have been investigated in IC. Acid species are hydrochloric acid and nitric acid. Acid content in standard sample are adjusted from 0.2 N to 1.0 N for HCl,and from 0.2 N to 2.5 N for HNO_3. Significant effect was observed at the concentration above 0.8 N for HCl and 1.5 N for HNO_3 as shown in Figure 9. Chromatograms showed broadening and splitting pattern due to the high concentrations of acids. Therefore the influence of the acid cannot be considered negligible, although further work is needed.

Analysis of real sample. In order to evaluate on the developed digestion system,boiler feed water of Seochen power plant located in the West coast were digested and analyzed. The results are shown in Table 5 with good precision. Results show high concentration of Fe and Cu, because Seocheon power plant was operated again after a long shutdown. The concentration of Cu higher than that of Fe indicates needs of more examination of its boiler system.

Conclusion

The method described offers rapid and efficient sample preparation using microwave digestion for the determination of metal oxides in boiler feed water of power plants. The microwave digestion system reduces sample handling and make complete automation of the analysis possible. The open tubing method (OTM) and the restraint tubing method (RTM) were designed for microwave digestion system and tested to find the optimum conditions. RTM was 3 times quicker on the digestion time and 10 times higher on sample mass. The results of RTM agree well with those by conventional microwave open vessel in all cases; Fe and Cu show good agreement within about 6% of RSD, while Zn and Co more or less than 10% RSD. The concentration of samples analyzed by IC and compared with those of ICP-AES. The results of IC agree with those of ICP with less than 3% deviation. According to this study, the continuous flow microwave digestion system provides the proper dissolution method for the analysis of solid particulate sample directly in IC or ICP-AES.

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Conformations of 25,27-Diacyloxy-26,28-dialkyloxycalix[4]arenes

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1,3-Dimethyl and dipropyl ethers of *p-t*-butylcalix[4]arene and calix[4]arenes have been converted to the corresponding diesters, acetate and propionate, and their conformations are inferred based on the ^1H and ^{13}C NMR spectra. The presence of *t*-butyl groups is effective in maintaining the cone conformation on derivatization.

Introduction

Calixarenes, a class of synthetic macrocycles having phenolic residues in a cyclic array linked by methylene groups at the positions "ortho" to the hydroxy groups, have cavities of sufficient size to form host-guest complexes, thus, are particularly attractive compounds for attempting to construct systems that mimic the catalytic activity of the enzyme and have received a great deal of attention in recent years[1,2].

The cavity of calixarene is conformationally mobile and

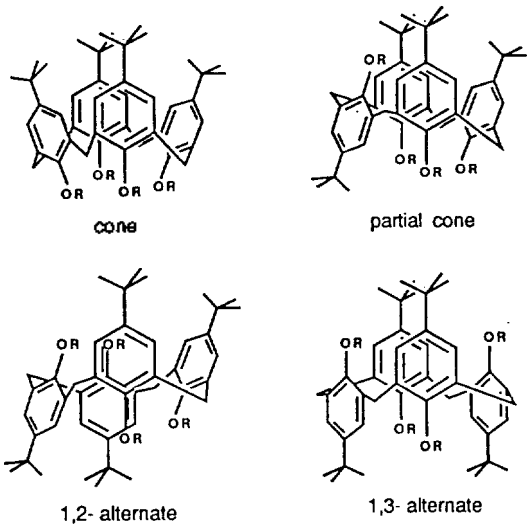


Figure 1. Conformations of Calix[4]arene.

exists as four possible conformational isomers; cone, partial cone, 1,2-alternate and 1,3-alternate[3] as shown on Figure 1.

Upon replacement of the phenolic hydrogens with sufficiently large groups, the calix[4]arenes become conformationally immobilized, existing as discrete conformational isomers[4,5].

Preorganization of the basket plays a potentially vital role in the design of calixarenes as enzyme mimics, for host-guest interactions depend on complementarity in shapes as well as functionality. In study of the aroylation of calix[4]arenes, Gutsche[6] showed that the particular conformation in which a calix[4]arene is fixed upon derivatization is dependent on the temperature, the solvent, the para substituent of the calixarene, and the reactivity of the aroylating agent. He also reported that the products of arylmethylation partition principally between the cone and partial cone conformers[7].

A recent study[8] of the acylation of *p-tert*-butylcalix[4]arene and calix[4]arenes showed that particular conformation in which a calix[4]arene is fixed upon derivatization is dependent on the presence of *t*-butyl groups at para position and the method of acylation. The present investigation is an extension of this earlier work and involves the conformational outcomes in the acylation of the calix[4]arene 1,3-dialkyl ethers.

Results and Discussions

The conformation of a calix[4]arene with ABAB substitution pattern at lower rim can be readily established on the bases of its ^{1}H and ^{13}C NMR spectra,[9,10] particularly of the peaks arising from the methylene groups joining the aromatic rings of the cyclic array. Table 1 shows the ^{1}H and ^{13}C NMR spectral patterns that would be expected to be observed for each of five conformers.

The diacyl esters of *p-tert*-butylcalix[4]arene 1,3-dialkylether, **3a-c**, were synthesized as shown in Scheme 1.

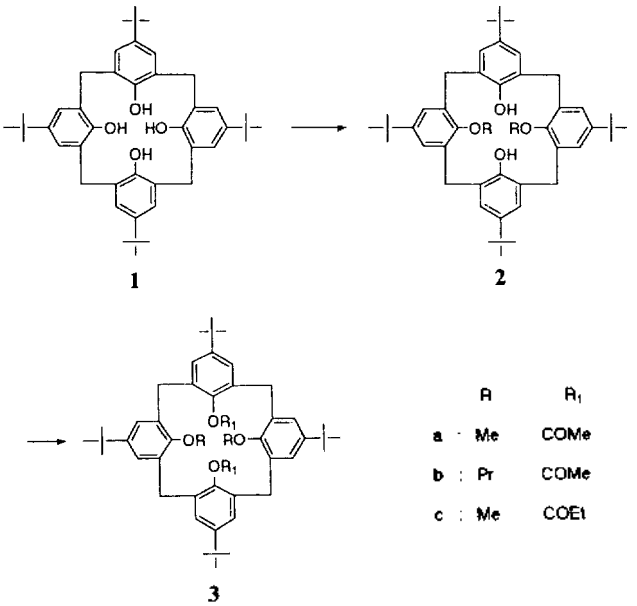
The diacetate of *p-tert*-butylcalix[4]arene 1,3-dimethylether **3a** can be obtained in 79% yield by treatment of a THF solution of **2a**, which was obtained in 86% yield by the published procedures[11], with NaH followed by the acetyl chloride. Diacetate **3a** displays a ^{1}H NMR spectrum that is commensurated with a cone conformation, showing two singlets arising from aryl protons, a pair of doublets arising from the methylene protons, one singlet arising from the methoxy protons, one singlet arising from the methyl protons adjacent to carbonyl group, and two singlets arising from the *t*-butyl protons. The ^{13}C NMR spectrum, which shows one peak from carbonyl carbons, 8 peaks from aromatic carbons, and only one peak at δ 31.40 from the methylene, also supports the cone conformation of **3a**.

The conformation of dipropionate **3b**, which is obtained in 77% yield by the similar method, is cone based on ^{1}H and ^{13}C NMR spectra.

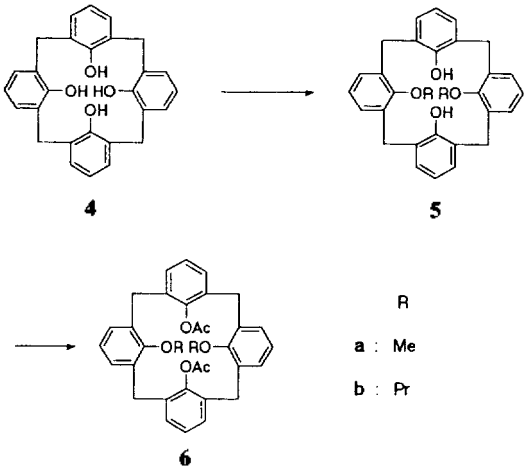
The methyl and ethyl ether of calix[4]arene are less con-

Table 1. ^{1}H-NMR and ^{13}C-NMR spectral patterns for the conformers of *p-t*-butylcalix[4]arene with ABAB type lower rim substitution

	^{1}H-NMR		^{13}C-NMR		
	CH_2	*t*Bu	Aromatic	CH_2	C=O
Cone	One pair of doublet	Two singlets	8	1	1
Partial cone (ester down)	Two pairs of doublet	Three singlets	14	2	2
Partial cone (ether down)	Two pairs of doublet	Three singlets	14	2	1
1,3-Alternate	One pair of doublet	Two singlets	8	1	1
1,2-Alternate	Two pairs of doublets or three pairs of doublets	Two singlets	12	2	1



Scheme 1. Synthesis of diacylesters of *p-t*-butylcalix[4]arene 1,3-dialkyl ethers.



4 5 6

Scheme 2. Synthesis of diacetates of calix[4]arene 1,3-dialkyl ethers.

formationally mobile than the parent compound. To complete immobilization of calix[4]arene, the acyl ester of calix[4] arene 1,3-dipropyl ether **3b** is prepared. In the early stage of this investigation, *p-tert*-butylcalix[4]arene 1,3-dipropyl ether **2b** was tried to prepare using the similar procedure for the preparation of **2a**, however, the yield was low and monopropyl ether was accompanied by **2b** and the separation was very tedious. Treatment of a DMF solution of **1** with $Ba(OH)_2 \cdot 8H_2O$ followed by propylbromide produces **2b** in 79% yield as a cone conformer. It was reported by Shinkai[12] that the alkylation reaction in the presence of $Ba(OH)_2 \cdot 8H_2O$ and BaO afforded only trialkylated calix[4]arene in cone conformation. However, when *p-tert*-butylcalix[4]arene was treated with propylbromide under the Shinkai's conditions, dipropylated calix[4]arene was obtained as the major product along with a small amount of tripropylated one. Treatment of a THF solution of **2b** with NaH followed by acetyl chloride affords ester **3b** in 79% yield as a cone conformer. The preparation of the same compound was reported by Ungaro[13] without detailed physical data. They found that there is a strong metal ion control of stereoselectivity, sodium giving exclusively derivatives in the cone conformation and thallium exclusively partial cone compounds.

After selective methylation at lower rim, the difference in reactivity between phenol rings and anisole rings can be utilized for the selective functionalization at the para positions of calix[4]arene. In this respect, 25,27-diacyloxy-26,28-dialkoxycalix[4]arenes in fixed cone conformation are even more interesting because the reactivity difference between two kinds of benzene rings is greater than calixarene 1,3-dialkyl ether. Therefore two 25,27-diacyloxy-26,28-dialkoxycalix[4]arenes are synthesized as shown in Scheme 2.

Compound **5a** was prepared as a cone conformer by following the published procedures[10], which involves treatment of the acetone solution of calix[4]arene 4 with K_2CO_3 and MeI. A solution of **5a** in THF was treated with NaH followed by acetyl chloride to afford **6a** in 93% yield. The ^1H NMR spectrum of **6a** shows four sets of doublets arising from the methylene protons, a singlet arising from the methoxy protons, and two singlets from the methyl groups adjacent to carbonyl, which is commensurated with the partial cone conformation, in which one of the ester benzene ring is inverted. The ^{13}C NMR spectrum shows 14 peaks from aryl carbons, one peak from methoxy carbons, and two peaks at δ 37.30 and 30.30 from the methylene carbons, which also support the partial cone. The reaction is carried out under reflux conditions dose not give difference in yield and stereochemistry, but produces the partial cone conformer in 90% yield as the sole product. In the preparation of the same compound by the treatment of **5a** with acetic anhydride in the presence of conc sulfuric acid, the same conformer was produced in 80% yield. From the results of preparation of **3a** and **6a**, it is evident that the presence of *t*-butyl groups slow down the rate of conformational interconversion, effectively maintaining the cone conformation on derivatization as reported by Gutsche[7]. Cone conformer of the diacetate of calix[4] arene 1,3-dipropyl ether is prepared by a similar procedure. Treatment of a DMF solution of **5b** with $Ba(OH)_2 \cdot 8H_2O$ and propyl bromide produces 25,27-diacetoxy-26,28-dipropyloxycalix[4]arene in 71% yield as a cone conformer. In this preparation, no tripropyl ether was produced as the case of preparation of **2b**. Treatment of a THF solution of **5b** with NaH and acetyl chloride produces **6b** in 71% yield. The conformation of **6b** is cone based on the ^1H and ^{13}C NMR spectra.

Table 2. ^1H and ^{13}C-NMR Spectral Patterns of 25,27-diacyoxy-25,28-dialkyloxy Derivatives of Calix[4]arenes

Compound	^1H NMR			^{13}C NMR				Conformation
	ArH	CH_2	*t*Bu	C=O	Ar	CH_2	*t*Bu	
3a	Two Singlets	One Pair of Doublet	Two Singlets	1	8	1 (31.40)	2	Cone
3b	Two Singlets	One Pair of Doublet	Two Singlets	1	8	1 (31.40)	2	Cone
3c	Two Singlets	One Pair of Doublet	Two Singlets	1	8	1 (31.02)	2	Cone
6a	Multiplet	Two Pairs of Doublet	–	2	14	2 (37.30) (30.30)	–	Partial Cone
6b	Multiplet	One Pair of Doublet	–	1	8	1 (30.57)	–	Cone

Experimental

Melting points of all compounds were taken in sealed and evacuated capillary tubes on an Syblon thermolyne apparatus with polarizing microscope and were not corrected. IR spectra were determined on a Nicolet Impact 400 FT-IR spectrometer as KBr pellet. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini 300 (300 and 75 MHz) instrument. Chemical shifts are recorded as δ values in parts per million relative to TMS (δ 0.0) as an internal standard. TLC analyses were carried out on silica gel plates (absorbent thickness 250 μm). Flash chromatography[14] was carried out with E. Merck silica gel (230-400 mesh ASTM). Elution rate were 2 in/min.

5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-dimethoxycalix[4]-arene (2a) was prepared by the published procedure[11,15]. A heated suspension of *p-tert*-butylcalix[4]arene (1) (2.00 g, 2.70 mmol, 1 mole equivalent of toluene was occuluded) and K_2CO_3 (460 mg) in acetone (150 mL) was stirred for 20 min and added MeI (3.0 mL, 48 mmol) dropwise and then refluxed for 20 h. After solvent was evaporated, the resulting waxy solid was treated with dil HCl, extracted with chloroform. The organic layer was washed with water, dried over $MgSO_4$, and evaporated *in vacuo*. The oily residue was recrystallized from chloroform and methanol to afford 1.57 g (86%) of the desired product as a colorless crystalline solid; mp. 268℃; IR (KBr) 3450 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 7.20 (s, 2, OH), 7.07 (s, 4, ArH), 6.76 (s, 4, ArH), 4.28 (d, 4, CH_2, J=13.2 Hz), 3.95 (s, 6, OCH_3), 3.33 (d, 4, CH_2, J=13.2 Hz), 1.30 (s, 18, tBu), 0.93 (s, 18, *t*Bu); ^{13}C NMR ($CDCl_3$) δ 151.41, 150.71, 147.03, 141.69, 132.41, 128.04, 125.65, 125.18 (Ar), 63.40 (OCH_3), 33.68, 33.63 ($\underline{C}(CH_3)_3$), 31.50 ($C(\underline{C}H_3)_3$), 31.17 ($ArCH_2Ar$), 30.78 ($C(\underline{C}H_3)_3$).

5,11,17,13-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-dipropyloxycalix[4]-arene (2b). To a stirred solution of **1** (3.00 g, 4.05 mmol, 1 mole equivalent of toluene is occuluded) and $Ba(OH)_2 \cdot 8H_2O$ (2.26 g) in DMF (40 mL), propyl bromide (1.4 mL, 15.4 mmol) was added dropwise. After the mixture was heated at 90℃ for 2 h, conc NH_4OH (20 mL) was added, followed by water (100 mL). The product was extracted twice with 50 mL portions of chloroform and the organic layer was worked up with usual way. The residue was recrystallized from chloroform and hexane to afford 2.35 g (79%) of the desired product as a crystalline solid; mp. 206-207℃; IR (KBr) 3530 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 7.18 (s, 2, OH), 7.09 (s, 4, ArH), 6.56 (s, 4, ArH), 4.37 (d, 4, CH_2, J=13.2 Hz), 3.27 (d, 4, CH_2, J=13.2 Hz), 3.79 (t, 4, OCH_2, J=6.9 Hz), 1.95 (sextet, 4, CH_2, J=6.9 Hz), 1.36 (s, 18, *t*Bu), 1.13 (t, 6, CH_3, J=6.9 Hz), 0.86 (s, 18, *t*Bu); ^{13}C NMR ($CDCl_3$) δ 151.95, 150.92, 145.20, 138.20, 132.41, 129.68, 125.73, 125.11 (Ar), 77.78 (OCH_3), 33.92, 33.63 ($\underline{C}(CH_3)_3$), 31.49, 30.85 ($ArCH_2Ar$), 31.16 ($C(\underline{C}H_3)_3$), 23.17 (CH_2), 10.51 (CH_3).

25,27-Dihydroxy-26,28-dipropyloxycalix[4]arene (5b). To a stirred solution of calix[4]arene **4** (2.28 g, 5.38 mmol) and $Ba(OH)_2 \cdot 8H_2O$ (3.00 g, 9.51 mmol) in DMF (50 mL), propyl bromide (1.5 mL, 16.5 mmol) was added dropwise. After the mixture was heated at 80℃ for 2 h, the reaction mixture was treated as the same method as **2b**. A recrystallization of the crude product from chloroform and hexane affords 1.93 g (71%) of the pure product as a crystalline solid; mp. 294-295℃; IR (KBr) 3300 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 8.31 (s, 2, OH), 7.07 (d, 4, ArH, J=7.5 Hz), 6.94 (d, 4, ArH, J=7.5 Hz), 6.74 (t, 2, ArH, J=7.5 Hz), 6.61 (t, 2, ArH, J=7.5 Hz), 4.34 (d, 4, CH_2, J=12.9 Hz), 4.00 (t, OCH_2), 3.40 (d, 4, CH_2, J=12.9 Hz), 2.09 (sextet, 4, CH_2), 1.33 (t, 6, CH_3); ^{13}C NMR ($CDCl_3$) δ 153.61, 152.13, 139.65, 129.05, 128.55, 128.30, 125.39, 119.05 (Ar), 78.26 (OCH_2), 31.22 ($ArCH_2Ar$), 23.25 (CH_2), 10.62 (CH_3).

Preparation of Di-acylesters of Calix[4]arene 1, 3-dialkyl ethers. To a stirred solution of *p-tert*-butylcalix[4]arene 1,3-dialkyl ether or calix[4]arene 1,3-dialkylether (1.50 mmol) and NaH (0.25 g, 2 mole equivalent per OH) in THF (70 mL), was added dropwise a solution of acetyl chloride or propionyl chloride (5 mole equivalent per OH) in THF (30 mL) and the mixture was stirred at room temperature for 2.5 h. After solvent was evaporated, the resulting residue was treated with 50 mL water, extracted with chloroform. The organic layer was washed with water, dried over Na_2SO_4, and evaporated the solvent. The slightly waxy residue was recrystallized from chloroform and methanol to afford the desired product as a colorless crystalline solid.

5,11,17,23-Tetra-*tert*-butyl-25,27-diacetoxy-26,28-dimethoxycalix[4]-arene (3a). yield 79%; mp. 314℃; IR (KBr) 1748 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 7.12 (s, 4, ArH), 6.95 (s, 4, ArH), 3.82 (d, 4, CH_2, J=16 Hz), 3.65 (d, 4, CH_2, J=16 Hz), 2.99 (s, 6, OCH_3), 1.59 (s, 3, $COCH_3$), 1.29 (s, 18, *t*Bu), 1.26 (s, 18, *t*Bu); ^{13}C NMR ($CDCl_3$) δ 169.21 (C=O), 147.63, 145.09, 134.09, 132.94, 126.47, 126.42, 126.11, 125.61 (Ar), 57.77 (OCH_3), 34.25, 34.16 ($\underline{C}(CH_3)_3$), 31.81, 31.51, ($C(\underline{C}H_3)_3$), 31.40 ($ArCH_2Ar$), 20.87 ($COCH_3$).

5,11,17,23-Tetra-*tert*-butyl-25,27-diacetoxy-26,28-dipropyloxycalix[4]-arene (3b). yield 79%; mp. 244-245℃; IR (KBr) 1750 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 7.17 (s, 4, ArH), 6.61 (s, 4, ArH), 4.03 (d, 4, CH_2, J=13 Hz), 3.60 (t, 4, OCH_2, J=7.5 Hz), 3.18 (d, 4, CH_2, J=13 Hz), 2.17 (s, 6, $COCH_3$), 1.88 (sextet, 4, CH_2, J= 7.5 Hz), 1.35 (s, 18, *t*Bu), 1.03 (t, 6, CH_3, J=7.5 Hz), 0.83 (s, 18, *t*Bu); ^{13}C NMR ($CDCl_3$) δ 172.92 (C=O), 154,74, 152.10, 147.85, 144.62, 135.09, 132.39, 125.56, 124.21 (Ar), 77.83 (OCH_3), 33.83, 33.40 ($C(\underline{C}H_3)_3$, 31.56, 30.88 ($C(\underline{C}H_3)_3$), 31.40 ($ArCH_2Ar$), 22.27 (CH_2), 21.81 ($COCH_3$), 10.31 (CH_3).

5,11,17,23-Tetra-*tert*-butyl-25,27-dimethoxy-26,28-dipropionyloxycalix[4]arene (3c). yield 77%; mp. 298℃; IR (KBr) 1744 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 7.12 (s, 4, ArH) 6.92 (s, 4, ArH), 3.80 (d, 4, CH_2, J=15.9 Hz), 3.63 (d, 4, CH_2, J=15.9 Hz), 3.01 (s, 6, OCH_3), 1.81 (q, 4, $COCH_2$), 1.29 (s, 18, *t*Bu), 1.25 (s, 18, *t*Bu), 0.91 (t, 6, CH_3); ^{13}C NMR ($CDCl_3$) δ 172.16 (C=O), 155.97, 146.96, 145.64, 144.72, 133.86, 132.56, 126.02, 125.97 (Ar), 57.35 (OCH_3), 33.82, 33.78 ($\underline{C}(CH_3)_3$), 30.30, 31.18 ($C(\underline{C}H_3)_3$, 31.02 ($ArCH_2Ar$), 25.95 ($COCH_2$), 8.21 (CH_3).

25,27-Diacetoxy-26,28-dimethoxycalix[4]arene (6a). yield 93%; mp. 298℃; IR (KBr) 1744 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 7.43-6.67 (m, 12, ArH), 3.90 (d, 2, CH_2, J=15 Hz), 3.89 (d, 2, CH_2, J=13.2 Hz), 3.63 (s, 6, OCH_3), 3.60 (d, 2, CH_2, J=15 Hz), 3.24 (d, 2, CH_2, J=13.2 Hz), 1.83 (s, 3, $COCH_3$), 1.55 (s, 3, $COCH_3$); ^{13}C NMR ($CDCl_3$) δ 172.31, 168.89 (C=O), 156.36, 148.67, 148.29, 135.61, 134.18, 133.42, 132.79, 130.14, 129.74, 129.39, 128.64, 125.86, 125.24, 122.86 (Ar), 60.24 (OCH_3), 37.30, 30.30 ($ArCH_2Ar$), 20.94, 20.80 ($COCH_3$). The same product was prepared by the published

procedure[10]. To a heated solution of **5a** (1.00 g, 2.21 mmol) in acetic anhydride (30 mL), was added a drop of conc sulfuric acid and the mixture was refluxed for 1 h. The reaction mixture was poured into 200 mL of ice water, and stirred for 3 h. The resulting precipitate was collected by filtration and recrystallized from chloroform and methanol to afford 1.00 g (84%) of the desired product.

25,27-Diactoxy-26,28-dipropyloxycalix[4]arene 6b. yield 77%; mp. 226-227°C; IR (KBr) 1756 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 6.95 (d, 4, ArH, J=7.5 Hz), 6.77 (t, 2, ArH, J=7.5 Hz), 6.70 (s, 6, ArH), 4.10 (d, 4, CH_2, J=13 Hz), 3.89 (t, 4, OCH_2, J=8.1 Hz), 3.27 (d, 4, CH_2, J=13 Hz), 2.59 (s, 6, $COCH_3$), 1.96 (sextet, 4, CH_2, J=7.2 & 8.1 Hz), 0.99 (t, 6, CH_3, J=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 170.66 (C=O), 155.91, 146.32, 134.90, 133.92, 129.13, 128.01, 125.19, 123.08 (Ar), 77.24 (OCH_2), 30.57 ($ArCH_2Ar$), 21.56 (CH_2), 9.83 (CH_3).

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Large Acceleration Effects of Mono-6-(alkylamino)-β-cyclodextrins on the Cleavage of *p*-Nitrophenyl α-Methoxyphenylacetate

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Kinetic studies of the deacylation reactions of *p*- and *m*-nitrophenyl esters of (*R* or *S*)-α-methoxyphenylacetic acid were performed in β-CD, mono-6-deoxy-6-[*N*-(2-aminoethyl)]amino-β-CD (β-CDen) and mono-6-deoxy-6-[*N*-(2-aminoethyl)-2-aminoethyl]amino-β-CD (β-CDdien) media. The binding constants (K) of the substrates to the hosts and the rate constants (k_ψ^{CD}) for the complexed substrates were determined. k_ψ^{CD} values are highly dependent on the hosts and the substrates, whereas differences in K values among them are modest. The *p*-nitrophenyl esters show larger acceleration by β-CDen and β-CDdien than the corresponding *m*-isomers, while the *m*-isomers are more reactive than the *p*-isomers in β-CD media. This is taken as an indication that the amino groups attached to the primary side of β-CD participate in the deacylation reaction.

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides composed of six or more α-1,4-linked D-glucopyranose units and possess hydrophobic cavities. They have attracted great interest as enzyme mimics because CDs form inclusion complexes with a variety of substrates and exhibit large catalytic activity for many kinds of reactions.[1] The cleavage of aryl esters in basic solution is the most widely investigated of such CD-catalyzed reactions. Bender and his coworkers established that the cleavage of the ester within an inclusion complex takes places by acyl transfer from the ester to a hydroxyl group of the cyclodextrin.[2] It has also been shown that the catalytic effects of CDs on the ester cleavage is greater for *meta*-substituted aryl esters than for *para*-substituted ones.[2-5] CD cavity has a chiral environment and induces stereoselective reactions for complexed substrates.[1] Enantiomeric selectivities have been found in the deacylation of complexed optically active esters.[3,5,6] To improve catalytic activity and enantioselectivity, modified CDs have been extensively used.[3,7-10]