Tetrahedron Vol. 49, No. 27, pp. 6019-6024, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00
Pergamon Press Ltd

Regioselective Synthesis of Calixcrowns Derived from *p-tert*-Butylcalix[5]arene

Dagmar Kraft, Ralf Arnecke, Volker Böhmer*, Walter Vogt

Institut für Organische Chemie, Johannes Gutenberg Universität Mainz, J.-J.-Becher Weg 34 SB1, D-6500 Mainz, Germany

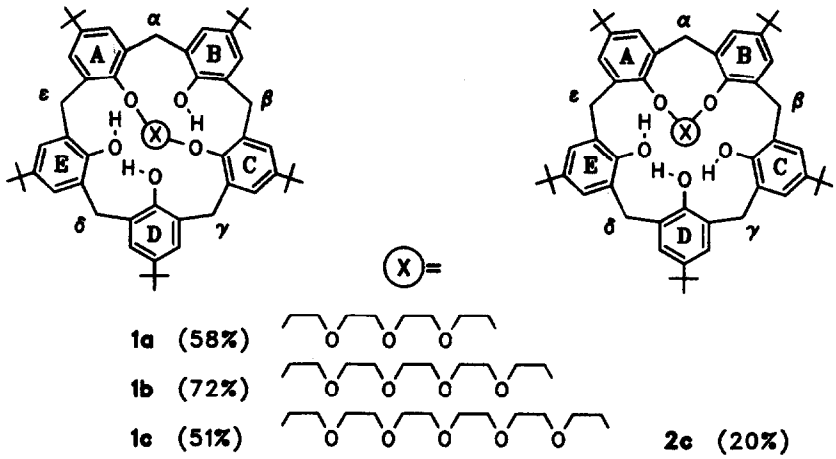
(*Received in Germany* 25 *January* 1993)

Abstract: Alkylation of *p-tert*-butylcalix[5]arene with oligoethylene glycol-ditosylates in the presence of CsF affords the 1,3-bridged calix[5]crowns **1a-c** in 51 to 72% yield. In the case of hexaethylene glycol the isomeric 1,2-bridged calix[5]crown-7 **2c** was obtained additionally. The calixcrowns were further modified by alkylation of the remaining hydroxyl groups.

The generic family of calixcrowns combines the structural elements of calixarenes and crown ethers through the bridging of phenolic oxygens of a calixarene by a polyether chain. The first calixcrowns were obtained by the reaction of oligoethylene glycol-ditosylates with calix[4]arenes, which leads to the connection of two opposite oxygens (1,3-crowns)[1-3]. The remaining two phenolic oxygens may be used to introduce further ligating functions[2], to fix certain conformations (cone, partial cone, 1,3-alternate)[4,5] or to span a second polyether chain, leading in the latter case to a double crown in the 1,3-alternate conformation[4]. Macrocyclic compounds in which two calix[4]arene subunits are connected by polyether chains have been reported too[6]. Recently single and double crowns of calix[4]arenes in which adjacent phenolic oxygens are connected (1,2-crowns)[7], have been prepared in a stepwise procedure. While the rapid progress in selective functionalization of calix[6]arenes[8] has led also to crown ether derivatives of calix[6]arenes in which the oxygens in 1,3- or 1,4-position are connected[9], less attention has been given to calix[5]arenes. We report here the first examples for crown ether derivatives of *p-tert*-butylcalix[5]arene which also represent the first selectively O-alkylated derivatives of calix[5]arenes[10].

Synthesis

First reactions of *p-tert*-butylcalix[5]arene[11] with oligoethylene glycol-ditosylates were carried out in refluxing benzene with KOtBu as a base in analogy to the synthesis of calixcrowns derived from *p-tert*-butylcalix[4]arene[1,2,4]. Various modifications of these conditions always led to complex and unseparable mixtures, as was the case with Cs_2CO_3 in THF. The 1,3-crown ether derivatives **1a-c** were finally obtained by reaction of *p-tert*-butylcalix[5]arene with tetra- to hexaethylene glycol-ditosylate in boiling acetonitrile under dilution conditions using CsF as a base, conditions which were successfully applied also to the preparation of crown ethers from other phenols[12-14]. The yield of pure products easily isolated and purified by flash chromatography was in the range of 51% (**1c**) to 72% (**1b**). In the case of hexaethylene glycol the isomeric 1,2-bridged calixcrown **2c** could be additionally isolated in 20% yield.



Structure and conformation

The FD mass spectra of **1** and **2** prove the formation of mono crown ethers, their molecular ion was found with 100% abundance in all cases. The further assignment of their structure was done on the basis of ^{1}H NMR (and ^{13}C NMR) spectra, which is not quite trivial.

Like in the case of calix[4]arenes two monocrowns are possible in which adjacent or distal oxygens are connected. In contrast to calix[4]crown ethers, however, both calix[5]crown ethers possess just <u>one</u> symmetry plane, while the 1,3-crown of a calix[4]arene (in the cone conformation) has <u>two</u>. Thus, compound **1** contains three different phenolic units A/C, E/D and B (ratio 2:2:1) and three different methylene bridges α/ß, γ/ε and δ (ratio 2:2:1), but the same is true for the isomeric compound **2** (A/B, E/C, D and ε/ß, δ/γ and α respectively). Therefore, both isomers cannot be distinguished *a priori* by the multiplicity of their NMR signals.

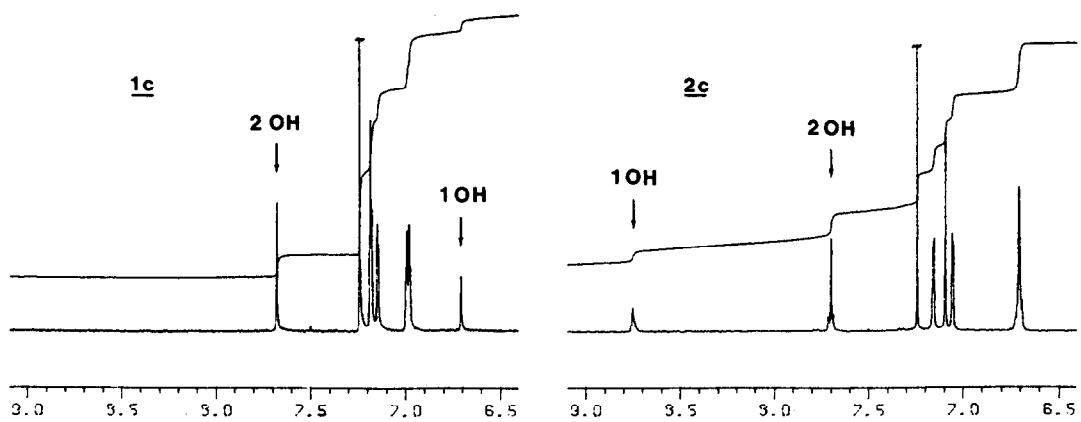


Figure 1. Section of the ^{1}H NMR spectra of compounds **1c** and **2c** (400 MHz, $CDCl_3$). The OH signals are indicated by arrows.

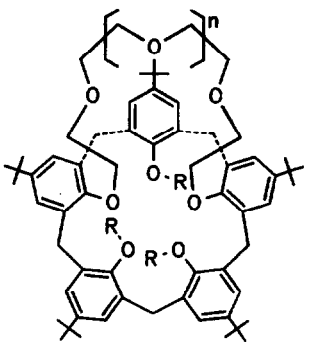
The distinction is possible, however, regarding the signals of the phenolic OH groups. In a 1,3-crown **1** the single OH group of unit B is "isolated" from the other two adjacent OH groups of D/E. Due to the stronger intramolecular hydrogen bonding the latter protons should experience a stronger downfield shift. In a 1,2-crown **2** the single OH group of unit D is in the middle of a continuous row of intramolecular hydrogen bonded OH groups, and their signal should appear at lower field in comparison to the signals of E/C. Indeed the two isomeric crown-7 derivatives (**1c** and **2c** which could be isolated in pure form) exhibit this expected ^{1}H NMR behaviour.

The major product showed two signals for OH at 7.69 and 6.70 with the ratio 2:1 (Figure 1) and therefore we assume it is **1c**. The other isomer, with OH signals at 8.76 and 7.70 ppm in the ratio 1:2 therefore must be **2c**. Similar NMR patterns as for **1c** are observed for the crown-5 and crown-6 derivatives which we assign as **1a** (OH signals at 7.89 and 7.16 ppm, ratio 2:1) and **1b** (OH signals at 7.76 and 6.88 ppm, ratio 2:1). Thus, we believe that the structure of the new crown ethers **1a-c** and **2c** (which is further corroborated by their ^{13}C NMR spectra) can be unambiguously attributed, although suitable crystals for an X-ray analysis have not yet been obtained.

Calixcrowns **1** and **2** assume a cone like conformation in which the maximum amount of intramolecular hydrogen bonding is possible. This may be deduced from the expected chemical shifts found for the aromatic protons (in the range of 7.22-6.71 ppm) and the *t*-butyl groups (1.33-0.82 ppm), as well as from three pairs of doublets (ratio 2:2:1) for the Ar-CH_2-Ar groups in the usual region (4.61-4.11 and 3.43-3.34 ppm).

Further derivatives

Alkylation of the remaining hydroxyl groups in **1** should lead to neutral ionophores as in the case of other calixcrowns. Exhaustive methylation was easily achieved by reaction with methyl iodide in THF using NaH as a base. The trimethyl ethers **3a** and **3b** were obtained in 89 and 65% yield, respectively. According to their ^{1}H NMR spectra, which show for instance three pairs of doublets (ratio 2:2:1) for the diastereotopic Ar-CH_2-Ar methylene protons, the trimethyl ethers assume the cone conformation. Since by analogy to calix[4]arenes it must be supposed that the methoxy groups can pass through the calixarene annulus, this seems to be the most stable conformation.



3a (89%) R=Me, n=1
3b (65%) R=Me, n=2
4a (31%) R=CH_2COOEt, n=1

If larger residues are attached to the oxygens, they cannot pass through the calix[5]arene annulus. This conformational fixing may lead to a complex mixture of products. In comparison to diether derivatives of 1,3-crowns of calix[4]arenes, where three conformational isomers are possible, six conformational isomers in principle exist for triethers derived from **1**. These are: all *syn* (corresponding to cone), all *anti* (corresponding to 1,3-alternate) and four *syn-anti* conformers, two of which are chiral[15]. This may be one reason that up to now only in the case of **1a** suitable conditions have been found for the alkylation with ethyl bromoacetate. Reaction in boiling acetonitrile in the presence of Cs_2CO_3 led to the corresponding triester **4a** in the cone-conformation, which was isolated chromatographically with a moderate yield of 31%. The conformational assignment is based on arguments analogous to those discussed above.

First extraction experiments[16] (neutral picrates, water / CH_2Cl_2) with **3** and **4** show a preference for the complexation of the larger alkali cations. We especially hope that by further (selective) functionalization at the phenolic OH groups a fine tuning of these complexation properties may be possible.

EXPERIMENTAL

Crown ethers 1: A suspension of *p-tert*-butylcalix[5]arene (1 mmol) and CsF (5 mmol) in CH_3CN (40 ml) was refluxed for 1 h. Then a solution of the corresponding oligoethylene glycol-ditosylate (1 mmol) in CH_3CN (40 ml) was added over a 8 h period. The mixture was refluxed for another 15 h before the solvent was removed. The crude product was taken up in $CHCl_3$ and washed with brine. The organic layer was dried over $MgSO_4$, filtered and after evaporation of the solvent the product was purified by flash chromatography (CH_2Cl_2/acetone).

1,3-Calix[5]crown-5 (1a): yield 58%; mp. 248°C; MS-FD, *m/z* 969.3 (M^+, calc. 968.6).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2 H, OH), 7.22 (s, 2 H, ArH), 7.19 (d, 2 H, ^4J = 2.3 Hz, ArH), 7.16 (d, 2 H, ^4J = 2.1 Hz, ArH) and (s, 1 H, OH), 7.15 (d, 2 H, ^4J = 2.4 Hz, ArH), 7.12 (d, 2 H, ^4J = 2.2 Hz, ArH), 4.45 (d, 2 H, ^2J = 13.8 Hz, $ArCH_2Ar$), 4.37 (d, 2 H, ^2J = 13.7 Hz, $ArCH_2Ar$), 4.25 (d, 1 H, ^2J = 13.9 Hz, $ArCH_2Ar$), 4.18-3.97 (m, 16 H, O-CH_2CH_2-O), 3.40 (d, 1 H, ^2J = 13.8 Hz, $ArCH_2Ar$), 3.384 (d, 2 H, ^2J = 13.8 Hz, $ArCH_2Ar$), 3.38 (d, 2 H, ^2J = 13.9 Hz, $ArCH_2Ar$), 1.33 (s, 9 H, $C(CH_3)_3$), 1.26 (s, 18 H, $C(CH_3)_3$), 1.09 (s, 18 H, $C(CH_3)_3$);

^{13}C NMR (100.6 MHz) δ 150.6 (Ar-C 35), 149.9 (Ar-C 33,32), 149.3 (Ar-C 31,34), 147.2 (Ar-C 11,29), 142.3 (Ar-C 17,23), 141.3 (Ar-C 5), 132.1 (Ar-C 1,9,13,27), 126.9, 126.2 (Ar-C 3,7,15,19,21,25), 126.15, 126.08 (Ar-C 10,12,28,30), 125.9, 125.2 (Ar-C 4,6,16,18,22,24), 75.6 (Ar-O-CH_2), 72.0 (Ar-O-$(CH_2)_2$-O-CH_2), 70.9 (Ar-O-$(CH_2)_2$-OCH_2-CH_2), 69.9 (Ar-O-CH_2CH_2), 34.2, 33.8 (CH_2 2,8,14,20,26), 31.7 ($C(CH_3)_3$), 31.6, 31.2 ($C(CH_3)_3$), 30.2, 29.8 ($C(CH_3)_3$).

1,3-Calix[5]crown-6 (1b): yield 72%; mp. 138-140°C; MS-FD, *m/z* 1013.6 (M^+, calc. 1012.6).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (br s, 2 H, OH), 7.20 (s, 2 H, ArH and pseudo s, 2 H, ArH), 7.16 (d, 2 H, ^4J = 2.4 Hz, ArH), 7.03 (d, 2 H, ^4J = 2.2 Hz, ArH), 7.01 (d, 2 H, ^4J = 2.3 Hz, ArH), 6.88 (br s, 1 H, OH), 4.44 (d, 2 H, ^2J = 13.9 Hz, $ArCH_2Ar$), 4.42 (d, 2 H, ^2J = 13.9 Hz, $ArCH_2Ar$), 4.24 (d, 1 H, ^2J = 13.9 Hz, $ArCH_2Ar$), 4.16 (br s, 6 H, O-CH_2CH_2-O), 4.02-3.77 (m, 14 H, O-CH_2CH_2-O), 3.41 (d, 1 H, ^2J = 13.9 Hz, $ArCH_2Ar$), 3.38 (d, 2 H, ^2J = 13.9 Hz, $ArCH_2Ar$), 3.37 (d, 2 H, ^2J = 14.4 Hz, $ArCH_2Ar$), 1.33 (s, 9 H, $C(CH_3)_3$), 1.26 (s, 18 H, $C(CH_3)_3$), 1.00 (s, 18 H, $C(CH_3)_3$);

^{13}C NMR (100.6 MHz) δ 150.4 (Ar-C 35), 150.1 (Ar-C 33,32), 149.3 (Ar-C 31,34), 147.0 (Ar-C 11,29), 142.4 (Ar-C 17,23), 141.4 (Ar-C 5), 132.2, 132.1 (Ar-C 1,9,13,27), 126.9, 126.5, 126.4 (Ar-C 3,7,15,19,21,25), 126.1 (Ar-C 10,12,28,30), 125.8, 125.6, 125.0 (Ar-C 4,6,16,18,22,24), 75.0 (Ar-O-CH_2), 71.6, 71.2 (Ar-O-$(CH_2)_2$O-$(CH_2)_2$-OCH_2), 70.3 (Ar-O-CH_2CH_2), 34.1, 33.83 (CH_2 2,8,14,26), 33.86 (CH_2 20), 31.7 ($C(CH_3)_3$), 31.6, 31.1 ($C(CH_3)_3$), 30.3, 30.0 ($C(CH_3)_3$).

1,3-Calix[5]crown-7 (1c): yield 51%; mp. 120-121.5°C; MS-FD, *m/z* 1058.3 (M^+, calc. 1056.7).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 2 H, OH), 7.20 (s, 2 H, ArH), 7.19 (d, 2 H, ^4J = 3.3 Hz, ArH), 7.15 (d, 2 H, ^4J = 2.4 Hz, ArH), 6.99-6.97 (m, 4 H, ArH), 6.70 (s, 1 H, OH), 4.46 (d, 2 H, ^2J = 14.0 Hz, $ArCH_2Ar$), 4.38 (d, 2 H, ^2J = 14.0 Hz, $ArCH_2Ar$), 4.23 (d, 1 H, ^2J = 14.0 Hz, $ArCH_2Ar$), 4.23-4.14 (m, 4 H, O-CH_2CH_2-O), 4.08-4.06 (m, 4 H, O-CH_2CH_2-O), 3.96-3.80 (m, 8 H, O-CH_2CH_2-O), 3.78-3.72 (m, 4 H, O-CH_2CH_2-O), 3.70-3.66 (m, 4 H, O-CH_2-CH_2-O), 3.40 (d, 1 H, ^2J = 13.9 Hz, $ArCH_2Ar$), 3.39 (d, 2 H, ^2J = 14.1 Hz, $ArCH_2Ar$), 3.37 (d, 2 H, ^2J = 14.1 Hz, $ArCH_2Ar$), 1.33 (s, 9 H, $C(CH_3)_3$), 1.27 (s, 18 H, $C(CH_3)_3$), .0.96 (s, 18 H, $C(CH_3)_3$);

^{13}C NMR (100.6 MHz) δ 150.32 (Ar-C 35), 150.27 (Ar-C 33,32), 149.2 (Ar-C 31,34), 147.0 (Ar-C 11,29), 142.4 (Ar-C 17,23), 141.6 (Ar-C 5), 132.4, 132.3 (Ar-C 1,9,13,27), 127.0, 126.7, 126.4 (Ar-C 3,7,15,19,21,25), 126.1, 126.0

(Ar-C 10,12,28,30), 125.7, 125.5, 124.9 (Ar-C 4,6,16,18,22,24), 74.6 (Ar-O-CH_2), 71.3, 71.1 (Ar-O(CH_2)$_2$-O(CH_2)$_2$), 70.8, 70.6 (Ar-O(CH_2)$_2$-O(CH_2)$_2$-O(CH_2)$_2$), 70.3 (Ar-O-CH_2CH_2), 34.0, 33.8 (CH_2 2,8,14,26), 33.9 (CH_2 20), 31.7 (C(CH_3)$_3$), 31.6, 31.1 (C(CH_3)$_3$), 30.4, 30.1 ($C(CH_3)_3$).

1,2-Calix[5]crown-7 (2c): yield 20%; mp. 244-245°C; MS-FD, *m/z* 1057.5 (M^+, calc. 1056.7).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1 H, OH), 7.70 (s, 2 H, OH), 7.16 (d, 2 H, ^4J = 2.4 Hz, ArH), 7.10 (s, 2 H, ArH), 7.06 (d, 2 H, ^4J = 2.4 Hz, ArH), 6.71 (s, 4 H, ArH), 4.61 (d, 1 H, ^2J = 15.1 Hz, $ArCH_2Ar$), 4.33 (d, 2 H, ^2J = 14.5 Hz, $ArCH_2Ar$), 4.24-4.21 (m, 2 H, O-CH_2-CH_2-O), 4.11 (d, 2 H, ^2J = 14.0 Hz, $ArCH_2Ar$), 3.98-3.57 (m, 22 H, O-CH_2-CH_2-O), 3.43 (d, 1 H, ^2J = 15.4 Hz, $ArCH_2Ar$), 3.42 (d, 2 H, ^2J = 14.0 Hz, $ArCH_2Ar$), 3.34 (d, 2 H, ^2J = 14.6 Hz, $ArCH_2Ar$), 1.26 (s, 18 H, C(CH_3)$_3$), 1.21 (s, 9 H, C(CH_3)$_3$), 0.82 (s, 18 H, C(CH_3)$_3$);

^{13}C NMR (100.6 MHz) δ 152.0 (Ar-C 34,32), 148.8 (Ar-C 31,35), 147.8 (Ar-C 33), 146.1 (Ar-C 5,29), 143.0 (Ar-C 17), 142.5 (Ar-C 11,23), 133.5, 133.2 (Ar-C 1,3,7,27), 127.1, 126.6 (Ar-C 9,13,15,19,21,25), 126.2, 125.5 (Ar-C 4,30 / 6,28), 125.4, 125.2, 124.6 (Ar-C 10,24 / 12,22 / 16,18), 72.7 (Ar-O-CH_2), 71.2, 71.0 (Ar-O(CH_2)$_2$-O(CH_2)$_2$), 70.8, 70.7 (Ar-O(CH_2)$_2$-O(CH_2)$_2$-O(CH_2)$_2$), 70.6 (Ar-O-CH_2CH_2), 33.85, 33.78, 31.74 (CH_2 2,8,14,20,26), 31.7 ($C(CH_3)_3$), 31.6, 31.0 (C(CH_3)$_3$), 31.4 (C(CH_3)$_3$), 30.8 ($C(CH_3)_3$).

Trimethyl ether 3a: A mixture of crown ether **1a** (0.2 mmol) and NaH (5 mmol) in THF (10 ml) was stirred for 30 min at room temperature. Then MeI (12 mmol) was added. After 9 h at room temperature, the reaction mixture was poured in 0.5 n HCl (40 ml), followed by extraction with $CHCl_3$. It was worked up as usual and purified by flash chromatography (diethyl ether); yield 89%; mp. 225°C; MS-FD, *m/z* 1011.8 (M^+, calc. 1011.4).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, 2H, ^4J = 1.9 Hz, ArH), 7.05 (s, 2 H, ArH), 7.04 (d, 2 H, ^4J = 1.9 Hz, ArH), 6.93 (d, 2 H, ^4J = 1.9 Hz, ArH), 6.76 (d, 2 H, ^4J = 1.9 Hz, ArH), 4.52 (d, 2 H, ^2J = 13.7 Hz, $ArCH_2Ar$), 4.36 (d, 2 H, ^2J = 14.0 Hz, $ArCH_2Ar$), 3.92 (d, 1 H, ^2J = 14.8 Hz, $ArCH_2Ar$), 4.09-3.54 (m, 16 H, O-(CH_2CH_2)-O), 3.65 (d, 1 H, ^2J = 14.8 Hz, $ArCH_2Ar$), 3.37 (d, 2 H, ^2J = 14.0 Hz, $ArCH_2Ar$), 3.29 (d, 2 H, ^2J = 13.9 Hz, $ArCH_2Ar$), 3.02 (s, 3 H, OCH_3), 2.89 (s, 6 H, OCH_3), 1.24 (s, 9 H, C(CH_3)$_3$), 1.23 (s, 18 H, C(CH_3)$_3$), 1.17 (s, 18 H, C(CH_3)$_3$).

Trimethyl ether 3b: Crown ether **1b** (0.2 mmol) was treated as described for **1a**, except using different amounts of NaH (8 mmol) and MeI (1 mmol); yield 65%; mp. 217°C; MS-FD, *m/z* 1056.8 (M^+, calc. 1055.4).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, 2 H, ^4J = 2.4 Hz, ArH), 7.14 (s, 2 H, ArH), 7.11 (d, 2 H, ^4J = 2.4 Hz, ArH), 7.01 (d, 2 H, ^4J = 2.4 Hz, ArH), 6.75 (d, 2 H, ^4J = 2.2 Hz, ArH), 4.55 (d, 2 H, ^2J = 14.3 Hz, $ArCH_2Ar$), 4.05 (d, 1 H, ^2J = 14.8 Hz, $ArCH_2Ar$), 3.97 (d, 2 H, ^2J = 13.7 Hz, $ArCH_2Ar$), 3.82-3.42 (m, 20 H, O-CH_2-CH_2-O), 3.47 (d, 1 H, ^2J = 14.1 Hz, $ArCH_2Ar$), 3.45 (d, 2 H, ^2J = 13.9 Hz, $ArCH_2Ar$), 3.16 (d, 2 H, ^2J = 14.4 Hz, $ArCH_2Ar$), 2.86 (s, 6 H, OCH_3), 1.99 (s, 3 H, OCH_3), 1.34 (s, 9 H, C(CH_3)$_3$), 1.28 (s, 18 H, C(CH_3)$_3$), 1.00 (s, 18 H, C(CH_3)$_3$).

Triester 4a: To a solution of crown ether **1a** (150 mg, 0.15 mmol) in CH_3CN (35 ml) was added Cs_2CO_3 (147 mg, 0.45 mmol). The mixture was refluxed for 30-40 min. Then a solution of ethyl bromoacetate (150 mg, 0.9 mmol) in CH_3CN (25 ml) was added within 2.5 h. The reaction mixture was refluxed for another 4 h and worked up as usual. Purification was performed by flash chromatography ($CHCl_3$/ethanol = 5/1); yield 31%; mp. 116-117°C; MS-FD, *m/z* 1226.9 (M^+, calc. 1226.7).

^{1}H NMR (400 MHz) δ 7.29 (d, 2 H, ^4J = 2.3 Hz, ArH), 7.09 (d, 2 H, ^4J = 2.2 Hz, ArH), 7.02 (s, 2 H, ArH), 6.67 (br s, 2 H, ArH), 6.40 (br s, 2 H, ArH), 4.73 (d, 2 H, ^2J = 16.0 Hz, O-CH_2-CO), 4.64 (s, 2 H, O-CH_2-CO), 4.51 (d, 2 H, ^2J = 13.7 Hz, $ArCH_2Ar$), 4.40 (d, 2 H, ^2J = 14.2 Hz, $ArCH_2Ar$), 4.39 (d, 1 H, ^2J = 12.6 Hz, $ArCH_2Ar$), 4.34 (q, 4 H, ^3J = 7.1 Hz, CH_2CH_3), 4.29 (d, 2 H, ^2J = 15.8 Hz, O-CH_2-CO), 4.16 (q, 2 H, ^3J = 7.1 Hz, CH_2CH_3), 4.07-3.97 (m, 6 H, O-(CH_2)$_2$-O), 3.90-3.81 (m, 6 H, O-(CH_2)$_2$-O), 3.78-3.70 (m, 6 H, O-(CH_2)$_2$-O), 3.40 (d, 3 H, ^2J = 13.9 Hz, $ArCH_2Ar$), 3.30 (d, 2 H, ^2J = 14.3 Hz, $ArCH_2Ar$), 1.35 (t, 6 H, ^3J = 7.1 Hz, CH_2CH_3), 2.25 (s, 18 H, C(CH_3)$_3$), 1.24 (t,

3 H, ^3J = 7.1 Hz, CH_2CH_3), 1.07 (s, 9 H, $C(CH_3)_3$), 0.72 (s, 18 H, $C(CH_3)_3$);

^{13}C NMR (100.6 MHz) δ 169.9 (C=O), 169.5 (C=O), 153.0 (Ar-C 35), 151.7, 151.6 (Ar-C 31,34 / 33,32), 147.2, 146.5 (Ar-C 11,29 / 17,23), 145.9 (Ar-C 5), 133.4, 133.3 (Ar-C 1,9 / 13,27), 132.8, 132.4, 131.4 (Ar-C 3,7 / 15,25 / 21,25), 127.1, 126.4 (Ar-C 10,30 / 12,28), 125.8 (Ar-C 16,18,22,24), 125.2 (Ar-C 4,6), 73.3 (O-CH_2-CO), 72.6 (O-CH_2-CO), 71.0 (Ar-O-CH_2), 70.8 (Ar-O$(CH_2)_2$-OCH_2-CH_2), 69.9 (Ar-O$(CH_2)_2$-OCH_2), 69.7 (Ar-O-CH_2CH_2), 61.9 (OCH_2CH_3), 61.1 (OCH_2CH_3), 34.3, 34.0 (CH_2 2,8,14,26), 34.2 (CH_2 20), 31.5 ($C(CH_3)_3$), 31.3 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 29.5, 28.3 ($C(CH_3)_3$), 14.3 (CH_2CH_3).

Acknowledgement: These studies were supported by the Deutsche Forschungsgemeinschaft and the European Community. We are grateful to Prof. C. D. Gutsche, who kindly provided us with an improved procedure for the preparation of *p-tert*-butylcalix[5]arene prior to publication[11b] and to Prof. M. A. McKervey for sending us a first sample of this compound.

REFERENCES AND NOTES

1) Alfieri, C.; Dradi, E.; Pochini, A.; Ungaro, R.; Andreetti, G. D. *J. Chem. Soc., Chem. Commun.* **1983**, 1075-1076.
2) Ungaro, R.; Pochini, A.; Andreetti, G. D. *J. Incl. Phenom.* **1984**, *2*, 199-206.
3) The barium complex of calix[4]crown-5 was recently shown to catalyze transacylation reactions: R. Cacciapaglia, Casnati, A.; Mandolini, L.; Ungaro, R. *J. Am. Chem. Soc.* **1992**, *114*, 10956-58.
4) Ghidini, E.; Ugozzoli, F.; Ungaro, R.; Harkema, S.; El-Fadl, A. A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1990**, *112*, 6979-6985.
5) Dijkstra, P. J.; Brunink, J. A. J.; Bugge, K.-E.; Reinhoudt, D. N.; Harkema, S.; Ungaro, R.; Ugozzoli, F.; Ghidini, E. *J. Am. Chem. Soc.* **1989**, *111*, 7567-7575.
6) a) Asfari, Z.; Abidi, R.; Arnaud, F.; Vicens, J. *J. Incl. Phenom. Mol. Recog. Chem.* **1992**, *13*, 163-169.
b) Asfari, Z.; Weiss, J.; Vicens, J. *Pol. J. Chem.* **1992**, *66*, 709-711.
7) Arduini, A.; Casnati, A.; Dodi, L.; Pochini, A.; Ungaro, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1597-1598.
8) a) Casnati, A.; Minari, P.; Pochini, A.; Ungaro, R. *J. Chem. Soc., Chem. Commun.* **1991**, 1413-1414.
b) Rogers, J. S.; Gutsche, C. D. *J. Org. Chem.* **1992**, *57*, 3152-3159.
c) Kanamathareddy, S.; Gutsche, C. D. *J. Org. Chem.* **1992**, *57*, 3160-3166.
d) Neri, P.; Foti, M.; Ferguson, G.; Gallagher, J. F.; Kaitner, B.; Pons, M.; Molins, M. A.; Giunta, L.; Pappalardo, S. *J. Am. Chem. Soc.* **1992**, *114*, 7814-7821.
e) Moran, J. K.; Roundhill, D. M. *Inorg. Chem.* **1992**, *31*, 4213-4215.
9) Ungaro, R.; Pochini, A. private communication.
10) Various penta-O-alkylated derivatives in the cone-conformation have been synthesized recently, McKervey, M. A. private communication.
11) a) Ninagawa, A.; Matsuda, H. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 65-67.
b) Stewart, D. R.; Gutsche, C. D. *Org. Prep. Proced. Int.*, in press.
12) Czech, B. P.; Czech, A.; Bartsch, R. A. *J. Heterocyclic Chem.* **1985**, *22*, 1297-1300.
13) Armstrong, D. W.; Ward, T. J.; Czech, A.; Czech, B. P.; Bartsch, R. A. *J. Org. Chem.* **1985**, *50*, 5556-5559.
14) Kraft, D.; Cacciapaglia, R.; Böhmer, V.; El-Fadl, A. A.; Harkema, S.; Mandolini, L.; Reinhoudt, D. N.; Verboom, W.; Vogt, W. *J. Org. Chem.* **1992**, *57*, 826-834.
15) The prefix *syn* and *anti* describes the situation of the O-alkyl groups with respect to the polyether chain.
16) Arnaud, F.; Schwing, M.-J.; Fanni, S. unpublished results.