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Syntheses of Ditopic Calix[4]arene Receptor Molecules Containing Silicon on the Upper Rim

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Calix[4]arene molecules containing two and four silicon atoms appended to the upper rim of the cone conformation were synthesized via hydrosilation of the corresponding di- and tetra-*p*-allyl calixarene ethers. The *p*-allyl calixarene ethers were prepared via the well known Claisen rearrangement which transferred the allyl groups originally on the lower rim of the cone to the upper rim. The silated calix[4]arenes were designed to function as ditopic receptor molecules that will bind cations through the oxygen atoms at the lower rim and anions through the silicon atoms on the upper rim. The hydrosilation reaction provided an easy method for introducing different functionality on the silicon atoms in order to attenuate their relative stability and Lewis acidity.

Keywords: Calix[4]arenes, silicon, hydrosilation, ditopic, receptor

INTRODUCTION

Calixarenes are cyclic oligomers of *t*-butylphenol and formaldehyde which posses an upper rim defined by the para positions of the phenol moieties and a lower rim defined by the oxygen atoms [1]. Calix[4]arenes remain at the forefront of active research into non-bonded, host-guest interactions principally because they may be manipulated to assume specific conformations which may then serve as a molecular scaffold for constructing binding sites for different types of substrates. Furthermore, calix[4]arenes in the cone conformation (the most commonly utilized shape) may be functionalized on either rim of the cone or basket which provides two potential sites for complexation. By far the most extensively investigated areas involve the complexation of cations, and to a lesser extent, neutral molecules [2]. However, the complexation of anions has lagged, in part, due to the relative scarcity of stable, Lewis-acid-functionalized calixarenes [3].

One method for imparting Lewis acidity into the calixarene host is the incorporation of metal atoms. Previously reported examples of metallacalixarenes have focused on either the formation of π-arene-metal complexes [4] or by bonding metal atoms such as titanium [5a], niobium [5b], aluminium [5c], silicon [5d] and zinc [5e] to the oxygen atoms located at the lower rim. Silicon has also been incorporated into the framework of calixarenes where the

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silicon atoms act as bridges between the aromatic nuclei [6]. Incorporation of silicon atoms is particularly attractive since the complexation of anions by tetravalent silicon compounds has been thoroughly investigated and reviewed [7]. To date, there have been no reports of calixarenes in which the silicon atoms are bonded to the upper rim of the basket. Herein we report the syntheses and characterizations of two silicon-containing calix[4]arenes in which the silicon atoms have been introduced to the upper rim via the hydrosilation of pendant allyl groups [8]. The result is the formation of a ditopic, neutral, Lewis acidic, host with convergent binding sites for anions and cations.

RESULTS AND DISCUSSION

The syntheses of the *p*-diallyl and tetraallyl calix[4]arenes were accomplished by following the sequence of reactions shown in Figures 1 and 2. Both syntheses rely on the dealkylated calix[4]-arene **2**, as the principal starting material, which was obtained in multigram quantities using procedures described by Gutsche *et al.* [9, 10].

Synthesis of 5,17-dipropenyl-25,27-dipropoxy-26,28-dipentoxy calix[4]arene (6)

The dially ether compound, 25,27-dihydroxy-26,28-dipropenyloxy calix[4]arene, **3**, was prepared from the dealkylated compound **2** in good yield and high purity by suspending the calixarene in refluxing acetonitrile followed by the addition of 1.1 mole equivalents of K_2CO_3 and 2.2 mole equivalents of allyl bromide (see Fig. 1) [11]. This provided a calix[4]arene molecule which was held in the cone conformation as evidenced by the AB quartet observed for the diastereotopic hydrogens on the methylene carbons connecting the aromatic rings. 25,27-Dipropoxy-26,27-dipropenyloxy calix[4]arene, **4**, was obtained by treatment of **3** with an excess of NaH and 1-iodopropane in DMF. The diallyl-dipropyl ether **4**, which was determined to also assume the cone conformation, was isolated in 68% yield by pouring a concentrated solution of crude **4** into methanol to precipitate the product. The Claisen rearrangement of **4**, in which the allyl groups were transferred from the lower to the upper rim, provided **5** (5,17-dipropenyl-25,27-dipropoxy calix[4]arene) in 53.8% yield after chromatography on silica gel. The cone conformation was unaffected throughout the remaining steps in the synthesis. Compound **5** was converted into the tetraalkyl ether **6** by treatment with an excess of sodium hydride and 1-bromopentane in DMF. This compound, 5,17-dipropenyl-25,27-dipropoxy-26,28-dipentoxy calix[4]arene, was isolated in 80% yield after chromatography as a white solid. The choice of using two different alkyl groups on the lower rim was driven by the fact that the compound **6** is a crystalline solid in the cone conformation. It should be noted that care must be taken at this

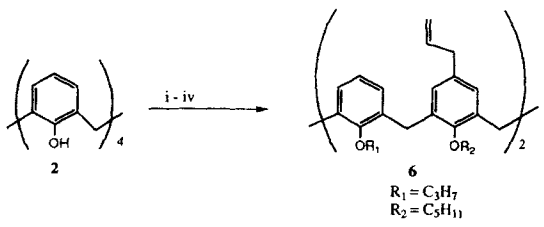

FIGURE 1 Synthetic sequence for the formation of the *p*-diallyl calix[4]arene ether **6**. i) 1.1 equiv. K_2CO_3/2.2 equiv. allyl bromide; ii) excess NaH/excess 1-iodopropane; iii) *N,N*-diethylaniline/reflux; iv) excess NaH/excess 1-bromopentane.

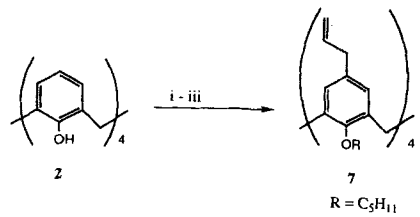

FIGURE 2 Synthetic sequence for the formation of the *p*-tetraallyl calix[4]arene ether **7**. i) excess NaH/excess allyl bromide; ii) *N,N*-diethylaniline/reflux; iii) excess NaH/excess 1-bromopentane.

stage in the synthesis to ensure that the terminal double bond of the allyl groups do not isomerize to the internal alkene in the presence of the sodium hydride. This was accomplished by using dry DMF as the solvent and performing the reaction at room temperature.

Synthesis of 5,11,17,23-tetrapropenyl-25,26,27, 28-tetrapentoxy calix[4]arene (7)

We have also synthesized the *p*-tetraallyl-tetrapentoxy calixarene ether **7** in a manner similar to that used in the synthesis of **6**, but with one less synthetic step, (see Fig. 2). This symmetrical compound allowed for the incorporation of four silicon atoms on the upper rim. The dealkylated calixarene **2** was converted into the 25,26,27,28-tetrapropenyloxy ether by treatement with excess NaH and allyl bromide in DMF [12]. This compound was then subjected to the Claisen rearrangement conditions to yield 5,11,17,23-tetrapropenyl calix[4]arene which existed as a mixture of isomers at room temperature on an 80 MHz NMR spectrometer. The tetra-*p*-allyl compound was converted to the tetrapentoxy ether **7**, by the reaction with excess NaH and 1-bromopentane to yield a viscous oil which was recrystallized to afford a white crystalline solid. The ^{1}H and ^{13}C spectra for **7** corroborate the structural assignment and confirm the cone conformation.

Hydrosilation Reactions

All of the hydrosilation reactions were carried out in freshly distilled toluene and catalyzed by the addition of 0.05 mole equivalents of chloroplatinic acid. Typically 2 mole equivalents of silane were added per allyl group. As shown in Figure 3, the two principle silation products **8** and **9** were obtained by hydrosilation of **6** and **7**, respectively, with dimethylphenyl silane. This compound was chosen to be the hydrosilation reagent for two reasons. One is that the products **8** and **9** would be hydrolytically stable and

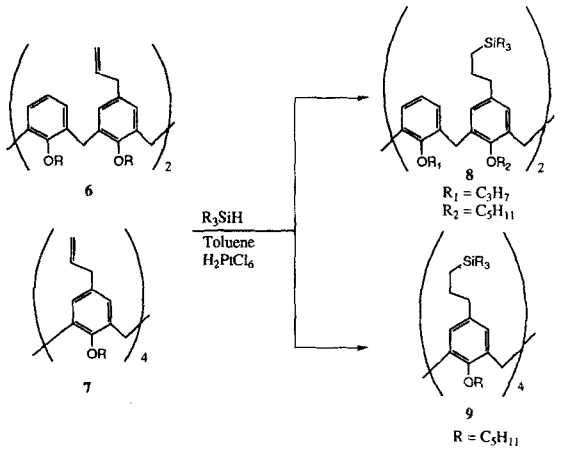

FIGURE 3 Hydrosilation reactions of di- and tetra-*p*-allyl calix[4]arenes.

amenable to obtaining satisfactory elemental analyses. The second reason is that the phenyl groups may be cleaved easily in the presence of carbon tetrachloride to afford a more Lewis acidic host. The hydrosilation methodology was extended to reactions of **6** and **7** with triphenyl-, methyldiethoxy-, dimethylethoxy-, dimethylchloro- and diphenylfluorosilane.

The substituents in the silane affected the reaction times significantly. The halosilanes were the most reactive, followed by the ethoxysilanes and the least reactive were the trialkylsilanes. Unfortunately, the highly reactive silanes yielded the most hydrolytically unstable products and obtaining satisfactory elemental analyses was not possible. The regioselectivity of the hydrosilations involving the halo and alkoxy silanes was very high with the silicon atoms being bonded to the terminal carbons of the allyl groups. Conversely, the least reactive silanes, with the most hydrolytic stability, gave mixtures of regioisomeric products (approximately 4:1). The major isomer in both cases was the one in which the silicon atoms were bonded to the terminal carbons of the three carbon chain. The isomers could be separated on silica gel, thus providing analytically pure samples of **8** and **9**. In all cases, the cone conformation of the calix[4]arene was maintained throughout the

syntheses as evidenced by the characteristic AB quartet for the diastereotopic methylene hydrogens on the carbon atoms connecting adjacent aromatic rings.

MATERIALS AND METHODS

General Procedures

All purchased compounds were used as received without further purification with the exception of the silanes, which were distilled prior to use. *N,N*-dimethylformamide (DMF) was dried over molecular sieves at least three days prior to use. Toluene was dried over sodium metal and freshly distilled prior to use in the hydrosilation reactions. All ^{1}H spectra were referenced to internal TMS or residual $CHCl_3$ and all ^{13}C spectra were referenced to residual $CHCl_3$. All reactions were carried out under an inert atmosphere of argon. Melting points are uncorrected.

5,11,17,23-tetra-t-butyl-25,26,27,28-tetrahydroxy calix[4]arene (1)

p-t-Butyl calix[4]arene was prepared by the procedure described by Gutsche *et al.* [9]. In a three neck 3 L round bottom flask fitted with a mechanical stirrer was added 150 g (1 mol) *t*-butylphenol and 93.35 mL (1.25 mol) of formalin. The mixture was heated to 130°C for 15 minutes. To this solution was added 1.795 g (0.045 mol) of sodium hydroxide dissolved in a minimum amount of water. The temperature was increased to 150°C and the mixture began to foam. The heat was removed after an additional 15 minutes of heating and the contents were allowed to cool to a glassy yellow solid. One liter of phenyl ether was added and a water-cooled condenser was fitted onto the round bottom flask. The contents of the flask were heated to reflux for 2 hours under a steady stream of argon gas to remove water from the reaction mixture. The mixture was cooled to room temperature and 2 liters of ethyl acetate were added to precipitate the calixarene. The solution was filtered and the solid was washed with 2 × 400 mL of ethyl acetate, 400 mL acetic acid, and an additional 400 mL of ethyl acetate to yield 90.93 g (56.2%) *p-t*-Butylcalix[4]arene.

25,26,27,28-tetrahydroxy calix[4]arene (2)

Dealkylated calix[4]arene was prepared by the method described by Gutsche *et al.* [10] *p-t*-Butylcalix[4]arene (45 g, 69.3 mmol) was suspended in one liter of toluene. To this was added 39.48 g (420 mmol) phenol and 74.76 g (560 mmol) aluminum trichloride. The reaction stirred for 9 hours at room temperature. The reaction was quenched by the addition of 300 mL of water. The contents were poured into a separatory funnel and the toluene layer was washed with 2 × 200 mL of 1 N HCl and 100 mL of brine then dried over $MgSO_4$. The solution was concentrated under reduced pressure to approximately 100 mL and then poured into 500 mL of methanol. The precipitated dealkylated calixarene was collected by filtration and dried to yield 25.5 g (85.7%).

26,28-propenyloxy calix[4]arene (3)

The symmetrically disubstituted calixarene was prepared according to the methods described by Ungaro *et al.* [11]. In a flame dried 1 liter round bottom flask, 24.5 g (57.7 mmol) of **2** were suspended in 300 mL of acetonitrile. To this was added 8.77 g (63.47 mmol) of K_2CO_3 and 11 mL (126.94 mmol) of allyl bromide. The mixture was heated at reflux for 12 hours after which time the solvent was removed under vacuum and the residue was taken up in 300 mL of $CHCl_3$. The chloroform solution was washed with 2 × 200 mL of 1 N HCl, 200 mL brine and dried over $MgSO_4$. The solution was filtered and concentrated to approximately 50 mL and poured into 500 mL of

methanol. The precipitated product was collected by filtration to yield 23.5 g (80.8%) of the lower rim di-allyl calixarene **(3)**.

25,27-dipropoxy-26,28-propenyloxy calix[4]arene (4)

In a flame-dried, 1L round bottom flask, 23.5 g (46.6 mmol) of **3** was dissolved in 500 mL of dry DMF. To this was added 4.47 g (186.4 mmol) of sodium hydride which had been washed twice with hexane to remove the mineral oil. The reaction flask was lowered into a 80°C oil bath and 18.2 mL (186.4 mmol) of iodopropane was added via syringe. After 16 hours, the solvent was removed under vacuum and the residue was taken up in 500 mL of CH_2Cl_2 and washed with 2 × 250 mL of 1N HCl and 250 mL of brine. The CH_2Cl_2 solution was dried over $MgSO_4$, filtered and concentrated under vacuum to approximately 50 mL then poured into 500 mL of methanol. The precipitated product was collected by filtration to yield 18.6 g (67.9%) of the pure product **4**; *mp* = 182–183. ^{1}H NMR δ 7.1–6.9 (*m*, 6H), 6.6–6.2 (*m*, 8H), 5.3–5.1 (*m*, 4H), 4.6 and 3.2 (AB *q*, 8H, *J* = 13.0 Hz), 4.5 (*d*, 4H, *J* = 7 Hz), 3.8 (*t*, 4H, *J* = 4 Hz), 1.9 (*m*, 4H), 1.1 (*t*, 6H, *J* = 4 Hz); ^{13}C NMR δ 156.8, 155.6, 136.9, 136.3, 133.6, 128.6, 127.6, 122.2, 122.0, 116.5, 77.0, 75.6, 31.2, 23.5, 10.7; Anal. Calcd for $C_{40}H_{44}O_4$: C, 81.60; H, 7.53. Found: C, 81.77; H, 7.55.

5,17-dipropenyl-25,27-dipropoxy calix[4]arene (5)

The Claisen rearrangement of compound **4** was performed by the method described by Gutsche *et al.* [12]. In a flame-dried 500 mL round bottom flask 18.6 g (31.6 mmol) of compound **4** was dissolved in 80 mL of *N,N*-diethylaniline. The mixture was heated at reflux for 12 hours. The mixture was then poured into 500 mL of an ice-conc. HCl solution then transferred to a separatory funnel and was extracted with 200 mL of CH_2Cl_2. The organic layer was washed with 2 × 200 mL of 6N HCl, 200 mL of brine and dried over $MgSO_4$. The solvent was removed under vacuum and the crude material was chromatographed on silica gel (50/50 $CHCl_3$/hexane; r_f = 0.8) to yield 10 g (53.8%) of compound **5**; *mp* = 197–198°C. ^{1}H NMR δ 8.3 (*s*, 2H), 7.2–6.8 (*m*, 10H), 6.4–5.8 (*m*, 2H) 5.3–5.1 (*m*, 4H), 4.5 and 3.4 (AB *q*, 8H, *J* = 13.0 Hz), 3.4 (*d*, 4H, *J* = 7 Hz), 4.1 (*t*, 4H, *J* = 4 Hz); 2.2 (*m*, 4H), 1.4 (*t*, 6H, *J* = 4 Hz); ^{13}C NMR δ 151.1, 150.7, 137.5, 132.8, 129.2, 128.0, 127.6, 127.2, 124.3, 114.2, 77.4, 38.6, 30.6, 22.6, 10.0; Anal. Calcd for $C_{40}H_{44}O_4$: C, 81.60; H, 7.53. Found: C, 81.40; H, 7.54.

5,17-dipropenyl-25,27-dipropoxy-26,28-dipentoxy calix[4]arene (6)

Into a flame-dried 500 mL round bottom flask was placed 2 g (3.4 mmol) of **5** and 150 mL of dry DMF. To this was added 0.33 g (13.6 mmol) of sodium hydride that was washed with hexane to remove the mineral oil. The flask was placed in an 80°C oil bath and to it was added 1.7 mL (13.6 mmol) of 1-bromopentane. The contents of the flask were heated for 24 hours. The solvent was removed under vacuum and the residue was taken up in 300 mL of $CHCl_3$ and the solution was washed with 2 × 200 mL of 1N HCl and 200 mL of brine then dried over $MgSO_4$. The filtered solution was concentrated to a viscous oil which was chromatographed on silica gel (40/60 $CHCl_3$/hexane; r_f = 0.9) to yield 2 g (80%) of **6** as a clear oil. The oil was recrystallized from absolute ethanol to yield a white solid; *mp* = 82–83°C. MS 751 ($M + NA^+$) ^{1}H NMR δ 6.6 (*s*, 4H), 6.4 (*s*, 6H), 5.7 (*m*, 2H) 5.08–4.86 (*m*, 4H), 4.5 and 3.1 (AB *q*, 8H, *J* = 13.0 Hz), 3.8 (*d* of *t* 8H), 3.05 (*d*, 4H, *J* = 7 Hz), 2.0 (*m*, 8H), 1.4 (*m*, 8H) 1.0 (*d* of *t*, 12H); ^{13}C NMR δ 156.1, 155.4, 138.2, 135.4, 134.4, 132.8, 128.4, 127.7, 121.9, 114.9, 76.7, 74.9, 39.5, 31.0, 29.8, 29.6, 28.3, 23.3, 22.7, 14.1, 10.5; Anal. Calcd for $C_{50}H_{64}O_4$: C, 82.38; H, 8.85. Found: C, 82.57; H, 9.07.

5,11,17,23-tetrapropenyl-25,26,27,28-tetrapentoxy calix[4]arene (7)

The upper rim 5,11,17,23-tetraallyl calix[4]arene was obtained in 82% yield according to the procedures outlined by Gutsche *et al.* [12]. Into a 500 mL round bottom flask was placed 4.0 g (6.8 mmol) of the upper rim tetraallyl calix[4]arene dissolved in 200 mL of dry DMF. To this was added 1.64 g (68 mmol) of sodium hydride which had been washed with hexanes to remove the mineral oil. The contents of the flask were stirred at room temperature for 30 minutes and to them was added 6.8 mL (54 mmol) of 1-bromopentane. The reaction mixture was stirred 15 hours at room temperature and the solvent was removed under vacuum. The residue was redissolved in 200 mL of chloroform and washed with 3×100 mL of 1N HCl and 100 mL of brine. The organic solution was dried over MgSO4 filtered and concentrated to yield a viscous oil. The oil was chromatographed on silica gel (80% hexane/20% chloroform) to yield 4.61 g (78%) of **7** as a clear oil. The oil was recrystallized from absolute ethanol and methylene chloride to yield 4 grams of a white crystalline compound; *mp* = 55 – 56°C. MS = 887 $(M + Na^+)$ ^{1}H NMR $CDCl_3$ δ 6.38 (*s*, 8H), 6.0–5.6 (*m*, 4H), 5.0–4.6 (*m*, 8H), 4.4 and 3.0 (AB *q*, 8H, J = 13.0 Hz), 3.8 (*t*, 8H), 3.05 (*d*, 8H, J = 7 Hz), 2.0 (*m*, 8H) 1.4 (*m*, 8H), 1.4 (*m*, 16H), 1.0 (*d* of *t*, 12H); ^{13}C NMR δ 154.73, 138.21, 134.64, 132.74, 128.21, 114.71, 75.11, 39.37, 30.88, 29.89, 28.41, 22.77, 14.10. Anal. Calcd for $C_{60}H_{80}O_4$: C, 83.28; H, 9.32. Found: C, 83.56; H, 9.48.

Representative Procedure for Hydrosilation Reactions

Typically, 100 mg of either the *p*-diallyl and tetraallyl calix[4]arenes (**6** and **7**) were dissolved in 10 mL of freshly distilled toluene. To these solutions was added 0.05 mole equivalents of chloroplatinic acid dissolved in 0.5 mL of isopropanol. Two mole equivalents of dimethylethoxysilane were added per allyl group via syringe and the reactions were strirred at RT until all of the starting material was consumed (12–72 h). During the early stages of the reactions gas was evloved and the color of the solution turned from clear to green. During the latter stages of the reactions precipitation of platinum occurred. After the reaction was complete, activated carbon was added to the solution to help remove the colloidal platinum and the solutions were filtered and concentrated under reduced pressure to provide quantitative yields of the silated calixarenes as viscous oils. The silated products (**8** and **9**) produced from the *p*-allyl calix[4]arenes, (**6** and **7**), with dimethylphenyl silane, were chromatographed on silica gel (hexane-chloroform, 85:15) to yield analytically pure samples. The isolated yields for **8** and **9** from the hydrosilation reactions were 61% and 72%, respectively. The overall yields of **8** and **9** were 14% and 42%, respectively starting from the dealkylated calixarene **2**. The proton and carbon spectra for these two silated calix[4]arenes are listed below along with their elemental analyses.

5,17-[1-(dimethylphenylsilyl)-n-propyl]-25,27-dipropoxy-26,28-dipentoxy calix[4]arene (8)

^{1}H NMR $CDCl_3$ δ 7.8–7.3 (*m*, 10H), 6.81 (*s*, 4H), 6.46 (*s*, 6H), 4.5 and 3.2 (AB quartet, 8H, J = 13 Hz), 4.12 (*t*, 4H), 3.89 (*t*, 4H) 2.61 (*t*, 4H), 2.2–0.8 (*m*, 24H), 1.2–0.8 (*m*, 12H), 0.42 (*s*, 12H). 13C $CDCl_3$ δ 155.84, 155.53, 139.64, 135.81, 135.50, 134.12, 133.62, 128.79, 127.80, 121.98, 75.52, 75.00, 39.09, 31.15, 29.90, 28.36, 26.06, 23.54, 22.96, 15.40, 14.32, 10.83, –2.97. Anal. Calcd for $C_{66}H_{84}O_4Si_2$: C, 79.32; H, 8.47. Found C, 79.17; H, 8.72.

5,11,17,23-[1-(dimethylphenylsilyl)-n-propyl]-25,26,27,28-tetrapentoxy calix[4]arene (9)

^{1}H NMR $CDCl_3$ δ 7.7–7.2 (*m*, 20H), 6.42 (*s*, 8H), 4.40 and 3.15 (AB quartet, 8H, J = 13 Hz), 3.94 (*t*,

8H), 2.35 (*t*, 8H) 1.96 – 1.19 (*m*, 40H), 0.98 (*t*, 12H), 0.33 (*t*, 12H). ^{13}C $CDCl_3$ δ 155.56, 140.02, 135.30, 134.48, 133.55, 132.89, 128.72, 127.68, 75.01, 39.14, 31.05, 29.93, 28.46, 25.94, 22.82, 15.46, 14.15, – 2.93. Anal. Calcd for $C_{92}H_{128}O_4Si_4$: C, 78.34; H, 9.14. Found C, 78.71; H, 8.87.

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