Synthesis of C-Alkyl Calix[4]arenes. 3. Acid-Catalyzed Rearrangement of 2,6-Dimethoxycinnamate Prior to Tetramerization to Calix[4]arenes

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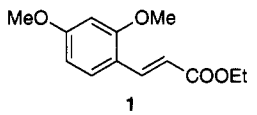
In our continuing studies concerning the versatility of the acid-catalyzed conversion of cinnamates to calix[4]resorcinarenes, we have demonstrated that 2,6-dimethoxycinnamic acid ethyl ester **3** undergoes an interesting rearrangement to afford the same calix[4]resorcinarenes as those obtained from the 2,4-dimethoxy isomer **1**. The experimental results were substantiated by molecular mechanics calculations.

Introduction

In previous studies we have shown that etheral BF_3 catalyzes the conversion of (*E*)-2,4-dimethoxycinnamic acid esters to the corresponding mixture of calix[4]-resorcinarenes stereoisomers.[1,2] Thus, ethyl ester **1** gave the 1,2-alternate **2a**, the flattened-cone (**2b**), and the 1,3-alternate (**2c**) stereoisomers. The relationship between the nature of the ester and the stereoisomer distribution in the reaction mixture has been discussed in a previous paper.[2] In order to evaluate the versatility of the above reaction and to obtain calix[4]resorcinarenes similar to **4**, that is those bearing the oxygen functions in the inner cavity, we repeated our generalized procedure with (*E*)-2,6-dimethoxycinnamic acid ethyl ester (**3**).



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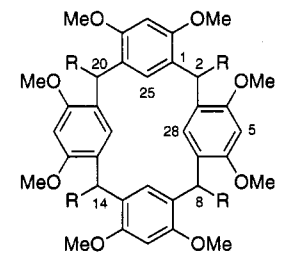
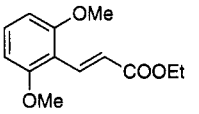
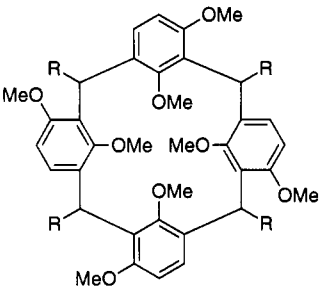


R	stereoisomer
2 CH_2COOEt	**a** 1.2 alternate
16 H	**b** flattened cone
	c 1.3 alternate



3
15 $\Delta^{7,8}$ dihydro



R
4 CH_2COOEt
17 H

Results

Treatment of **3** (1 mol) in $CHCl_3$ with $BF_3{\cdot}Et_2O$ (1.5 mol) at reflux for 2 h afforded the products **2a**, **2b**, and **2c**, which had been previously obtained under similar reaction conditions from the isomeric (*E*)-2,4-dimethoxy-cinnamic acid ethyl ester (**1**) rather than the expected structures, **4**. The three stereoisomers were obtained in an overall yield of 67% and in a relative ratio 1:1:1. Also isolated (expt A, Table 1) were the (*E*)-2,4-dimethoxy-cinnamic acid ethyl ester (**1**) and the dimeric compound **5** (*vida infra*).

These results suggested that the reaction may proceed *via* rearrangement of **3** to **1** before tetramerization. Similarly, 2,6-dimethyl-4-hydroxybenzyl alcohol (**6**) was reported to give upon treatment with $AlCl_3$ the calix[4]-arene **9** instead of the expected regioisomer **7**.[3] The authors assumed that **6** could rearrange to **8**, with subsequent conversion to **9** (Scheme 1).

To better define the migration of the side chain in **3**, we performed a series of experiments under a variety of conditions (temperature, equivalents of etheral BF_3 and reaction time) and monitored the experiments by pre-

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(1) Botta, B.; Iacomacci, P.; Di Giovanni, M. C.; Delle Monache, G.; Gacs-Baitz, E.; Botta, M.; Tafi, A.; Corelli, F.; Misiti, D. *J. Org. Chem.* **1992**, *57*, 3259.
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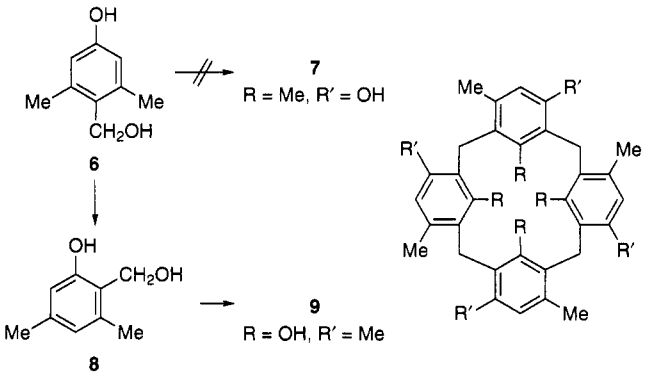
Table 1. Summary of Experiments Performed with 2,6-Dimethoxycinnamic Acid Ethyl Ester (3) and Results Obtained

reaction conditions	expts A	B	C_1	C_2	C_3	D	E
substrate/$BF_3{\cdot}Et_2O$	1:1.5	1:1.5	1:3	1:3	1:3	1:3	1:3
temperature	reflux	room	room	room	room	4 °C	−20 °C
time	2 h	1 day	4 h	8 h	4 days	4 days	4 days
product	% yield						
starting ester **3**	1	92	9	4	1	6	75
2,4-dimethoxy isomer **1**	3						
dimer **5**	6	2	3	2		9	6
dimer **11**						1	
trimer **10**		3	1	2		1	16
tetramer **2a**	23		12	16	14	8	
tetramer **2b**	21		16	28	35	11	
tetramer **2c**	23		12	18	21	15	
total calixarenes	67		40	63	71	33	

Scheme 1



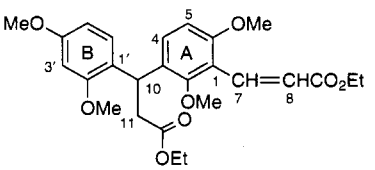
parative-TLC purification and ^1H NMR spectral analysis. The results obtained are summarized in Table 1.

At room temperature with a 1:1.5 ratio of substrate to $BF_3{\cdot}Et_2O$ (expt B), only a trace reaction was observed. Increasing the Lewis acid concentration to a 1:3 substrate/$BF_3{\cdot}Et_2O$ ratio and reacting for 4 h afforded, together with the dimer **5** and the calix[4]arenes **2a**−**c**, a new product, which was assigned the trimeric structure **10** (*vide infra*).

After 8 h, under the same conditions as above, the reaction mixture afforded **2a**, **2b**, and **2c** in 63% overall yield and in a 1:2:1 relative ratio. Finally, after 4 days, calix[4]arenes **2a**−**c** were isolated in a 70% overall yield and in *ca.* 1:3:2 ratio.

The observed increase in the yield of the thermodynamic stereoisomer **2b** (flattened-cone conformation) with reaction time at the expense of **2a** (1,2-alternate isomer) are in agreement with our earlier studies.[2]

When the reaction was carried out at 4 °C, with a 1:3 substrate/$BF_3{\cdot}Et_2O$ ratio (expt E), over a 4 day period, the following products were isolated: recovered (*E*)-2,6-dimethoxycinnamic acid ethyl ester (**1**), the dimer **5** in the *Z*-form, a new dimer (**11**) in which both the 2,4- and



11

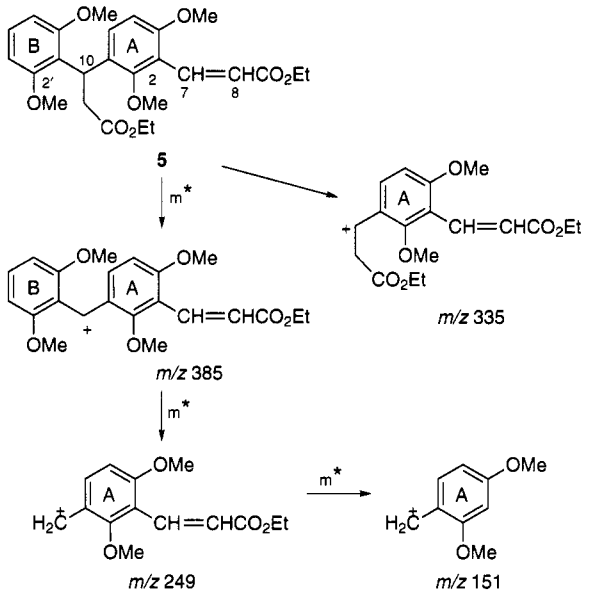
2,6-disubstituted aromatic rings were present, the trimer **10** (mostly in the *Z*-form), and the calixarenes **2a**−**c**.

Table 2. ^1H NMR Data of Dimers 5 (*E* and *Z* Form) and 11[a]

proton	5 *E* form	5 *Z* form	11 *Z* form
4	7.31, d (8.8)	7.25, d (8.8)	7.25, d (8.5)
5	6.62, d	6.56	6.54, d
7	7.95, d (16)	6.87, d (12.5)	6.88, d (12.5)
8	6.86, d	6.03, d	6.04, d
OCH_2	4.24, q (7)	4.00, q (7)	4.06, q (7)
CH_3	1.32, t	1.09, t	1.23, t
10	5.40, dd (8.5, 8)	5.37, t (8)	5.03, t (8)
11a	3.21, dd (15, 8.5)	3.19, dd (15, 8)	2.97, d
11b	3.02, dd	3.00, dd	
OCH_2	4.01, q (7)	3.77, q (5)	4.01, q (7)
CH_3	1.10, t	0.97, t	1.11, t

[a] All signals showed the appropriate integrate intensities. Coupling constants, in parentheses, are given only once.

Scheme 2. Dimer 5 and Mass Fragments



The structures of products **5** and **11** followed from normal assignment of proton signals in ^1H NMR spectra (Table 2), which revealed the presence of the saturated C(10)H−C(11)H_2 grouping, the substitution patterns of A (substituted) and B (unsubstituted) aromatic rings, and the (*E*)- or (*Z*)-arrangement of the C(7)−C(8) double bond.

A further confirmation of the structure of the dimers is revealed by mass spectra fragmentation, which can be rationalized and summarized for compound **5** as shown in Scheme 2. The fragmentation begins with the loss of one of the three substituents of the bridged C(10)-methine, the most favored being the loss of the alkyl side chain. The tropylium-like ion so formed undergoes the loss of neutral fragments (the B-ring and the olefinic chain) and leads to the base peak (a dimethoxytropylium ion) at *m/z* 151.

The proposed pathway is confirmed by the presence of the appropriate metastable peaks and by the comparison with the fragmentations of dimers which differ either in the number of methoxyl groups in the benzene rings[4,5] or in the nature of the ester groups.[1,2] In both cases the fragments are shifted, as expected, by the different substitution patterns.

(4) Botta, B.; Iacomacci, P.; Vinciguerra, V.; Delle Monache, G.; Gacs-Baitz, E.; Botta, M.; Misiti, D. *Chem. Pharm. Bull.* **1990**, *38*, 3238.

(5) (*E*)-2,4,6-Trimethoxycinnamic acid methyl ester gave under the same conditions of expt A dimeric and trimeric compounds similar to **5** and **10**.

Table 3. ^1H and ^{13}C NMR Data of Trimer 10 (Z Form)[a]

carbon	δ_C	δ_H[b]	long-range connected carbon
1	118.15	–	
2	157.11	–	
3	128.34	–	
4	131.07	7.63 (d, 9)	$^3J_2$, $^3J_6$
5	104.55	6.52 (d, 9)	
6	155.53		
7	133.25	6.82 (d, 12)	
8	122.83	5.97 (d, 12)	$^3J_1$, $^2J_9$
9	167.36		
10	36.50	5.49 (d, 11.5)	$^3J_2$, $^3J_4$, $^3J_{1'}$, $^2J_3$
11	49.98	4.20 (dd, 11.5, 8.5)	$^3J_{1'}$, $^3J_{12}$, $^3J_{14}$, $^2J_{10}$
12	173.79	–	
13	33.94	4.31 (ddd, 11.5, 8.5, 4.5)	$^3J_{10}$, $^3J_{15}$, $^3J_{2''}$, $^3J_{6''}$, $^2J_{14}$, $^2J_{1''}$
14	37.14	2.86 (dd, 15, 11)	$^2J_{15}$
		1.82 (dd, 15, 4.5)	$^2J_{15}$
15	172.74	–	
1'	119.15	–	
2'	159.32[c]	–	
3'	104.26	6.43 (br d, 8)	
4'	127.74	7.08 (t, 8)	
5'	104.26	6.43 (br d, 8)	
6'	158.08[c]	–	
1''	119.22	–	
2''	159.59[d]	–	
3''	104.72	6.43 (br d, 8)[e]	
4''	127.84	7.03 (t, 8)	
5''	104.72	6.39 (br d, 8)[e]	
6''	158.56[d]	–	

[a] The carbon and proton signals were correlated through HECTOR (^1J) and INEPTL (^2J and ^3J) experiments. The signals due to the OMe and OEt groups are not reported. [b] In parentheses: multiplicities and coupling constants in hertz. [c–e] In the same resonance envelope may be interchanged.

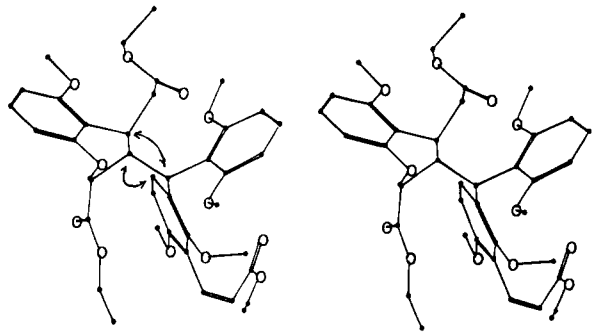
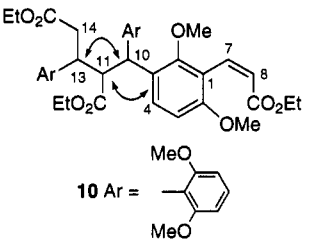


Figure 1. 3-D representation of trimer **10** obtained by minimization with MM2 calculation.

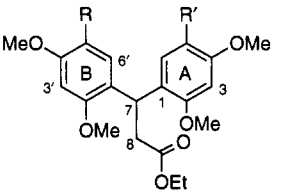
With regard to compound **10**, ^1H and ^{13}C NMR data (Table 3), combined with the presence of a molecular peak at *m/z* 708 in the mass spectrum, were in agreement with the trimeric molecular formula $C_{39}H_{48}O_{12}$.

The distribution of the proton signals in the aromatic-olefinic region of the ^1H NMR spectrum (Table 3) indicated that in only one aromatic ring has the H-3 proton been substituted, while one double bond (in the predominant *Z*-form) is still present. For confirmation, a COSY spectrum and evidence from detailed decoupling experiments revealed the partial aliphatic structure $CH_a-CH_b-CH_c-CH_2$, where the CH_a methine must be linked to two aromatic rings because of the value (δ 5.49) of its chemical shift, whereas the methylene is very likely linked to a carbonyl ($COOCH_2CH_3$) due to the large difference in the chemical shifts, δ 2.86 and 1.82, respectively, of the two geminal protons.

The resulting structure **10** and the assignment of proton and carbon signals in ^1H and ^{13}C NMR spectra were supported by a HECTOR measurement and a series of INEPTL experiments, as summarized in Table 3. Finally, the transoid relationship (J = 11 Hz) between H-10 (H_a) and H-11 (H_b) protons was confirmed by DIFNOE experiments, which showed the proximity of H-10 to H-13 (H_c) and of H-11 to the H-4 aromatic proton. Notably, these findings are in agreement with the 3D model (Figure 1) obtained by minimization of structure **10** with the MM2 program.



In order to confirm the formation of 2,4-dimethoxycinnamic acid ethyl ester in the reaction mixture, we repeated experiment A in the presence of 1,2,4-trimethoxybenzene, which was expected to act as a trap for the above molecule, according to the postulated mechanism of the dimerization reaction.[4] As a result (see expt F in the Experimental Section), three diarylpropanoates were isolated and assigned the structures **12–14** on the basis of spectral data (Table 4). The three compounds contain two aromatic moieties, with either 2,4-dimethoxy or 2,4,5-trimethoxy substituents, linked by the C-3 carbon of a propanoate unit.



	R	R'
12	H	H
13	OMe	H
14	OMe	OMe

Discussion

Experiments B and E reveal that under mild conditions the 2,6-dimethoxycinnamic ethyl ester (**3**) also yields a dimer, which for the 2,4-dimethoxy isomer has been demonstrated to be the intermediate of the tetramerization reaction.[2]

By contrast, the dimer **5** gives subsequently the trimer **10**, in which a third molecule of monomer is linked to the aliphatic chain, thus blocking the tetramerization. Moreover, the dimer **5** by direct treatment with $BF_3{\cdot}Et_2O$ gave only polymeric material.

Calix[4]arene tetramers **2a–c** were obtained only under those conditions in which the 2,4-dimethoxy isomer **1** can be formed (expts A, C, and D). In two of the above experiments, compound **1** was also isolated either as such (expt A) or linked to a molecule of 2,6-dimethoxycinnamate as in the dimer **11** (expt D). The drastic conditions of experiment C1 prevented the isolation of **1**, which under such conditions is entirely converted in the tetramers **2a–c**.[2]

Notably the distribution of tetramers **2a–c** in the reaction mixtures of experiments C1, C2, and C3 is very similar to that obtained starting from 2,4-dimethoxy

Table 4. Spectral Data of Diarylpropanoates Isolated from the Reaction Mixture of Experiment F

	δ_C		
carbon[a]	**12**	**13**	**14**
1	124.05	123.93	123.05
2	158.06	158.00	151.43
3	98.69	98.67	97.99
4	159.13	159.21	147.90
5	103.57	103.63	142.55
6	128.73	128.74	113.03
7	38.67	38.67	38.62
8	34.14	34.79	35.40
CO	172.58	172.50	172.43
OCH_2	60.00	60.06	60.12
Me	14.13	14.12	14.19
1′	124.05	123.14	123.05
2′	158.06	151.48	151.43
3′	98.69	98.17	97.99
4′	159.13	147.82	147.90
5′	103.57	142.55	142.55
6′	128.73	113.03	113.03
proton[a,b]	δ_H		
3	6.42, d (2)	6.42, d (2)	6.49, s
5	6.41, dd	6.40, dd	
6	7.02, d (8)	7.04, d (8)	6.78, s
7	5.03, t (8)	5.02, t (8)	5.01, t (8)
8a	2.97, d	3.02, dd (15, 8)	3.02, d
8b		2.96, dd	
OCH_2	4.01, q (7)	4.02, q (7)	4.02, q (7)
Me	1.09, t	1.10, t	1.11, t
3′	6.42	6.49, s	6.49
5′	6.41		
6′	7.02	6.76, s	6.78
EIMS	*m/z* (rel intensity)		
M	374 (24)	404 (41)	434 (50)
M − CH_2COOEt	287 (100)	317 (100)	347 (100)
B tropylium	151 (55)	181 (17)	181 (48)
A tropylium		151 (38)	

[a] The signals of methoxy groups are not reported. [b] The signals showed the appropriate integrated intensities. Coupling constants, in parentheses, are given only once.

isomer, thus suggesting that calixarenes **2a−c** have the same precursor.

Finally, the findings of experiment F cleared up the formation of isomer **1** by an intermolecular rearrangement which involves, as intermediates, 1,3-dimethoxybenzene and the propanoate unit, both derived from **3**. The unsaturated side chain appears to be essential for rearrangement of **3** to **1**. In fact, the olefinic double bond of the side chain of **3** was reduced and the product **15** showed no reaction upon treatment with BF_3 etherate in a 1:1.5 ratio at room temperature for 18 h.

Molecular Modeling Studies

In order to establish whether the putative calix[4]-resorcinarene **4** could be a stable compound, molecular mechanics calculations were undertaken. The calculations were performed with the MODEL program[6] which employs a generalized MM2 force field on a VAX6100. The five minimized conformations[2] **16a−e** (Table 5) of the calixarene nucleus lacking the side chain (**16**) were used as input structures. The substitution pattern of each conformation was changed into that of the regioisomer expected from the 2,6-dimethoxycinnamic acid ester, that is, structure **17**. The structures of conformers **17a−e** (Figure 2) were then minimized and submitted to conformational analysis.

Table 5. Energies of MM2(MODEL)-Minimized Conformations of 17

conformation relative to **16**	*E* (kcal/mol) **16**	*E* (kcal/mol) **17**	calcd equilibrium mixture (%)
a flattened cone	86.7	93.3	0.19
b flattened partial cone 1	87.6	89.6	98.93
c flattened partial cone 2	89.1	96.6	0.00
d 1,3-alternate	87.8	92.4	0.88
e 1,2-alternate	90.0	96.6	0.00

Since the input conformations had been obtained by an exhaustive conformational analysis,[2] the search was restricted to the four methoxy groups of the lower ring.

A statistical search was performed, maintaining all the default conditions suggested by the MODEL program. In particular, the dipole−dipole electrostatic calculation was chosen without electrostatic cut off and with a van der Waals interaction cut off of 7 Å; a dielectric constant of 1.0 was employed.

A comparison between the energies calculated for each conformation of the two regioisomers is reported in Table 5.

In summary, the data suggest that the structure **16** is more stable, regardless of the kind of conformer, when compared to structure **17**. These results are in agreement with those reported in the literature for the tetramethyl ethers of *p*-methyl- and the *p-tert*-butyl[4]-calixarenes.[7]

Analogously, our calculations show that the van der Waals contributions to the total energy (Table 6) are responsible for the higher stability of the flattened partial cone 1 conformer **17b**.

Fitting experiments among the five conformers of both **16** and **17** have also been carried out considering only the carbon atoms of the cavity. The RMS values generally fall in the range 0.2−0.5 Å, suggesting that the geometry of each conformer of **17** is similar to that of the corresponding isomer of **16** with the exception of the flattened partial cone 2 (**17c**). In this case, the steric repulsions between the methoxy groups require a significant distortion of the overall structure so as to approach the 1,2-alternate (**17e**) conformation. In fact, the energies calculated for both **17e** and **17c** (Table 4) reveal that these conformers are the least stable and are unlikely to exist to any significant extent in gas, liquid, or solid states.

In additional studies, the relative stabilities of the two regioisomers **2** and **4** were evaluated by calculation of the heats of formation (ΔH_f) using the MMX program.[8] This program is derived from MM2 with the MMP1 subroutine incorporated for the delocalized π electron system. However the calculations performed on the calixarenes **2** and **4** did not incorporate the π system because of the high number of π atoms. The ΔH values for **2** and **4** (−613.5 and −562.1 kcal/mol, respectively; Table 7) were calculated from eq 1, where BE is the bond

$$\Delta H_f = \text{energy} + \text{BE} + \text{PFC} \qquad (1)$$

energy term and PFC is the partition function contribu-

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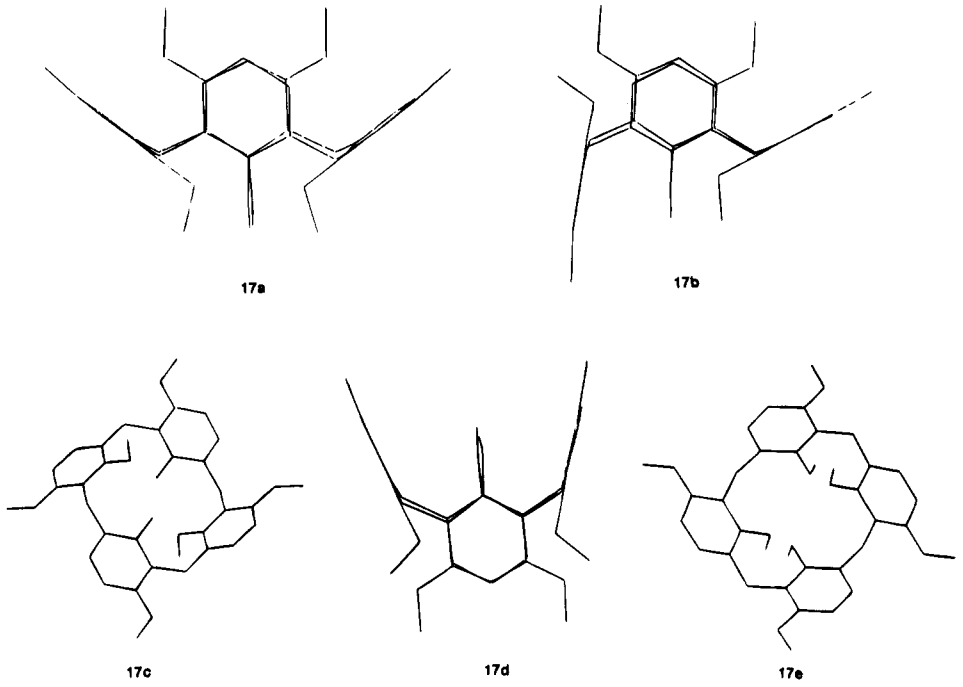

Figure 2. Minimized conformations of **17** *via* MODEL–MM2 calculations.

Table 6. Partial Contributions to the Total Energies of MM2(MODEL)-Minimized Conformations of 17[a]

	E	STR	BND	S–B	TOR	VDW	DIP
17a	93.3	5.7	16.6	−0.2	29.3	41.4	0.4
17b	89.6	5.4	16.9	−0.1	28.5	39.7	−0.8
17c	96.6	5.7	19.6	0.1	28.2	42.3	0.7
17d	92.4	5.5	19.2	0.1	29.6	39.8	−1.7
17e	96.6	5.7	19.5	0.1	28.2	42.4	0.7

[a] *E*, total energy; STR, energy of stretching; BND, energy of bending; S–B, energy of stretching–bending; TOR, torsional energy; VDW, energy of van der Waals; DIP, dipole energy.

Table 7. Heats of Formation (kcal/mol) of Tetramers 2 and 4 Calculated by MMX Program

	ΔH_f	*E* steric	BE	*E* strain
2	−613.5	60.7	−676.6	24.3
4	−562.1	112.1	−676.6	75.8

tion (2.4 kcal/mol).[8] Because the BE values for calixarenes **2** and **4** are the same, the greater stability of **2** can be attributed to the difference in strain energy.

In addition, we have calculated the heats of formation of the starting monomers **1** ($\Delta H_1 = -145.2$ kcal/mol) and **3** ($\Delta H_3 = -144.9$ kcal/mol), in relation to those of **2** and **4** (*vide supra*). It is clear that the conversion **1** → **2** is a strongly favored reaction ($\Delta H_2 - 4\Delta H_1 = -32.7$ kcal/mol), whereas tetramerization of **3** to **4** ($\Delta H_4 - 4\Delta H_3 = +17.5$ kcal/mol) is not.

In summary, all the above data suggest that the formation of calixarene **2**, regardless of whether **1** or **3** is employed as starting materials, will be favored over that of **4**.

Conclusions

In conclusion, it seems that the monomer **3** can follow two different reaction pathways. The first route (**3** → **5** → **10**) leads to the formation of dimer **5**, which then reacts with another equivalent of monomer to give the trimer **10**. The latter, on further treatment, is assumed to undergo polymerization, since longer reaction times afford only highly polar (base line on TLC) decomposition products.

The alternate path implies the rearrangement of **3** to **1**. As the latter is formed, it may undergo conversion to calixarenes (**1** → **2a–c**) or react with **3**, producing compound **11** (**1** → **11**). Product distribution suggests that path **3** → **1** → **2a–c** is the most favorable.

While our molecular mechanics study does not favor the route **3** → **4**, the data in Table 6 suggest that **4** could exist as a stable compound in the flattened partial cone 1 conformation and thus may be formed by an alternate route.

Experimental Section

General. Melting points (uncorrected): Kofler apparatus. ^{1}H and ^{13}C NMR (300 MHz and 75 MHz, TMS as internal standard, in $CDCl_3$ solutions): Varian Gemini 300 spectrometer. EIMS (direct inlet): VG7070 EQ spectrometer.

Synthesis of 2,6-Dimethoxycinnamic Acid Ethyl Ester (3). To a stirred solution of 2,6-dimethoxybenzaldehyde (1 g, 6 mmol) in absolute EtOH (20 mL) in the presence of anhydrous K_2CO_3 (2.5 g) was added triethyl phosphonoacetate (1.5 mL, 7.2 mmol), and the mixture was heated at reflux for 3 h. The reaction mixture was concentrated under vacuo and added with H_2O, affording a precipitate which was filtered and dried to give 1.38 g (97%) of 2,6-dimethoxycinnamic acid ethyl ester (**3**), mp 56 °C: ^{1}H NMR ($CDCl_3$) δ 8.14 (1H, d, J = 16 Hz, H-α), 6.88 (1H, d, J = 16 Hz, H-β).

General Procedure for Experiments A–E. To a solution of 2,6-dimethoxycinnamic acid ethyl ester (**3**, 118 mg, 0.5 mmol) in 3 mL of $CHCl_3$ was added BF_3Et_2O, 0.1 mL (0.75 mmol, expts A–B) or 0.2 mL (1.5 mmol, expts C–E), and the mixture was stirred at the temperature indicated in Table 1 for the time therein reported. The reaction mixture was diluted with MeOH and dried. The residue was fractionated by silica gel column chromatography, eluting with *n*-hexane/CH_2Cl_2/EtOAc, 5:3:2, to give the products listed in Table 1. The tetramers **2a–c** were recovered together, and the relative ratio of the three stereoisomers was evaluated by integration of the appropriate signals in the ^{1}H NMR spectra. Compounds **2a**, **2b**, and **2c** were identified by comparison with authentic samples (^{1}H and ^{13}C NMR spectra and co-TLC).

Experiment F. To a solution of 2,6-dimethoxycinnamic acid ethyl ester (**3**, 48 mg, 0.2 mmol) and 1,2,4-trimethoxybenzene (100 mg, 0.6 mmol) in 2 mL of $CHCl_3$ was added

$BF_3{\cdot}Et_2O$, 0.4 mL (0.3 mmol), and the mixture was held at reflux for 2 h. The reaction mixture was diluted with MeOH and dried. The residue was fractionated by silica gel column chromatography, eluting with $CHCl_3$ and $CHCl_3$/EtOAc, 95:5, to give recovered 1,2,4-trimethoxybenzene (40 mg), **12** (14 mg), **13** (18 mg), and **14** (15 mg). Further polar compounds were not examined.

Dimer 5: oil; EIMS *m/z* (rel intensity) 472 $[M]^+$ (35), 427 $[M - OEt]^+$ (8), 398 $[M - HCOOEt]^+$ (21), 385 $[M - CH_2COOEt]^+$ (65), 335 [M − B ring]$^+$ (26), 249 [385 − B ring]$^+$ (17), 151 [249 − HC=CCOOEt]$^+$ (100).

Trimer 10: vitreous solid; EIMS *m/z* (rel intensity) 708 $[M]^+$ (58), 663 $[M - OEt]^+$ (38), 634 $[M - HCOOEt]^+$ (100), 471 [M − 237] (11), 425 [471 − EtOH]$^+$ (40), 385 [A and B ring, tropylium ion]$^+$ (100), 249 [385 − B ring]$^+$ (20), 237 [C ring, tropylium ion]$^+$ (20), 191 [237 − EtOH]$^+$ (23), 165 (22), 151 [249 − HC=CCOOEt]$^+$ (100).

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Supplementary Material Available: Complete ^1H and ^{13}C NMR data for compounds **5** and **10**−**14** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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