.12 (d, 2, CH_2), 2.91 (s, 3, OH); R_f (petroleum ether/acetone, 3:1) 0.30.

Anal. Calcd for $C_{38}H_{29}BrO_3$: C, 74.39; H, 4.76. Found: C, 74.17; H, 4.68.

3-[3-(3-Bromo-5-phenylsalicyl)-5-phenylsalicyl]-5-phenyl-2-hydroxybenzyl Alcohol (7). A mixture of 1.94 g (3.2 mmol) of **6** and 60 mL of 37% formaldehyde was stirred in an ice bath, treated with 2.47 g (44 mmol) of KOH, and stirred at room temperature for 6 days. The product was worked up as described above for **5** (flash chromatography with 5:2 hexane/acetone as the eluent) to give 1.50 g (73%) of **7** as a colorless powder after recrystallization from $CHCl_3$/hexane: mp 143–145 °C; IR (KBr) 3250 (br, OH stretching), 875 cm^{-1} (1,2,3,5-tetrasubstituted Ar); ^1H NMR ($CDCl_3$) δ 7.48–7.08 (m, 21 Ar H), 5.45 (br, 4, OH), 4.92 (s, 2, CH_2OH), 4.02 (d, 2, CH_2); R_f (hexane/acetone, 10:7) 0.93.

Anal. Calcd for $C_{39}H_{31}BrO_4$: C, 72.78; H, 4.86. Found: C, 72.35; H, 4.79.

2-[3-[3-(3-Bromo-5-phenylsalicyl)-5-phenylsalicyl]-5-phenylsalicyl]-4-phenylphenol (8). A mixture of 2.08 g (3.2 mmol) of **7** and 27 g (482 mmol) of *p*-phenylphenol in 100 mL of xylene was heated to 120 °C, treated dropwise over a period of 6 h with 10 mL of concentrated HCl, and refluxed for 24 h. The product was isolated and purified as described above for **4** to yield 1.63 g (81%) of **8** as a colorless powder after recrystallization from $CHCl_3$/hexane: mp 166–168 °C; IR (KBr) 3260 (br, OH stretching), 880 (1,2,3,5-tetrasubstituted Ar), 830 cm^{-1} (1,2,4-trisubstituted Ar); ^1H NMR (acetone-d_6) δ 7.58–6.91 (m, 29, Ar H), 4.16 (s, 4, OH), 4.14 (s, 6, CH_2); R_f (petroleum ether/acetone, 2:1) 0.34.

Anal. Calcd for $C_{51}H_{39}BrO_4$: C, 76.98; H, 4.94. Found: C, 76.80; H, 5.22.

3-[3-[3-(3-Bromo-5-phenylsalicyl)-5-phenylsalicyl]-5-phenylsalicyl]-5-phenyl-2-hydroxybenzyl Alcohol (9). To a suspension of 3.48 g (4.4 mmol) of **8** in 150 mL of 37% formaldehyde cooled in an ice bath was added 5.88 g (105 mmol) of KOH, and the mixture was stirred at 35 °C for 6 days. The product was isolated and purified as described above for **5** (flash chromatography with 2:1 hexane/acetone as the eluent) to yield 1.43 g (46%) of **9** as a colorless powder after two recrystallizations from $CHCl_3$/hexane: mp 150–152 °C; IR (KBr) 3150 (br, OH stretching), 880 cm^{-1} (1,2,3,5-tetrasubstituted Ar); ^1H NMR (acetone-d_6) δ 7.55–7.20 (m, 28, Ar H), 4.87 (d, 2, CH_2OH), 4.47 (br, 5, OH), 3.99 (s, 6, CH_2); R_f (petroleum ether/acetone, 8:5) 0.28. A pure analytical sample could not be obtained, because **9** decomposes when dried under vacuum at room temperature.

(16) Boiling points are uncorrected. Melting points of all compounds melting above 250 °C were taken in sealed and evacuated capillary tubes on a Mel-Temp apparatus (Laboratory Devices, Cambridge, MA) by using a 500 °C thermometer calibrated against a thermocouple (accuracy ±1 C). Infrared (IR) spectra were determined on a Perkin-Elmer 283B spectrometer. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Hitachi Perkin-Elmer R-24B spectrometer on a JEOL FX-100 spectrometer, and carbon nuclear magnetic resonance spectra (^{13}C NMR) were also obtained with the latter instrument. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane (δ 0.00) as an internal standard. Mass spectra[17] were obtained on a Varian MAT-311A instrument. Osmometric molecular weight determinations[18] were made on a Wescan Model 232A apparatus by using concentrations of ca. 10^{-3} M in $CHCl_3$. Microanalyses were carried out by Industrial Testing Laboratories, St. Louis, MO. Thin-layer chromatographic analyses were carried out on silica gel plates (absorbant thickness 250 μm). Flash chromatography[10] was carried out with E. Merck silica gel (230–400-mesh ASTM) on columns of diameters 80 mm (for more than 5 g of sample, 50 mm (for 1–5 g of sample), and 30 mm (for less than 1 g of sample) filled to a height of 6 in. Elution rates were 2 in./min; fractions of 125 mL were collected from the two larger columns and of 50 mL from the smallest column.

(17) We are indebted to Ralph Fuhrop of the Monsanto Co, St Louis, MO, for carrying out the mass spectral determinations.

(18) We are indebted to Alice Gutsche for carrying out the osmometric molecular weight determinations.

3-[3-[3-(5-Phenylsalicyl)-5-phenylsalicyl]-5-phenylsalicyl]-5-phenyl-2-hydroxybenzyl Alcohol (10). A solution of 1.67 g of **9** in 35 mL of CH_3OH, 5 mL of dioxane, and 3.12 mL of 20% aqueous KOH was placed in a hydrogenation apparatus, 0.7 g of Raney nickel W-2 catalyst[19] was added, and the system was flushed and filled with hydrogen. The reaction mixture was stirred at room temperature until the calculated amount of H_2 had been taken up (ca. 6 h), and the product was then isolated in a conventional fashion and obtained, after flash chromatography and recrystallization from $CHCl_3$/petroleum ether (bp 35–60 °C), as 1.06 g (70%) of a colorless powder: mp 142–143 °C dec; IR (KBr) 3260 (br, OH stretching), 878 (1,2,3,5-tetrasubstituted Ar), 820 cm^{-1} (1,2,4-trisubstituted Ar); ^1H NMR δ 7.60–6.92 (m, 29, Ar H), 4.91 (s, 2, CH_2OH), 4.12 (s, 6, CH_2), 3.75 (br, 5, OH); R_f (petroleum ether/acetone, 5:3) 0.37.

Anal. Calcd for $C_{52}H_{42}O_5 \cdot 0.1CHCl_3$: C, 82.48; H, 5.55. Found: C, 82.35; H, 5.55.

Longer drying at room temperature under vacuum to remove the small amount of $CHCl_3$ adhering to the compound resulted in decomposition.

5,11,17,23-Tetraphenyl-25,26,27,28-tetrahydroxycalix[4]-arene (11). To a 5-L three-necked flask fitted with a condenser, addition funnel, and nitrogen/vacuum inlet was added a mixture of 1.5 L of acetic acid and 5 mL of concentrated HCl. The system was evacuated and filled with nitrogen, the contents were brought to reflux, and a solution of 0.847 g of **10** in 160 mL of acetic acid and 80 mL of $CHCl_3$ was added dropwise (5 drops/min) over a period of 24 h. At intervals of 12 h an additional 5 mL of concentrated HCl was added until the reaction mixture contained a total of 20 mL. The mixture was refluxed for 53 h, and the acetic acid was then removed by distillation under reduced pressure. The brown residue was dissolved in 100 mL of $CHCl_3$, washed with water, dried over anhydrous $MgSO_4$, and decolorized with charcoal. Evaporation of the $CHCl_3$ gave a brown residue which was indicated by TLC to be a mixture of three compounds. In a flash chromatographic separation the fastest and next fastest moving components were eluted together (4.6:1 pentane/acetone as the eluent), the eluate was evaporated, and the residue was twice triturated with boiling CH_3OH. Recrystallization of the CH_3OH-insoluble material from $CHCl_3$/petroleum ether (b p 35–60 °C) gave 0.11 g (13%) of **11** as colorless crystals: mp 407–409 °C dec; IR (KBr) 3170 (br, OH stretching), 870 (1,2,3,5-tetrasubstituted Ar), 755 and 690 cm^{-1} (monosubstituted Ar); ^1H NMR ($CDCl_3$) δ 10.46 (s, 1, OH), 7.43–7.24 (m, 7, Ar H), 4.15 (br, 2, CH_2); ^{13}C NMR ($CDCl_3$) 148.8 (8%, Ar), 140.6 (3.5%, Ar), 135.7 (6%, Ar), 128.6 (43%, Ar), 128.4 (22%, Ar), 128.0 (50%, Ar), 126.9 (48%, Ar), 126.8 (29%, Ar), 32.2 (18%, CH_2); osmometric mol wt ($CHCl_3$, 37 °C) 733 (calcd 728); mass spectrum (EI, 90 eV), m/e 728; R_f (petroleum ether/acetone, 2:1) 0.62.

Anal. Calcd for $C_{52}H_{40}O_4$: C, 85.59; H, 5.53. Found: C, 85.37; H, 5.59.

13,19,25-Triphenyl-10*H*,16*H*,22*H*,28*H*-5,9:11,15:17,21:23,-27-tetramethenobenzocyclohexacosene-8,29,30,31-tetrol (12).[20] The slowest moving component in the flash chromatographic separation described above was recrystallized from $CHCl_3$/hexane and obtained as 0.235 g (28%) of a colorless powder containing a trace of an impurity. When this material was dissolved in $CHCl_3$ and allowed to stand at room temperature for a few hours, a pure sample of **12** separated as colorless crystals: mp 256–285 °C; IR (KBr) 3520 and 3290 (OH stretching), 878 (1,2,3,5-tetrasubstituted Ar), 820 (1,2,4-trisubstituted Ar), 725 (1,2-disubstituted Ar), 760 and 692 cm^{-1} (monosubstituted Ar); ^1H NMR (acetone-d_6) δ 7.80–6.87 (m, 14, Ar H), 4.22 (br, 2, OH), 4.17 (s, 1, CH_2), 4.12 (s, 1, CH_2), 3.95 (s, 1, CH_2), 3.77 (s, 1, CH_2); osmometric mol wt ($CHCl_3$, 37 °C) 767 (calcd for **12** with $^1/_8$ mol of $CHCl_3$, 744).

Anal. Calcd for $C_{52}H_{40}O_4 \cdot 1/8\ CHCl_3$: C, 84.15; H, 5.45. Found: C, 84.00; H, 5.49.

10,16,22-Triphenylhexacyclo[24.2.2.2.$1^{2,6}$.$1^{8,11}$.$1^{14,18}$.$1^{20,24}$]tetratriconta-2,4,6(34),8,10,12(33),14,16,18(32),20,22,24-(31),26,28,29-pentadecaene-5,31,32,33-tetrol (13).[20] The CH_3-OH-soluble component of the fastest and next fastest moving components in the flash chromatographic separation described above precipitated when the volume of CH_3OH was reduced by evaporation. After recrystallizations from CH_3OH followed by $CHCl_3$/petroleum ether (bp 36–60 °C) 0.26 g (31%) of a colorless powder was obtained: mp 193–195 °C dec; IR (KBr) 3400 (br, OH stretching), 875 (1,2,3,5-tetrasubstituted Ar), 795 (1,4-disubstituted Ar), 755 and 690 cm^{-1} (monosubstituted Ar); ^1H NMR ($CDCl_3$) δ 7.60–7.11 (m, 4, Ar H and OH), 4.00 (m, 1, CH_2); osmometric mol wt ($CHCl_3$, 37 °C) 726 (calcd 729); R_f (petroleum ether/acetone, 2:1) 0.67.

Anal. Calcd for $C_{52}H_{40}O_4$: C, 85.59; H, 5.53. Found: C, 85.09; H, 5.59.

Registry No. **1**, 92-69-3; **2**, 92-03-5; **3**, 16396-76-2; **4**, 81535-85-5; **5**, 81535-86-6; **6**, 81535-87-7; **7**, 81535-88-8; **8**, 81535-89-9; **9**, 81535-90-2; **10**, 81535-91-3; **11**, 60705-63-7; **12**, 81535-92-4; **13**, 81535-93-5.

(19) Mozingo, R. "Organic Syntheses"; Wiley: New York, 1955; Collect Vol. III, p 181.

(20) We are indebted to Dr. Kurt L. Loening, Nomenclature Director of Chemical Abstracts Service, for assistance with the nomenclature of this compound.