added and the pH kept neutral (pH paper) by addition of NaOH (0.50 N). After 7 days, 98 mL (49 mmol) of the alkaline solution had been consumed. The aqueous phase containing mostly 1 was separated and extracted continuously with diethyl ether (175 mL). The ethereal extract was concentrated to a solid (>99% ee) which was recrystallized from hot toluene (10 mL) to afford crystalline (*R*)-1, 2.4 g (42%, 84% of theory): mp 107.5–108.5 °C (lit.[28] 113–114 °C from acetone/hexane); ee > 99.8%; $[\alpha]_D^{20}$ = −35.0° (*c* 0.30, CH_3OH) [lit.[29] −36.9° (H_2O)]; ^1H NMR δ 3.68 (br s, 2), 3.31 (m, 2), 1.94 (m, 2), 1.69 (m, 2), 1.23 (m, 4). The hexane phase containing mostly 1-diacetate was dried over $MgSO_4$, filtered, and concentrated. Purification on silica gel eluted with 5:1 hexane/ethyl acetate followed by Kugelrohr distillation under water aspirator vacuum gave (*S*)-1-diacetate as a colorless oil, 3.8 g (38%, 76% of theory), >99% ee; $[\alpha]_D^{20}$ = +16.1° (*c* 0.42, CH_3OH) [lit.[29] +12.4° ($CHCl_3$)]; ^1H NMR δ 4.82 (m, 2), 2.03 (m, 8), 1.75 (m, 2), 1.38 (m, 4). The monoester (3.7 mol %, 94.6% ee *R*) was present in both the aqueous and hexane phases as shown by TLC.

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Registry No. (*R*)-1, 1072-86-2; (*S*)-1, 57794-08-8; (±)-1, 54383-22-1; (±)-1 diacetate, 79416-44-7; (±)-1 monoacetate, 62921-46-4; esterase, 9013-79-0; cholesterol esterase, 9026-00-0; lipase, 9001-62-1.

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Calixarenes. 26. Selective Esterification and Selective Ester Cleavage of Calix[4]arenes

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Methods have been developed for converting *p-tert*-butylcalix[4]arene (**1a**) in high yield to the 25-monoester **7**, the 25,26-diesters **5** and **6**, the 25,27-diester **4a**, and the 25,26,27-triesters **2** and **3** in which the aryl groups are 3,5-dinitrophenyl moieties. Concomitantly, methods have emerged whereby these esters can be selectively cleaved or rearranged. By appropriate choice of reaction conditions the 25,27-diester **4a** can be selectively cleaved with imidazole bases to the monoester **7** or rearranged to the 25,26-diester **5**; the triesters **2** and **3** can be converted to their conformationally related 25,26-diesters **5** (a chiral compound) and **6**. The effects of variations in solvent, organic base, and reaction time on the conversion of **4a** to **7**, along with semiquantitative kinetic data, suggest that two or more molecules of the imidazole are involved in the activated complex of the rate-determining step in the aminolysis. These syntheses provide easy access to the mono-, di-, and triesters, thus expanding the techniques for obtaining selectivity para-substituted calixarenes via selective de-*tert*-butylation. Thus, removal of three, two, or one *tert*-butyl group, respectively, from the monoester **7**, the diesters **4a** and **5**, and the triester **2** yields the corresponding mono-, di-, and tri-*tert*-butylated analogues **12a–d**. Acylation of **12b**, for example, can be effected at the vacated para positions to produce the diacylcalix[4]arenes **15a** and **15b**. Collectively, the system provides an example of how careful control of reaction conditions can be used to advantage in determining product formation.

As part of a program involving the synthesis of "double cavity" calixarenes[1] the 25,27-bis(3,5-dinitrobenzoyl) ester of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (generally abbreviated as *p-tert*-butylcalix[4]arene) (**1a**) has been prepared and its complexation properties studied. Instead of forming a complex with the putative guest imidazole, however, the ester undergoes cleavage, thereby providing the starting point for the present investigation, which has led to an interesting sequence of events that makes possible the selective esterification of calix[4]arenes and the selective cleavage of esterified calix[4]arenes. As frequently happens when a research program takes an unexpected turn, the scheme of subsequent events has not been orderly. The following discussion, therefore, is a nonchronological account of how the salient features of the final picture emerged. In this discussion the procedures for preparing various esters of calix[4]arenes are first presented, followed by a commentary on the conformations of the esters, a detailed consideration of the amine-induced cleavage of the 25,27-diester, and a conclusion that summarizes the ester forming/ester cleaving processes that can be induced by the proper choice of reaction conditions.

Synthesis of 3,5-Dinitrobenzoates of *p-tert*-Butylcalix[4]arene. The procedures that are outlined below represent an end result rather than a starting point in the present investigation. They are the harvest partly of serendipity and partly of rational designs based on the various observations that are described in later sections of this paper.

25,26,27-Tris(3,5-dinitrobenzoates). *p-tert*-Butylcalix[4]arene (**1a**) was shown by Gutsche and Lin[2] to react with benzoyl chloride in the presence of pyridine to yield the tribenzoate of **1a**. 3,5-Dinitrobenzoyl chloride behaves in a qualitatively comparable fashion to yield a mixture containing some of the triester. Much more effective as the base, however, is 1-methylimidazole in acetonitrile solution which gives a 90% yield of the cone conformer of 25,26,27-tris((3,5-dinitrobenzoyl)oxy)-28-hydroxy-

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[‡] Authors to whom correspondence regarding the X-ray analyses should be sent.

(1) Gutsche, C. D.; See, K. A. *J. Am. Chem. Soc.*, in press.
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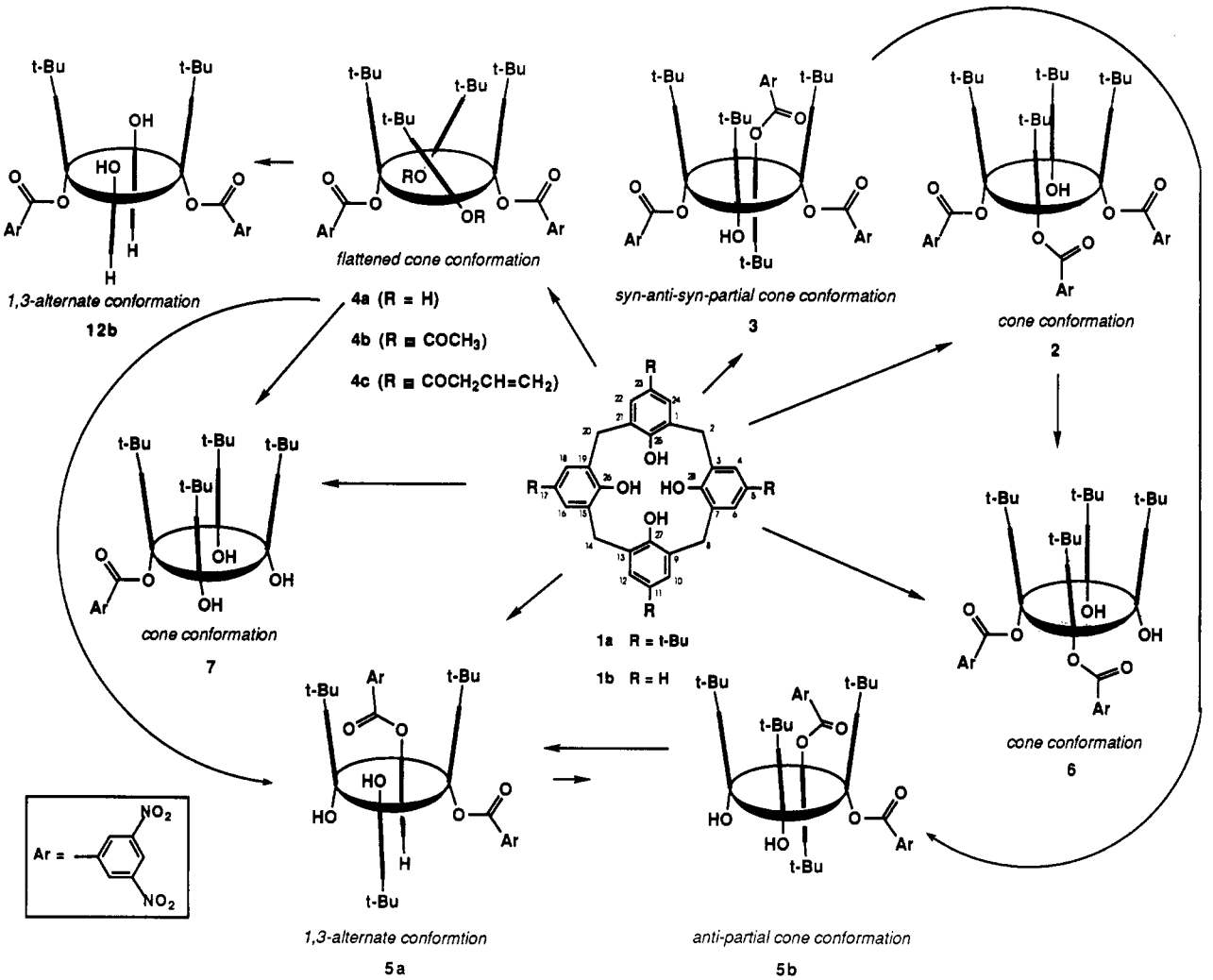
0022-3263/91/1956-7256$02.50/0

Scheme I



5,11,17,23-tetra-*tert*-butylcalix[4]arene (**2**). To obtain high yields it is necessary that the reaction proceed only 2–4 h, because longer times cause a slow disappearance of the triester and the formation of a diester (see later discussion). The success of 1-methylimidazole is dependent on its ability to act as an effective base but a poor ester-cleaving agent (see later discussion) for imidazole under the same conditions produces a mixture of products containing only a trace of the triester. When the 3,5-dinitrobenzoylation is carried out in the manner just described but with chloroform in place of acetonitrile as the solvent, a 60% yield is obtained of the triester as the syn-anti-syn partial cone[3] (**3**) rather than the cone conformer (**2**), which is present only as a minor side product. The factors governing the conformational outcome of derivatizations of calix[4]arenes are not yet well understood and are the subject of continuing study.[4,5]

25,27-Bis(3,5-dinitrobenzoates). *p-tert*-Butylcalix[4]arene (**1**) has been shown by previous work in this laboratory to react with para-substituted benzoyl chlorides in the presence of either $AlCl_3$ or NaH to form the tetraaroylates,[4] and it was anticipated that 3,5-dinitrobenzoyl chloride would behave in a similar fashion. Surprisingly, no tetrakis(3,5-dinitrobenzoate) is found, the major product being the 25,27-diester. A more convenient procedure leading to the same diester uses 3,5-dinitrobenzoic acid in the presence of $(C_6H_5O)POCl_2$ which affords an 80% yield of 5,11,17,23-tetra-*tert*-butyl-25,27-bis((3,5-dinitrobenzoyl)oxy)-26,28-dihydroxycalix[4]arene (**4a**). The diester **4a** (flattened cone conformation) is susceptible to selective de-*tert*-butylation, as discussed in a later section, to yield 11,23-di-*tert*-butyl-25,27-bis((3,5-dinitrobenzoyl)oxy)-26,28-dihydroxycalix[4]arene (**12b**), which adopts the 1,3-alternate conformation.

25,26-Bis(3,5-dinitrobenzoates). The diaroylates carrying the ester groups on adjacent aromatic residues can be made by direct aroylation of *p-tert*-butylcalix[4]arene **1a** (method a), by selective cleavage of the cone conformer of the triester (method b), or by rearrangement of the 25,27-diester (method c). In method a the treatment of *p-tert*-butylcalix[4]arene **1a** with 20 equiv of imidazole and 2 equiv of 3,5-dinitrobenzoyl chloride in refluxing chloroform for 1 h (or 6 h at room temperature) gives an 80–90% yield of the 1,3-alternate conformer of 5,11,17,23-tetra-*tert*-butyl-25,26-bis((3,5-dinitrobenzoyl)-oxy)-27,28-dihydroxycalix[4]arene (**5**). The use of acetonitrile as the solvent or 1-methylimidazole as the base significantly lowers the yield of this diester. Treatment of **1** with 27 equiv of 1-methylimidazole in acetonitrile for 20 h at room temperature gives a 90% yield of the cone

(3) Three isomers are possible for a triester in the partial cone conformation. They can be designated, in terms of the spatial relation (syn/anti) between the unesterified ring (as the reference) and the esterified rings, as all-anti, syn-syn-anti, and syn-anti-syn.

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Table I. Synthetic Procedures for the Preparation of 3,5-Dinitrobenzoyl Esters 2, 3, 4a, 5, 6, and 7 from *p-tert*-Butylcalix[4]arene (1a)

base	equiv of base	equiv of ArCOCl	solvent	time, h	product	yield, %
1-butylimidazole	15	1.3	acetonitrile	24	monoester 7	83
1-butylimidazole	27	2.3	acetonitrile	24	1,2-diester 6	90
imidazole	20	2.0	chloroform	6	1,2-diester 5	80
pyridine	20	2.0	chloroform	96	1,3-diester 4a	95
1-methylimidazole	20	4.0	chloroform	48	triester 3	70
1-methylimidazole	10	4.0	acetonitrile	6	triester 2	95

conformer 6 of the 25,26-diester. In method b treatment of the cone conformer of the triester 2 with 15 equiv of imidazole in chloroform solution selectively removes one of the ester groups to produce the cone conformer of the 25,26-diester 6 in 75% yield; treatment of the partial cone conformer of the triester 3 with 3 equiv of imidazole in chloroform gives the 1,3-alternate conformer of the diester 5 in 85% yield. In method c the treatment of the 25,27-diester 4a with 2–4 equiv of imidazole in chloroform solution affords a 65% yield of the same 25,26-diester 5 that is obtained by selective cleavage of the partial cone conformer of the triester (see above).

25-Mono(3,5-dinitrobenzoate). The observation that initiated the work described in this paper was the cleavage of the 25,27-diester to a monoester in the presence of imidazole, the details of which are outlined in the next section. The best preparative procedure that has evolved makes use of 10 equiv of imidazole in a chloroform–acetonitrile solution for 1 h, which yields 5,11,17,23-tetra-*tert*-butyl-25-((3,5-dinitrobenzoyl)oxy)-26,27,28-trihydroxycalix[4]arene (7) in 70% yield accompanied by only a small amount of the completely cleaved product 1a. The monoester can also be prepared by direct aroylation of 1a in 80% yield by using 2 equiv of 3,5-dinitrobenzoyl chloride in the presence of 20 equiv of 1-butylimidazole in acetonitrile solution for 16 h. A minor product of the reaction, easily removed by trituration, is the cone conformer of the 25,26-diester 6.

The conditions for preparing the mono-, di-, and triesters starting with *p-tert*-butylcalix[4]arene 1a are summarized in Table I.

Conformations of the 3,5-Dinitrobenzoates of Calix[4]arenes. 25,26,27-Tris(3,5-dinitrobenzoates). The triesters 2 and 3 possess similar ^{1}H NMR spectral patterns, showing three singlets arising from the *p-tert*-butyl hydrogens, four doublets arising from the methylene hydrogens, and two envelopes arising from the aromatic hydrogens, compatible with either a cone (2) or a partial cone conformation (3). The definitive assignment of the partial cone conformation to one of these compounds is made on the basis of X-ray crystallography (see Figure 1), leaving the assignment of the cone conformation to the other compound. These assignments are also in agreement with the difference in rates of the imidazole-induced cleavage of triesters 2 and 3 in which the cleavage is facilitated by a phenolic OH group proximate to the ester carbonyl function (see later discussion).

25,27-Bis(3,5-dinitrobenzoates). The ^{1}H NMR spectrum of the 25,27-diester 4a shows a pair of resonances arising from the *tert*-butyl protons (1:1 ratio) and a pair of doublets arising from the methylene hydrogens, compatible with a cone conformation. X-ray crystallography of 4a confirms this conclusion and shows that the two aryl rings carrying the free OH groups are splayed outward to give a "flattened cone" (see Figure 2), the flattening probably facilitated by transannular hydrogen bonding between the OH groups at positions 26 and 28. The two OH oxygen atoms and the two ester oxygen atoms lie within 0.25 Å of a common plane and form an approximate

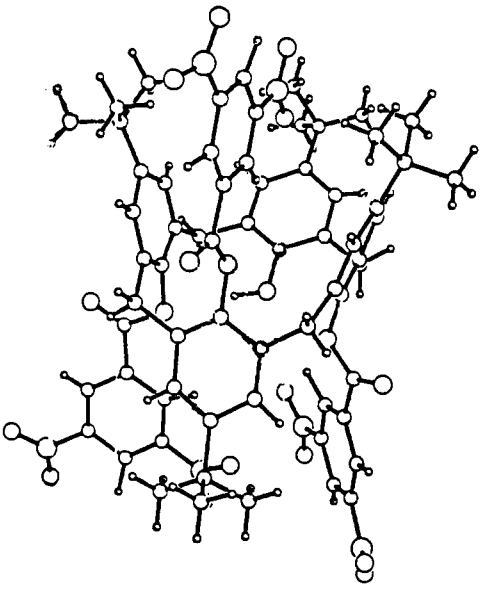


Figure 1. X-ray crystallographic structure of the partial cone conformer of the 25,26,27-triester 3.

parallelogram, with sides ranging between 2.817 (4) and 3.262 (7) Å. The interior angles of the parallelogram average 62.3° at the ester oxygen and 114.6° at the OH oxygen, with diagonal 3.164 (6) Å between the OH oxygen atoms. The aryl rings carrying the OH groups form dihedral angles of 33.1 (2) and 43.1 (2)° with the parallelogram plane, while the aryl rings carrying ester groups are much more upright, forming analogous dihedral angles of 87.4 (2) and 80.7 (2)°. In the ^{1}H NMR spectrum of 12b, the di-*tert*-butyl analogue of 4a, a much more closely spaced pair of doublets arising from the *tert*-butyl hydrogens and a singlet arising from the methylene hydrogens is observed, compatible with a 1,3-alternate conformation. Although the hydrogens on the methylene groups of 12b are nonequivalent, they are in similar environments (ca. equally proximate to oxygen atoms), and the chemical shift between them is rather small. This conclusion is supported by the X-ray crystallographic structure (see Figure 2) which shows that the molecule lies on a crystallographic 2-fold rotation axis and adopts a 1,3-alternate conformation in which the 4.950 (5) Å distance between the OH groups precludes hydrogen bonding. The aryl rings bearing the OH groups tilt away from the symmetry axis only slightly more than those bearing the *tert*-butyl and ester groups; the two aryl rings bearing the OH groups form a dihedral angle of 14.0 (3)°, while those bearing the *tert*-butyl and ester groups form a 5.4 (8) Å dihedral angle. A molecular modeling study[6] along with an examination of CPK models indicates that the tetra-*tert*-butyl compound in the 1,3-alternate conformation exhibits some nonbonded interference between the aroyl residues (at positions 11 and 23) and the *tert*-butyl groups (at positions

(6) Silicon Graphics IRIS-4D/210VGX with CHARMm and QUANTA programs.

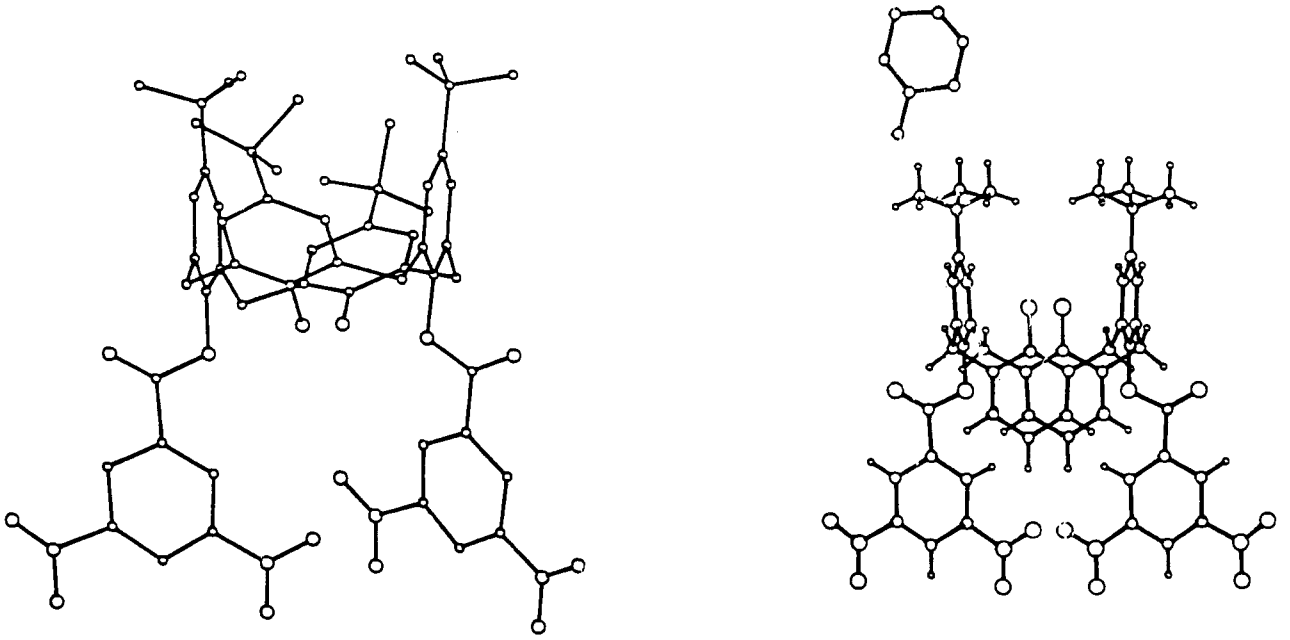


Figure 2. X-ray crystallographic structures of the 25,27-diesters containing four *p-tert*-butyl groups (**4a**) (left-hand structure) and two *p-tert*-butyl groups (**12b**) (right-hand structure).

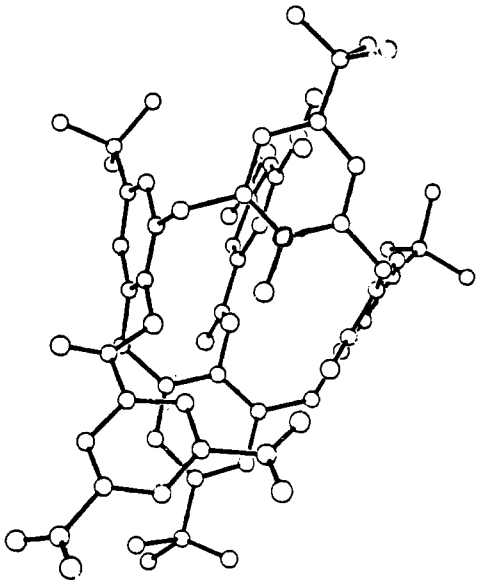


Figure 3. X-ray crystallographic structure of the partial cone conformer of the 25,26-diester **5b**.

5 and 17) but that this interference disappears when hydrogen occupy positions 5 and 17.

25,26-Bis(3,5-dinitrobenzoates). The ^{1}H NMR spectrum of the 25,26-diester **5** prepared directly from **1a** (method a) displays two singlets (1:1 ratio) arising from the *tert*-butyl hydrogens along with two singlets and two doublets arising from the methylene hydrogens, corresponding to either a 1,3-alternate or a 1,2-alternate conformation for **5**. The stability of **5** to amine-induced cleavage, which is facilitated by a proximate phenolic OH group (see later discussion), is in good accord with a 1,3-alternate conformation. This conclusion is also supported by NOE studies of **5** in $CHCl_3$ in which saturation of the protons at C-2 and C-6 of the 3,5-dinitrobenzoyl ring enhances the resonance of the *tert*-butyl group on the phenolic ring, the C-2,6 protons being closer to the *tert*-butyl groups in the 1,3-alternate than in the 1,2-alternate conformation. It is surprising, therefore, that the X-ray structure of this compound, displayed in Figure 3, shows

Table II. ^{1}H NMR Data for Esters 2, 3, 4a, 5a, 6, and 7

ester	conformation	CH_2 Resonances	*tert*-butyl resonances
triester **2**	cone	four doublets	1.44 (ArOR), 1.38 (ArOH), 0.93 (2 ArOR)
triester **3**	partial cone	four doublets	1.27 (ArOH), 0.85 (ArOR), 0.65 (2 ArOR)
25,26-diester **5a**	1,3-alternate	two doublets, two singlets	0.96 (ArOH), 0.77 (ArOR)
25,26-diester **6**	cone	six doublets	1.17 (ArOH or ArOR), 1.13 (ArOR or ArOH)
25,27-diester **4a**	cone	two doublets	1.33 (ArOH), 0.93 (ArOR)
monoester **7**	cone	four doublets	1.39 (ArOR), 1.34 (ArOH), 0.77 (2 ArOH)

it to be in a partial cone conformation. This is attributed to a barrier for the 1,3-alternate to partial cone conversion that is low enough to allow the partial cone conformer to crystallize from a solution even though the 1,3-alternate conformer is the major species at equilibrium. The ^{1}H NMR spectrum of the 25,26-diester prepared by methods b and c (see above) shows two singlets (1:1 ratio) arising from the *tert*-butyl groups and six doublets arising from the methylene hydrogens, corresponding to a cone conformation. Spectra measured up to 60 °C in $CDCl_3$ and 120 °C in DMSO-d_6 show no coalescence of the methylene hydrogens, indicating that the compound is conformationally inflexible over these temperature ranges.

25-Mono(3,5-dinitrobenzoate). The ^{1}H NMR spectrum of the monoester **7** contains three singlets (2:1:1 ratio) arising from the *tert*-butyl hydrogens and four doublets arising from the methylene hydrogens. Though not definitive, this pattern is compatible with a cone conformation, which is reasonable since the progenitor compound **4a** is known to exist in a flattened cone conformation.

Table II summarizes the data for the methylene and *tert*-butyl portions of the ^{1}H NMR spectra for these esters, the δ values for the *tert*-butyl resonances providing a useful means for semiquantitatively assaying the product distribution in crude reaction mixtures.

Table III. Solvent Dependence of the Rate of Conversion of 4a to 7 in the Presence of 4-Methylimidazole

solvent	$t_{1/2}$ for disappearance of 4a, min	solvent	$t_{1/2}$ for disappearance of 4a, min
benzene	<1.0	tetrahydrofuran	1.8
toluene	<1.0	pyridine	2.0
bromobenzene	<1.0	acetonitrile + methanol	3.5
		chloroform	4.0
acetonitrile	<1.0	dimethyl sulfoxide	8.5
acetone	1.8		

Amine-Induced Cleavage of 3,5-Dinitrobenzoates of Calix[4]arenes. When the complexation properties of **4a** toward imidazole were tested[1] it was observed that the host molecule disappears, and the mono(3,5-dinitrobenzoate) of *p-tert*-butylcalix[4]arene **7** takes its place. The course of the conversion is easily monitored by ^{1}H NMR spectroscopy, the two *p-tert*-butyl resonances (ratio 1:1) of **4a** being replaced by the three *p-tert*-butyl resonances (ratio 2:1:1) of **7**. Only after the solution has remained for 12 or more hours at room temperature does the spectrum ultimately change to show a single *p-tert*-butyl resonance characteristic of *p-tert*-butylcalix[4]arene **1a** itself. When the tris(3,5-dinitrobenzoate) of *p-tert*-butylcalix[4]arene, subsequently shown to possess the cone conformation (**2**) (see above), was treated in a similar manner it was also found to undergo cleavage, although in a much less clean fashion, to yield a mixture of products showing a multiplicity of *p-tert*-butyl resonances. Our curiosity was piqued by these results and led us to undertake a more detailed study of the effects of the solvent, the amine, and the structure and conformation of the starting ester on the course of the ester aminolysis reaction.

Effect of Solvent. In the presence of 4-methylimidazole the rate of conversion of **4a** to **7** in various solvents, as shown in Table III, is much slower in DMSO than in benzene. With *n*-butylamine as the base, however, the reaction proceeds very slowly in $CDCl_3$, benzene, or toluene but rapidly in DMSO-d_6. Thus, with the aliphatic amine the increase in rate appears to parallel the solvent polarity, whereas with imidazole the response is approximately the inverse of this order.

Many studies of amine-induced cleavages of esters in aqueous and semiaqueous systems are reported in the literature, the products in these cases being the result of hydrolysis. Although much less attention has been devoted to ester cleavages in nonaqueous systems, an example related to the present case was reported by Menger[7] who found that benzamidine is a much better nucleophile for cleavage of *p*-nitrophenyl acetate in chlorobenzene solution than is *n*-butylamine. He attributed this to the ability of benzamidine to act as a proton transfer agent as well as a nucleophile, thereby leading to a neutral activated complex. *n*-Butylamine, lacking the proton-transferring ability of imidazole, can act only as a nucleophile to produce a charged or charge-separated activated complex that would be expected to be more stable in a polar solvent (i.e. an aqueous system) than in a nonpolar solvent (i.e. chlorobenzene). A similar situation obtains in the present system in which the much greater rate of imidazole-induced cleavage compared with *n*-butylamine-induced cleavage in nonpolar solvents can be attributed to the bifunctional character of imidazole.

Effect of Imidazole. When acetonitrile-d_3 is used as the solvent along with 20 equiv of the imidazole it is found that 4-methylimidazole (pK_a 7.4) cleaves the diester **4a** to the monoester **7** 2.5 times faster than imidazole (pK_a 7.0), 18 times faster than 2-methylimidazole (pK_a 7.9), and 2000 times faster than 1-methylimidazole (pK_a 6.9). It is interesting to note that although 2-methylimidazole is ca. 3 times more basic than 4-methylimidazole, it is considerably less effective as a cleavage reagent, suggesting that subtle steric factors must come into play. It is perhaps surprising that 1-methylimidazole, which is constrained to form a quaternary cleavage product, is only ca. 800 times less effective than imidazole.

(7) Menger, F. M. *J. Am. Chem. Soc.* **1966**, *88*, 3081.

Table IV. Half-Lives ($t_{1/2}$) for the Conversion of 4a to 9 in the Presence of Various Bases in CD_3CN Solution

base no. 1	equiv	base no. 2	equiv	$t_{1/2}$ for disappearance of 4a, min
imidazole	10			12
	20			1.5
4-methylimidazole	10			4
	20			<1
2-methylimidazole	10			75
	20			10
1-methylimidazole	10			>10 000
	20			~10 000
n-butylamine	10			≫60
	20			>60
TMEDA	20			≫4420
aniline	20			≫4420
imidazole	10	4-methylimidazole	10	<1
imidazole	10	2-methylimidazole	10	1.5
imidazole	10	1-methylimidazole	10	10
imidazole	10	*n*-butylamine	10	5
4-methylimidazole	10	2-methylimidazole	10	<1
4-methylimidazole	10	1-methylimidazole	10	2
2-methylimidazole	10	1-methylimidazole	10	38

Several cleavage reactions involving the conversion of **4a** to **7** were carried out using pairs of bases, with the results noted in Table IV. Inspection of these data reveals that the observed rates are not directly additive from the rates of the individual bases that were used. For example, the mixture of 10 equiv of imidazole ($t_{1/2}$ of 12 min) and 10 equiv of 2-methylimidazole ($t_{1/2}$ of 75 min) might have been expected to show a $t_{1/2}$ of 10.3 min. Instead, it shows a value of 1.5 min, which is virtually identical with that of 20 equiv of imidazole. Similarly, the mixture of 10 equiv of imidazole ($t_{1/2}$ of 12 min) and 10 equiv of *n*-butylamine ($t_{1/2}$ much greater than 60 min) shows a $t_{1/2}$ value of 5 min, only ca. 3 times short of being identical with that of 20 equiv of imidazole. These results indicate that several processes must be occuring in the overall transformation and that they respond in different fashions to different amines; viz. one process involving nucleophilic attack of the amine on the carbonyl function of the ester and one or more processes involving proton transfers.

Effect of Conformation. The first example in this investigation of a conformational effect on the rate of ester cleavage was observed with the 25,27-bis(3,5-dinitrobenzoate) of di-*p-tert*-butylcalix[4]arene (**5**) (1,3-alternate conformation) which reacts almost 7 times less rapidly than its tetra-*p-tert*-butyl counterpart (**4a**) (cone conformation). In **12b** the phenolic OH groups are farther from the carbonyl moieties than in **4a**, suggesting that the phenolic OH group plays a part in the overall process. This conclusion is reinforced by the fact that the tetraesters **4b** and **4c** show no tendency whatsoever to undergo cleavage in the presence of imidazole under the conditions that rapidly cleave **4a**. Similar differences in the rate of ester cleavage have been observed for other members of this family, as illustrated by the data in Table V, and can be interpreted in terms of the distance between the phenolic OH and ester carbonyl groups. For example, the 25,26-bis(3,5-dinitrobenzoate) of *p-tert*-butylcalix[4]arene (**5**) undergoes im-

Table V. Half-Times ($t_{1/2}$) for the Ester Cleavage Reactions of Mono-, Bis-, and Tris(3,5-dinitrobenzoyl) Esters of *p-tert*-Butylcalix[4]arene

compound	conformation	$t_{1/2}$ for disappearance of starting material, min
triester 2	cone	5.7
triester 3	partial cone	70
25,27-diester 4a	flattened cone	1.5
25,26-diester 5a	1,3-alternate	4300
25,26-diester 6	cone	60
monoester 7	cone	220

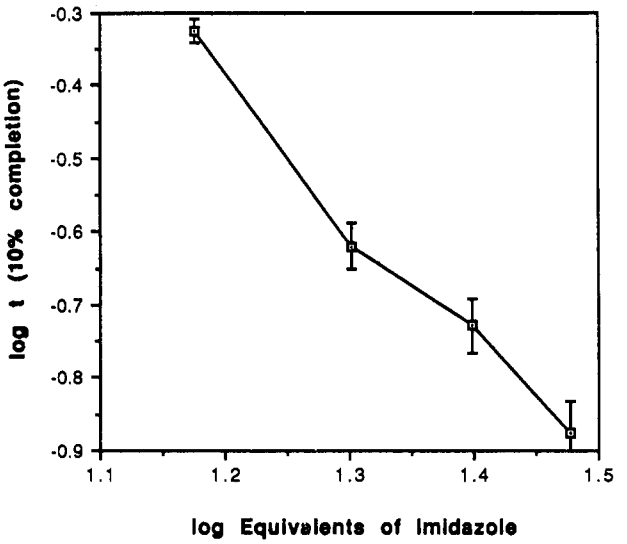


Figure 4.

idazole-induced cleavage almost 2900 times less rapidly than **4a**, attributable to the 1,3-alternate conformation of **6a** in which the phenolic OH groups are not proximate to the ester carbonyls. Also, the 12-fold greater rate of ester cleavage for the triester in the cone (**2**) than in the syn-anti-syn partial cone conformation (**3**) follows this same trend, though less dramatically so. The rather slow rates of ester cleavage shown by the cone conformer of the 25,26-diester **6** and the monoester **5** seem surprising but may be due to the OH groups in these compounds being adjacent not only to the ester carbonyl groups but also to other neighboring phenolic OH groups. In cases where the ester cleavage is particularly fast (i.e. **4a** and **2**), the phenolic OH group is proximate to the ester carbonyl group but *not* to a neighboring phenolic OH group.

Semiquantitative Kinetic Studies. Although a detailed kinetic analysis is beyond the scope of the present investigation, attempts have been made to establish the order of the reaction with respect to the amine. The best-fit straight line drawn through the data points of a plot of log time vs log equivalents of imidazole (see Figure 4) for cleavage reactions of **4a** carried to 10% completion has a slope of ca. −1.7. Insertion of this number in the equation[8] "order of reaction (n) = 1 − slope" gives a value

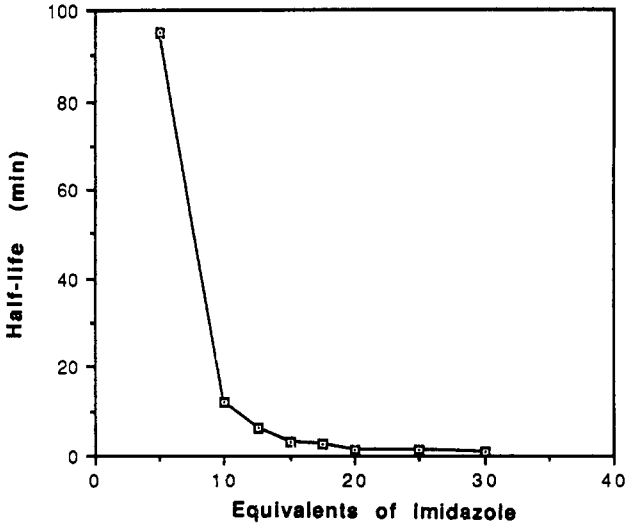


Figure 5.

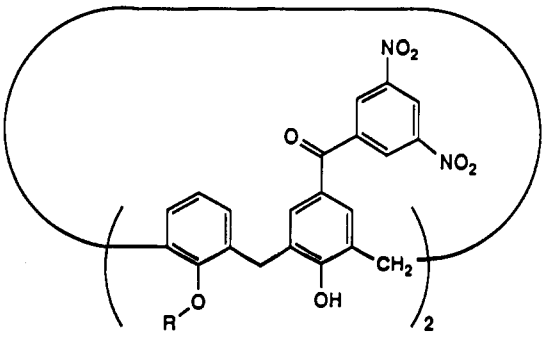
of 2.7. The fractional order may simply be the result of experimental error; it may arise from a pair of simultaneous pathways of different order; or it may indicate that for the particular concentrations of imidazole used to obtain these data the reaction is changing from third-order to pseudo-second order. Some indication that the last of these possibilities might play a role is seen in Figure 5 where a plot of the rate of cleavage of **4a** vs the amount of imidazole present shows a break in the region of 10–15 equiv of imidazole, the addition of more imidazole beyond this point having relatively little effect on the rate.

De-*tert*-butylation and Para Substitution Reactions. De-*tert*-butylation. To establish the general utility of the partially esterified calixarenes as precursors for the synthesis of calixarenes selectively substituted in the para positions, de-*tert*-butylations of several of the compounds described in this paper were carried out. Treatment of the esters with a 20-fold excess of $AlCl_3$ in toluene solution results in removal of the *tert*-butyl groups para to the free phenolic moieties, leaving intact those para to the esterified phenolic moieties. In this fashion the monoester **7** produces the mono-*tert*-butyl compound **12a**, the diesters **4a** and **5** produce the di-*tert*-butyl compounds **12b** and **12c**, and the triester **2** produces the tri-*tert*-butyl compound **12d**, the yields of de-*tert*-butylation products ranging from 54 to 89%. It is interesting to note that de-*tert*-butylation occurs even in CH_2Cl_2 solution (presumably with the formation of isobutene) although somewhat more sluggishly than in toluene. For example, the dimethyl ether of *p-tert*-butylcalix[4]arene (**8a**)[11] is converted in this fashion to the di-*tert*-butyl analogue **8b** under mild conditions[1] and to the completely de-*tert*-butylated analogue **8c** under more strenuous conditions.

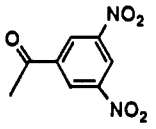
Para Acylation and Aroylation. The dimethyl ether **8c** reacts with 3,5-dinitrobenzoyl chloride in the presence of $AlCl_3$ in refluxing $CHCl_3$ to give the diketone **14a** along with a small amount of the monoaroylated compound. In similar fashion the diester **13**, prepared by 3,5-dinitrobenzoylation of calix[4]arene **1b**, yields the diaroyl compound **14b** upon treatment with 3,5-dinitrobenzoyl chloride and $AlCl_3$. The di-*tert*-butyl analogue **12b**, prepared by selective de-*tert*-butylation of **4a** as described above, affords the diacyl compounds **15a** and **15b** upon treatment with acryloyl chloride and γ-chlorobutanoyl chloride, re-

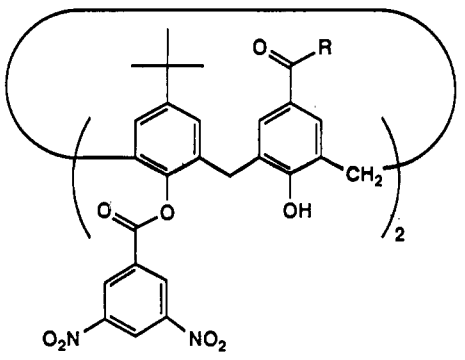
(8) Frost, A. H.; Pearson, R. B. *Kinetics and Mechanism*, 2nd ed.; John Wiley and Sons: New York, 1961.
(9) Zinke, A.; Ziegler, E. *Ber.* **1944**, *77*, 264.
(10) *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Vicens, J., Böhmer, V., Eds.; Kluwer Academic Publishers: Dordrecht, 1991. Gutsche, C. D. *Calixarenes*; Stoddart, J. F., Ed.; Royal Society of Chemistry: London, 1989. Gutsche, C. D. In *Calixarenes and the Art of Molecular Basketmaking*; Izatt, R. M., Christensen, J. J., Eds.; John Wiley & Sons, Inc.: New York, 1987; pp 93–165. Gutsche, C. D. In *Host Guest Complex Chemistry: Macrocycles*; Vögtle, F.; Weber, E., Eds.; Springer-Verlag: Berlin, 1985; pp 375–421.
(11) Gutsche, C. D.; Dhawan, B.; Levine, J. A.; No, K. H.; Bauer, L. J. *Tetrahedron* **1983**, *39*, 409.

spectively, in the presence of $AlCl_3$.



14a R = CH_3

14b R = 



15a R = $CH{=}CH_2$

15b R = $CH_2CH_2CH_2Cl$

Other Reactions of Calixarenes, Calixarene Ethers, and Calixarene Esters. 25,27-Bis((3,5-dinitro-4(*R*)-benzoyl)oxy) Esters. Three 25,27-bis((3,5-dinitrobenzoyl)oxy) esters carrying substituents at the 4-position of the aroyloxy ring were synthesized by the procedures described above for **4a** including the methyl compound **9a**, (dimethylamino)ethyl compound **9b**, and vinyl compound **9c**.

Reaction of *p-tert*-Butylcalix[4]arene with $SOCl_2$. From some of the imidazole-induced reactions of *p-tert*-butylcalix[4]arene (1) with 3,5-dinitrobenzoyl chloride small amounts of a compound were isolated that possessed an ^1H NMR spectrum corresponding to a calixarene in the 1,2-alternate conformation and showing an equivalent set of *p-tert*-butyl resonances. The IR spectrum indicated the absence of free OH groups, and the mass spectrum showed a strong signal at *m/e* 649, corresponding to **1a**, along with weak signals at 697 and 745. These data are in agreement with the bis-cyclic sulfite structure **10**, and it was subsequently shown that the same product can be obtained in excellent yield by treatment of **1a** with $SOCl_2$. Heating or treating **10** with MeOH removes the sulfite groups and converts **10** back to **1a**. Formation of **10** in the esterification reactions is obviously due to residual $SOCl_2$ used in the commercial preparation of 3,5-dinitrobenzoyl chloride.

Trisheptanoyl Ester of *p-tert*-Butylcalix[4]arene. To test the generality of the triester-forming process a reaction was carried out between **1a** and an aliphatic acid chloride. Under the same conditions used for the preparation of **2**, treatment of *p-tert*-butylcalix[4]arene with heptanoyl chloride and 1-methylimidazole in acetonitrile solution affords the triester **11** in 90% yield.

Discussion

The first preparation of a calixarene derivative was reported by Zinke and Ziegler in 1944.[9] Since then many other derivatives have appeared in the rapidly burgeoning literature of these compounds.[10] Of the three ring sizes of calixarenes that currently are readily accessible, the most assiduously studied are the calix[4]arenes. Although in many cases these cyclic tetramers form the completely substituted products of derivatization, such as the tetraacetate, the tetramethyl ether, etc. there is a growing list of examples in which partially derivatized products can be isolated. In the case of ether derivatives, for example, the 25,27-disubstituted compounds, first reported by Gutsche and co-workers,[11] have been exploited in interesting fashions by others for the preparation of calix crown ethers,[12,13] calixspherands,[13] and a variety of calix[4]arenes substituted at two of the para positions of the aryl rings.[14] The triethyl ether of *p-tert*-butylcalix[4]arene has been obtained by the acid-induced selective cleavage of the tetraethyl ether,[15] and the X-ray crystallographic structure of the triacetate of *p-tert*-butylcalix[4]arene has been reported.[16] To date, partially esterified calixarenes have not been exploited in comparable fashion, one of the few examples being the use of the tribenzoate by Gutsche and Lin[2] for the preparation of 5-allylcalix[4]arene.

Since benzoyl chloride and 4-nitrobenzoyl chloride react with *p-tert*-butylcalix[4]arene to yield the tetraesters, the absence of any tetraester in the aroylation with 3,5-dinitrobenzoylating agents might logically be ascribed to steric interference between the aryl residues (for products in the cone conformation) or between the aryl and *tert*-butyl residues (for products in the 1,3-alternate conformation). The tendency for the system to avoid the *tert*-butyl/3,5-dinitrobenzoyl interaction is well illustrated by the change in conformation from flattened cone to 1,3-alternate that occurs upon the removal of the *tert*-butyl groups at the 5- and 17-positions in the conversion of **4a** to **12b**. However, the triester **2** *can* be prepared in excellent yield under appropriate conditions, and inspection of CPK models suggests that the additional interference that would result from the introduction of a fourth aryl residue to form the tetraester should be no greater than that resulting from the addition of the third aryl residue. That solubility factors might also play a role in calixarene esterifications is shown by the 4-nitrobenzoylation of *p-tert*-butylcalix[6]arene which yields a mixture of tetra- and pentaesters, while that of *p*-allylcalix[6]arene under the same conditions yields the hexaester;[17] the greater solubility of the *p*-allyl esters keeps the products in solution throughout the course of the reaction. It has already been

(12) Ungaro, R.; Pochini, A.; Andreetti, G. D. *J. Inclusion Phenom.* **1984**, *2*, 19.

(13) 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.

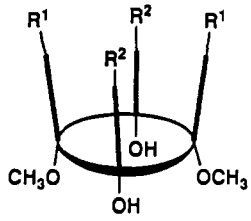
(14) van Loon, J.-D.; Arduini, A.; Coppi, L.; Verboom, W.; Pochini, A.; Ungaro, R.; Harkema, S.; Reinhoudt, D. N. *J. Org. Chem.* **1990**, *55*, 5639–46. Beer, P. D. Keefe, A. D.; Drew, M. G. B. *J. Orgmet. Chem.* **1989**, *378*, 437.

(15) Böhmer, V.; Vogt, W.; Harris, S. J.; Leonard, R. G.; Collins, E. M.; Deasy, M.; McKervey, M. A.; Owens, M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 431.

(16) Zhang, P.; Guo, F.; Huang, Z. *Huaxue Xuebao* **1989**, *47*(8), 731; *Chem. Abstr.* **1990**, *112*, 178299y.

(17) Rogers, J. S.; Gutsche, C. D. unpublished observations.

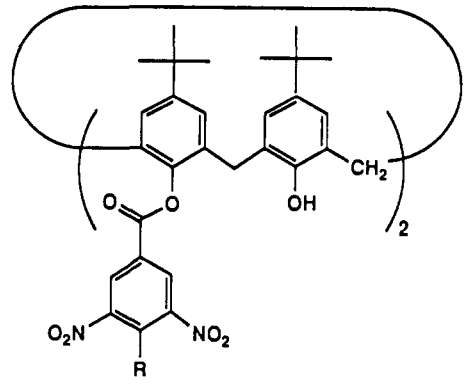
Chart I



8a $R^1 = R^2 = t\text{-Bu}$

8b $R^1 = t\text{-Bu}, R^2 = H$

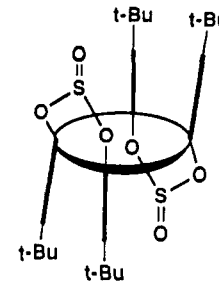
8c $R^1 = R^2 = H$



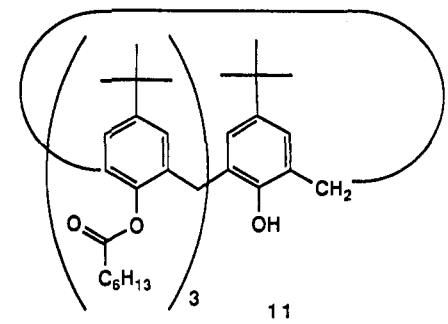
9a (R = CH_3)

9b (R = $CH_2CH_2N(CH_3)_2$)

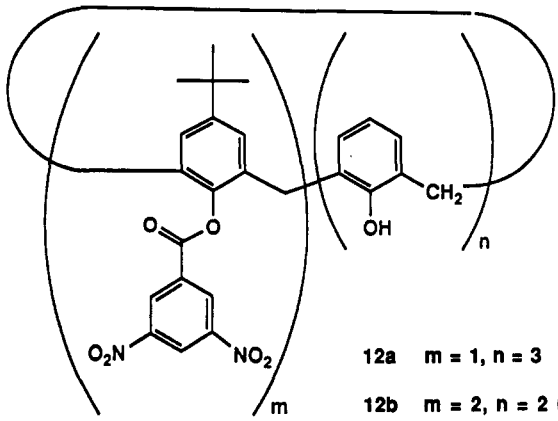
9c (R = $CH{=}CH_2$)



10



11



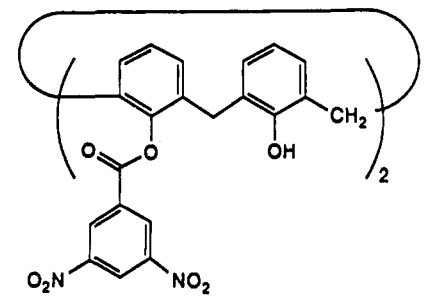
12a m = 1, n = 3

12b m = 2, n = 2 (25,27-diester)

12c m = 2, n = 2 (25,26-diester)

12d m = 3, n = 1

1b ⟶



13

suggested (see above) that the formation of the triester when 1-methylimidazole is used is due to the ability of this base to interact with the aroyl chloride and scavenge the HCl while remaining an ineffective ester cleaving reagent. The triester, once it forms under these conditions, remains intact, in contrast to reactions involving imidazole which cleaves the initially formed triester to lower esters. The formation of triester rather than tetraester might be ascribed to the inability of 1-methylimidazole to remove the proton from the remaining OH group of the triester.

The 25,27-diester of *p-tert*-butylcalix[4]arene **4a** is available in excellent yield by procedures that do *not* employ an amine (see above). The compound assumes a flattened cone conformation in which the 3,5-dinitrobenzoyl moieties are at an angle of ca. 45° to one another, thereby minimizing steric interference between them. Under conditions that *do* employ an amine, however, the 25,27-diester is no longer the major product but is superseded by other 3,5-dinitrobenzoates of **1**, depending on the particular amine and reaction conditions that are used. The details of the aminolysis (see previous section) are compatible with a process involving a neutral activated complex (reaction facilitated by nonpolar solvents) in which a neighboring phenolic residue, presumably in its oxyanionic form, plays an important part. The kinetic data discussed above, indicating that the order of the reaction with respect to imidazole is 2 or greater, suggest that the imidazole plays more than one role, certainly performing as a nucleophile {to yield *N*-(3,5-dinitrobenzoyl)imidazole as an aminolysis product} and probably also acting as a proton transfer agent. Without attempting to specify the mechanism in detail, we suggest that 1 equiv of imidazole is involved in forming the calixarene oxyanion, another in acting as a nucleophile to form a tetrahedral intermediate, and a third in assisting the decomposition of the tetrahedral intermediate by facilitating the necessary proton transfers. Such a picture implies that the rate-determining step is the break-down of the tetrahedral intermediate, catalyzed by imidazole and preceded by the equilibrium processes involving the formation of the calixarene oxyanion and tetrahedral intermediate.

$$1 + \text{Im} \rightleftarrows \text{IMH}^+ + 1^-$$

$$1^- + \text{Im} \rightleftarrows [\text{tetrahedral intermediate}]$$

$$[\text{tetrahedral intermediate}] \xrightarrow{\text{Im}} \text{product}$$

The facile aminolysis of the 25,27-diester to the monoester raised the hope of achieving a similarly selective cleavage of the triester **2** to a 25,26-diester. However, under the conditions that smoothly convert **4a** to **7** the triester gives a mixture of compounds which is shown by HPLC analysis to contain starting triester **2**, 25,27-diester **4a**, *p-tert*-butylcalix[4]arene **1a**, two compounds subsequently identified as 25,26-diesters (**5**, **6**), and monoester **7**. The diesters are formed in yields too low to make isolation and purification feasible on a preparative scale, the initial structure proofs at this point of the investigation

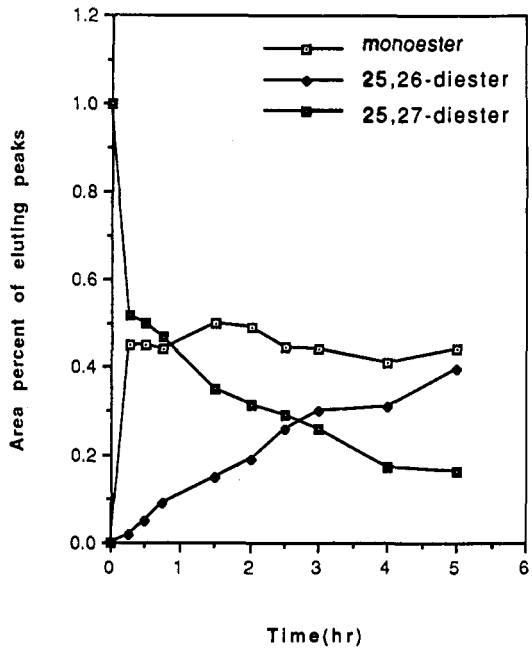


Figure 6.

depending on ^1H NMR analyses of small samples. Ultimately, however, these structure assignments were verified when larger amounts of the 25,26-diesters were obtained by direct preparation from **1**.

It was eventually realized that the high yield conversion of **4a** to **7** is dependent on the reaction conditions. Thus, when the amount of imidazole is reduced and/or the solvent changed from chloroform–acetonitrile to pure chloroform the product no longer is the monoester but is a 25,26-diester in which a 3,5-dinitrobenzoyl moiety has migrated from the 27-position to the 26-position. The composition of the reaction mixture as a function of time was determined by means of HPLC and ^1H NMR analyses, the results of which are shown in Figure 6. These reveal that there is a rapid initial disappearance of the starting 25,27-diester **4a** concomitant with a rapid formation of the monoester **7** but that as time progresses and the 25,27-diester **4a** continues to disappear, the amount of monoester **7** remains more or less constant, and the amount of 25,26-diester **5** continuously increases. It was concluded from these data that the 25,26-diester is *not* formed via intramolecular rearrangement but by reesterification of the monoester by the *N*-(3,5-dinitrobenzoyl)imidazole produced in the initial cleavage reaction. This is also supported by the results obtained when $CHCl_3$ containing a small amount of EtOH is used as the solvent. Initially, this was an inadvertent experiment arising from a change in brands of $CHCl_3$ from one in which butene was the stabilizer to one in which EtOH was used for this purpose. With the EtOH-containing $CHCl_3$ no 25,26-diester was obtained, only the monoester **7** along with ethyl 3,5-dinitrobenzoate. This is the result of the more rapid reaction of the *N*-(3,5-dinitrobenzoyl)imidazole produced in the aminolysis of **4a** with EtOH than with **7**.

The formation of the 25,26-diester through reesterification of the monoester by *N*-(3,5-dinitrobenzoyl)imidazole suggested that appropriate choice of solvent and amine might provide a method for preparing the various esters observed in these cleavage processes by *direct* aroylation of *p-tert*-butylcalix[4]arene with 3,5-dinitrobenzoyl chloride. As illustrated by the procedures discussed in the first section of this paper, this does, indeed, prove to be the case. In the presence of 1-alkylimidazoles **1a** is converted to the

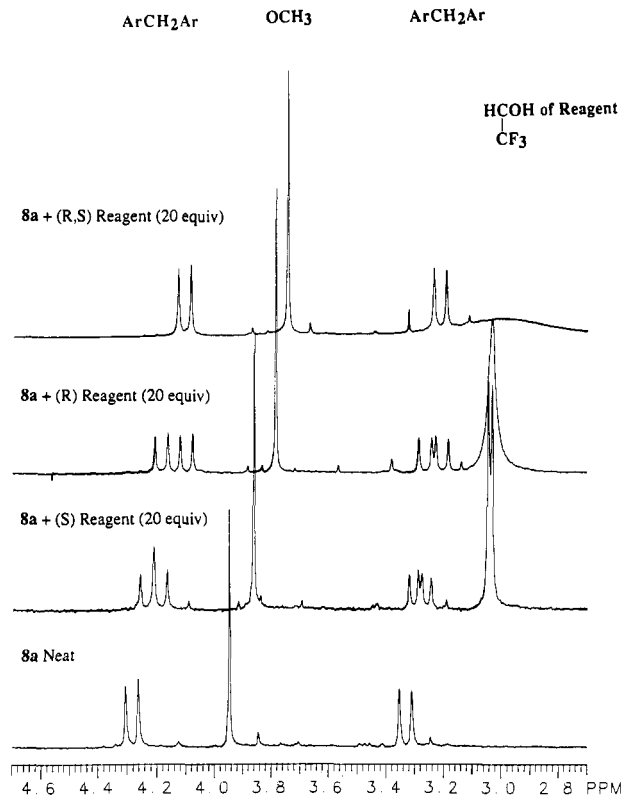


Figure 7.

triester **2** in 90% yield, these amines being effective proton-transfer reagents but ineffective nucleophiles for ester cleavage. In the presence of imidazole, **1a** is converted to the alternate conformer of the 25,26-diester **5**, the cone conformer of the 25,26-diester **6**, or the monoester **7** in good to excellent yields, depending on the amount of imidazole used, the duration of the reaction, and the solvent. This provides a preparatively useful route to these otherwise difficulty accessible types of compounds.

The 25,26-diesters are especially interesting because they are chiral if the ester moieties are on opposite sides of the molecule. This, in fact, was the original motivation for exploring the aminolysis of the triester which we had hoped would be clean and selective but which, instead, yields a mixture. Prior to the present work the only examples of 25,26-derivatives of calix[4]arenes were the dipyridyl ethers prepared by Bottino et al.[18] and by Shinkai and co-workers[19] and the phthaloyl ester prepared by van Loon et al.[20] One of the standard methods for determining whether or not a compound is chiral is to observe the effect on its ^1H NMR spectrum of adding a chiral complexing agent. Most of the chiral reagents with which **5** and **6** were tested showed no doubling of the resonance patterns, presumably due to a failure of sufficiently strong complexes to form. Pirkle's reagent [(*R*)- or (*S*)-2,2,2-trifluoro-1-(9-anthryl)-ethanol] with **5** and **6**, on the other hand, does produce a doubling of the resonances, indicative of inherently chiral structures for these compounds. However, this result is tempered by the fact that achiral calix[4]arenes can also behave in an apparently similar fashion. For example, the 25,27-dimethyl ether of *p-tert*-butylcalix[4]arene (**8a**)[11]

(18) Bottino, F.; Giunta, L.; Pappalardo, S. *J. Org. Chem.* **1989**, *54*, 5407.

(19) Shinkai, S.; Otsuka, T.; Araki, K.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 4055.

(20) van Loon, J.-D.; Kraft, D.; Ankone, M. J. K.; Verboom, W.; Harkema, S.; Vogt, W.; Böhmer, V.; Reinhoudt, D. N. *J. Org. Chem.* **1990**, *55*, 5176–79.

shows a similar doubling of resonances when mixed with Pirkle's reagent. As illustrated in Figure 7, in the presence of either the *R* or *S* enantiomer of the reagent the doublets arising from the methylene hydrogens of **8a** change to quartets and are shifted upfield. With the *R,S* reagent only the upfield shift is observed, without the resonance doubling. Compound **8a** possesses a plane of symmetry passing through atoms 23, 25, 27, 11, making C-2 and C-8 enantiotopic with C-20 and C-14, respectively. In the presence of the chiral complexing agent these pairs of methylenes become diastereotopic and anisochronous. As noted many years ago by Pirkle and co-workers,[21] *J* coupling between nuclei that are diastereotopic and anisochronous is characteristic for the meso form of a compound, in contrast to a (+) or (−) enantiomer, for which *J* coupling is not induced by the shift reagent. However, if the *J*-coupled groups are far from one another in the molecule, the coupling will be too small to be detectable, as is the case with the 25,27-diether **8a**. Thus, failure to observe coupling in the doubled resonances from **5** and **6** cannot be taken as absolute proof that these 25,26-diesters are racemates rather than meso compounds.

The interaction of calix[4]arenes with 3,5-dinitrobenzoyl chloride in the presence of amines as well as the interaction of the 3,5-dinitrobenzoates of calix[4]arenes with amines present interesting, striking, and useful examples of how reaction conditions can play a critical role in product formation. Although the precise details of the reactions involved in these interrelated processes are not yet understood, it seems probable that the determining factor is the competition between kinetic and thermodynamic control, with conformational and strain factors playing important roles. The most important practical aspect of the present work is that it provides additional tools for the synthesis of selectively functionalized calix[4]arenes.

Experimental Section[22,23]

Cone Conformer of 5,11,17,23-Tetra-*tert*-butyl-25,26,27-tris((3,5-dinitrobenzoyl)oxy)-28-hydroxycalix[4]arene (2). A 1.3-g (2-mmol) sample of *p-tert*-butylcalix[4]arene[24] was mixed with 1.6 mL (20 mmol) of 1-methylimidazole and 1.8 g (8 mmol) of 3,5-dinitrobenzoyl chloride in 100 mL of CH_3CN in a 200-mL flask. The contents were stirred at room temperature for 6 h and then acidified with 100 mL of 1 N HCl. After the mixture had been stirred vigorously for 1 h the precipitate was removed by filtration and dried under vacuum to give 2.3 g (95%) of **2** as a pale yellow powder: mp 331–333 °C; ^{1}H NMR ($CDCl_3$) δ 9.12 (m, 8, ArH of $ArNO_2$), 8.70 (t, 1, *J* = 2.1 Hz, ArH of $ArNO_2$), 7.44 (s, 2, ArH), 7.23 (s, 2, ArH), 6.76 (d, 2, *J* = 3.3 Hz, ArH), 6.74 (d, 2 *J* = 3.3 Hz, ArH), 4.30 (br s, 1 OH), 4.18 (d, 2 *J* = 14.1 Hz, $ArCH_2Ar$), 3.87 (d, 2, *J* = 13.8 Hz, $ArCH_2Ar$), 3.58 (d, 2, *J* = 13.8 Hz, $ArCH_2Ar$), 3.49 (d, 2, *J* = 14.1 Hz, $ArCH_2Ar$), 1.44 (s, 9, $C(CH_3)_3$), 1.38 (s, 9, $C(CH_3)_3$), 0.93 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{65}H_{62}N_6O_{19}$: C, 63.41; H, 5.08; N, 6.83. Found: C, 63.59; H, 5.08; N, 6.82.

Partial Cone Conformer of 5,11,17,23-Tetra-*tert*-butyl-25,26,27-tris((3,5-dinitrobenzoyl)oxy)-28-hydroxycalix[4]-arene (3). A 1.3-g (2-mmol) sample of *p-tert*-butylcalix[4]-arene[24] was mixed with 3.2 mL (40 mmol) of 1-methylimidazole and 1.8 g (8 mmol) of 3,5-dinitrobenzoyl chloride in 50 mL of $CHCl_3$ in a 100-mL flask. The contents were stirred for 48 h at room temperature and then acidified with 50 mL of 1 N HCl. The organic layer was separated, dried over Na_2SO_4, and filtered. The solvent was evaporated, and the residue was triturated with MeOH. The pale yellow gellike precipitate was removed by filtration and dried to give 1.7 g (70%) of **3**. Crystallization from toluene gave yellow rhombs: mp 285–287 °C; ^{1}H NMR ($CDCl_3$) δ 8.98 (m, 3, ArH of $ArNO_2$), 8.89 (d, 4, *J* = 2.1 Hz, ArH of $ArNO_2$), 7.82 (br s, 2 O_2NArH), 7.12 (s, 2, ArH), 7.08 (s, 2, ArH), 7.04 (d, 2, *J* = 2.1 Hz, ArH), 6.65 (d, 2, *J* = 2.1 Hz, ArH), 5.87 (s, 2, OH), 4.16 (d, 2, *J* = 17.1 Hz, $ArCH_2Ar$), 3.93 (d, 4, *J* = 14.4 Hz, $ArCH_2Ar$), 3.64 (d, 2, *J* = 14.7 Hz, $ArCH_2Ar$), 1.27 (s, 9, $C(CH_3)_3$), 0.85 (s, 9, $C(CH_3)_3$), 0.65 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{65}H_{62}N_6O_{19}$: C, 63.41; H, 5.08; N, 6.83. Found: C, 63.64; H, 5.03; N, 6.75.

Flattened Cone Conformer of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis((3,5-dinitrobenzoyl)oxy)-26,28-dihydroxycalix-[4]arene (4a). (a) Dichloro Phenyl Phosphate–DMF Procedure. A 0.75-g (4-mmol) sample of dichloro phenyl phosphate was mixed with 0.6 mL of DMF at ice-bath temperature, and 0.85 g (4 mmol) of 3,5-dinitrobenzoic acid in 40 mL of CH_2Cl_2 was added, followed by 1.0 g (1.5 mmol) of *p-tert*-butylcalix[4]arene[24] and 0.5 mL (15 mmol) of pyridine. The reaction mixture was stirred at room temperature for 12 h, and 30 mL of 1 N HCl was then added with vigorous stirring. The organic layer was separated, dried over Na_2SO_4, and filtered, and the solvent was evaporated. The residue was triturated with MeOH to leave a pale yellow gellike precipitate which was dried and recrystallized from toluene to give 1.2 g (75%) of **3** as yellow rhombs: mp 302–304 °C; ^{1}H NMR ($CDCl_3$) δ 9.60 (d, 4, *J* = 2.1 Hz, ArH of $ArNO_2$), 9.22 (t, 2, *J* = 2.1 Hz, ArH of $ArNO_2$), 7.17 (s, 4, ArH), 6.82 (s, 4, ArH), 5.20 (s, 2, OH), 3.95 (d, 4, *J* = 14.1 Hz, $ArCH_2Ar$), 3.47 (d, 4, *J* = 14.1 Hz, $ArCH_2Ar$), 1.33 (s, 18, $C(CH_3)_3$), 0.93 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{58}H_{60}N_4O_{14}$: C, 67.17; H, 5.83; N, 5.40. Found: C, 67.24; H, 5.84; H, 5.44.

(b) $AlCl_3$ Procedure. A mixture of 3.0 g (4.6 mmol) of **1a**, 6.0 g (26 mmol) of 3,5-dinitrobenzoyl chloride, and 3.0 g (23 mmol) of anhydrous $AlCl_3$ in 250 mL of CH_2Cl_2 containing 20 mL of DMF was stirred at room temperature for 12 h. The mixture was cooled in an ice bath and treated, with stirring, with 50 mL of 3 N HCl. The product **4a** was obtained as described above as 3.2 g (67%) of yellow, feathery crystals after recrystallization from $CHCl_3$–MeOH.

(c) Pyridine Procedure. A 1.5-g (2.3-mmol) sample of **1a**, 1.1 g (4.8 mmol) of 3,5-dinitrobenzoyl chloride, and 3.7 mL (46 mmol) of pyridine were mixed in 100 mL of $CHCl_3$. The suspension was stirred at room temperature for 96 h; then, 75 mL of 1 N HCl was added, and the mixture was worked up as described above to give 2.5 g (95%) of **4a**.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis((3,5-dinitrobenzoyl)oxy)-26,28-diacetoxycalix[4]arene (4b). Three drops of concd H_2SO_4 were added to a suspension of 2.0 g (1.9 mmol) of **4a** in 25 mL of acetic anhydride, and the mixture was stirred at room temperature for 18 h. It was then poured onto ice, and 50 mL of $CHCl_3$ was added. The $CHCl_3$ solution was washed with $NaHCO_3$, dried over $CaCl_2$, concentrated, and treated with MeOH. Upon standing, 1.7 g (80%) of **4b** separated as tiny white rhombs: mp >311 °C dec; ^{1}H NMR ($CDCl_3$) δ 9.21 (t, 2, *J* = 2.1 Hz, NO_2ArH), 9.09 (d, 4, *J* = 2.1 Hz, NO_2ArH), 7.33 (s, 2, ArH), 7.01 (d, 2, *J* = 2.1 Hz, ArH), 6.98 (d, 2, *J* = 2.1 Hz, ArH), 6.79 (s, 2, ArH), 3.80 (m, 6, $ArCH_2Ar$), 3.42 (d, 2, *J* = 13.5 Hz, $ArCH_2Ar$), 1.89 (s, 3, $COCH_3$), 1.37 (s, 9, $C(CH_3)_3$), 1.20 (s, 3, $COCH_3$), 1.18 (s, 18, $C(CH_3)_3$), 0.82 (s, 9, $C(CH_3)_3$). Anal. Calcd for $C_{62}H_{64}N_4O_{16}$: C, 66.42; H, 5.75; N, 5.00. Found: C, 66.34; H, 5.80; N, 4.99.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis((3,5-dinitrobenzoyl)oxy)-26,28-bis(acrolyloxy)calix[4]arene (4c). A 1.00-g (1.00-mol) sample of **4a** was added to a suspension of 0.66 g (8.0 mmol) of acryloyl chloride and 0.88 g (6.7 mmol) of $AlCl_3$ in 100 mL of CH_2Cl_2. The mixture was stirred 7 h at ice-bath tem-

(21) Kainosho, M.; Ajisaka, K.; Pirkle, W. H.; Beare, S. D. *J. Am. Chem. Soc.* **1972**, *94*, 5924.

(22) The melting points of all compounds above 250 °C were taken in sealed and evacuated capillary tubes on a Mel-Temp apparatus (Laboratory Devices, Cambridge, MA) using a 500 °C thermometer calibrated against a thermocouple. Flash chromatography[23] was carried out using J. T. Baker 40-mm silica gel. Thin-layer chromatography was carried out on 250-mm silica plates. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Varian XL-300 spectrometer. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane (δ 0.00) as an internal standard. Microanalyses were carried out by Desert Laboratories, Tucson, AZ. Analytical samples were dried at least 36 h at 140 °C and 1–2 mm of pressure. In some instances solvent of crystallization was retained, considerably affecting the elemental analysis. Those instances in which solvent of crystallization is retained the best fits between the analytical values and the appropriate increment of solvent were sought. The presence of these substances was qualitatively supported by the appearance of characteristic resonances in the ^{1}H NMR spectrum of the host compound.

(23) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(24) Gutsche, C. D.; Iqbal, M. *Org. Synth.* **1989**, *69*, 234.

perature and 14 h at room temperature, following which it was treated with 100 mL of cold H_2O and worked up to give 0.95 g of a white powder. Recrystallization from $CHCl_3$–MeOH gave 0.60 g (55%) of **4c** as fine, colorless needles: mp >302 °C dec; ^1H NMR ($CDCl_3$) δ 9.33 (d, 4, J = 2.1 Hz, NO_2ArH), 9.28 (t, 2, J = 2.1 Hz, NO_2ArH), 7.32 (s, 4, ArH), 6.93 (m, 2, COCH=C), 6.73 (s, 4, ArH), 6.46 (d, 2, J = 15.8 Hz, C=CH_2), 5.59 (d, 2, J = 12.0 Hz, C=CH_2), 3.77 (d, 4, J = 13.2 Hz, $ArCH_2Ar$), 3.38 (d, 4, J = 13.2 Hz, $ArCH_2Ar$), 1.40 (s, 18, $C(CH_3)_3$), 0.92 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{64}H_{64}N_4O_{16}$: C, 67.12; H, 5.63; N, 4.89. Found: C, 66.81; H, 5.72; N, 4.94.

1,3-Alternate Conformer of 5,11,17,23-Tetra-*tert*-butyl-25,26-bis((3,5-dinitrobenzoyl)oxy)-27,28-dihydroxycalix[4]arene (5). (a) Procedure a. A 1.3-g (2-mmol) sample of *p-tert*-butylcalix[4]arene[24] was treated with 2.7 g (40 mmol) of imidazole and 1.0 g (4 mmol) of 3,5-dinitrobenzoyl chloride in 50 mL of $CHCl_3$ in a 100-mL flask. The contents were stirred at room temperature for 6 h and then made acidic with 50 mL of 1 N HCl. The organic layer was separated, dried over Na_2SO_4, and filtered. The solvent was evaporated, and the residue was triturated with MeOH. The yellow precipitate was removed by filtration and dried to give 1.6 g (80%) of **5** as a yellow powder. An analytical sample of **5** was obtained by recrystallization from $CHCl_3$–MeOH as pale orange rhombs: mp >260 °C dec; ^1H NMR ($CDCl_3$) δ 9.10 (t, 2, J = 2.1 Hz, ArH of $ArNO_2$), 8.39 ((br s, 4, ArH or $ArNO_2$), 7.21 (d, 2, J = 2.2 Hz, ArH), 7.07 (d, 2, J = 2.2 Hz, ArH), 6.76 (s, 4, ArH), 6.50 (br s, 2, OH), 3.94–3.82 (m, 8, $ArCH_2Ar$), 0.96 (s, 18, $C(CH_3)_3$), 0.77 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{58}H_{60}N_4O_{14}$: C, 67.17; H, 5.83; N, 5.40. Found: C, 67.23; H, 5.89; N, 5.26.

(b) Procedure b. A 3.7-g (3-mmol) sample of triester **3** was treated with 0.63 g (9 mmol) of imidazole in 100 mL of $CHCl_3$. The solution was stirred for 20–24 h, and 75 mL of 1 N HCl was then added. The mixture was vigorously stirred for 5 min and allowed to settle. The organic layer was separated, washed with brine, and dried over Na_2SO_4. The solvent was evaporated until a solid separated, at which point the suspension was cooled and the solid *p-tert*-butylcalix[4]arene (starting material) was removed by vacuum filtration. The mother liquor was concentrated and triturated with MeOH. The yellow precipitate was removed by filtration to give 2.5 g (80%) of **5** suitable for use without further purification.

(c) Procedure c. A 3.1-g (3-mmol) sample of the 25,27-diester **4a** was mixed with 0.80 g (12 mmol) of imidazole in 100 mL of $CHCl_3$ in a 200-mL round-bottomed flask. The solution was stirred at room temperature for 20–24 h, and 75 mL of 1 N HCl was then added. The mixture was vigorously stirred for 5 min and allowed to settle, and the organic layer was separted, washed with brine, and dried over Na_2SO_4. The solution was concentrated under vacuum until solid began to appear and then cooled, and the precipitate consisting of starting material **1** was removed by filtration. The filtrate was concentrated, MeOH was added, and 2.5 g (80%) of essentially pure 25,26-diester **5** was separated by filtration.

Cone Conformer of 5,11,17,23-Tetra-*tert*-butyl-25,26-((dinitrobenzoyl)oxy)-27,28-dihydroxycalix[4]arene (6). (a) Procedure a. A 1.2-g (1.0-mmol) sample of triester **2** was treated with 1.02 g (15.0 mmol) of imidazole in 75 mL of $CHCl_3$. The contents were stirred at room temperature for 20 min, after which 50 mL of 1 N HCl was added. The organic layer was separated, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was crystallized from $CHCl_3$–MeOH to give fine, yellow flowerettes: mp >175 °C dec; ^1H NMR ($CDCl_3$) δ 9.23 (d, 4, J = 2.1 Hz, ArH of $ArNO_2$), 9.04 (t, 2, J = 2.1 Hz, ArH of $ArNO_2$), 7.10 (d, 2, J = 2.4 Hz, ArH), 7.04 (d, 2, J = 2.4 Hz, ArH), 7.02 (d, 2, J = 2.4 Hz, ArH), 6.96 (d, 2, J = 2.4 Hz, ArH), 5.73 (s, 2, OH), 4.18 (d, 2, J = 14.4 Hz, $ArCH_2Ar$), 4.13 (d, 1, J = 13.8 Hz, $ArCH_2Ar$), 3.83 (d, 1, J = 14.4 Hz, $ArCH_2Ar$), 3.60 (d, 1, J = 13.8 Hz, $ArCH_2Ar$), 3.59 (d, 1, J = 14.4 Hz, $ArCH_2Ar$), 3.45 (d, 1, J = 14.4 Hz, $ArCH_2Ar$), 1.17 (s, 18, $C(CH_3)_3$), 1.13 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{58}H_{60}N_4O_{14}$: C, 67.17; H, 5.83; N, 5.40. Found: C, 67.16; H, 5.87; N, 5.58.

(b) Method b. A 2.0-g (3-mmol) sample of *p-tert*-butylcalix-[4]arene was mixed with 6.4 mL (80 mmol) of 1-methylimidazole and 2.0 g (8 mmol) of 3,5-dinitrobenzoyl chloride in 100 mL of CH_3CN in a 200-mL flask. The contents were stirred at room temperature for 20 h and then made acidic by adding 50 mL of 2 N HCl. The suspension was stirred overnight, after which a yellow precipitate appeared which was separated by filtration and dried to give 2.8 g (90%) of **6** as a yellow powder.

5,11,17,23-Tetra-*tert*-butyl-25-((3,5-dinitrobenzoyl)oxy)-26,27,28-trihydroxycalix[4]arene (7). (a) Procedure a. A 1.0-g (0.96-mmol) sample of 25,27-diester **4a** was suspended in $CHCl_3$ in a 100-mL Erlenmeyer flask while 0.68 g (10.0 mmol) of imidazole was suspended in 20 mL of CH_3CN in another flask. The imidazole solution was added to the calixarene solution, and the contents were stirred at room temperature for 30 min after which 40 mL of 1 N HCl was added. The organic layer was separated, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was crystallized from $CHCl_3$–MeOH to give 0.4 g (50%) of monoester **7** as fine yellow needles: mp >170 °C dec; ^1H NMR ($CDCl_3$) δ 9.03 (s, 1, ArH of $ArNO_2$), 8.51 (s, 1, OH), 8.18 (br s, 2, ArH of $ArNO_2$), 7.44 (s, 2, ArH), 7.17 (s, 2, ArH), 5.98 (s, 2, OH), 6.93 (s, 2, ArH), 6.57 (s, 2, ArH), 4.02 (d, 2, J = 13.9 Hz, $ArCH_2Ar$), 3.97 (d, 2, J = 15.8 Hz, $ArCH_2Ar$), 3.82 (d, 2, J = 15.8 Hz, $ArCH_2Ar$), 3.63 (d, 2, J = 13.9 Hz, $ArCH_2Ar$), 1.40 (s, 9, $C(CH_3)_3$), 1.34 (s, 9, $C(CH_3)_3$), 0.77 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{51}H_{58}N_2O_9$: C, 72.66; H, 6.93; N, 3.32. Found: C, 72.14; H, 6.86; N, 3.32.

(b) Procedure b. A 2.0-g (3-mmol) sample of *p-tert*-butylcalix[4]arene[24] was mixed with 3.5 mL (45 mmol) of 1-methylimidazole and 0.9 g (4 mmol) of 3,5-dinitrobenzoyl chloride in 100 mL of CH_3CN in a 200-mL round-bottomed flask. The mixture was stirred at room temperature for 24 h and acidified with 50 mL of 2 N HCl. The mixture was stirred vigorously until a precipitate began to appear. The precipitate was removed by filtration to give 2.1 g (83%) of the monoester **7**, which was recrystallized from $CHCl_3$–MeOH to give an analytical sample as fine needles.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis((3,5-dinitro-4-methylbenzoyl)oxy)-26,28-dihydroxycalix[4]arene (9a). A mixture of 3.0 g (4.6 mmol) of *p-tert*-butylcalix[4]arene,[24] 9.8 g (40 mmol) of 3,5-dinitro-4-methylbenzoyl chloride, 3.0 g (23 mmol) of $AlCl_3$, 20 mL of DMF, and 200 mL of CH_2Cl_2 was stirred in a 500-mL round-bottomed flask for 20 h at room temperature. The mixture was worked up to give 4.0 g of crude product as an off-white solid which was recrystallized from $CHCl_3$–MeOH to afford 3.8 g (77%) of **9a** as pale yellow feathery crystals: mp >290 °C dec; ^1H NMR ($CDCl_3$) δ 9.10 (s, 4, ArH of $ArNO_2$), 7.17 (s, 4, ArH), 6.80 (s, 4, ArH), 5.13 (s, 2 OH), 3.95 (d, 4, J = 13.2 Hz, $ArCH_2Ar$), 3.46 (d, 4, J = 13.2 Hz, $ArCH_2Ar$), 2.68 (s, 6, $ArCH_3$), 1.33 (s, 18, $C(CH_3)_3$), 0.90 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{60}H_{64}N_4O_{14}$: C, 67.66; H, 6.06; N, 5.26. Found: C, 67.69; H, 5.80; N, 5.29.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis((3,5-dinitro-4-(β-(dimethylamino)ethyl)benzoyl)oxy)-26,28-dihydroxycalix[4]arene (9b). A 3.0-mL (20.0-mmol) sample of dichloro phenyl phosphate and 1.2 mL (15.6 mmol) of DMF were mixed at ice-bath temperature to give a white slurry. To this was added 1.9 g (8.0 mmol) of 3,5-dinitro-4-(β-(dimethylamino)ethyl)benzoic acid and 60 mL of CH_2Cl_2; the mixture was stirred at room temperature for 10 min and was treated with 2.0 g (3.0 mmol) of *p-tert*-butylcalix[4]arene[24] followed 10 min later with 2.4 mL (30 mmol) of pyridine. The solution was stirred at room temperature for 12 h, treated with 50 mL of 0.5 N HCl, and worked up to yield 2.1 g of a yellow powder. Recrystallization from MeOH–*i*-PrOH produced 2.0 g (57%) of the dihydrochloride of **9b** as light orange needles: mp >200 °C dec, ^1H NMR ($CDCl_3$) δ 9.19 (s, 4, O_2NArH), 7.16 (s, 4, ArH), 6.78 (s, 4, ArH), 5.01 (s, 2, OH), 3.93 (d, 4, J = 14.1 Hz, $ArCH_2Ar$), 3.66 (br s, 8, CH_2CH_2N), 3.45 (d, 4, J = 14.1 Hz, $ArCH_2Ar$), 3.03 (s, 12, $N(CH_3)_2$), 1.33 (s, 18, $C(CH_3)_3$), 0.91 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{66}H_{76}N_6O_{14}\cdot 2HCl$: C, 63.40; H, 6.29; N, 6.72. Found: C, 62.77; H, 6.07; N, 6.46.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis((3,5-dinitro-4-vinylbenzoyl)oxy)-26,28-dihydroxycalix[4]arene (9c) was prepared from *p-tert*-butylcalix[4]arene[24] and 3,5-dinitro-4-vinylbenzoic acid by the procedure described above for **9b** and was obtained in 70% yield, after recrystallization from toluene, as light yellow rhombs: mp >230 °C dec; ^1H NMR ($CDCl_3$) δ 9.14 (s, 4, O_2NArH), 7.17 (s, 4, ArH), 7.05 (m, 2, CH=CH_2), 6.81 (s, 4, ArH), 5.58 (d, 2, J = 11.7 Hz, CH=CH_2), 5.41 (d, 2, J = 17.7 Hz, CH=CH_2), 5.17 (s, 2, OH), 3.96 (d, 4, J = 14.1 Hz, $ArCH_2Ar$), 3.48 (d, 4, J

= 14.1 Hz, $ArCH_2Ar$), 1.45 (s, 18, $C(CH_3)_3$), 0.92 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{62}H_{64}N_4O_{14}$: C, 68.37; H, 5.92; N, 5.14. Found: C, 67.83; H, 5.91; N, 5.46.

Disulfite of *p-tert*-Butylcalix[4]arene (10). A 1.3-g (20-mmol) sample of *p-tert*-butylcalix[4]arene[24] was mixed with 2.3 mL (28 mmol) of 1-methylimidazole and 1.5 mL of $SOCl_2$ in 100 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 24 h during which time the initially cloudy solution cleared. After the addition of H_2O, the layers were separated and the CH_2Cl_2 layer worked up to give 1.1 g of crude material. This was triturated with cold CH_2Cl_2, which left unreacted starting material undissolved, and the triturate was evaporated to give 0.8 g (54%) of clean product along with an additional 0.4 g (27%) by concentration of the filtrate. An analytical sample was obtained as small, colorless rhombs by recrystallization from $CHCl_3$–MeOH: mp >270 °C dec; mass spec (EI) *m/e* 745 (M + 1), 697 (M + 1 − SO), 649 (M + 1 − 2SO; e.g. M + 1 for **1a**); ^1H NMR ($CDCl_3$) δ 7.16 (dd, 8, J = 2.4 Hz, ArH), 4.48 (d, 2, J = 13.8 Hz, $ArCH_2Ar$), 4.03 (s, 4, $ArCH_2Ar$), 3.48 (d, 2, J = 13.8 Hz, $ArCH_2Ar$), 1.30 (s, 36, $C(CH_3)_3$). Anal. Calcd for $C_{44}H_{52}O_6S_2$: C, 71.32; H, 7.07. Found: C, 71.34; H, 7.09.

5,11,17,23-Tetra-*tert*-butyl-25,26,27-tris(heptanoyloxy)-28-hydroxycalix[4]arene (11) was prepared by the procedure described above for the triester **2** and obtained in 90% yield as colorless rhombs after crystallization from $CHCl_3$–MeOH: mp 225–227 °C; ^1H NMR ($CDCl_3$) δ 7.23 (s, 2, ArH), 7.11 (s, 2, ArH), 6.72 (d, 2, J = 2.4 Hz, ArH), 6.63 (d, 2, J = 2.4 Hz, ArH), 4.04 (s, 1 OH), 3.81 (d, 2, J = 14.1 Hz, $ArCH_2Ar$), 3.66 (d, 2, J = 13.5 Hz, $ArCH_2Ar$), 3.45 (d, 2, J = 14.1 Hz, $ArCH_2Ar$), 3.26 (d, 2, J = 13.5 Hz, $ArCH_2Ar$), 3.06 (t, 2, J = 7.2 Hz, CH_2CO), 2.64 (m, 6, CH_2CH_2, CH_2CO), 1.77 (m, 6, CH_2CH_2), 1.37 (s, 9, $C(CH_3)_3$), 1.36 (s, 9, $C(CH_3)_3$), 1.33 (m, 16, CH_2CH_2), 0.93 (m, 9, CH_3), 0.91 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{65}H_{92}O_7$: C, 79.22; H, 9.41. Found: C, 78.80; H, 9.62.

5-*tert*-Butyl-25-((3,5-dinitrobenzoyl)oxy)-26,27,28-trihydroxycalix[4]arene (12a). To a suspension of 3.8 g (27.9 mmol) of $AlCl_3$ in 50 mL of toluene was added 0.80 g (1.0 mmol) of monoester **7**. The mixture was stirred for 1 h at room temperature, and 50 mL of cold H_2O was then added with vigorous stirring. The water layer was separated and washed with $CHCl_3$, and the organic layers were combined and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was triturated with ether to leave 0.6 g (89%) of a dark brown powder. This was dissolved in 50 mL of $CHCl_3$, heated to boiling, and treated with decolorizing charcoal. To the hot, filtered solution MeOH was added, and upon cooling **12a** precipitated as dark brown rhombs: mp >270 °C dec; ^1H NMR ($CDCl_3$) δ 9.02 (t, 1, J = 2.1 Hz, O_2NArH), 8.01 (br s, 2, O_2NArH), 7.86 (br s, 1, OH), 7.50 (s, 2, ArH), 7.18 (d, 2, J = 7.5 Hz, ArH), 6.92 (t, 1, J = 7.5 Hz, ArH), 6.84 (d, 2, J = 7.5 Hz, ArH), 6.59 (br s, 2, OH), 6.43 (d, 2, J = 7.5 Hz, ArH), 6.06 (t, 2, J = 7.5 Hz, ArH), 4.06 (d, 2, J = 14.1 Hz, $ArCH_2Ar$), 4.05 (d, 2, J = 16.2 Hz, $ArCH_2Ar$), 3.82 (d, 2, J = 16.2 Hz, $ArCH_2Ar$), 3.52 (d, 2, J = 14.1 Hz, $ArCH_2Ar$), 1.44 (s, 9, $C(CH_3)_3$). Anal. Calcd for $C_{39}H_{34}N_2O_9$: C, 69.43; H, 5.08; N, 4.15. Found: C, 68.88; H, 5.06; N, 3.94.

5,17-Di-*tert*-butyl-25,27-bis((3,5-dinitrobenzoyl)oxy)-26,28-dihydroxycalix[4]arene (12b). To a suspension of 9.0 g (66 mmol) of anhydrous $AlCl_3$ in 200 mL of toluene in a 500-mL flask was added 2.5 g (2.4 mmol) of 5,11,17,23-tetra-*tert*-butyl-25,27-bis((3,5-dinitrobenzoyl)oxy)-26,28-dihydroxycalix[4]arene (**4a**). The mixture was stirred for 15 min at room temperature, and 150 mL of cold H_2O was added with vigorous stirring. The aqueous layer was separated and washed with $CHCl_3$, and the organic layers were combined, dried over Na_2SO_4, and concentrated under vacuum. Filtration of the cooled solution yielded 2.1 g (86%) of **12b** as pale yellow crystals: mp >285 °C dec; ^1H NMR ($CDCl_3$) δ 9.29–9.25 (m, 6, ArH of $ArNO_2$), 7.07 (s, 4, ArH), 6.98 (d, 4, J = 7.8 Hz, ArH), 6.68 (t, 2, J = 7.8 Hz, ArH), 4.70 (s, 2, OH), 3.84 (d, 4, J = 14.1 Hz, $ArCH_2Ar$), 3.65 (d, 4, J = 14.1 Hz, $ArCH_2Ar$), 1.12 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{50}H_{44}N_4O_{14}$: C, 64.93; H, 4.80; N, 6.06. Found: C, 65.23; H, 4.75; N, 5.82.

5,11-Di-*tert*-butyl-25,26-bis((3,5-dinitrobenzoyl)oxy)-27,28-dihydroxycalix[4]arene (12c) was prepared from the 25,26-diester (1,3-alternate conformer) **5** by the procedure described above for the preparation of **12a** and obtained in 54% yield as very small yellow crystals after MeOH-induced precipitation from the toluene-$CHCl_3$ solution: mp >290 °C; ^1H NMR ($CDCl_3$) δ 9.13 (t, 2, J = 2.1 Hz, O_2NArH), 8.27 (br s, 4, O_2NArH), 7.24 (d, 2, J = 2.1 Hz, ArH), 7.01 (d, 2, J = 2.1 Hz, ArH), 6.81 (d, 2, J = 2.4 Hz, ArH), 6.62 (d, 2, J = 7.5 Hz, ArH), 6.26 (t, 2, J = 7.5 Hz, ArH), 6.24 (s, 2, OH), 3.93–3.79 (m, 8, $ArCH_2Ar$), 0.80 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{50}H_{44}N_4O_{14}\cdot{}^1/_2C_7H_8$ (toluene observed in ^1H NMR): C, 66.18; H, 4.98; N, 5.77. Found: C, 65.92; H, 4.86; N, 5.85.

5,11,17-Tri-*tert*-butyl-25,26,27-tris((3,5-dinitrobenzoyl)-oxy)-28-hydroxycalix[4]arene (12d) was prepared from the triester (cone conformer) **2** by the procedure described above for the preparation of **12a** and obtained in 77% yield as very small yellow crystals after crystallization from $CHCl_3$–MeOH: mp 308–310 °C; ^1H NMR ($CDCl_3$) δ 9.16 (br s, 2, O_2NArH), 9.05 (br s, 6, O_2NArH), 8.73 (br s, 1, O_2NArH), 7.44 (s, 2, ArH), 7.21 (d, 2, J = 7.5 Hz, ArH), 6.94 (t, 1, J = 7.5 Hz, ArH), 6.77 (m, 4, ArH), 4.30 (s, 1, OH), 4.13 (d, 2, J = 14.4 Hz, $ArCH_2Ar$), 3.84 (d, 2, J = 14.1 Hz, $ArCH_2Ar$), 3.58 (d, 2, J = 14.4 Hz, $ArCH_2Ar$), 3.54 (d, 2, J = 14.1 Hz, $ArCH_2Ar$), 1.45 (s, 9, $C(CH_3)_3$), 0.95 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{61}H_{54}N_6O_{19}$: C, 62.35; H, 4.63; N, 7.15. Found: C, 62.46; H, 4.73; N, 6.90.

25,27-Bis((3,5-dinitrobenzoyl)oxy)-26,28-dihydroxycalix-[4]arene (13). A mixture containing 2.0 g (4.7 mmol) of calix-[4]arene,[24] 6.8 g (29.4 mmol) of 3,5-dinitrobenzoyl chloride, and 3.4 g (26.0 mmol) of $AlCl_3$ in 150 mL of CH_2Cl_2 and 10 mL of DMF in a 300-mL round-bottomed flask was allowed to stand at room temperature for 3 h and then worked up to give 2.4 g (66%) of **13** as pale yellow crystals after crystallization from toluene: mp 180–182 °C; ^1H NMR ($CDCl_3$) δ 9.47 (d, 4, J = 2.1 Hz, O_2NArH), 9.27 (t, 2, J = 2.1 Hz, O_2NArH), 7.11 (d, 4, J = 7.5 Hz, ArH), 6.98 (s, 4, ArH), 6.80 (t, 2, J = 7.5 Hz, ArH), 5.04 (s, 2, OH), 3.93 (d, 4, J = 14.4 Hz, $ArCH_2Ar$), 3.63 (d, 4, J = 14.4 Hz, $ArCH_2Ar$). Anal. Calcd for $C_{42}H_{28}N_4O_{14}$: C, 62.07; H, 3.47; N, 6.89. Found: C, 62.18; H, 3.22; N, 6.58.

5,17-Bis((3,5-dinitrobenzoyl)oxy)-25,27-dihydroxy-26,28-dimethoxycalix[4]arene (14a). To a slurry of 2.0 g (15.0 mmol) of $AlCl_3$ and 3.3 g (14.3 mmol) of 3,5-dinitrobenzoyl chloride in 50 mL of $CHCl_3$ in a 100-mL round-bottomed flask was added 1.0 g (1.8 mmol) of **8c**. The mixture was refluxed for 90 min, cooled, treated with 30 mL of 0.1 N HCl, and vigorously stirred until the color changed from burgundy to orange. The product was worked up in the usual fashion and purified by flash chromatography using CH_2Cl_2 as eluant (R_f 0.19) to give 0.9 g (60%) of **14a** as a yellow powder: mp >320 °C dec; ^1H NMR ($CDCl_3$) δ 9.25 (t, 2, J = 2.1 Hz, O_2NArH), 9.13 (s, 2, OH), 8.93 (d, 4, J = 2.1 Hz, O_2NArH), 7.64 (s, 4, ArH), 7.01 (m, 6, ArH), 4.46 (d, 4, J = 13.2 Hz, $ArCH_2Ar$), 4.07 (s, 6, OCH_3), 3.52 (d, 4, J = 13.2 Hz, $ArCH_2Ar$). Anal. Calcd for $C_{44}H_{32}N_4O_{14}$: C, 62.86; H, 3.84; N, 6.66. Found: C, 62.81; H, 3.69; N, 6.34.

5-(3,5-Dinitrobenzoyl)-25,27-dihydroxy-26,28-dimethoxycalix[4]arene was obtained from the flash chromatography of the reaction mixture described above (R_f 0.28) as 0.20 g (20%) of a yellow powder: mp 299–301 °C dec; ^1H NMR ($CDCl_3$) δ 9.24 (t, 1, J = 1.8 Hz, O_2NArH), 9.05 (s, 1, OH), 8.92 (d, 2, J = 1.8 Hz, O_2NArH), 7.96 (s, 1, OH), 7.62 (s, 4, ArH), 7.09 (d, 2, J = 7.5 Hz, ArH), 6.99–6.83 (m, 4, ArH), 6.69 (t, 2, J = 7.5 Hz, ArH), 4.46 (d, 2, J = 13.2 Hz, $ArCH_2Ar$), 4.30 (d, 2, J = 13.2 Hz, $ArCH_2Ar$), 4.02 (s, 6, OCH3), 3.48 (d, 2, J = 13.5 Hz, $ArCH_2Ar$), 3.45 (d, 2, J = 13.2 Hz, $ArCH_2Ar$). Anal. Calcd for $C_{37}H_{30}N_2O_9$: C, 68.72; H, 4.68; N, 4.33. Found: C, 68.68; H, 4.51; N, 4.19.

5,17-Bis(3,5-dinitrobenzoyl)-25,27-dihydroxy-26,28-bis-((3,5-dinitrobenzoyl)oxy)calix[4]arene (14b). To a slurry of 1.5 g (11.3 mmol) of $AlCl_3$ and 3.2 g (14.0 mmol) of 3,5-dinitrobenzoyl chloride in 40 mL of $CHCl_3$ in a 100-mL round-bottomed flask was added 0.8 g (1.1 mmol) of **13**. The mixture was refluxed 20 h, cooled, treated with 30 mL of 0.1 N HCl, and worked up to yield 0.8 g (70%) of **14b** as small yellow crystals after recrystallization from acetone–MeOH: mp >210 °C dec; ^1H NMR (DMSO-d_6) δ 9.10 (s, 2, $O_2NArHCOAr$), 8.96 (s, 4, $O_2NArHCOAr$), 8.55 (s, 4, $O_2NArHCO_2Ar$), 7.92 (s, 2, $O_2NArHCO_2Ar$), 7.60 (s, 4, ArH), 7.13 (d, 4, J = 7.2 Hz, ArH), 6.97 (t, 2, J = 7.2 Hz, ArH), 3.95 (d, 4, J = 14.1 Hz, $ArCH_2Ar$), 3.78 (d, 4, J = 14.1 Hz, $ArCH_2Ar$). Anal. Calcd for $C_{56}H_{32}N_8O_{24}$: C, 56.01; H, 2.69; N, 9.33. Found: C, 55.71; H, 2.60; N, 8.31.

5,17-Di-*tert*-butyl-11,23-diacryloyl-25,27-bis((3,5-dinitrobenzoyl)oxy)-26,28-dihydroxycalix[4]arene (15a). A slurry

of 1.0 g (7.5 mmol) of $AlCl_3$, 1.0 mL (12.0 mmol) of acryloyl chloride, and 0.7 g (0.8 mmol) of **5** in 50 mL of $CHCl_3$ was refluxed 1 h and worked up to give 0.74 g of crude product. Recrystallization from $CHCl_3$–MeOH afforded 0.55 g (60%) of **15a** as small, dark yellow crystals: mp >250 °C dec; ^1H NMR ($CDCl_3$) δ 9.22 (t, 2, J = 2.1 Hz, O_2NArH), 9.10 (d, 4, J = 2.1 Hz, O_2NArH), 7.64 (s, 4, ArH), 7.13 (s, 4 ArH), 6.99 (m, 2, COCH=C), 6.27 (m, 2, COC=CH), 5.77 (m, 2, COCH=C), 5.44 (s, 2, OH), 3.92 (d, 4, J = 15.0 Hz, $ArCH_2Ar$), 3.77 (d, 4, J = 15.0 Hz, $ArCH_2Ar$), 1.14 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{56}H_{48}N_4O_{16}\cdot{}^3/_5CHCl_3$: C, 61.54; H, 4.43; N, 5.07. Found: C, 61.78; H, 4.32; N, 5.26.

5,17-Di-*tert*-butyl-11,23-bis(γ-chlorobutyryl)-25,27-bis-((3,5-dinitrobenzoyl)oxy)-26,28-dihydroxycalix[4]arene (15b). A slurry of 1.0 g (7.5 mmol) of $AlCl_3$, 0.7 mL (6.6 mmol) of γ-chlorobutyryl chloride, and 0.7 g (0.8 mmol) of **5** in 75 mL of CH_2Cl_2 was stirred 2 h at ice-bath temperature and then worked up to yield 0.55 g (60%) of **15b** as small, dark yellow crystals after recrystallization from $CHCl_3$–MeOH: mp >204 °C dec; ^1H NMR ($CDCl_3$) δ 9.25 (t, 2, J = 2.1 Hz, O_2NArH), 9.11 (d, 4 J = 2.1 Hz, O_2NArH), 7.62 (s, 4, ArH), 7.15 (s, 4, ArH), 5.45 (s, 2, OH), 3.90 (d, 4, J = 14.7 Hz, $ArCH_2Ar$), 3.77 (d, 4, J = 14.7 Hz, $ArCH_2Ar$), 3.58 (t, 4, J = 6.0 Hz, CCH_2CH_2Cl), 2.89 (t, 4, J = 7.2 Hz, $COCH_2CH_2Cl$), 2.05 (m, 4, $CH_2CH_2CH_2$), 1.16 (s, 18, $C(CH_3)_3$). Anal. Calcd for $C_{58}H_{54}Cl_2N_4O_{16}$: C, 61.43; H, 4.80; N, 4.94. Found: C, 61.21; H, 4.77; N, 4.78.

X-ray Crystallography of 3 and 5b. The data were collected on a Nicolet R3M/μ update of $P2_1$ diffractometer. The intensity data in the ω-scan mode were collected using a variable scan rate (4–29.3°/min) and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Lattice parameters were obtained from a least-squares refinement of 25 reflections. Data collected within the range $3 \le 2\theta \le 55°$. Lorenz polarization corrections were applied; no absorption correction was made with **3** and a ψ-scan absorption correction was applied to **5b**. The structures were solved by direct methods and refined by a block-cascade least-squares technique. Hydrogen atoms were located in difference maps, but only selected atoms were refined while the remainder were allowed to ride at fixed positions on the attached heavy atom. The computer programs were supplied by Nicolet Instrument Co for Desktop 30 Microeclipse and Nova 4/C configuration. Atomic scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography*.[25]

Compound 3: $C_{65}H_{62}N_6O_{19}\cdot 1.5C_7H_8$, FW = 1369.55, triclinic space group $P\bar{1}$ with a = 12.905 (12) Å, b = 14.916 (13) Å, c = 21.751 (2) Å, α = 105.30 (7), β =92.90 (8), γ = 114.03 (7)°, V = 3629 (6) Å^3 with Z = 2, and D_x(calcd) = 1.250 g/cm^3. Two crystals of dimensions 0.40 × 0.25 × 0.20 and 0.43 × 0.28 × 0.20 mm were used. A total of 10025 reflections were measured of which 9505 were independent and 5293 had $I > 3\sigma(I)$. There are 1.5 molecules of toluene in the asymmetric unit. The structure was refined to R = 0.111 and R_w = 0.142 for 1019 parameters and 5293 reflections with S = 1.338, $(\Delta/\sigma)_{max}$ = 0.034 and the largest peaks in the final difference map of 0.75 and −0.44 e/Å^3. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + 0.000690F_o^2]^{-1}$. The phenolic hydrogen is internally hydrogen bonded to an ester oxygen atom (O(1a)··O(1d) = 3.074 (10) Å, O(1a)··H(10d) = 2.10 (5) Å, O(1A)··H(10d)–O(1d) = 158 (3)°.

Compound 5b: $C_{58}H_{60}N_4O_{14}$, FW = 1037.15, monoclinic space group $P2_1/c$ with a = 14.993 (3) Å, b = 24.544 (5) Å, c = 15.054 (3) Å; β = 95.03 (2)°; V = 5518 (2) Å^3; Z = 4; D_x(calcd) = 1.248 g cm^{-3}; μ = 0.84 cm^{-1}; $F(000)$ = 2192. A crystal of dimensions 0.38 × 0.30 × 0.25 mm was used. A total of 7748 reflections yielded 7210 independent reflections of which 3799 had intensities greater than $3\sigma(I)$. The structure was refined to R = 0.0931 and R_w = 0.0683 with 816 parameters and 3799 reflections giving S = 1.666, $(\Delta/\sigma)_{max}$ = 0.26, and the largest peaks in the final difference map of −0.30 and +0.38 eÅ^3. One *tert*-butyl group is disordered.

(25) *International Tables for X-ray Crystallography*; Birmingham: Kynoch Press: Birmingham (present distributor Kluwer Academic Publishers, Dordrecht), 1974; Vol. IV.

X-ray Crystallography of 4a and 12b. X-ray data were collected on an ENRAF-Nonius CAD4 diffractometer equipped with Cu Kα radiation (λ = 1.54184 Å) and a graphite monochromator. Crystals were sealed in capillaries containing mother liquor. The θ–2θ scans were made at variable rate 1.1–3.3 deg min^{-1}. Lattice parameters were obtained by least-squares refinement using the setting angles of 25 reflections having $25 < \theta < 30°$. Data were collected within the angular limits $2 < \theta < 75°$, one quadrant for the monoclinic crystal **12b** and one hemisphere for the triclinic crystal **4a**. Data reduction included corrections for decay (22% with **4a**), background, Lorentz polarization, and absorption by ψ-scans. Structures were solved by direct methods and refined by full-matrix least-squares, treating non-hydrogen atoms anisotropically and including hydrogen atoms as fixed contributinos except where noted below. The function minimized in least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the weights were $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$. A secondary extinction coefficient g was refined, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c. The SDPVAX programs were used for all calculations, and scattering factors were taken from the *International Tables for X-ray Crystallography*.[25] Specifics for the two crystals are as follows.

Compound 4a: $C_{58}H_{60}N_4O_{14}\cdot C_7H_8$, FW = 1129.2, triclinic space group $P\bar{1}$, a = 14.460 (2) Å, b = 14.906 (6) Å, c = 17.201 (7) Å, α = 85.74 (3), β = 68.50 (3), γ = 65.05 (3)°, V = 3113 (2) Å^3, Z = 2, D_c = 1.204 g cm^{-3}, T = 23 °C, μ = 6.6 cm^{-1}, pale yellow crystals 0.30 × 0.40 × 0.55 mm. A total of 12908 reflections were measured, of which 12689 were unique, and 4981 were considered observed with $I > 3\sigma(I)$ and were used in the refinement. Hydrogen atoms were placed in calculated positions except for those of the OH groups, which were located by difference maps, and those of the solvent, which were ignored. The structure was refined to convergence with R = 0.074, R_w = 0.074, S = 1.899, g = 6.3 (2) × 10^{-7}, and maximum deviations 0.37 and −0.41 eÅ^{-3} in the final difference map.

Compound 12b: $C_{50}H_{44}N_4O_{14}\cdot 2C_7H_8$, FW = 1109.2, monoclinic space group $C2/c$, a = 25.955 (3), b = 16.029 (3), c = 15.296 (2) Å, β = 112.39 (1)°, V = 5873 (2) Å^3, Z = 4, D_c = 1.254 g cm^{-3}, μ = 6.9 cm^{-1}, T = 23 °C, pale yellow crystals 0.30 × 0.45 × 0.45 mm. A total of 6394 reflections was measured, of which 6044 were unique and 3298 were considered observed with $I > 1\sigma(I)$ and were used in the refinement. Toluene C atoms were refined isotropically. Calixarene H atoms were placed in calculated positions, but the OH hydrogen atoms were not located, and solvent H atoms were ignored. Convergence was achieved with R = 0.107, R_w = 0.111, S = 3.615, g = 7.3 (9) × 10^{-7}, and the largest deviations in a final difference map of 0.85 and −0.52 e Å^{-3}.

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Registry No. **1a**, 60705-62-6; **2**, 137258-32-3; **3**·1.5C_7H_8, 137331-14-7; **4a**·C_7H_8, 137258-34-5; **4b**, 137258-35-6; **4c**, 137258-36-7; **5a**, 137258-37-8; (±)-**5b**, 137429-15-3; **6**, 137258-38-9; **7**, 137258-39-0; **9a**, 137258-40-3; **9b**, 137258-41-4; **9c**, 137258-42-5; **10**, 137300-22-2; **11**, 137258-43-6; **12a**, 137258-44-7; **12b**·2C_7H_8, 137258-46-9; **12c**, 137258-47-0; **12d**, 137258-48-1; **13**, 137258-49-2; **14a**, 137258-50-5; **14b**, 137258-52-7; **15a**, 137258-53-8; **15b**, 137258-54-9; TMEDA, 110-18-9; 3,5-$(O_2N)_2C_6H_3COCl$, 99-33-2; 1-butylimidazole, 4316-42-1; imidazole, 288-32-4; pyridine, 110-86-1; 1-methylimidazole, 616-47-7; 4-methylimidazole, 822-36-6; 2-methylimidazole, 693-98-1; butylamine, 109-73-9; aniline, 62-53-3; dichloro phenyl phosphate, 36291-18-6; 5-(3,5-dinitrobenzoyl)-25,27-dihydroxy-26,28-dimethoxycalix[4]arene, 137258-51-6.

Supplementary Material Available: Tables of coordinates, bond distances, bond angles, and anisotropic thermal parameters for **3**, **5**, **4a**, and **12b** (43 pages). Ordering information is given on any current masthead page.