Study of Calixarenes, V[1]

Friedel-Crafts Reaction of Calixarenes

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Received July 19, 1993

Key Words: Calixarenes / Friedel-Crafts reaction, selective

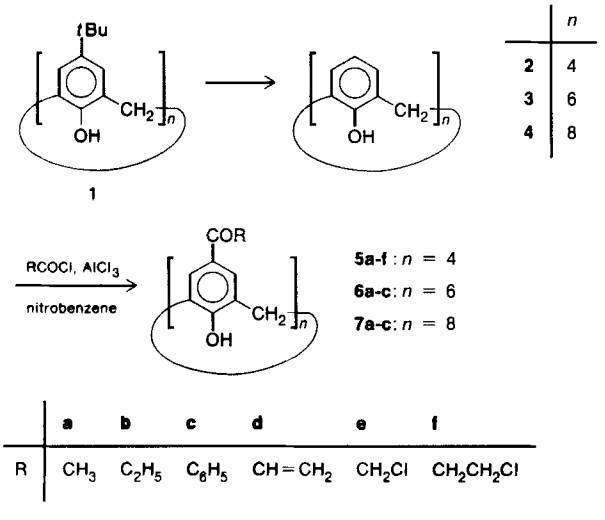
The *para*-acylation of calix[4]arene (**2**), calix[6]arene (**3**), and calix[8]arene (**4**) by Friedel-Crafts reaction with a wide variety of acyl chlorides leads to **5**–**7** in moderate to good yields. Friedel-Crafts reaction of 26,28-dimethoxycalix[4]-arene (**8**) gave products **9** selectively disubstituted in the *para*-positions of phenol rings.

Calixarenes are cavity-containing macrocyclic compounds which are attracting increasing interest because of their potential for forming host-guest complexes and acting as enzyme mimics, especially if appropriately functionalized[2,3].

By the proper choice of reaction conditions *p-tert*-butylcalix[*n*]arenes (n = 4, 6, 8) **1** can be easily prepared in good yields by the base-induced condensation of *p-tert*-butylphenol with formaldehyde[4,5]. As aluminium chloride-catalyzed removal of the *tert*-butyl group proceeds in excellent yields[6,7], **2**–**4** are readily available starting materials for the introduction of functional groups into the calixarene framework.

Gutsche and others have developed several routes to functionalize calixarenes on the "upper rim", including the electrophilic substitution reaction as represented by the preparation of *p*-sulfonatocalixarenes[8], the *para* Claisen rearrangement route for the preparation of *p*-allylcalixarenes[9], and the formation of a Mannich base in the *para* position[10]. The Friedel-Crafts reaction is a convenient and widely used method for the introduction of functional groups into aromatic rings. However, acetylation and benzoylation of calix[4]arene (**2**) under Friedel-Crafts conditions, using acetyl or benzoyl chloride and aluminium chloride in dichloromethane, yield only *O*-substituted products[7]. Friedel-Crafts acetylation can take place in the *para*-position in the case of calix[4]arene methyl ether; unfortunately, the process is complicated by concomitant demethylation[7]. So far, the *para* acylation of calixarenes by Friedel-Crafts reaction has not been achieved in providing the functionalized calixarenes. However, the *para* acylation of calixarenes performed by *O*-acylation followed by Fries rearrangement has been reported[11–13], and it has been indicated that higher temperature should be used for this process[11], or this reaction is only suitable for some higher acyl chlorides and not for acetoxycalixarene[12]. The selective Friedel-Crafts acetylation and benzoylation of 26,28-dimethoxycalix[4]arene (**8**) have been reported in a short communication[14]. In this paper we report in detail on the results of the Friedel-Crafts reaction of calixarenes[15] and the selective Friedel-Crafts reaction of 26,28-dimethoxycalix[4]-arene[16].

By optimizing the reaction conditions, especially by choice of reaction solvent and the molar ratio of aluminium chloride to calixarene, we have achieved a *para* acylation of calixarenes by Friedel-Crafts reaction. We have found that nitrobenzene and a mixture of nitromethane and 1,1,2,2-tetrachloroethane (volume ratio 1:4) are suitable reaction solvents, and that the optimum molar ratio of aluminium chloride to calixarene (calculated on one phenolic unit) is 2:1. The reaction is carried out at ambient temperature for a given period and monitored by TLC. The reaction mixture is worked up in the usual way to give the *para*-acylated products in moderate to good yields. This procedure is applicable to calix[4]arene (**2**), calix[6]arene (**3**), and calix[8]arene (**4**) and a wide variety of acyl chlorides. In general, the use of propionyl chloride gives a considerably higher yield of the *para*-acylated product than that of acetyl and benzoyl chlorides.



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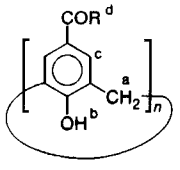
The constitution of the products **5**, **6**, and **7** is confirmed by elemental analyses and that of **5** also by mass spectra, but these are same for the *O*-substituted products. The evidences for the acylation in the *para* position with respect to the hydroxy group for products **5**–**7** are: (1) In the IR spectra, a strong absorption of a ketonic carbonyl group linked to the phenyl ring is observed at 1638–1672 cm^{-1} and a broad absorption of a phenolic hydroxy group at 3170–3300 cm^{-1}, and no absorption of an ester carbonyl group in the region of ca. 1750 cm^{-1}. (2) In the ^{1}H-NMR specta (Table 1), there appears a broad peak of a phenolic hydroxy group at δ = 5.0–8.5 and a singlet signal of an aromatic proton (except R = C_6H_5) at δ ca. 7.70. (3) The ^{13}C-NMR spectra (Table 2) exhibit the signal of the ketonic carbonyl carbon at δ = 187.7–198.7.

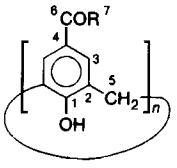
Table 1. ^{1}H-NMR data (δ values) of **5**–**7** in [D_6]DMSO at 60°C with TMS as internal standard



	H^a	H^b	H^c	H^d
5a	3.96 (s)	7.73 (s)	7.74 (s)	2.38 (s)
5b	3.96 (s)	6.84 (s)	7.74 (s)	2.81 (q), 1.01 (t)
5c	3.96 (s)	6.16 (s)	7.32–7.57 (m)	
5d	4.00 (s)	8.28 (s)	7.86 (s)	5.80–6.60 (m)
5e	3.92 (s)	8.00 (s)	7.75 (s)	4.82 (s)
5f	3.98 (s)	8.47 (s)	7.78 (s)	3.33 (t), 3.83 (t)
6a	3.93 (s)	5.04 (s)	7.64 (s)	2.34 (s)
6b	3.93 (s)	5.50 (s)	7.64 (s)	2.76 (q), 1.00 (t)
6c	3.96 (s)	7.30 (s)	7.28–7.64 (m)	
7a	3.98 (s)	5.60 (s)	7.53 (s)	2..28 (s)
7b	3.97 (s)	6.24 (s)	7.58 (s)	2.74 (q), 0.95 (t)
7c	3.96 (s)	7.20 (s)	7.28–7.54 (m)	

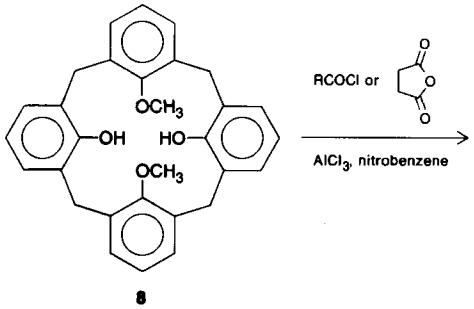
The methylene protons of Ar–CH_2–Ar in the cyclic tetramers **5** in the ^{1}H-NMR spectra measured at 60°C in [D_6]DMSO show a singlet signal. This indicates that compound **5** possesses a rapidly interconverting cone or a 1,3-alternate conformation. However, an X-ray diffraction analysis shows that **5b** exhibits a cone conformation[17]. Therefore, the interconversion of this conformation for tetramer **5** occurring by the rotation of the aryl group around the C-2/C-6 axis[18] at the measured temperature is most probable. This is another evidence for the free hydroxy group on the benzene ring, because it causes little hindrance to this rotation through the center of the macrocyclic ring, and, if the hydroxy group is esterified, the other larger groups give rise to a hindrance of this rotation or make it virtually impossible. In a fashion similar to **5**, the methylene protons of the Ar–CH_2–Ar group in cyclic hexamers **6** and octamers **7** show a singlet signal, too. The ^{13}C-NMR spectra of the *para*-acylated calixarenes **5**, **6**, and **7** show a very simple pattern[4,18]. Due to the symmetry of the cyclic oligomers only four aromatic carbon signals, one methylene carbon signal, and the signals of COR are observed.

Table 2. ^{13}C-NMR data (δ values) of **5**–**7** in [D_6]DMSO at 60°C with TMS as internal standard

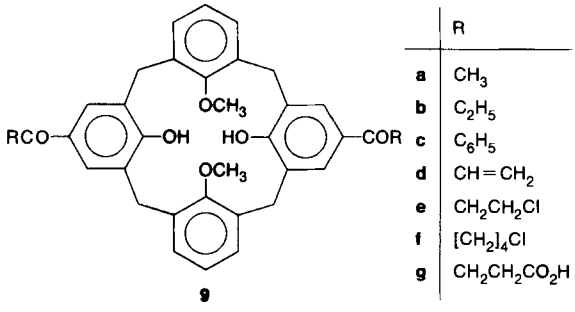


	C-1	C-2	C-3	C-4	C-5	C-6	C-7
5a	156.7	128.7	128.9	129.1	30.8	195.5	25.7
5b	155.7	128.8	128.4	129.1	30.7	198.3	30.4, 8.1
5c	157.1	128.3	127.9	128.5	30.9	193.8	137.9, 130.8, 129.0, 131.2
5d	157.5	128.2	129.2	129.8	31.1	187.7	128.8, 132.5
6a	156.6	127.1	128.7	133.1	30.4	195.6	25.3
6b	156.6	128.4	127.3	128.8	30.4	198.6	30.4, 8.2
6c	157.0	128.0	127.4	130.8	30.8	193.8	137.8, 128.7, 127.7, 131.1
7a	156.2	128.2	126.4	128.4	29.8	195.2	25.0
7b	156.9	128.5	127.1	128.7	30.5	198.7	30.5, 8.3
7c	157.6	127.4	127.3	130.3	30.7	193.7	137.9, 128.4, 127.4, 130.8

Concerning the mechanism of formation of the *para*-acylated products **5**–**7**, a Fries rearrangement of the primarily formed *O*-acylation products seems reasonable. However, it has been reported that *p*-acetylcalix[4]arene is formed by a Fries rearrangement only by heating calix[4]arene tetraacetate with aluminium chloride at 150°C[11], or this process is only suitable for some higher acyl chlorides and not for acetoxycalixarene[12]. We have also attempted to effect a Fries rearrangement of the *O*-acylated calixarene to the *para*-acylated calixarene under the same reaction conditions, but these attempts have failed. We assume that the hydroxy group of calixarene first forms a complex with aluminium chloride which preferentially undergoes Friedel-



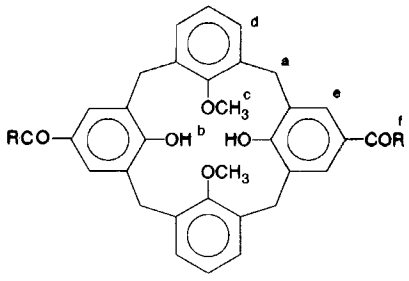
8



9

	R
a	CH_3
b	C_2H_5
c	C_6H_5
d	$CH=CH_2$
e	CH_2CH_2Cl
f	$[CH_2]_4Cl$
g	$CH_2CH_2CO_2H$

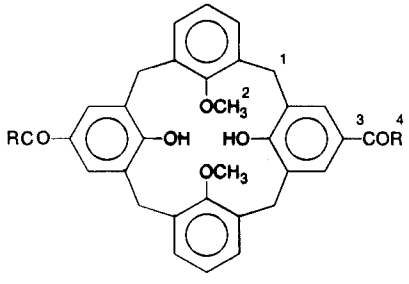
Table 3. ^{1}H-NMR data (δ values) of **8** and **9** in $CDCl_3$ with TMS as internal standard



	H^a	H^b	H^c	H^d	H^e	H^f
8	3.30 (d), 4.23 (d)	7.55 (s)	3.90 (s)	6.43–7.03 (m)		
9a	3.40 (d), 4.20 (d)	8.32 (s)	3.88 (s)	6.63–6.91 (m)	7.63 (s)	2.47 (s)
9b[a]	3.48 (d), 4.22 (d)		3.94 (s)	6.55–6.83 (m)	7.83 (s)	3.03 (q), 1.23 (t)
9c	3.40 (d), 4.25 (d)	8.47 (s)	3.93 (s)	6.70–6.95 (m)	7.35–7.72 (m)	
9d	3.40 (d), 4.20 (d)	8.43 (s)	3.92 (s)	6.62–6.90 (m)	7.65 (s)	5.80–6.50 (m)
9e	3.42 (d), 4.24 (d)	8.48 (s)	3.92 (s)	6.68–6.97 (m)	7.71 (s)	3.34 (t), 3.85 (t)
9f	3.44 (d), 4.27 (d)	8.45 (s)	3.95 (s)	6.73–6.98 (m)	7.73 (s)	2.92 (t), 1.85 (quin), 3.55 (t)
9g[b]	3.57 (d), 4.15 (d)	8.70 (s)	3.88 (s)	6.82–7.05 (m)	7.82 (s)	3.17 (t), 6.73 (s)

[a] In CF_3CO_2D. – [b] In $[D_6]$DMSO.

Table 4. ^{13}C-NMR data (δ values) of **8** and **9** in $CDCl_3$ with TMS as internal standard



	C-1	C-2	C-3	C-4	C-aromatic
8	31.2	63.5			153.4, 153.2, 132.9, 129.0, 128.5, 128.3, 125.2, 119.1
9a	31.1	63.6	196.5	26.1	157.9, 153.2, 132.1, 129.5, 129.3, 129.2, 127.9, 125.5
9b[a]	32.2	64.7	196.5	32.9, 10.3	160.7, 154.6, 133.2, 132.7, 131.3, 130.8, 129.0, 127.6
9c	31.0	63.7	195.5	157.6, 152.9, 131.5, 129.6, 127.7, 125.5	138.6, 132.2, 131.6, 129.3, 128.6, 128.0,
9e	31.2	63.6	195.1	41.0, 39.2	158.4, 153.2, 132.1, 130.0, 129.4, 128.4, 128.2, 125.6
9f	31.1	63.6	198.1	44.7, 37.0, 32.1, 21.9	157.9, 153.1, 132.1, 129.4, 129.2, 128.6 127.8, 125.5
9g[b]	32.6	63.3	196.5	173.6, 30.1, 27.9	153.1, 152.7, 132.4, 129.0, 128.2, 128.1, 127.6, 125.2

[a] In CF_3CO_2D. – [b] In $[D_6]$DMSO.

Crafts acylation in the *para* position under the reaction conditions used by us. This can also explain why the 2:1 molar ratio of aluminium chloride to the phenolic unit should be used in the above Friedel-Crafts reaction.

When 26,28-dimethoxycalix[4]arene (**8**) is used as a substrate to undergo the Friedel-Crafts reaction under the conditions used above, the reaction takes place smoothly, and diacylated products determined by mass spectrometry and elemental analyses are produced in good to excellent yields, although the reagents have been used in excess. The presence of a phenolic hydroxy group observed at 3250–3300 cm^{-1} in the IR and at δ = 8.32–8.70 in the ^{1}H-NMR spectra and the occurrence of a ketonic carbonyl group at 1640–1665 cm^{-1} in the IR and at δ = 195.0–196.5 in the ^{13}C-NMR spectra indicate that the acylation has taken place at the phenyl ring and excludes *O*-substitution for the products. There are two *para* positions of the phenol rings and also two *para* positions of the anisole rings in **8**. An X-ray diffraction analysis of **9e** demonstrates unambiguously that the substitution has taken place in the *para* positions of the phenol rings[16,19].

The selective substitution of **8** has been reported[20–22], and the position attacked is consistent with our above result. The acylation occurs in the *para* position of the phenolic ring which is also consistent with the above-mentioned mechanism for the Friedel-Crafts reaction involving complex formation between aluminium chloride and the phenolic hydroxy group. However, No and Hong have reported that Friedel-Crafts acetylation and benzoylation of **8** afford the diametrically acylation products in the *para* positions of the anisole ring[14]. We consider that the conclusion drawn by them is not so convicing, because the

structure of such acylated products cannot be conclusively determined by spectral data only.

When succinic anhydride is used instead of acyl chloride, the disubstituted product **9g** with carboxyl groups is obtained.

The ^{1}H- and ^{13}C-NMR data of **8** and **9** are listed in Tables 3 and 4, respectively. The ^{1}H-NMR spectra of **9** show a typical AB pattern for the methylene bridge protons. It is indicated that compounds **9** exist in the cone conformation, and this has also been ascertained by an X-ray diffraction analysis[16].

This work was supported by the *National Natural Science Foundation of China.*

Experimental

IR: Perkin-Elmer 782. – ^{1}H- and ^{13}C-NMR: Jeol FX-100. – MS: AEI MS-50. – Melting points are uncorrected. – Elemental analyses: Analytical Laboratory of our Institute.

General Procedure for the Synthesis of **5**–**7**: 5.0 mmol (6.0 mmol in the case of **6**) of acyl chloride was dropped into a mixture of 1.25 mmol of **2** (1.0 mmol of **3** in the case of **6** and 0.625 mmol of **4** in the case of **7**) and 10 mmol (12 mmol in the case of **6**) of anhydrous aluminium chloride in 25 ml of nitrobenzene with stirring. The mixture was continuously stirred at room temp. for 3–22 h (according to different calixarene and acyl chloride used). The reaction was stopped by the addition of 20 ml of dilute hydrochloric acid, and nitrobenzene was removed by steam distillation. The solid product was recrystallized from acetone.

5,11,17,23-Tetraacetyl-25,26,27,28-tetrahydroxycalix[4]arene (**5a**): 296 mg (40%) was obtained from 530 mg (1.25 mmol) of **2**, 393 mg (5.0 mmol) of acetyl chloride, and 1.34 g (10 mmol) of $AlCl_3$ after a reaction time of 5 h; m.p. >330°C. – IR (KBr): $\tilde{\nu}$ = 3200 cm^{-1} (OH), 1665 (CO), 1590. – MS (FAB), *m/z*: 593 [M$^+$ + 1]. – $C_{36}H_{32}O_8$ (592.6): calcd. C 72.96, H 5.44; found C 72.95, H 5.61.

25,26,27,28-Tetrahydroxy-5,11,17,23-tetrapropionylcalix[4]arene (**5b**): 710 mg (88%) was obtained from 530 mg (1.25 mmol) of **2**, 465 mg (5.0 mmol) of propionyl chloride, and 1.34 g (10 mmol) of $AlCl_3$ after a reaction time of 3 h; m.p. >300°C. – IR (KBr): $\tilde{\nu}$ = 3230 cm^{-1} (OH), 1672 (CO), 1598. – MS (FAB), *m/z*: 649 [M$^+$ + 1]. – $C_{40}H_{40}O_8$ (648.7): calcd. C 74.05, H 6.22; found C 74.05, H 6.08.

25,26,27,28-Tetrahydroxy-5,11,17,23-tetrabenzoylcalix[4]arene (**5c**): 378 mg (36%) was obtained from 530 mg (1.25 mmol) of **2**, 705 mg (5.0 mmol) of benzoyl chloride, and 1.34 g (10 mmol) of $AlCl_3$ after a reaction time of 20 h; m.p. 176–178°C. – IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} (OH), 1662 (CO), 1588. – MS (FAB), *m/z*: 841 [M$^+$ + 1]. – $C_{56}H_{40}O_8$ (840.9): calcd. C 79.98, H 4.79; found C 79.55, H 5.02.

5,11,17,23-Tetraacryloyl-25,26,27,28-tetrahydroxycalix[4]arene (**5d**): 416 mg (52%) was obtained from 530 mg (1.25 mmol) of **2**, 455 mg (5.0 mmol) of acryloyl chloride, and 1.34 g (10 mmol) of $AlCl_3$ after a reaction time of 15 h; m.p. >300°C. – IR (KBr): $\tilde{\nu}$ = 3170 cm^{-1} (OH), 1665 (CO), 1593. – MS (FAB), *m/z*: 641 [M$^+$ + 1]. – $C_{40}H_{32}O_8$ (640.7): calcd. C 74.99, H 5.03; found C 74.95, H 5.58.

5,11,17,23-Tetrakis(chloroacetyl)-25,26,27,28-tetrahydroxycalix[4]arene (**5e**): 640 mg (70%) was obtained from 530 mg (1.25 mmol) of **2**, 565 mg (5.0 mmol) of chloroacetyl chloride, and 1.34 g (10 mmol) of $AlCl_3$ after a reaction time of 6 h; m.p. 208–210°C. – IR (KBr): $\tilde{\nu}$ = 3220 cm^{-1} (OH), 1670 (CO), 1590. – MS (FAB), *m/z*: 729 [M$^+$ + 1].

5,11,17,23-Tetrakis(3-chloropropionyl)-25,26,27,28-tetrahydroxycalix[4]arene (**5f**): 640 mg (65%) was obtained from 530 mg (1.25 mmol) of **2**, 635 mg (5.0 mmol) of 3-chloropropionyl chloride, and 1.34 g (10 mmol) of $AlCl_3$ after a reaction time of 6 h; m.p. 216°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3220 cm^{-1} (OH), 1660 (CO), 1585. – MS (FAB), *m/z*: 785 [M$^+$ + 1].

5,11,17,23,29,35-Hexaacetyl-37,38,39,40,41,42-hexahydroxycalix[6]arene (**6a**): 374 mg (42%) was obtained from 637 mg (1.0 mmol) of **3**, 472 mg (6.0 mmol) of acetyl chloride, and 1.60 g (12 mmol) of $AlCl_3$ after a reaction time of 14 h; m.p. >310°C. – IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} (OH), 1660 (CO), 1585. – $C_{54}H_{48}O_{12}$ (888.9): calcd. C 72.96, H 5.44; found C 72.79, H 5.88.

37,38,39,40,41,42-Hexahydroxy-5,11,17,23,29,35-hexapropionylcalix[6]arene (**6b**): 778 mg (80%) was obtained from 637 mg (1.0 mmol) of **3**, 556 mg (6.0 mmol) of propionyl chloride, and 1.60 g (12 mmol) of $AlCl_3$ after a reaction time of 3 h; m.p. >330°C. – IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} (OH), 1665 (CO), 1580. – $C_{60}H_{60}O_{12}$ (973.1): calcd. C 74.05, H 6.22; found C 74.08, H 6.09.

5,11,17,23,29,35-Hexabenzoyl-37,38,39,40,41,42-hexahydroxycalix[6]arene (**6c**): 504 mg (40%) was obtained from 637 mg (1.0 mmol) of **3**, 844 mg (6.0 mmol) of benzoyl chloride, and 1.60 g (12 mmol) of $AlCl_3$ after a reaction time of 22 h; m.p. 258–260°C. – IR (KBr): $\tilde{\nu}$ = 3220 cm^{-1} (OH), 1638 (CO), 1590. – $C_{84}H_{60}O_{12}$ (1261.3): calcd. C 79.98, H 4.79; found C 79.69, H 5.35.

5,11,17,23,29,35,41,47-Octaacetyl-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene (**7a**): 378 mg (48%) was obtained from 530 mg (0.625 mmol) of **4**, 393 mg (5.0 mmol) of acetyl chloride, and 1.34 g (10 mmol) of $AlCl_3$ after a reaction time of 13 h; m.p. >300°C. – IR (KBr): $\tilde{\nu}$ = 3240 cm^{-1} (OH), 1660 (CO), 1585. – $C_{72}H_{64}O_{16}$ (1185.2): calcd. C 72.96, H 5.44; found C 73.03, H 5.61.

49,50,51,52,53,54,55,56-Octahydroxy-5,11,17,23,29,35,41,47-octapropionylcalix[8]arene (**7b**): 690 mg (85%) was obtained from 530 mg (0.625 mmol) of **4**, 465 mg (5.0 mmol) of propionyl chloride, and 1.34 g (10 mmol) of $AlCl_3$ after a reaction time of 4 h; m.p. >300°C. – IR (KBr): $\tilde{\nu}$ = 3270 cm^{-1} (OH), 1670 (CO), 1590. – $C_{80}H_{80}O_{16}$ (1297.4): calcd. C 74.05, H 6.21; found C 74.10, H 6.00.

5,11,17,23,29,35,41,47-Octabenzoyl-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene (**7c**): 473 mg (45%) was obtained from 530 mg (0.625 mmol) of **4**, 705 mg (5.0 mmol) of benzoyl chloride, and 1.34 g (10 mmol) of $AlCl_3$ after a reaction time of 22 h; m.p. 213–215°C. – IR (KBr): $\tilde{\nu}$ = 3270 cm^{-1} (OH), 1640 (CO), 1592. – $C_{112}H_{80}O_{16}$ (1681.8): calcd. C 79.98, H 4.79; found C 79.34, H 5.02.

25,27-Dihydroxy-26,28-dimethoxycalix[4]arene (**8**): Prepared as described in ref.[21]

General Procedure for the Synthesis of **9**: 453 mg (1.0 mmol) of **8** was dissolved in 20 ml of nitrobenzene, and 1.07 g (8 mmol) of $AlCl_3$ was added to the solution, then 6 mmol of acyl chloride was added dropwise. The mixture was stirred at room temp. for 12 h, and the reaction was stopped by the addition of 20 ml of dilute hydrochloric acid. Nitrobenzene was removed by steam distillation. The solid product obtained was recrystallized from chloroform.

11,23-Diacetyl-25,27-dihydroxy-26,28-dimethoxycalix[4]arene (**9a**): 348 mg (65%) was obtained from 453 mg (1.0 mmol) of **8** and 472 mg (6.0 mmol) of acetyl chloride, m.p. >300°C. – IR (KBr):

$\tilde{\nu}$ = 3260 cm^{-1} (OH), 1660 (CO), 1590. – MS, *m/z* (%): 536 [M^+] (39), 535 (100), 520 (25), 505 (20), 493 (19), 253 (24), 121 (42). – $C_{34}H_{32}O_6$ (536.6): calcd. C 76.10, H 6.01; found C 75.60, H 6.15.

25,27-Dihydroxy-26,28-dimethoxy-11,23-dipropionylcalix[4]arene (**9b**): 525 mg (93%) was obtained from 453 mg (1.0 mmol) of **8** and 556 mg (6.0 mmol) of propionyl chloride; m.p. >300°C. – IR (KBr): $\tilde{\nu}$ = 3280 cm^{-1} (OH), 1660 (CO), 1590. – MS, *m/z* (%): 564 [M^+] (99), 535 (100), 507 (9), 253 (29), 121 (13). – $C_{36}H_{36}O_6$ (564.7): calcd. C 75.60, H 6.15; found C 75.69, H 5.70.

11,23-Dibenzoyl-25,27-dihydroxy-26,28-dimethoxycalix[4]arene (**9c**): 382 mg (58%) was obtained from 453 mg (1.0 mmol) of **8** and 844 mg (6.0 mmol) of benzoyl chloride, m.p. >300°C. – IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} (OH), 1660 (CO), 1585. – MS (FAB), *m/z*: 661 [M^+ + 1]. – $C_{44}H_{36}O_6$ (660.7): calcd. C 79.98, H 5.49; found C 79.69, H 5.66.

11,23-Diacryloyl-25,27-dihydroxy-26,28-dimethoxycalix[4]arene (**9d**): 380 mg (68%) was obtained from 453 mg (1.0 mmol) of **8** and 543 mg (6.0 mmol) of acryloyl chloride, m.p. >300°C. – IR (KBr): $\tilde{\nu}$ = 3280 cm^{-1} (OH), 1660 (CO), 1580. – MS (FAB), *m/z*: 561 [M^+ + 1]. – $C_{36}H_{32}O_6$ (560.6): calcd. C 77.12, H 5.75; found C 76.85, H 5.37.

11,23-Bis(3-chloropropionyl)-25,27-dihydroxy-26,28-dimethoxycalix[4]arene (**9e**): 550 mg (87%) was obtained from 453 mg (1.0 mmol) of **8** and 762 mg (6.0 mmol) of 3-chloropropionyl chloride, m.p. >300°C. – IR (KBr): $\tilde{\nu}$ = 3280 cm^{-1} (OH), 1660 (CO), 1585. – MS (FAB), *m/z*: 633 [M^+ + 1]. – $C_{36}H_{34}Cl_2O_6$ (633.5): calcd. C 68.25, H 5.41; found C 68.02, H 5.52.

11,23-Bis(5-chloropentanoyl)-25,27-dihydroxy-26,28-dimethoxycalix[4]arene (**9f**): 613 mg (89%) was obtained from 453 mg (1.0 mmol) of **8** and 930 mg (6.0 mmol) of 5-chloropentanoyl chloride, m.p. 253–255°C. – IR (KBr): $\tilde{\nu}$ = 3270 cm^{-1} (OH), 1640 (CO), 1590. – MS (FAB), *m/z*: 689 [M^+ + 1]. – $C_{40}H_{42}Cl_2O_6$ (689.7): calcd. C 69.66, H 6.14; found C 68.68, H 5.52.

11,23-Bis(3-carboxypropionyl)-25,27-dihydroxy-26,28-dimethoxycalix[4]arene (**9g**): 475 mg (73%) was obtained from 453 mg (1.0 mmol) of **8** and 600 mg (6.0 mmol) of succinic anhydride, m.p. >300°C. – IR (KBr): $\tilde{\nu}$ = 3250 cm^{-1} (OH), 1720, 1705 (OCO), 1665 (CO), 1585. – $C_{38}H_{36}O_{10}$ (652.7): calcd. C 69.93, H 5.56; found C 68.85, H 5.85.

[1] Part IV: Z.-T. Huang, G.-Q. Wang, *Synth. Commun.* **1993**, *23*.
[2] C. D. Gutsche, *Acc. Chem. Res.* **1983**, *16*, 161–170.
[3] C. D. Gutsche, *Top. Curr. Chem.* **1984**, *123*, 1–47.
[4] C. D. Gutsche, B. Dhawan, K. H. No, R. Muthukrishnan, *J. Am. Chem. Soc.* **1981**, *103*, 3782–3792.
[5] C. D. Gutsche, M. Iqbal, D. Stewart, *J. Org. Chem.* **1986**, *51*, 742–745.
[6] C. D. Gutsche, J. A. Levine, P. K. Sujeeth, *J. Org. Chem.* **1985**, *50*, 5802–5806.
[7] C. D. Gutsche, L.-G. Lin, *Tetrahedron* **1986**, *42*, 1633–1640.
[8] S. Shinkai, S. Mori, H. Koreishi, T. Tsubaki, O. Manabe, *J. Am. Chem. Soc.* **1986**, *108*, 2409–2416.
[9] C. D. Gutsche, J. A. Levine, *J. Am. Chem. Soc.* **1982**, *104*, 2652–2653.
[10] C. D. Gutsche, K. C. Nam, *J. Am. Chem. Soc.* **1988**, *110*, 6153–6162.
[11] K. H. No, Y. Noh, Y. Kim, *Bull. Korean Chem. Soc.* **1986**, *7*, 442–444; cf. C. D. Gutsche, *Calixarenes*, The Royal Society of Chemistry, **1989**, p. 138.
[12] T. Arimura, S. Shinkai, T. Matsuda, Y. Hirata, H. Satoh, O. Manabe, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3733–3734.
[13] S. Shinkai, T. Nagasaki, K. Iwamoto, A. Ikeda, G.-X. He, T. Matsuda, M. Iwamoto, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 381–386.
[14] K. No, M. Hong, *J. Chem. Soc., Chem. Commun.* **1990**, 572–573.
[15] The primarily results have been published in a communication: Z.-T. Huang, G.-Q. Wang, *Chin. Chem. Lett.* **1992**, *3*, 485–488.
[16] The primarily obtained results have been published in a communication: Z.-T. Huang, G.-Q. Wang, *J. Chem. Soc., Perkin Trans. 1, Perkin Commun.* **1993**, 167–168.
[17] J.-H. Weng, H.-M. Wu, X.-Y. Lin, G.-Q. Wang, Z.-T. Huang, *Chin. J. Struct. Chem.* **1993**, *12*, 93–96.
[18] C. D. Gutsche, B. Dhawan, J. A. Levine, K. H. No, L. J. Bauer, *Tetrahedron* **1983**, *39*, 409–426.
[19] The details will be published elsewhere.
[20] J. D. van Loon, A. Arduini, W. Verboom, R. Ungaro, G. J. van Hummel, S. Harkema, D. N. Reinhoudt, *Tetrahedron Lett.* **1989**, *30*, 2681–2684.
[21] J. D. van Loon, A. Arduini, L. Coppi, W. Verboom, A. Pochini, R. Ungaro, S. Harkema, D. N. Reinhoudt, *J. Org. Chem.* **1990**, *55*, 5639–5646.
[22] W. Verboom, A. Durie, R. J. M. Egberink, Z. Asfari, D. N. Reinhoudt, *J. Org. Chem.* **1992**, *57*, 1313–1316.

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