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## SYNTHESIS OF ESTER GROUP—CONTAINING p-tert-BUTYLCALIXCROWNS

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Abstract: A series of ester group — containing calixcrowns 3a-e has been prepared by the reaction of p-tert-butyl-calixarenes 1a, b with an appropriate oligoethylene glycol bischloroacetate. An improved procedure for the synthesis of p-tert-butylcalix[4]crown-5 4 was developed.

Calixarenes are becoming an important class of compounds in supramolecular chemistry <sup>1, 2</sup>. In particular, p-tert-butylcalix [4] arene **1a**, which is easily accessible in large quantities<sup>3</sup>, is a very convenient substructure for the synthesis of molecular or cation receptors and carriers. Unfunctionalized p-tert-butylcalix [4] arene has very little ionophoric activity for alkali metal cations, but its tetraesters or tetraketones exhibit high affinity for alkali metal cations and high selectivity for Na<sup>+</sup>.<sup>4</sup> It was found that the ester groups play an important role in the complex formation<sup>5</sup>. On the other hand, the calixcrowns—1, 3-bridged calix [4] arenes via polyoxyethylene on the lower rim—are novel macrobicylic compounds (possess both hy-

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drophilic and lipophilic cavities), and can form complexes with alkali metal cations selectively<sup>6, 7, 8</sup>. Thus, it is attractive to study the ester group—containing calixcrowns. When the polyoxyethylene bridge is long enough, as in **3d**, it may be possible that the ester carbonyl groups point into the crown cavity and complex with cations.



The synthesis of 1,3-dihydroxy-p-tert-butylcalixcrowns has generally been achieved from the reactions of p-tert-butylcalix[4]arene with oligoethylene glycol ditosylates using KOBu<sup>t</sup> as the base<sup>6, 8</sup>. The yields of the calixcrowns depended on the addition rate of KOBu<sup>t</sup> and the ditosylates<sup>8</sup>. Recently, we have developed an improved procedure using K<sub>2</sub>CO<sub>3</sub> as the base. p-t-Butylcalix[4]crown-5 **4** has been obtained in 70% yield by refluxing a mixture of p-tert-butylcalix[4]arene **1a**, tetraethylene glycol ditosylate and K<sub>2</sub>CO<sub>3</sub> in benzene for 24 hours. Using K<sub>2</sub>CO<sub>3</sub> instead of KOBu<sup>t</sup>

#### CALIXARENES

as the base, the procedure was simplified (don't need slow addition), and the yield of **4** was improved from  $53\%^{8}$  to 70%. Furthermore, K<sub>2</sub>CO<sub>3</sub> is cheaper and can be treated more conveniently than KOBu<sup>1</sup>.

Recently, we have designed and prepared a series of ester group—containing calixcrowns 3a-e. Calixcrowns 3a-e were obtained in reasonable yields (3a, 27%; 3b, 37%; 3c, 40%; 3d, 49%; 3e, 14%) by the cyclocondensation of the corresponding calixarene 1 and oligoethylene glycol bischloroacetate 2 using K<sub>2</sub>CO<sub>3</sub> as the base and KI as the catalyst. These reactions were completed in refluxing benzene within 2-3 days. However, no calixcrown 3b could be detected by TLC analysis when the reaction of 1a with 2b had been carried on for 1 day in the absence of KI. Using toluene or acetonitrile as the solvent in the place of benzene, the reaction time was reduced, but the yield of calixcrown 3b was much poorer.

The structures of the ester group—containing calixcrowns **3a-e** were identified by mass spectra, <sup>1</sup>H NMR spectra, IR spectra and elemental analyses. The <sup>1</sup>H NMR spectra of all these calixcrowns show a typical AB pattern (J = 13 - 14 Hz) for the methylene bridge protons, indicating that **3a-e** are 1, 3-bridged and exist in the cone conformation<sup>9</sup>.

#### **EXPERIMENTAL**

Melting points are uncorrected. <sup>1</sup>H NMR spectra were recorded on a EM 360L instrument in CDCl<sub>3</sub> with TMS as internal standard. Mass spectra were obtained using a KRATOS ZAB HF-HF spectrometer. Elemental analyses were carried out on a MOD 1106 autoanalyzer. IR spectra were recorded on a Nicolet 170 SX FT-IR instrument. All chemicals were reagent grade and used without further purification. Compounds **1a<sup>3</sup>**, **1b<sup>10</sup>** were prepared according to the literature. Compounds **2a-d** were prepared by heating the mixture of the corresponding polyethylene glycol and slightly excessive chloroacetyl chloride in nearly quantitative yields<sup>11</sup>.

5,11,17,23-Tetra-tert-buty1-25,27-dihydroxy-26,28-(3', 6'-dioxa-2',7'-dioxooctylene)dioxy-calix [4] arene(3a).

A mixture of **1a**-toluene (1.75g, 2.36 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (0.75g, 5.4 mmol), glycol bischloroacetate **2a** (0.54g, 2.5 mmol) and KI (0.7g, 4 mmol) in 200 ml of benzene was refluxed for 2.5 days. After the suspension was cooled to room temperature and filtered, the filtrate was evaporated under reduced pressure. The residue was submitted to column chromatography (silica gel, 200—300 mesh, CH<sub>2</sub>Cl<sub>2</sub>—Et<sub>2</sub>O=10 : 1 v/v) to give **3a**. Recrystallization from petroleum ether (60—90°C) afforded 0.50g (0.63 mmol) of **3a** as white powder in 27% yield. mp 209 -212°C; MS (EI), m/e 791 ((M+1)<sup>+</sup>, 10%); IR (KBr), 3408 (OH), 1751 (OCO) cm<sup>-1</sup>; <sup>1</sup>H NMR (60MHz),  $\delta$ 7.20 (s, 2H, OH), 7.07 (s, 4H, ArH), 6.85 (s, 4H, ArH), 4.72 (s, wide, 8H, OCH<sub>2</sub>), 4. 40 (d, J=13Hz, 4H, ArCH<sub>2</sub>Ar, H<sub>ax</sub>), 3. 25 (d, J=13Hz, 4H, ArCH<sub>2</sub>Ar, H<sub>eq</sub>), 1.18 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.87 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd. for C<sub>50</sub> H<sub>62</sub>O<sub>8</sub>: C 75.92; H 7.90. Found: C 75.53; H 7.98.

## 5,11,17,23 — Tetra-tert-buty 1-25,27-dihydroxy-26,28-(2',10'-dioxo-3',6',9'-trioxaundecylene)dioxy-calix[4]arene (3b).

As described for **3a**, 1.80g (2.16 mmol) of **3b** was obtained from 4.30g (5.80 mmol) of **1a**-toluene, 1.55g (5.99 mmol) of **2b** and 1.75 g (12.7 mmol) of K<sub>2</sub>CO<sub>3</sub> in 280 ml of benzene in the presence of KI (1.0 g). The reaction time was 30 hours. **3b**: yield 37%; mp 237-240°C; MS (FAB), m/e 834 (M<sup>+</sup>, 28%); IR (KBr), 3456 (OH), 1740 (OCO) cm<sup>-1</sup>; <sup>1</sup>H NMR,  $\delta7$ .11 (s, 4H , ArH), 6.97 (s, 2H, OH), 6.87 (s, 4H, ArH), 4.27 (s, 4H, OCH<sub>2</sub>CO), 4.57 – 3.80 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>O and ArCH<sub>2</sub>Ar, H<sub>ax</sub>), 3.25 (d, J=13 Hz, 4H, ArCH<sub>2</sub>Ar, H<sub>eq</sub>), 1.18 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.88 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd. for C<sub>52</sub>H<sub>66</sub>O<sub>9</sub>; C 74.79; H 7.97. Found; C 74.35; H 8.06. 5, 11, 17, 23-Tetra-tert-buty1-25, 27- dihydroxy- 26, 28- (2', 13'dioxo-3', 6', 9', 12'-tetraoxatetradecylene)dioxy-calix[4]arene (3c).

As described for **3a**, 0.93g (1.1 mmol) fine crystals of **3c** were obtained from 1.98g (2.67 mmol) of **1a**-toluene, 0.87g (2.9 mmol) of **2c** and 0.86g (6.2 mmol) of  $K_2CO_3$  in 200 ml of benzene in the presence of KI (0.8g). The reaction time was 48 hrs. **3c**: yield 40%; mp 205–208°C; MS (EI), m/e 879 ((M + 1)<sup>+</sup>, 100%); IR (KBr), 3456 (OH), 1741 (OCO) cm<sup>-1</sup>; <sup>1</sup>H NMR, 7.22(s, 2H, OH), 7.04 (s, 4H, ArH), 6.92 (s, 4H, ArH), 4.79 (s, 4H, OCH<sub>2</sub>CO), 4.63–3.73(m, 16H, OCH<sub>2</sub>CH<sub>2</sub>O and ArCH<sub>2</sub>Ar, H<sub>ax</sub>), 3. 27 (d, J = 14Hz, 4H, ArCH<sub>2</sub>Ar, H<sub>eq</sub>), 1.15 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.95 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd. for C<sub>54</sub>H<sub>70</sub>O<sub>10</sub>: C 73.78; H 8.03. Found: C 73.80; H 8.19.

## 5,11,17,23-Tetra-tert-buty1-25,27-dihydroxy-26,28-(2',16'-dioxo-3',6',9',12',15'-pentaoxaheptadecylene)dioxy-calix[4]arene (3d).

As described for 3a, 1.03g (1.12 mmol) of 3d was obtained from 1.68g (2.27 mmol) of 1a-toluene, 0.83g (2.4 mmol) of 2d and 0.73g (5.3 mmol) of  $K_2CO_3$  in 200 ml of benzene in the presence of KI (0.8g).

The reaction time was 48 hrs. **3d**: yield 49%; mp 191-193°C; MS (EI), m/e 923 ((M+1)<sup>+</sup>, 100%); IR (KBr), 3456 (OH), 1746 (OCO) cm<sup>-1</sup>; <sup>1</sup>H NMR, 7. 12 (s, 4H, ArH), 7. 03 (s, 2H, OH), 6. 91 (s, 4H, ArH), 4. 77 (s, 4H, OCH<sub>2</sub>CO), 4. 60-3. 67 (m, 20H, OCH<sub>2</sub>CH<sub>2</sub>O, and ArCH<sub>2</sub>Ar, H<sub>ax</sub>), 3. 26 (d, J=14Hz, 4H, ArCH<sub>2</sub>Ar, H<sub>eq</sub>), 1. 18 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0. 89 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd. for C<sub>56</sub>H<sub>74</sub>O<sub>11</sub>: C 72. 86; H 8. 08. Found: C 73. 26; H 8. 17.

5,11,17,23-Tetra-tert-buty1-25, 27-bis (ethoxycarbonylmethoxy)-26, 28-(2', 16'-dioxo-3', 6', 9', 12', 15'-pentaoxaheptadecylene) dioxy-calix [4]arene (3e).

A mixture of 1b (0.81g, 1.0 mmol), 2d (0.36g, 1.0 mmol), anhydrous  $K_2CO_3(0.35g, 2.5 \text{ mmol})$  and KI (0.2g) in 70 ml of benzene was refluxed for 48 hrs. After the suspension was cooled and filtered, the filtrate was evaporated under reduced presure. The residue was submitted to chromatography (silica gel,  $CH_2Cl_2 - Et_20 = 1 : 1 v/v$ ) to give 3e. Recrystallization from acetonitrile afforded 0. 15g (0. 14 mmol) of 3e as colorless crystals. yield, 14%; mp 133 - 135°C; MS (FAB), m/e 1095  $((M+1)^+, 23\%)$ ; IR (KBr), 1760 (OCO) cm<sup>-1</sup>; <sup>1</sup>H NMR, 7. 17 (s, 4H, ArH), 6. 55 (s, 4H, ArH), 5. 15 (s, 6H, ArCH<sub>2</sub>CO), 4. 88 (s, 2H, ArCH<sub>2</sub>CO), 4. 55-4. 13 (m, 12H, COOCH<sub>2</sub> and ArCH<sub>2</sub>Ar, H<sub>ax</sub>), 3. 86 - 3. 55 (m, 12H, CH<sub>2</sub>OCH<sub>2</sub>), 3. 12 (d, J = 14Hz, ArCH<sub>2</sub>Ar, H<sub>eq</sub>), 1. 42-1. 18 (m, 24H, C(CH<sub>3</sub>)<sub>3</sub> and OCH<sub>2</sub>CH<sub>3</sub>), 0. 77 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd. for C<sub>64</sub>H<sub>86</sub>O<sub>15</sub>; C 70. 17; H 7. 91. Found: C 69. 70; H 7. 78.

# 5,11,17, 23-Tetra-tert-buty1-25,27-dihydroxy-26,28-(3',6',9')-triox-aundecylene)dioxy-calix[4]arene (4).

A mixture of **la**-toluene (7. 4g, 10 mmol), tetraethylene glycol ditosylate (5. 0g, 10 mmol) and  $K_2CO_3$  (3. 9g, 28 mmol) in 350 ml of benzene was refluxed for 24 hrs. Then, it was treated by the same procedure used for **3e**. 5. 6g Needles of **4** (7. 0 mmol) were obtained in 70% yield. mp 241-243°C (lit. <sup>8</sup>246 - 248°C); <sup>1</sup>H NMR (CCl<sub>4</sub>), 7. 57 (s, 2H, OH), 6. 96 (s, 4H, ArH), 6. 87 (s, 4H, ArH), 4. 33 (d, J=13Hz, 4H, ArCH<sub>2</sub>Ar, H<sub>ax</sub>), 4. 00 (s, wide, 8H, CH<sub>2</sub>CH<sub>2</sub>O), 3. 74 (s, wide, 8H, OCH<sub>2</sub>CH<sub>2</sub>O), 3. 15 (d, J=13Hz, 4H, ArCH<sub>2</sub>Ar, H<sub>eq</sub>), 1. 13 and 0. 93 (s, 18H each, C(CH<sub>3</sub>)<sub>3</sub>).

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