Monocyanomethylated thiacalix[4]arenes: synthesis and lower rim modification

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Dedicated to Prof. I. Beletskaya on the occasion of her 75th birthday

Abstract

The selective monocyanomethylation of *p*-R-thiacalix[4]arenes (R = H, *tert*-Bu) with chloroacetonitrile in the presence of Na_2CO_3 in DMF is described. Monocyanomethylated *p-tert*-butylthiacalix[4]arene has been synthetically exploited in the Ritter reaction with 1-adamantanol for the transformation to the corresponding amide. A thiacalix[4]arene having mixed amide and ester functionalities at the lower rim was synthesized by alkylation of 25-*N*-(1-adamantyl)carbamoylmethoxy-*p-tert*-butylthiacalix[4]arene with ethyl bromoacetate.

Keywords: Thiacalix[4]arenes, *O*-monocyanomethylation, Ritter reaction, adamantylamides

Introduction

Tetrathiacalix[4]arenes[1] are novel widely developed members of the calixarene family in which the methylene bridges are replaced by sulfur atoms. The introduction of a heteroatom as a bridge provides an additional opportunity to tune the ring size, conformational and binding properties of a macrocycle. Since the starting *p*-R-thiacalix[4]arenes (**1**, R = *tert*-butyl, *tert*-octyl, 1-adamantyl or phenyl)[2-5] are accessible now in multi-gram scale, these macrocycles have sparked a great deal of interest as building blocks in the synthesis of more complicated systems.

The regioselective alkylation and acylation of the lower rim hydroxyls of the classical calix[4]arenes have become important synthetic tools for the construction of a great variety of synthetic receptors. Unfortunately, similar regioselective reactions cannot be performed on the thiacalix[4]arene platform to the same extent of efficacy. The lower apparent differences in the OH acidities[6] of the thiacalix[4]arenes as compared to the classical ones prevents the regio- and stereoselective partial *O*-alkylation and acylation of thiacalix[4]arenes . As a result, the relatively

easy formation of tetralkylated thiacalix[4]arenes[7] or thiacalix[4](bis)crown ethers[8] takes place simply in the presence of alkali metal carbonates.

With respect to partial *O*-alkylation of thiacalix[4]arenes, only a few 25,27-dialkoxy-thiacalix[4]arenes[9], distally bridged thiacalix[4](mono)crown ethers[8b,c] and several partially acylated derivatives[10] have been prepared although in only moderate yields. Recently expedient routes to 1,3- and 1,2-diethers *via* the Mitsunobu reaction,[11] or *via* proximal O,O'-disiloxane bridge intermediates[12] have been proposed to overcome the problems encountered in base-mediated alkylations. In this paper we report the first examples of the selective monoalkylation of thiacalix[4]arene and some chemical transformation of the monocyanomethylated thiacalix[4]arenes.

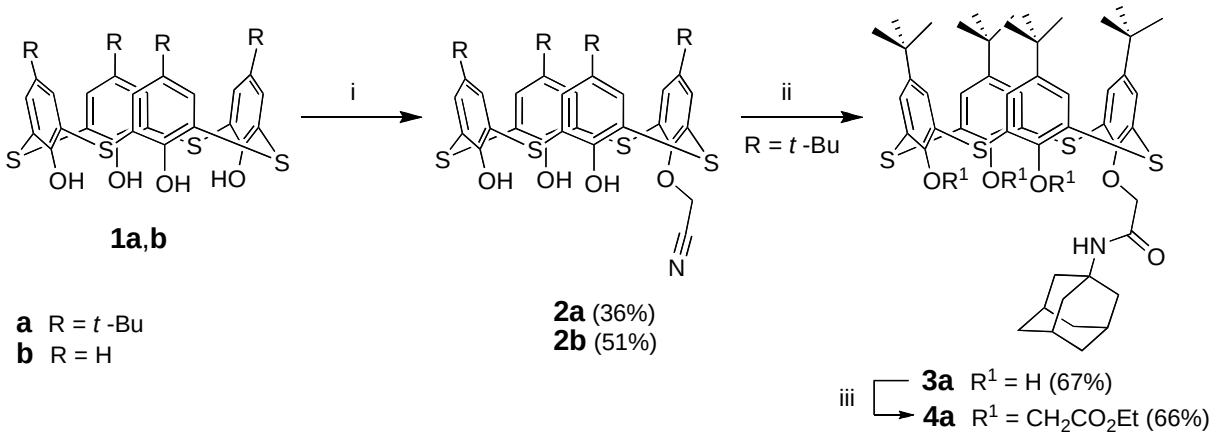
Results and Discussion

The products formed from the base-mediated alkylation of calixarenes are very sensitive to the choice of the reaction conditions. With this consideration in mind the reactions between *p*-R-thiacalix[4]arenes **1a** and **1b** (R = *tert*-Bu, H, respectively) and chloroacetonitrile was studied using the following different reaction conditions: (i) Method "**A**" = $ClCH_2CN/M_2CO_3$(M = Na, K)/NaI in refluxing acetone; (ii) method "**B**" = $ClCH_2CN/Cs_2CO_3$ in refluxing acetonitrile; and (iii) "**C**" = $ClCH_2CN/M_2CO_3$(M = Na, K)/NaI in DMF at 60 °C. When applied to the classical calix[4]arenes[13] method **A** produces distal dicyanomethoxy derivatives; procedure **B** has been proposed recently[14] for the synthesis of tetracyanomethoxy-*p*-H-calix[4]arene as a mixture of *cone* and *paco* conformers. In the case of thiacalix[4]arenes, it is known[15] that the alkylation of *p-tert*-butylthiacalix[4]arene **1a** with chloroacetonitrile conducted under the same conditions as used for the conventional calix[4]arene (**1a**/$ClCH_2CN/K_2CO_3$/NaI = 1:4:4:4) in acetone did not give the desired 1,3-dialkylated product but instead, formed a complex intractable mixture, and only the use of expensive Cs_2CO_3 (**1a**/$ClCH_2CN/Cs_2CO_3$/NaI = 1:3.5:1:3.5) in refluxing THF gave the 1,3- and 1,2-dialkylated products in 70 and <1% yields, respectively.

We found that reaction of *p*-(*tert*-butyl)thiacalix[4]arene **1a** using the modified reaction conditions **A** (**1a**/$ClCH_2CN/K_2CO_3$ or Na_2CO_3/NaI = 1:8:8:8) in refluxing acetone for up to 38 h afforded only a small amount of a mixture of cyanomethylated products, and mainly unreacted starting material (~90%). A similar reaction with **1b** (Na_2CO_3 as a base) proceeded faster with full conversion of parent thiacalix[4]arene, but led to a complex mixture of mono- and polyalkylated products. In this case, column chromatography afforded monocyanomethoxy-*p*-H-thiacalix[4]arene **2b** (~30%) and a mixture of regio- and conformational isomers of polycyanomethylated *p*-H-thiacalix[4]arenes (~40%). Under reaction conditions **B** (10 equiv. $ClCH_2CN$ and 10 equiv. Cs_2CO_3, 25 h) **1b** also underwent complete conversion into a mixture of cyanomethylated products, with lack of selectivity.

Unexpected results were obtained when procedure **C** was applied. It turned out that heating **1a** in DMF at 60 °C for 25 h in the presence of 10 equiv. $ClCH_2CN$, 10 equiv. Na_2CO_3 and 1

equiv. NaI formed the monocyanomethylated compound (~13%) only, and the 78% of starting material was recovered. The same result was obtained in the presence of K_2CO_3 as a base. By increasing of the molar ratio **1**/$ClCH_2CN$/Na_2CO_3/NaI up to 1:50:50:2 the yield of 25-cyanomethoxy-*p*-(*tert*-butyl)calix[4]arene **2a** was raised to 36%. Under these conditions polynitriles were not formed and only starting compound (53%) was recovered from the reaction. Using the same conditions, **1b** gave the desired mononitrile **2b** in high yield (~51%) accompanied with a small amount of polynitriles (~13%).



Scheme 1. (i) $ClCH_2CN$, Na_2CO_3, NaI, DMF, 60 °C; (ii) 1-adamantanol, CF_3CO_2H, $C_2H_4Cl_2$, 80 °C; (iii) $BrCH_2COOEt$, Na_2CO_3, acetone, reflux.

The structures of compounds prepared were proved by NMR measurements. The ^{1}H NMR spectrum of **2a** unambiguously reflected the ABBB ring symmetry of the monoalkylated thiacalix[4]arenes. The three singlets (1.28, 1.26 and 1.17 ppm in 2:1:1 ratio) for the *tert*-butyl groups, the one singlet (5.50 ppm) for the O*CH*$_2$CN group and splitting of the aromatic signals into two doublets (7.69 and 7.65 ppm with the typical *meta* coupling *J*=2.4 Hz) and two singlets (7.66 and 7.59 ppm) were all indicative for the monosubstituted structure of **2a**.

In contrast to thiacalix[4]arenes, *p*-(*tert*-butyl)calix[4]arene gave the 25,27-*syn*-dicyanomethoxy derivative in 62% yield using procedure **C**. The results obtained reconfirm the differences observed in the chemical behaviour of classical calix[4]arenes and their *thia*-analogues in their respective alkylation reactions. The monocyanomethylation of *p*-(*tert*-butyl)- and *p*-H-calix[4]arenes has been realized recently using an equimolar amounts of bromoacetonitrile and alkaline metal carbonates (1.0 equiv.)[16] or bis(tributyltin)oxide (0.5 equiv.)[17] as bases.

The success of the monoalkylation achieved enables the preparation of thiacalixarenes having mixed functionalities at the lower rim. This aim was successfully attained by using the Ritter reaction protocol for the transformation of nitriles to amides. Earlier we showed[18] that secondary and tertiary alcohols can be used as alkylation agents in the Ritter reaction in trifluoroacetic acid (TFA) for the lower-rim modification of 25,27-dicyanomethoxy-*p*-R-calix[4]arenes. It has now been found that heating 25-cyanomethoxy-*p*-(*tert*-butyl)-

thiacalix[4]arene **2a** with a twofold excess of 1-adamantanol in TFA-$C_2H_4Cl_2$ medium afforded 25-[*N*-(1-adamantyl)carbamoylmethoxythiacalix[4]arenes **3** in 67% yield.

^{1}H NMR spectra of monoamide **3** reflects practically the same splitting patterns for the aromatic and *tert*-butyl protons as were observed in the spectra of monocyanomethylated derivatives **2a**. In addition however, the broad signals of the adamantane protons in the 1.6-2.1 ppm region were clearly observed. The ^{13}C NMR spectra proved to be more informative for the identification of the adamantane fragment in this molecule since in accordance with the *mono*-substitution feature of the adamantane nucleus, four signals due to the adamantane fragment carbons were observed.

The synthesis of thiacalix[4]arene **4a** having mixed amide and ester functionalities at the lower rim was achieved by alkylation of 25-[*N*-(1-adamantyl)carbamoylmethoxythiacalix-[4]arenes **3a** with α-bromoethyl acetate (60 equiv.) in refluxing anhydrous acetone, in the presence of Na_2CO_3 (60 equiv.). The choice of sodium carbonate in preference to potassium carbonate was determined by the fact that sodium-containing compounds have been the usual bases used for the synthesis of cone conformers[7a,c] in thiacalixarene series. Although this reaction required a long refluxing period (40 h), the triester **4a** was isolated in good yield (66%) and with a complete stereoselectivity for the cone conformation, as was proved by ^{1}H and ^{13}C NMR analysis. The ^{1}H NMR spectrum of **4a** contained three signals due to the *tert*-butyl groups (1.14, 1.10, 1.06), four signals in the aromatic region consisting of two doublets (7.37 and 7.33 ppm) with a typical *meta*-coupling constant (J = 2.6 Hz) and two singlets (7.34 and 7.21 ppm). In the region for the -OCH_2CO- protons, two singlets for the -OCH_2CONHAd group and its counterpart, -OCH_2COOEt group, at 4.87 and 5.06 ppm respectively, were observed. The signals due to the methylene hydrogen atoms of the two remaining ester groups were split into two doublets at 5.29 and 5.09 ppm as a result of the H_A-H_B geminal interactions. The signals of the ethoxy group protons were evident as two sets of multiplets at 4.23 and 1.28 ppm.

In conclusion, we have demonstrated for the first time the selective mono-*O*-cyanomethylation of *p*-R-thiacalix[4]arenes (R = *tert*-Bu, H) with chloroacetonitrile using Na_2CO_3 as the base in the presence of NaI, in DMF, at 60 °C. Nitrile **2a** was converted into the corresponding amide **3a** in high yields by the Ritter reaction with adamantanol in trifluoroacetic acid, hence providing a simple access to a thiacalix[4]arene **4a** having mixed functionalities at the lower rim.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance 400 spectrometer with solvent signals as internal reference. Chemicals were commercial grade and were used without further purification. Preparative column chromatography was carried out on Kieselgel 40/60 (Merck), and TLC analysis was performed on DC Alufolien Kieselgel 60 F_{254}

plates (Merck) with UV development. Solvents were purified and dried according to standard procedures.

Synthesis of 25-cyanomethoxy-*p*-R-thiacalix[4]arenes 2. General procedure

A mixture of **1** (1 mmol), chloroacetonitrile (3.2 mL, 50 mmol), Na_2CO_3 (5.3 g, 50 mmol) and NaI (0.3 g, 2 mmol) in anhydrous DMF (40 mL) was stirred at 60 °C for 38 h. The solvent was removed under reduced pressure, and the residue was taken up in a chloroform/water mixture (1:1, 100 mL). After stirring for 1h the products were extracted with chloroform. The organic layers were combined, washed with water, dried over $MgSO_4$ and evaporated to dryness. The residue was treated with boiling ethanol followed by filtration of the starting material **1**. The filtrate was evaporated, the residue was purified by column chromatography on silica gel (hexane/ chloroform 1:1) to afford cyanomethylated derivatives **2**.

25-Cyanomethoxy-*p*-(*tert*-butyl)thiacalix[4]arene (2a). Colorless crystals (0.26 g, 36%); mp 193–195 °C. R_f = 0.4 ($CHCl_3$/EtOH = 10:1). ^{1}H NMR ($CDCl_3$): δ 9.18 (s, 1H, O*H*), 8.58 (s, 2H, O*H*), 7.69 (d, *J* = 2.4 Hz, 2H, Ar*H*), 7.65 (s, 2H, Ar*H*), 7.64 (d, *J* = 2.4 Hz, 2H, Ar*H*), 7.59 (s, 2H, Ar*H*), 5.50 (s, 2H, OCH_2), 1.28 [s, 18H, 2 C(CH_3)$_3$], 1.26 [s, 9H, [s, 9H, C(CH_3)$_3$], 1.17 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR ($CDCl_3$): δ 155.96, 155.73, 155.13, 150.11, 144.05, 143.87 (Ar*C*), 136.17, 135.92, 135.89, 135.67 (Ar*C*H), 128.19, 120.34, 120.18 (Ar*C*), 114.84 (OCH$_2$*C*N), 59.90 (O*C*H$_2$CN), 34.38, 34.05 [*C*(CH_3)$_3$], 31.17, 31.14, 30.79 [C(*C*H_3)$_3$]. Anal. calcd. for $C_{42}H_{49}NO_4S_4$ (760.12): C, 66.37 ; H, 6.50 %. Found: C, 66.06; H, 6.44 %.

25-Cyanomethoxy-*p*-*H*-thiacalix[4]arene (2b). White powder (0.27 g, 51%); mp 229–230°C; R_f = 0.35 ($CHCl_3$/EtOH = 10:1). ^{1}H NMR (DMSO-d_6): δ 7.51–7.45 (m, 4H, Ar*H*), 7.43 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.22 (d, *J* = 9.4 Hz, 2H, Ar*H*), 6.91 (t, *J* = 9.4 Hz, 1H, Ar*H*), 6.76 (t, *J* = 10.8 Hz, 2H, Ar*H*), 7.71 (d, *J* = 8.0 Hz, 2H, Ar*H*), 5.34 (s, 2H, OCH_2). ^{13}C NMR (DMSO-d_6): δ 158.01, 157.25, 156.36, (Ar*C*), 136.73, 136.10, 135.69, 133.85 (Ar*C*H), 130.37 (Ar*C*), 126.01 (Ar*C*H), 121.98, 121.89 (Ar*C*), 120.37, 120.23 (Ar*C*H), 116.65 (OCH$_2$*C*N), 56.09 (O*C*H$_2$CN). Anal. calcd. for $C_{26}H_{17}NO_4S_4$ (535.69): C, 58.30; H, 3.20 Found: C, 57.66; H, 3.09.

25-*N*-(1-Adamantyl)carbamoylmethoxy-*p*-(*tert*-butyl)thiacalix[4]arene (3a). A solution of **2a** (150 mg, 0.2 mmol), 1-adamantanol (60 mg, 0.4 mmol) in TFA/dichloroethane (1:1, 2 mL) was maintained at 60 °C for 8–20 h. On completion of the reaction, the solvents were removed at reduced pressure. The residue was triturated with ethanol, the solid product was filtered off and purified by column chromatography on silica gel (hexane/chloroform/ethanol) yielding colorless crystals 3a (120 mg, 67%); mp 284–286°C; R_f = 0.35 ($CHCl_3$/EtOH = 10:1). ^{1}H NMR ($CDCl_3$): δ 9.51 (s, 1H, OH), 9.10 (s, 2H, OH), 8.45 (s, 1H, CON*H*), 7.79 (d, *J* = 2.4 Hz, 2H, Ar*H*), 7.75 (s, 2H, Ar*H*), 7.71 (d*J* = 2.4 Hz, , 2H, Ar*H*), 7.69 (s, 2H, Ar*H*), 4.69 (s, 2H, OCH_2), 2.40 (m, 6H, AdCH_2), 2.24 (bs, 3H, AdC*H*),1.89–1.70 (m, 6H, AdCH_2), 1.33 [s, 18H, C(CH_3)$_3$], 1.32 [s, 9H, C(CH_3)$_3$], 1.26 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR ($CDCl_3$): δ 166.65 (*C*ONH), 157.12, 156.26, 155.69, 149.96, 144.42, 143.93 (Ar*C*), 136.86, 136.27, 136.02, 135.94 (Ar*C*H), 127.94, 120.59, 120.54, 119.52 (Ar*C*), 77.11 (O*C*H$_2$), 52.43 (AdC_1), 41.32 (Ad$C_{2,8,9}$), 36.35 (Ad$C_{4,6,10}$), 34.39, 34.15,

34.02 [*C*(CH_3)$_3$], 31.20, 31.11, 30.82 [C(*C*H_3)$_3$], 29.48 (Ad*C*$_{3,5,7}$). Anal. calcd. for $C_{52}H_{65}NO_5S_4$ (912.36): C, 68.46; H, 7.18. Found: C, 68.23; H, 7.03.

26,27,28-Tri(ethoxycarbonylmethoxy)-25-*N*-(1-adamantyl)carbamoylmethoxy-*p*-(*tert*-butyl)thiacalix[4]arene (4a). A mixture of **3a** (90 mg, 0.1 mmol), Na_2CO_3 (640 mg, 6 mmol) and ethyl bromoacetate (0.67 ml, 6 mmol) in dry acetone (10 mL) was refluxed under argon for 40 h. After cooling, the solid residue was removed by filtration and washed with dichloromethane. The organic solution was evaporated to dryness, the residue was washed with 0.2 N HCl and water, dried over P_2O_5 and purified by column chromatography on silica gel (hexane/chloroform/ethanol) to give **4a** (77 mg, 66%) as a colorless crystals, mp 152–155 °C. R_f = 0.35 ($CHCl_3$/EtOH 10:1). ^{1}H NMR ($CDCl_3$): δ 8.05 (s, 1H, CON*H*), 7.37 (d, *J* = 2.6 Hz, 2H, Ar*H*), 7.34 (s, 2H, Ar*H*), 7.33 (d, 2H, *J* = 2.6 Hz, 2H, Ar*H*), 7.21 (s, 2H, Ar*H*), 5.29 (d, *J* = 6.3 Hz, 2H,OC*H*$_2$COO), 5.09 (d, *J* = 6.3 Hz, 2H, OC*H*$_2$COO), 5.06 (s, 2H, OC*H*$_2$COO), 4.87 (s, 2H, OC*H*$_2$CONH), 4.23 (m, 6H, OC*H*$_2$CH$_3$), 2.19 (bs, 6H, AdC*H*$_2$), 2.09 (bs, 2H, AdC*H*), 1.77–1.66 (m, 6H, AdC*H*$_2$), 1.31–1.25 (m, 9H, OCH$_2$C*H*$_3$), 1.14 [s, 9H, C(CH$_3$)$_3$], 1.10 [s, 9H, C(CH$_3$)$_3$], 1.06 [s, 9H, C(CH$_3$)$_3$]. ^{13}C NMR ($CDCl_3$): δ 169.21 (*C*OO), 168.18 (*C*ONH), 159.05, 157.12, 156.55, 146.39, 146.21 (Ar*C*), 134.77, 134.48, 133.63, 133.25 (Ar*C*H), 129.45, 128.57, 128.09, 127.52 (Ar*C*), 75.53 (O*C*H$_2$CONH), 70.26, 70.03 (O*C*H$_2$COO), 60.67, 60.60 (O*C*H$_2$CH$_3$), 52.06 (Ad*C*$_1$), 41.28 (Ad*C*$_{2,8,9}$), 36.25 (Ad*C*$_{4,6,8}$), 34.05, 33.95 [*C*(CH$_3$)$_3$], 31.05, 30.99, 30.93 [C(*C*H$_3$)$_3$], 29.39 (Ad*C*$_{3,5,7}$), 14.03 (OCH$_2$*C*H$_3$). Anal. calcd. for $C_{64}H_{83}NO_{11}S_4$ (1170.63): C, 65.67; H, 7.15. Found: C, 65.08; H 6.98.

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