Heteroatom Chemistry
Volume 14, Number 4, 2003

Synthesis of *tert*-Butylcalix[4]arenes Modified with Germanium-Containing Side-Chains at the Lower Rim

Takayuki Sakurai and Yoshito Takeuchi

Department of Chemistry, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka-shi 259-1293, Japan

Received 16 December 2002; accepted 2 February 2003

ABSTRACT: *Bis-, tris-, and tetrakis-trimethylgermylpropanoyl esters of p-tert-butylcalix[4]arenes* **5**, **7**, *and* **8** *were synthesized and their conformations in solution were determined by* ^1H *and* ^{13}C *NMR spectroscopy. The characteristic pair of doublets from the Ar—CH$_2$—Ar methylene protons was observed, indicating that all the prepared calixarenes were in the cone conformation. These germylated calixarenes failed to exhibit any appreciable cation-capturing ability, indicating that further modification is required to make these compounds to be effective ditopic hosts.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:365–373, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10164

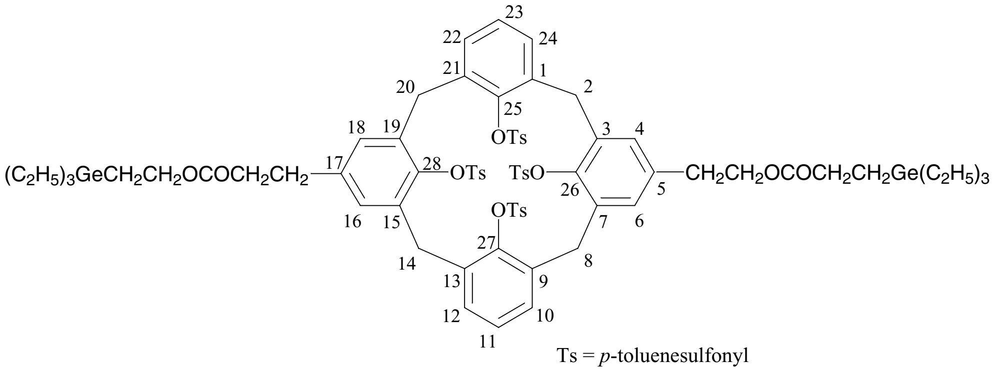
INTRODUCTION

For the last 10 years or so, in the field of host–guest chemistry, considerable attention has been focused on the synthesis and structure of a variety of ditopic hosts which can accommodate both a cation and an anion in different sites [1]. 5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (generally abbreviated as *p*-*tert*-butylcalix[4]arene) (**1**) and its derivatives are a class of macrocyclic compounds having a cavity in their center [2]. If **1** is appropriately functionalized, either on the upper or the lower rim, a very intriguing class of ditopic hosts is formed. Indeed, there are many reports on a variety of ditopic hosts including calixarenes modified with protonated azacrown, which acts as the binding site for anions [3]. The authors reported that the presence of K^+ enhances the binding ability toward Br^-.

In a previous communication [4], we reported the synthesis of a calixarene, 5,17-bis((2-(triethylgermylpropanoyloxy)ethyl)-25,26,27,28-tetrakis(*p*-toluenesulfonyl)oxy)calix[4]arene (**2**), in which the upper rim was modified with a germanium-containing moiety. We expected that **2** would act as a heteroditopic host with cation-capturing calixarene moiety and anion-capturing germanium moiety. We also expected that the cation-capturing property of calixarene moiety in **2** would be affected by the presence of Lewis-acidic germanium, which can aid in the capture of anions [5]. However, it was shown, that **2** failed to capture and transport cations. This was probably because of the presence of the bulky tosylate moieties in the lower rim, which reduces the size of the cavity.

Correspondence to: Yoshito Takeuchi; e-mail: yoshito@chem.kanagawa-u.ac.jp.

Contract grant sponsor: High-Tech Research Center Project, Ministry of Education, Culture, Sports, Science and Technology, Japan.



2

This prompted us to synthesize analogous compounds in which the lower rim is modified with a germanium-containing moiety rather than the upper rim.

RESULTS AND DISCUSSION

Synthesis

There are several methods available to introduce a germanium moiety into organic compounds. The following three methods are frequently used [6]:

i. Hydrogermylation of an alkene (Eq. (1)):

$$\mathrm{R{-}CH{=}CH_2 + R^1R^2R^3Ge{-}H \rightarrow R{-}CH_2{-}CH_2GeR^1R^2R^3} \qquad (1)$$

ii. Reaction between a lithio derivative of organogermanium compounds and a haloalkane (Eq. (2)):

$$\mathrm{R{-}X + R^1R^2R^3Ge{-}Li \rightarrow R{-}Ge\,R^1R^2R^3 + LiX} \qquad (2)$$

iii. Esterification of an alcohol or a phenol with a germanium-containing carboxylic acid or its derivative, such as a halide (Eq. (3)).

$$\mathrm{R{-}OH + R^1R^2R^3GeCH_2CH_2COX \rightarrow R{-}OCOCH_2CH_2GeR^1R^2R^3 + HX} \qquad (3)$$

Since esterification of **1** is well documented [7], method (iii) seems most appropriate to introduce a germanium moiety into the lower rim of **1**. On the basis of our previous experiences, the most suitable counterpart of **1** is either trialkyl- or triarylgermylpropanoic acid, or corresponding halides, which are obtainable starting from the reaction between trichlorogermane and acrylic acid [8]. We chose trimethylgermylpropanoyl chloride (**3**) for its better reactivity toward hydroxy compounds (Eq. (4)).

$$\mathrm{ROH + (CH_3)_3GeCH_2CH_2COCl \rightarrow ROCOCH_2CH_2Ge(CH_3)_3} \qquad (4)$$

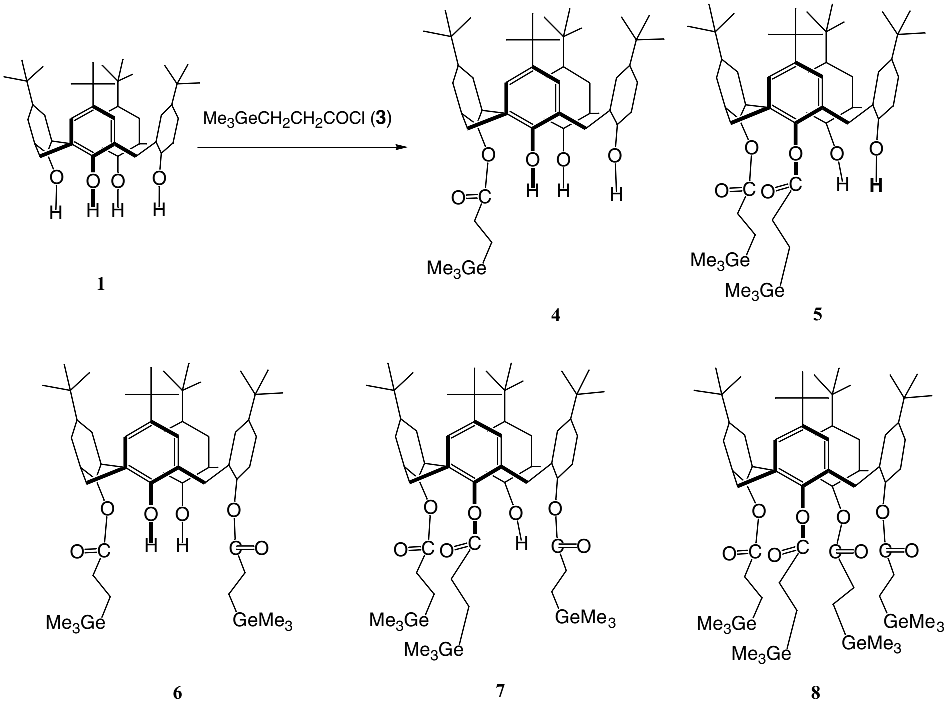
Usually this type of reaction is carried out in the presence of an appropriate base, such as NaH.

When **1** is made to react with **3**, five calixarenes, differently modified with the germanium moiety as is shown in Scheme 1, may be formed, viz., 5,11,17,23-tetra-*p*-*tert*-butyl-25-(trimethylgermylpropanoyl)-oxycalix[4]arene (**4**), 5,11,17,23-tetra-*p*-*tert*-butyl-25,26-bis((trimethylgermylpropanoyl)oxy)calix[4]-arene (**5**), 5,11,17,23-tetra-*p*-*tert*-butyl-25,27-bis((trimethylgermylpropanoyl)oxy)calix[4]arene (**6**), 5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27-tris((trimethylgermylpropanoyl)oxy)calix[4]arene (**7**), and 5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27,28-tetrakis((trimethylgermylpropanoyl)oxy)calix[4]arene (**8**). Each compound may have two or more different conformations, depending on the size and number of substituents in the lower rim [9].

Lin et al. [8] reported that the reaction of calix[4]arene with excess benzoyl chloride in the presence of NaH produced 25,27-dibenzoate. Following on from this report, we reacted **1** with various amounts of **3** in the presence of NaH.

The reaction between **1** and 1.2 molar equiv of **3** in the presence of 1.2 molar equiv of NaH (run 1, Table 1) gave 25-monoester **4** (8% by ^{1}H NMR) together with the concomitant formation of 25,27-diester **6** (20%). A large amount (ca. 64%) of unreacted **1** was also recovered. Purification of **4** was so difficult that we failed to obtain analytically pure **4**.

We reacted **1** with 2.2 and 3.2 molar equiv of **3** and NaH, respectively, (runs 2 and 3), expecting to obtain 25,26-diester **5** or **6**, and the 25,26,27-trimester **7**, respectively. In both cases, only **6** was



SCHEME 1 Synthesis of germylated calixarenes.

obtained and ^{1}H NMR detected a trace amount of **7**.

These results indicated that a large excess of **3** (and the base) was required for effective preparation of the triester. Thus, in run 4, a large excess (8.4 molar equiv) of **3** and 10 molar equiv of NaH were used. In this case also, the main product was **6** (52%), and only a trace amount **7** or **8** was present despite the large excess of **3** was used.

In run 5, a further excess (24.5 molar equiv) of NaH was used together with the same amount of **1** and **3** as in the run 4. The product of this reaction was a mixture of **7** (24%) and the 25,26,27,28-tetraester **8** (10%), which were separated by column chromatography. The tetraester **8** can be more conveniently obtained from triester **7**. Thus, in run 6, the triester **7** was treated with **3** and NaH to give **8** in 40% yield.

Altogether, the reactions between **1** and **3** in the presence of NaH tend to produce the di- or triester as the main products, regardless of the amount of NaH used. If the amount of NaH is relatively small, a small amount of monoester **4** was formed, while if it is used in a large excess, **8** was obtained as a minor product.

Gutsche and Lin reported that calix[4]arenes reacts with excess benzoyl chloride in pyridine to yield tribenzoates [10,11]. We attempted germylation under these conditions with differing amounts of **3**, expecting to obtain differently germylated esters selectively (runs 7–9).

In run 7, **1** was reacted with 1.3 molar equiv of **3** in pyridine. The result is a nearly quantitative recovery of **1**. In run 8, **1** was reacted with 2.3 molar equiv of **3** in pyridine in a similar manner. The recovery of **1** was ca. 50% and the rest was an intractable mixture of solid materials as revealed by ^{1}H NMR. In run 9 where a larger excess of **3** was used, only the triester **7** was obtained in a reasonable yield as was the case with the study by Lin et al. [10]. Thus, the use of pyridine as the base is not effective for the purpose of preparing **4** or **5**.

The results of runs 1–9 are summarized in Table 1.

To summarize, in the presence of NaH, the reaction between **1** and **3** has the following characteristics:

1. The esterification does not terminate at the monoester stage.
2. An excess of **3** seems necessary to prepare polyester.
3. Only the diester **6** was formed rather than diester **5**.

The reaction between **1** and **3** in pyridine has the following characteristics:

TABLE 1 Modification of Lower Rim with Germanium-Containing Moiety

				Yield (%)				
Run	*Calixarene*[a]	**3**[b]	*NaH*[b]	**4**	**5**	**6**	**7**	**8**
1[c]	**1**	1.2	1.2	8[d]		20[d]	–	–
2	**1**	2.2	2.2			75[d]	Trace	
3	**1**	3.2	3.2			54[d]	Trace	
4	**1**	8.4	10			52[d]		
5	**1**	8.4	24.5				24	10
6	**7**	6	4					40
7	**1**	1.3	Pyridine[e, f]					
8	**1**	2.3	Pyridine[e,g]					
9	**1**	4.2	Pyridine[e]				26	

[a] One molar amount.
[b] Relative to 1 molar amount of calixarenes.
[c] About 64% of unreacted **2** was recovered.
[d] Crude yield estimated by ^{1}H NMR.
[e] Pyridine was used as the base instead of NaH and no solvent was used.
[f] About 100% of unreacted **1** was recovered.
[g] About 50% of unreacted **1** was recovered.

1. Neither the monoester **4** nor the diesters **5** or **6** were obtained when 1 or 2 molar equiv of **3** were employed.
2. A large excess of **3** causes effective esterification.

NMR Spectra of **6**, **7**, *and* **8**, *and Their Structures in Solution*

The conformational behavior of calixarenes has been well investigated [11]. In the case of calix[4]arenes, conformational changes between cone, partial cone, 1,2-alternate, and 1,3-alternate conformers may effectively be analyzed by the characteristic behavior of the Ar—CH_2—Ar methylene protons, which appear as a pair of doublets in NMR spectra if the conformation is frozen in the cone. The ^{13}C chemical shift of the methylene carbon is also conformationally dependent [12,13]. In this regard, a thorough study of NMR spectra of prepared calixarenes was crucial to determine the conformation adopted.

For the purposes of discussion, it is convenient to classify the aromatic moieties of prepared calix[4]arenes into five groups:

A: The germylated aromatic residue with two germylated neighbors.
B: The germylated residue with one germylated and one ungermylated neighbors.
C: The germylated residue with two ungermylated neighbors.
D: The ungermylated residue with two germylated neighbors.
E: The ungermylated residue with two ungermylated neighbors

^{1}H NMR Spectra. Details of the assignment of ^{1}H NMR spectra are given hereafter.

1: The ^{1}H NMR spectrum of this compound has been reported previously [14]. There remains one important point to be discussed: to differentiate between axial and equatorial Ar—CH_2—Ar protons. The same is true for calix[4]arenes **6, 7**, and **8**. This point will be discussed in connection with the NMR spectrum of **7**.

8: Because of its symmetric structure, the ^{1}H NMR spectrum of **8** is less complicated compared to those of other calixarenes. A doublet of doublets (δ 3.25 and 3.75, J(H—H) = 13.3 Hz) is the characteristic peak for calix[4]arenes in the cone conformation [11], indicating that the germyl ester group is large enough to prohibit the inversion of the calixarene ring. The assignment of the other proton signals is also straightforward. Thus, of the two CH_2 groups in the $GeCH_2CH_2CO$ moiety, which form a characteristic pair of triplets, it is always the one closer to the germanium nucleus that resonates at higher field (i.e., at lower frequency). This rule can also be applied to distinguish between the $C(CH_3)_3$ and $Ge(CH_3)_3$ moieties. The ^{1}H NMR spectrum of **8** is given in Fig. 1.

6: There is only one doublet of doublets, δ 3.43 and 3.84, J(H—H) = 14.0 Hz, which again is due to Ar—CH_2—Ar methylene moiety and is the characteristic peak for calix[4]arenes in the cone conformation. This observation indicates that **6** is indeed 25,27-digermylated, not the 25,26-diester **5**, and that it is also in the cone conformation. If the compound obtained was 1,2-germylated, the Ar—CH_2—Ar methylene moiety should exhibit more than one set of AB quartets. There are two kinds of $C(CH_3)_3$ and aromatic protons (on rings **C** and **D**). These can be differentiated by comparison between the data for **1** and **8**.

7: In this compound there are three types of aromatic moieties, two **B**s and one **A** and **D**. However, there are only two types of the Ar—CH_2—Ar moieties, one between two germylated aromatic moieties and the other between one germylated and one ungermylated aromatic moiety. An assignment was made by comparing the shifts with those of **6** and **8**. Both methylene protons exhibit the characteristic pair of doublet for calixarenes in the cone conformation.

The assignment of germyl side-chain protons can be made based on the intensity (two ring **B** and only one ring **A**). Assignment of the $(CH_3)_3C$ protons is somewhat complicated, since there are only two signals of equal intensity for the two carbon nuclei,

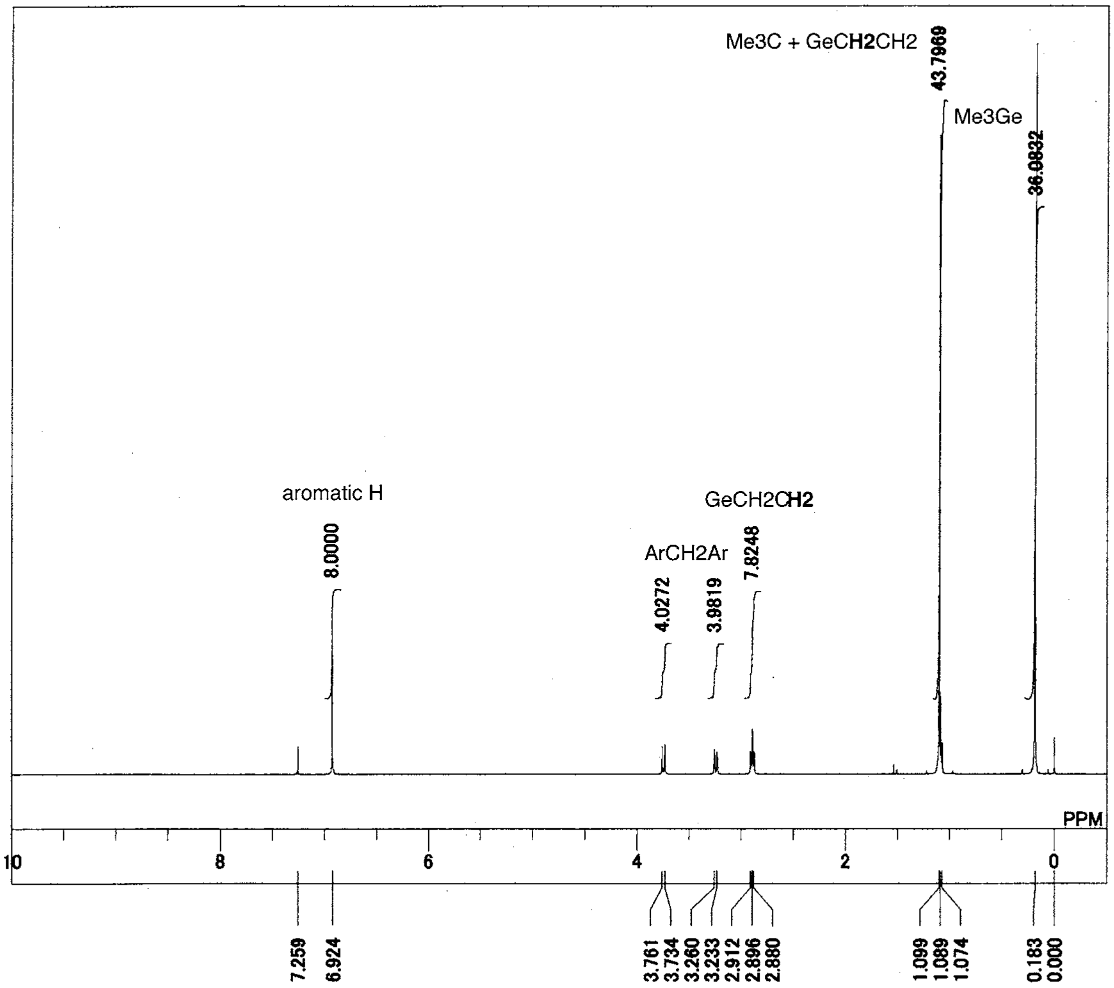


FIGURE 1 ^{1}H NMR spectrum (400 MHz) of **8**.

though three signals had been expected. The only possible explanation for this observation is that the two carbon signals of the $(CH_3)_3C$ group of rings **A** and **D** happen to have the same chemical shift. The peak at higher field was assigned to moiety **B** based on comparison with the data for the tribenzoate of **1** [7]. The authors assigned the peak at δ 0.93 to the *tert*-butyl group in type **B** rings, while one at δ 1.44 was assigned to one in a type-**A** ring. It is noteworthy that this similarity confirms that **7** is also in the cone conformation. If **7** is in the partial cone conformation, the *tert*-butyl proton of the type-B ring should resonate at higher field (δ 0.65 for the tribenzoate in a partial cone conformation [10]).

The assignment of aromatic protons is more complicated. In this case, two protons of the **B** moiety are nonequivalent, and in fact the spectrum gave an AB quartet (δ 6.61, 6.68, $J = 2.29$ Hz). The assignment was achieved by nuclear Overhauser effect (NOE) and H—H correlation spectroscopy (COSY) measurements. Thus, NOE experiment indicated that **D**–OH and the peak δ 3.85 are correlated, while the other methylene protons at δ 3.42 and 6.68 are correlated. These observations are in line with a previous report [13] that the equatorial proton of the Ar—CH_2—Ar methylene protons of calix[4]arenes always appear at higher field. It is very likely that this is also true for the other calix[4]arenes **1, 6,** and **8**. The observed correlations for **7** are shown in Fig. 2.

In Fig. 3, ^{1}H NMR chemical shifts of calixarenes **6, 7,** and **8** are given together with those of **1** for reference. Some of the assignments for **7** are tentative. In the figure are also marked the types of aromatic moieties.

^{13}C NMR Spectra. **1**: The ^{13}C NMR spectra of **2** has also been reported [14], but a complete assignment was not made. The assignments of Ar—CH_2—Ar, $\underline{C}(CH_3)_3$, and $C(\underline{C}H_3)_3$ were made by

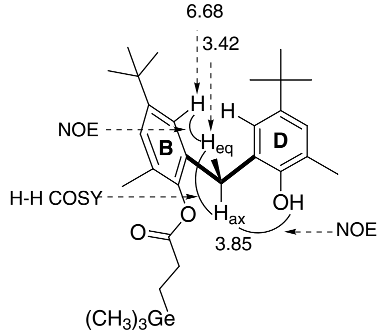


FIGURE 2 Correlations within rings **B** and **D** protons of **7**.

distortionless enhancement by polarization transfer (DEPT) experiments to remove any ambiguity. Full assignments of the aromatic carbon nuclei was achieved by heteronuclear multiple quantum correlation (HMBC) experiments. ^{13}C nuclei *ortho* to the OR moiety were detected by gated decoupling (without NOE).

8: Assignments of the germyl side-chain, $C(CH_3)_3$, and Ar—CH_2—Ar carbon nuclei were based on chemical shift considerations, and DEPT and H–C COSY experiments. Assignments of the aromatic carbon nuclei were made by HMBC experiments in which the Ar—$C\underline{H}_2$—Ar and $C(C\underline{H}_3)_3$ protons exhibited correlations with ^{13}C signals at δ 143.6 and 147.6, respectively. Here again, ^{13}C nuclei *ortho* to the OR moiety were detected by gated decoupling (without NOE).

Jaime et al. [13] reported that the ^{13}C chemical shifts of the Ar—CH_2—Ar methylene carbon changes with conformation. Thus, the chemical shift range for the cone conformer was δ 30.7–32.7 while that for the 1,3-alternate conformer was δ 36.9–38.2. The value for **8** indicates the cone conformation.

6: A full assignment of the ^{13}C NMR spectrum of **6** is more complicated and challenging but at the same time is necessary for the assignment of the spectrum of **7**. Firstly, ^1H and ^{13}C signals are classified into two groups belonging to either ring **C** or ring **D** by H–C COSY and HMBC experiments. The results are summarized in Table 2. Correlations essential to the assignment are selected.

Assignments of $\underline{C}(CH_3)_3$ and aromatic ^{13}C nuclei *para* to OR were made based on the correlation with $C(C\underline{H}_3)_3$ protons while assignments of other aromatic ^{13}C nuclei were made with the aid of correlations with aromatic H and OH (relative to ring **D**) protons. The correlation between $GeCH_2CH_2$ protons and ^{13}C signals at δ 29.8 proved that the ^{13}C signal is a part of the germyl side-chain and hence the signal at δ 33.1 is due to an Ar—CH_2—Ar moiety. On the basis of these data, a full assignment of all ^{13}C signals of **6** is now possible and is presented in Fig. 4.

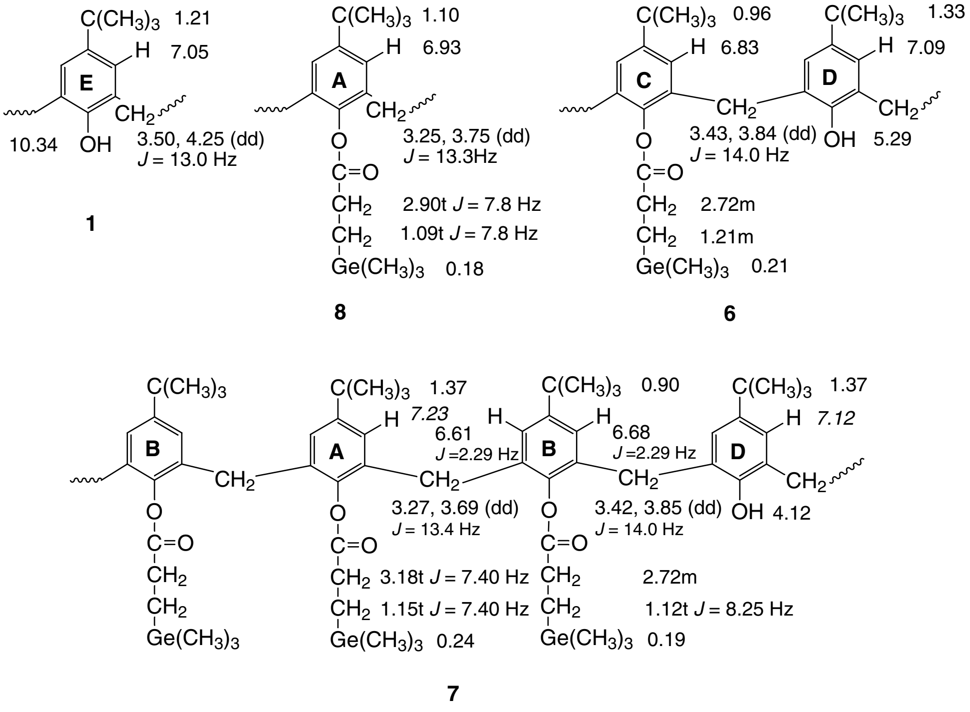


FIGURE 3 Assignments of ^1H NMR signals of calixarenes **1, 6, 7**, and **8**. Values in italics are of tentative assignments.

TABLE 2 Correlations Between ^1H and ^{13}C Signals Observed for **6** by H–C COSY and HMBC

Ring **C**			*Ring* **D**		
^1H	^{13}C	*Method*	^1H	^{13}C	*Method*
0.96	31.0	H–C COSY	1.33	31.8	H–C COSY
0.96	34.0	HMBC	1.33	33.995	HMBC
0.96	148.4	HMBC	1.33	142.3	HMBC
1.21	29.8	H–C COSY	–	–	–
2.72	29.8	HMBC	–	–	–
–	–	–	5.29	127.6	HMBC
–	–	–	5.29	150.2	HMBC
6.83	125.8	H–C COSY	7.09	125.3	H–C COSY
6.83	131.5	HMBC	7.09	125.3	HMBC
6.83	142.7	HMBC	7.09	150.2	HMBC

7: Assignment of the ^{13}C signals of **7** is much more complicated. There are three kinds of aromatic moieties (**A–B–D** = 1:2:1), and two kinds of germyl side-chains and Ar—CH_2—Ar moieties. The assignment of the germyl side-chains was achieved by H–C COSY experiments together with intensity considerations. Assignments of the twelve aromatic carbon signals was difficult and these remain unassigned. This is also true for assignments of the three kinds of *t*-Bu signals.

Figure 4 summarizes the assignments of the ^{13}C NMR spectra of these calixarenes although some of the assignments for **7** are tentative. It must be emphasized that the number of signals and the range of chemical shifts observed for **6, 7**, and **8** were consistent with their expected structures.

Ion Transport Properties. The cation transport ability of **6** and **7** determined using an H-tube test were previously described [4] for nitrates for the series Li^+, Na^+, K^+, Rb^+, Cs^+, and Ag^+. In all cases no cation transportation was seen. This may indicate that the cation-capturing capability of the calixarene cavity is not sufficiently strong.

CONCLUSION

We synthesized calix[4]arenes with a different number of germylated side-chains on the lower rim with the expectation that the modified calixarenes can

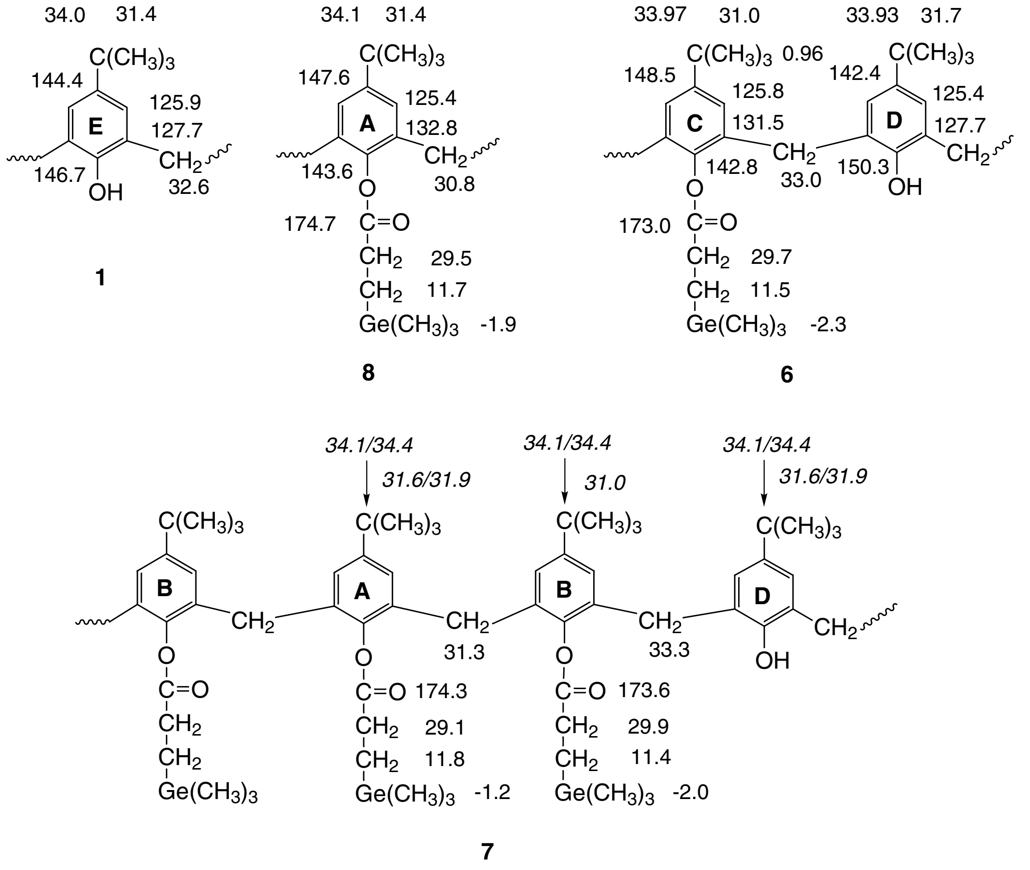


FIGURE 4 Assignments of ^{13}C NMR signals of calixarenes **2, 6, 7**, and **8**. Values in italics are of tentative assignments.

be a new class of ditopic host. These were found to adopt the cone conformation in solution, which is known to be favorable for capturing cations [2]. However, these calixarenes failed to capture and transport cations. The failure seems to be due to the weakness of cation capturing property of the calixarene moiety. Improvement may be achieved by introducing a more appropriate cation-capturing function into the calixarenes, such as a crown ether moiety. This expectation may be supported by some ditopic receptor reported by Gielen et al. [15] in which a crown acts as a cation receptor and a tin-containing moiety acts as an anion receptor. Studies along this line are currently in progress in our laboratory.

EXPERIMENTAL

Solvents were dried and purified in the conventional manner. Silica-gel column chromatography was performed on silica gel 7734 (Merck, 70–230 mesh). Melting points were determined on a Yanaco MP-S melting point apparatus and are uncorrected. NMR experiments were carried out on a JEOL EX 400 FT-NMR Spectrometer operating at 400 MHz for ^{1}H NMR or JEOL ECP 500 FT-NMR Spectrometer operating at 500 MHz for ^{1}H NMR. Sample concentrations were typically 10–30 mg/ml of solvents in a 5-mm (o.d.) sample tube with tetramethylsilane (TMS) as the internal standard. Elemental analysis was performed by the Elemental Analysis Laboratory, Department of Chemistry, Graduate School of Science, the University of Tokyo.

In all cases, separation was carried out with the aid of column and preparative chromatography. The eluents used were as follows: **4**, benzene–hexane = 5:2, $R_f = 0.80$; **6**, benzene–hexane = 3:1, $R_f = 0.28$; **7**, benzene–hexane = 5:1, $R_f = 0.43$; **8**, benzene–hexane = 5:1, $R_f = 0.32$.) Sometimes complete separation was impossible. This was particularly the case with **4**.

*Reaction Between Tetra-tert-butyl calix[4]arene(**1**) with Trimethylgermylpropanoyl Chloride (**3**) in the Presence of NaH*

Run 4: A mixture of 0.3 g (0.46 mmol) of **1**, THF (15 ml), DMF (2 ml), and NaH 0.11 g (4.58 mmol) was refluxed for 10 h. The mixture was added dropwise to 0.80 g (3.84 mmol) of **3** in 5 ml of THF, and refluxed for another 3 h. The mixture was allowed to cool to room temperature, and the solid material was filtered off. The solvent was removed in vacuo. The residue was dissolved in $CHCl_3$ (50 ml), and washed with water (25 ml) and saturated NaCl solution (25 ml), dried over Na_2SO_4, and evaporated. The residue was distilled in vacuo (90–105°C/1000 Pa) to remove yellow liquid and the remaining viscous material was recrystallized from $CH_2Cl_2{-}CH_3CH_2OH$ to give 0.24 g (52%) of 5,11,17,23-tetra-*p*-*tert*-butyl-25,27-bis((trimethylgermylpropanoyl)oxy)calix[4]arene (**6**) as colorless crystals, m.p. 280–285°C. Anal. calcd for $C_{56}H_{80}O_6Ge_2$: C, 67.64; H, 8.11. Found: C, 67.40, H, 8.07.

Run 5: A mixture of 0.3 g (0.46 mmol) of **1**, THF (15 ml), DMF (2 ml), and NaH (0.27 g; 11.25 mmol) was refluxed for 30 min. The mixture was added to 0.81 g (3.85 mmol) of **3** and refluxed for another 6 h. The mixture was allowed to cool to room temperature, and the solid was filtered off. The solvent was removed in vacuo and the residue was dissolved in a mixture of water (25 ml) and $CHCl_3$ (100 ml). The organic phase was washed with saturated NaCl solution (25 ml × 2), dried over Na_2SO_4, and evaporated. The residue was distilled in vacuo to remove the remaining starting material (**3**) (90–105°C/1000 Pa). The residue was washed with $CHCl_3$, CH_2Cl_2, and diethyl ether. Crystallization from $CH_2Cl_2{-}CH_3CH_2OH$ and then from $CHCl_3{-}CH_3OH$ produced 0.43 g of needles. These needles were subjected to chromatography (benzene–hexane, 5:1) to give 0.13 g (24%) of colorless needles of 5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27-tris((trimethylgermylpropanoyl)oxy)calix[4]arene (**7**) and 0.06 g (10%) of 5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27,28-tetrakis((trimethylgermylpropanoyl)oxy)calix[4]arene (**8**) as a colorless powder. **7**: m.p. 251–252°C, Anal. calcd for $C_{62}H_{92}O_7Ge_3$: C, 63.80; H, 7.95. Found: C, 63.77, H, 8.16. **8**: m.p. >300°C. Anal. calcd for $C_{68}H_{104}O_8Ge_4$: C, 60.95; H, 7.82. Found: C, 60.93, H, 7.75.

Direct Synthesis of **8** *from* **7**

Run 6: A mixture of 0.13 g (0.11 mmol) of **7**, THF (9 ml), DMF (1 ml), and NaH (0.011 g, 0.46 mmol) was stirred for 3 h. The mixture was added to 0.11 g (0.66 mmol) of **3** in THF (4 ml), and the stirring was continued for another 24 h. The mixture was then filtered and the solvent was removed in vacuo. The residue was dissolved in $CHCl_3$ (60 ml), and washed with water (20 ml × 2) and saturated NaCl solution (50 ml), dried over Na_2SO_4, and evaporated. The residue was washed with CH_3OH to leave a white powder, which was recrystallized from $CH_2Cl_2{-}CH_3CH_2OH$ to give 0.06 g (40%) of **8**.

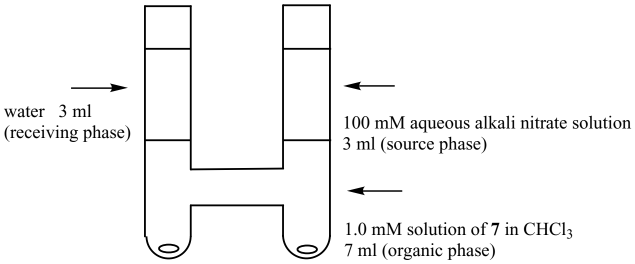


FIGURE 5 Cation transport measurement by H-tube method.

*Reaction Between Tetra-tert-butylcalix[4]-arene(**1**) with Trimethylgermylpropanoyl Chloride (**3**) in Pyridine*

Run 7: A sample of **1** (0.20 g, 0.31 mmol) in pyridine (10 ml) was added to **3** (0.146 g, 0.70 mmol) in pyridine (2 ml) at 30°C. The mixture was stirred for 5 h at 50°C. After cooling, the colorless precipitate (0.13 g) was collected and identified as **1** by ^{1}H NMR. The filtrate was acidified with hydrochloric acid, and the colorless powder was filtered off, from which **1** (0.6 g) was recovered.

Run 8: The reaction was carried out in the same manner as that of run 7 except that the amount of **3** was larger (0.146 g, 0.70 mmol). After cooling, **1** (0.10 g) was recovered. The residue obtained by evaporating pyridine from the filtrate was an intractable mixure.

Run 9: A sample of **1** (0.17 g, 0.26 mmol) in 12 ml of pyridine was stirred and **3** (0.25 g, 1.09 mmol) was added at room temperature, and the mixture was gently warmed for 5 h. The resulting mixture was poured onto ice, to which water was added. The precipitated white powder was filtered off. This powder was dissolved in $CHCl_3$ and the solution was filtered to remove undissolved residue and evaporated. The residue was treated with hexane, and the solid was filtered off, and hexane was evaporated and the residue was crystallized from CH_2Cl_2—CH_3OH to give 0.08 g (26%) of needles of **7**.

Cation Transport Experiments

Cation transport experiments on **6** and **7** were carried out using an H-tube test (Fig. 5) [2]. A chloroform solution of **6** or **7** was added to the bottom of the H-tube and aqueous nitrate solution (100 mmol/dm^3, 3 ml) was added to the right arm of the H-tube (source phase). Pure H_2O was added to the left arm of the H-tube (receiving phase). A small magnetic bar was placed in the bottom of each arm and was stirred. The whole apparatus was kept at 25°C for 24 h. The amount of cations in the receiving arm was measured by atomic absorption spectroscopy. A blank test was also performed, where no host was dissolved in the organic layer. Virtually no cations were detected in H_2O in the receiving arm.

REFERENCES

[1] Dietz, M. J.; Shang, M.; Smith. B. D. J Am Chem Soc 2000, 122, 6201.

[2] Gutsche, C. D. Calixarenes, The Royal Society of Chemistry: Cambridge, 1989.

[3] Tuntulai, T.; Poompradub, S.; Thavornyuikarn, P.; Jaiboon, N.; Ruangpornvisuti, V.; Chaicdhit, N.; Asari, Z.; Vicens, J. Tetrahedron Lett 2001, 42, 5541.

[4] Takeuchi, Y.; Sakurai, T.; Tanaka, K. Main Group Metal Chem 2000, 23, 313.

[5] (a) Ogawa, K.; Aoyagi, S.; Takeuchi, Y. J. Chem Soc, Perkin Trans 2 1993, 2389; (b) Aoyagi, S.; Tanaka, K.; Takeuchi, Y. J Chem Soc, Perkin Trans 2 1994, 355; (c) Aoyagi, S.; Ogawa, K.; Takeuchi, Y. J Chem Soc, Perkin Trans 2 1995, 1549.

[6] Suzuki, R.; Matsumoto, T.; Tanaka, K;.Takeuchi, Y.; Taketomi, T. J Organomet Chem 2001, 636, 108.

[7] See, K. A.; Fronczek, F. R.; Watson, W. H.; Kashyap, R. P.; Gutsche, C. D. J Org Chem 1991, 56, 7256.

[8] Kakimoto, N.; Akiba, M.; Takada, T. Synthesis 1985, 3, 272.

[9] Iwamoto, K.; Shinkai, S. J Org Chem 1991, 56, 4955.

[10] Shu, C.-M.; Lie, W.-C.; Ku, M.-C.; Tang, F.-S.; Yeh, M.-L.; Lin, L.-G. J Org Chem 1994, 59, 3730.

[11] Gutsche, C. D.; Bauer, L. J. Tetrahedron Lett 1981, 22, 4763.

[12] Iwamoto, K.; Shinkai, S. J Org Chem 1992, 57, 7066.

[13] Jaime, C.; Mendoza, J. M.; Prados, P.; Nieto, P. M.; Sanchez, C. J Org Chem 1991, 56, 3372.

[14] Gutsche, C. D.; Dhawan, B.; No, K. H.; Muthukrishnan, R. J Am Chem Soc 1981, 103, 3782.

[15] (a) Kemmer, M.; Ghys, L.; Gielen, M.; Biesemans, M.; Tieknik, E. R. T.; Willem, R. J Organomet Chem 1999, 582, 195; (b) Kemmer, M.; Biesemans, M.; Gielen, M.; Martins, J. C.; Gramlich, V.; Willem, R. Chem—Eur J 2001, 7, 4686.