Alkylation Products of a Calix[8]arene Trianion. Effect of Charge Redistribution in Intermediates

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The behavior of a well-defined calix[8]arene trianion under alkylation conditions was investigated by reacting the tetraethylammonium salt of *p-tert*-butylcalix[8]arene trianion with *p*-methylbenzyl bromide. Chromatography of the reaction mixture afforded the following derivatives in order of decreasing yields: 1,3,5,7-tetrakis-, 1,3-bis-, 1,3,5-tris-, 1,2,4-tris-, and mono(*p*-methylbenzyl)-*p-tert*-butylcalix[8]arene, besides trace amounts of 1,4- and 1,5-disubstituted compounds. Comparable results were obtained using *p-tert*-butylbenzyl bromide. The observed regioselectivity has been explained by assuming that after each alkylation step the left negative charge is redistributed, by exchange equilibria, over the remaining phenolic groups with preferential localization at those positions where contiguous H-bond stabilization is possible and the electrostatic repulsion is minimized. The occurrence of protonation/deprotonation equilibria allows the formation of 1,3,5,7-tetrasubstituted calix[8]arene.

Introduction

The behavior of calixarenes[1] in the base-promoted alkylation at the phenolic hydroxyls is a crucial aspect of their chemistry, whose understanding is a premise for better control of the reaction.[2] In fact, it has been largely demonstrated that the influence of the nature of the base (cation identity and strength) is of paramount importance in determining the stereo- and regiochemical outcome of the reaction.[3] Thus, calix[4]arenes often give preferentially the tetrasubstituted cone or partial cone atropisomers in the presence of NaH or, respectively, Cs_2CO_3,[4] while in their partial alkylation the use of K_2CO_3 affords selectively 1,3-disubstituted derivatives[5] and that of NaH the 1,2-regioisomers.[6] Moreover, in the arylmethylation of calix[6]arenes NaH leads to the preferential formation of 1,2,4,5-tetrasubstituted and KH that of 1,4-disubstituted derivatives,[2,7] while 1,2,3- or 1,3,5-trisubstitution is observed with either K_2CO_3 or CsF.[8] Analogously, the nature of the base has a strong effect in the product distribution in the reactions leading to both calix[4]-crown[9] and calix[8]crown ethers.[10]

In order to rationalize these data the factor to be considered first is the nature of the base, since in the presence of weak or strong bases monoanions or, respectively, polyanions are preferentially produced, thus driving the reaction through diverse pathways with the formation of variously substituted derivatives.[3−6] Thus, it is commonly agreed that, in the presence of CsF or K_2CO_3, calix[*n*]arenes originate monoanions[3,5c] which evolve mainly in accordance to the so-called *alternate alkylation* route.[11] Differently, in the presence of strong bases (hydroxides or hydrides) polyanions are usually formed[12,13] whose evolution is not yet fully understood.[2,4d,6,14] In many instances even the level of deprotonation is unclear, making immaterial any further argumentation.

In the case of calix[8]arenes we have demonstrated that alkylation in the presence of weak bases is mainly driven by the preferential formation of monoanions

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stabilized by two flanking hydrogen bonds leading to 1,3,5,7-tetraalkyl derivatives.[11,15] The use of strong bases that should originate polyanions[12,13] usually leads to exhaustive substitution or, with limiting amounts of electrophile, to complex mixtures. In these instances either the level of deprotonation and/or the behavior of the formed polyanion is unknown. The study of the alkylation of a preformed, well-defined polyanion seems to be the best way to solve these questions. In principle it is expected that such a polyanion should behave differently from a monoanion, probably giving rise to products with different substitution patterns.

The preparation of a well-defined calix[8]arene polyanion has been described in a recent paper by Harrowfield *et al.* who have shown that treatment of a solution of *p-tert*-butylcalix[8]arene (**1**) in acetonitrile with aqueous tetraethylammonium hydroxide produces a triple deprotonation leading in good yield to the easily crystallized salt $(Et_4N^+)_3(\mathbf{1}^{3-})$.[13a] This appears an interesting subject for the study of the behavior of a formally noncoordinated calix[8]arene trianion in the presence of alkylating agents. Thus, we decided to investigate this reaction using *p*-methylbenzyl bromide as electrophile, since various fully characterized *p*-methylbenzyl ethers of *p-tert*-butylcalix[8]arene were available as reference compounds for products identification.[11]

Results and Discussion

The salt $(Et_4N^+)_3(\mathbf{1}^{3-})$, prepared by following the procedure of Harrowfield *et al.*,[13a] was purified by repeated recrystallization from CH_3CN. Its identification was based on elemental analysis and ^{13}C NMR spectroscopy, while integration of the ^1H NMR spectrum confirmed the correct 3:1 cation to anion ratio.[16] According to chemical intuition and molecular mechanics calculations,[17] the negative charges in $\mathbf{1}^{3-}$ should be preferentially located at the 1,3,6 relative positions in order to achieve the maximum hydrogen-bonding stabilization and minimum electrostatic repulsion. However, the appearance of three single resonances for the *t*-Bu, $ArCH_2Ar$, and ArH groups in the ^1H NMR spectrum[16] evidences that, in the NMR time scale, the charge is equally distributed over the eight phenolic groups.[13] Therefore a fast exchange equilibrium in the NMR time scale has to be accepted, as sketched in Figure 1.

In order to investigate the behavior of calix[8]arene trianion $\mathbf{1}^{3-}$ under alkylation conditions, a sample of this salt was dissolved in anhydrous THF/DMF (10:1 v/v) and reacted with 10 equiv of *p*-methylbenzyl bromide at reflux for 12 h. TLC analysis of the crude reaction mixture revealed a pattern similar to that observed in the alkylation of **1** catalyzed by weak bases,[11] while column chromatography gave the following compounds (isolated yields): **2** (5%), **3** (17%), **6** (12%), **7** (7%), and **8** (26%), besides trace amounts of **4** and **5** (Chart 1). Identification was based on spectral comparison with authentic samples available from previous work.[11]

Formation of 1,3,5-tri- and 1,3,5,7-tetrasubstituted derivatives by alkylation of calix[8]arene trianion $\mathbf{1}^{3-}$

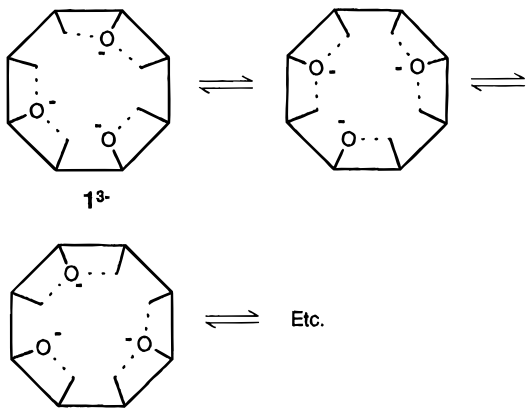
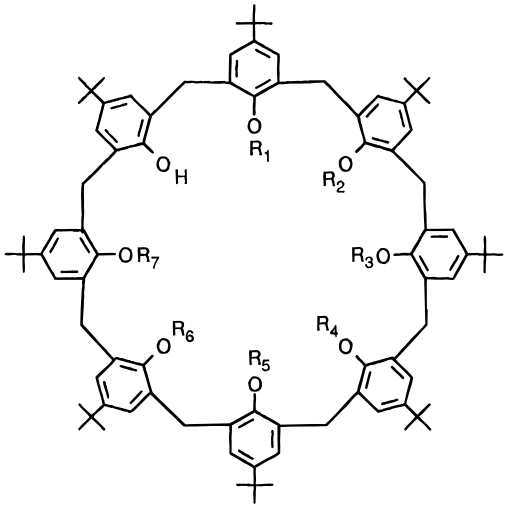


Figure 1. Exchange equilibrium for charge distribution for calix[8]arene trianion $\mathbf{1}^{3-}$.

Chart 1



Compd	R_1	R_2	R_3	R_4	R_5	R_6	R_7
1	H	H	H	H	H	H	H
2	MBn	H	H	H	H	H	H
3	MBn	H	MBn	H	H	H	H
4	MBn	H	H	MBn	H	H	H
5	MBn	H	H	H	MBn	H	H
6	MBn	H	MBn	H	MBn	H	H
7	MBn	MBn	H	MBn	H	H	H
8	MBn	H	MBn	H	MBn	H	MBn
2a	BBn	H	H	H	H	H	H
3a	BBn	H	BBn	H	H	H	H
6a	BBn	H	BBn	H	BBn	H	H
7a	BBn	BBn	H	BBn	H	H	H
8a	BBn	H	BBn	H	BBn	H	BBn

MBn ≡ *p*-Methylbenzyl; BBn ≡ *p-t*-Butylbenzyl

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(16) For completeness we report here the spectral data of the known salt $(Et_4N^+)_3(\mathbf{1}^{3-})$[13a] (see Experimental Section).

(17) Full minimization (MacroModel V4.5 computer program) of the five isomeric structures of $\mathbf{1}^{3-}$ in a pleated-loop conformation, using MM2 or Amber force-field with GB/SA model solvent (H_2O or $CHCl_3$), always favored 1,3,6-trianion by more than 5 kcal/mol with respect to the nearest higher energy isomer. The 1,3,6-charge localization in a calix[8]arene trianion was first suggested by Shinkai and co-workers (ref 13c).

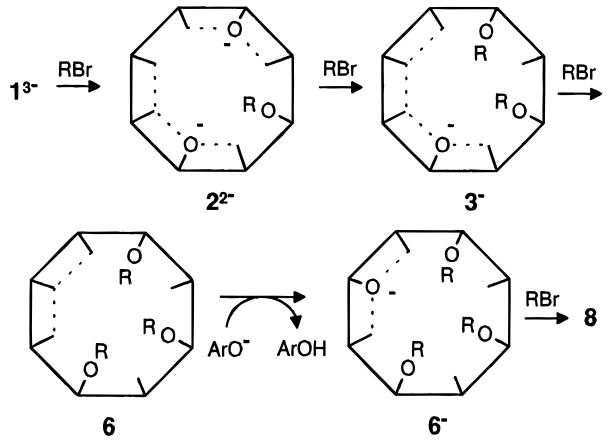

Figure 2. Proposed alkylation pathway for calix[8]arene trianion $\mathbf{1}^{3-}$.

appears somewhat surprising at first sight, since these compounds are characteristic products of the monoanionic pathway. In order to rationalize how these compounds are formed, we suggest the following mechanism. The first alkylation step of $\mathbf{1}^{3-}$ yields monoalkylated dianionic species $\mathbf{2}^{2-}$, which very likely adopts a preferential 3,7-charge distribution (Figure 2) in order to reduce electrostatic repulsion, with concomitant H-bond stabilization by flanking OH groups. Further alkylation of this dianion then originates the 1,3-dialkyl monoanion $\mathbf{3}^{-}$, with the charge localized at either position 5 or 6. In accordance with our previous study on the *alternate alkylation* of **1**, this intermediate gives preferentially the 1,3,5-trisubstituted derivative **6**, besides a small amount of 1,2,4-isomer **7**.[11]

According to chemical knowledge, 1,3,5-triether **6** should be a stronger acid than the conjugated species of $\mathbf{1}^{3-}$ or $\mathbf{2}^{2-}$ and therefore it may undergo an acid−base exchange with these anions still present in solution, followed by an alkylation step to give the 1,3,5,7-tetrasubstituted compound **8** (Figure 2). Of course, during the reaction several intermolecular protonation/deprotonation equilibria take place leading to a distribution from mono- to tetraalkylated products.[18] However, the observed regioselectivity indicates the preferential localization of the charge, in all intermediate anionic species, at those positions more stabilized by contiguous H-bonds and with lower electrostatic repulsion.[19]

This consideration should be independent of the nature of the electrophile,[20] making this approach of considerable usefulness from the synthetic point of view. Indeed, extending this reaction to *p-tert*-butylbenzyl bromide we isolated, besides to the expected 1,3,5,7-tetraether **8a**[15b] (25%), the hitherto unknown mono(*tert*-butylbenzyl) derivative **2a** (30%) and 1,3-bis(*tert*-butylbenzyl)calix[8]arene **3a** (33%). Their structures were readily assessed on the basis of the same arguments used in previous work for the structure assignments to **2** and **3**.[11] It is interesting to observe that previous attempts at isolating these compounds from the mixtures obtained by benzylation of **1** in the presence of CsF or K_2CO_3 have been unsuccessful because of their chromatographic overlapping with other polybenzyl compounds.[15b] Two other compounds were isolated in trace amounts for which, on the basis of ^{1}H NMR spectra, we suggest the structure of 1,3,5-tris(*tert*-butylbenzyl) derivative **6a** and 1,2,4-tris(*tert*-butylbenzyl)calix[8]arene **7a**. However, because of their minimal amounts and impure form they were not fully characterized.

In conclusion, the alkylation of a preformed and well-defined calixarene polyanion here described may be considered a general approach for a better understanding of their chemistry and a procedure of some synthetic utility. It has been evidenced that regioisomer distribution in the alkylation of a calix[8]arene trianion is similar to that observed when a monoanionic pathway is active. In the former instance, charge redistribution in intermediate species and occurrence of protonation/deprotonation equilibria are key factors for product distribution. The scope and extension of this approach to other calix[*n*]arene systems will be the subject of future studies.

Experimental Section

General Comments. Melting points are uncorrected. NMR spectra were taken on a Bruker AC-250 spectrometer operating at 250.13 (^{1}H) and 62.9 (^{13}C) MHz, using Me_4Si as internal standard. Elemental analyses were obtained from the Dipartimento di Scienze Farmaceutiche of the University of Catania. Column chromatography was performed using silica gel (kieselgel 60, 63−200 μm, Merck). Preparative TLC (PTLC) was carried out using silica gel plates (kieselgel 60 F_{254}, 1 mm, Merck). All chemicals were reagent grade and were used without further purification. Aqueous Et_4NOH (20%, w/v), anhydrous DMF, and THF were purchased from Aldrich. *p-tert*-Butylcalix[8]arene (**1**) was prepared by a literature procedure[21] while reference samples of *p*-methybenzyl calix[8]arenes (**2**−**8**)[11] and 1,3,5,7-tetrakis(*p-tert*-butylbenzyl) ether **8a**[15b] were available from previous work.

Preparation of Tetraethylammonium Salt of *p-tert*-Butylcalix[8]arene $(Et_4N^+)_3(\mathbf{1}^{3-})$. $(Et_4N^+)_3(\mathbf{1}^{3-})$ was prepared essentially according to the method of Harrowfield.[13a] To a suspension of *p-tert*-butylcalix[8]arene (2.0 g, 1.54 mmol) in CH_3CN (40 mL) was added 20% (w/v) aqueous Et_4NOH (12 mL), and the mixture was brought to reflux. While refluxing, additional aliquots of Et_4NOH were added until a clear solution was observed. Upon standing overnight in a refrigerator, the crystalline precipitate was collected by filtration, washed with cold CH_3CN, and recrystallized (×3) to give pure $(Et_4N^+)_3(\mathbf{1}^{3-})$ (0.70 g, 27%): ^{1}H NMR (250.13 MHz, $CDCl_3$, 340 K) δ 1.18 (t, J = 6.8 Hz, 36 H), 1.26 (s, 72 H), 3.13 (q, J = 6.8 Hz, 24 H), 3.90 (s, 16 H), 7.05 (s, 16 H); ^{13}C NMR (62.9 MHz, C_5D_5N, 296 K) δ 7.7 (q), 32.1 (q), 34.0 (t), 34.1 (s), 52.8 (t), 125.4 (d), 129.6 (s), 140.2 (s), 153.9 (s).

Alkylation of $(Et_4N^+)_3(\mathbf{1}^{3-})$ with *p*-Methylbenzyl Bromide. A solution of $(Et_4N^+)_3(\mathbf{1}^{3-})$ (350 mg, 0.21 mmol) and *p*-methylbenzyl bromide (400 mg, 2.2 mmol) in THF/DMF (10:1 v/v, 22 mL) was refluxed for 12 h. Evaporation of the solvent afforded a residue which was washed with 0.1 N HCl (30 mL) followed by MeOH (8 mL) and dried. The crude product was subjected to column chromatography (silica gel, elution with increasing concentrations of CH_2Cl_2 in petroleum ether) and, when needed, some of the pooled fractions were further purified by PTLC to give (isolated yields) **2** (15 mg, 5%), **3** (54 mg, 17%), **6** (41 mg, 12%), **7** (24 mg, 7%), and **8** (94 mg, 26%).

Alkylation of $(Et_4N^+)_3(\mathbf{1}^{3-})$ with *p-tert*-Butylbenzyl Bromide. *p-tert*-Butylbenzyl bromide (0,14 mL, 0.74 mmol) was reacted, under conditions similar to those above, with

(18) In principle, the occurrence of these equilibria could be demonstrated by mixing the salt with **2**, **3**, or **6**, while mathematical modeling could lead to the determination of relative acidities. However, these investigations remain beyond the purpose of the present work.

(19) It is worth mentioning that in the absence of preferential charge localization a large number of all possible regioisomers should be formed with a statistical distribution (one mono-, four di-, five tri-, and eight tetrasubstituted derivatives).

(20) However, it is to be expected that more reactive electrophiles could react also with less stable anions with loss of regioselectivity.

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$(Et_4N^+)_3(\mathbf{1}^{3-})$ (250 mg, 0.15 mmol) for 20 h. Purification by column chromatography (silica gel, elution with increasing concentrations of CH_2Cl_2 in petroleum ether) of the crude product afforded **2a** (64 mg, 30%), **3a** (78 mg, 33%), and **8a** (70 mg, 25%).

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49-[(4-*tert*-butylbenzyl)oxy]calix[8]arene-50,51,52,53,54,55,56-heptol (2a): mp > 400 °C dec; R_f 0.5 (CH_2Cl_2/petroleum ether, 2:3 v/v); ^{1}H NMR (250.13 MHz, C_6D_6, 350 K) δ 1.25, 1.26, 1.29, 1.33 (s, 27 H, 18 H, 9 H, 27 H, respectively), 3.75, 3.88, 3.97, 4.07 (s, 4 H each), 4.86 (s, 2 H), 7.10−7.28 (overlapped, 14 H), 7.32 (s, 2 H), 7.68 and 7.73 (AB, J = 8.7 Hz, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 310 K) δ 29.7 (t), 31.5 (q), 32.4, 32.6 (t), 34.0 (s), 78.1 (t), 125.2, 125.6, 125.8, 126.6 (d), 127.0, 127.6, 127.9, 128.1 (s), 128.7 (d), 133.0, 133.3, 143.1, 144.1, 144.5, 144.8, 146.7, 147.3, 148.7, 150.6 (s). Anal. Calcd. for $C_{99}H_{126}O_8$: C, 82.34; H, 8.79. Found: C, 82.19; H, 8.90.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,51-bis[(4-*tert*-butylbenzyl)oxy]calix[8]arene-50,52,53,54,55,56-hexol (3a): mp 163−165 °C; R_f 0.45 (CH_2Cl_2/petroleum ether, 2:3 v/v); ^{1}H NMR (250.13 MHz, C_6D_6, 340 K) δ 1.13, 1.30, 1.31, 1.38, 1.40 (s, 18 H, 18 H, 27 H, 18 H, 9 H, respectively), 3.93, 4.00, 4.22 (s, 8 H, 4 H, 4 H, respectively), 4.84 (s, 4 H), 7.16 (d, J = 2.3 Hz, 2 H), 7.17 (d, J = 2.3 Hz, 2 H), 7.19−7.28 (overlapped, 10 H), 7.29 (d, J = 2.2 Hz, 2 H), 7.39 and 7.46 (AB, J = 8.3 Hz, 8 H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 310 K) δ 29.7 (t), 31.3, 31.5 (q), 32.0, 32.1, 32.4 (t), 34.0, 34.3, 34.7 (s), 77.7 (t), 124.3, 125.1, 125.4, 125.6, 125.7 (d), 126.0 (s), 126.3, 126.8 (d), 127.0, 127.8, 128.0, 128.4 (s), 128.7(d), 132.0, 132.9, 133.0, 141.9, 143.1, 144.1, 144.4, 146.8, 147.1, 147.7, 149.0, 150.4, 151.0, 151.8 (s). Anal. Calcd for $C_{110}H_{140}O_8$: C, 83.08; H, 8.87. Found: C, 82.98; H, 9.02.

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