

- Chem. Soc.* 1993, 116, 3997.
- Nam, K. C.; Kim, J. M.; Kim, D. S. *Bull. Korean Chem. Soc.* 1995, 16, 186.
 - (a) Chang, S.-K.; Cho, I. J. *Che. Soc. Perkin Trans. I*, 1986, 211. (b) Sakaki, T.; Harada, T.; Deng, G.; Kawabata, H.; Kawahara, Y.; Shinkai, S. J. *Inclusion Phenomena and Molecular Recognition Chemistry*; 1992, 14, 285.
 - Gutche, C. D.; See, K. A. *J. Org. Chem.* 1992, 57, 4527.
 - No, K. H.; Hong, M. J. *Chem. Soc., Chem. Commun.* 1990, 572.
 - Nam, K. C.; Kim, D. S.; Yang, S. J. *Bull. Korean Chem. Soc.* 1992, 13, 105.
 - See, K. A.; Fronczek, F. R.; Watson, W. H.; Kashyap, R. P.; Gutche, C. D. *J. Org. Chem.* 1991, 56, 7256.
 - Jaime, C.; Mandoza, J. D.; Prados, P.; Nieto, P. M.; Sanchez, C. J. *J. Org. Chem.* 1991, 56, 3372.
 - 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.

Synthesis of Several Diester Group-Containing Calix[4]arenes

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Several ester group-containing calix[4]arenes were synthesized by the reaction of calix[4]arene and various acyl chlorides. Two or four ethyl succinyl units could be introduced into the calix[4]arene lower rim depending on the reaction conditions. But the mixture of three and four ethyl malonyl substituted calix[4]arenes were obtained and only three ethyl oxalyl units were introduced at the lower rim of calix[4]arene. Interestingly when calix[4]arene was treated with ethyl oxalyl chloride in the presence of aluminum chloride, two ethyl oxalyl units were introduced at the upper rim of calix[4]arene. The conformation of those ester-containing calix[4]arenes was presented based on the ^1H and ^{13}C NMR spectra.

Introduction

Since the modern discovery of calixarene by Gutsche¹ it has been developed as a variety of purpose such as host-guest chemistry,²⁻⁴ inclusion compounds,^{5,6} organic catalysts^{7,8} and certain metal ionophores.⁹ Recently a series^{10,11} of metal ionophores based on calixarenes were synthesized and utilized as a metal ion sensors. Most notable calixarene ionophores were prepared by McKervey *et al.*¹² They synthesized polyfunctional esters and ketones capable of showing ionophoric activity. The tetramer esters and ketones display peak selectivity for the sodium ion, and the hexaesters extract K^+ better than Na^+ . The octamers are the least effective ionophores. In that calixarene, the ethereal oxygen and the carbonyl oxygen are involved in the complex with the alkali metal.

We, however, focused more on the two oxygens in the diester groups than on the ethereal oxygen. For the purpose of developing effective metal ion ionophores we synthesized the several ester group-containing calix[4]arenes. Ethyl succinyl, ethyl malonyl, and ethyl oxalyl chloride were used as an ester group precursor. The conformation of the ester group-containing calix[4]arenes was discussed based on NMR spectra.

Results and Discussion

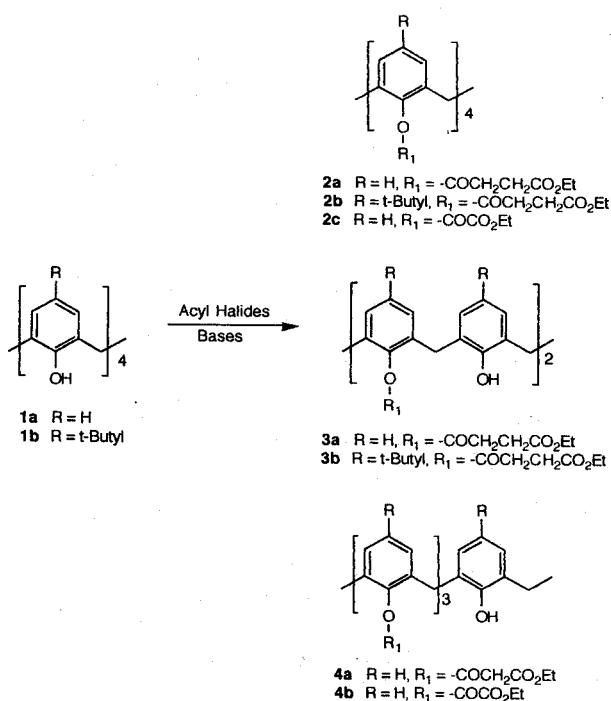
Reaction with Ethyl Succinyl Chloride. Calix[4]

arene **1a**, **1b** were treated with ethyl succinyl chloride in the presence of bases (Table 1). By controlled the amount of ethyl succinyl chloride, two or four ethyl succinyl groups were introduced at the lower rim of calix[4]arene. Figure 1 shows several O-acylation products prepared by the reaction of calixarene and acyl halides. Tetrasubstitution was occurred in the presence of excess ethyl succinyl chloride. Depending on the para substituents of calix[4]arene the conformation^{13,14} of tetraesters varied. If there are no para substituents, 1,3-alternate conformation products were obtained. On the other hand If there are bulky para substituents such as *p-t*-butyl group, cone conformation products were obtained. The conformation of calix[4]arenes **2a** and **2b** was confirmed by the NMR spectrum. The ^1H NMR spectrum of **2a** shows a multiplet at 7.0-7.2 ppm for the aromatic protons, and a quartet at 4.16 and a triplet at 1.28 ppm for the ethoxy protons, a singlet at 3.75 for the bridged methylene protons, and two triplets at 1.98 and 2.50 ppm for the two succinyl methylene protons. A singlet for the bridge methylene protons is characteristic for the 1,3-alternate conformation. The only one bridge methylene carbon peak appears at 37.4 ppm, indicating that the four phenol rings are all anti orientated.¹⁵ Therefore it is 1,3-alternate conformation. But, the ^1H NMR spectrum of **2b** shows a singlet at 6.95 ppm for the aromatic protons, a quartet at 4.17 ppm and a triplet at 1.28 ppm for the ethoxy protons, a pair of doublets at 4.00 and 3.28 ppm for the bridged methylene protons, two triplets at 3.20 and 2.74 ppm for the succinyl methylene protons, and a sing-

Table 1. Products by the reaction of calix[4]arene and various acylhalides

Comp	Acyl halide	Base	Solvent	Position of substituent (No)	Time (h)	Yield (%)	Conformation
2a	EtCO(CH ₂) ₂ COCl	NaH	THF	O-(4)	2.5	47	1,3-alternate
2b	EtCO(CH ₂) ₂ COCl	NaH	THF	O-(4)	3.5	48	cone
3a	EtCO(CH ₂) ₂ COCl	pyridine	THF	O-(2)	1	60	cone
3b	EtCO(CH ₂) ₂ COCl	pyridine	THF	O-(2)	5	55	cone
2c	EtCOCH ₂ C	pyridine	THF	O-(4)	2	0 ^b	1,3-alternate
4a	OCl			O-(3)			partial cone
4b	EtCOCOCi	pyridine	THF	O-(3)	1	45	partial cone
5	EtCOCOCi	AlCl ₃ ^a	CH ₂ Cl ₂	C-(2)	2	69	cone

^aLewis acid. ^b2c : 4a = 2 : 1, approximately.

**Figure 1.** O-Acylation Products by the Reaction of Calix[4]arene and Various Acyl Halides in the Presence of Bases.

let at 1.08 ppm for the *t*-butyl protons. The ¹³C NMR spectrum of **2b** shows no peaks at around 37 ppm which are the characteristic band for the anti oriented phenol ring, indicating there is only syn orientated phenol ring present. Therefore it exists in a cone conformation. It has been observed that *p*-*t*-butylcalix[4]arene tends to be fixed as a cone conformation when the large substituent was placed at the lower rim of calix[4]arene and when the metal cation (Na⁺) present in the base used serves as a template.¹⁶

Disubstitution¹⁷ was occurred with 2.5 equivalents of ethyl succinyl chloride in the presence of pyridine. The ¹H NMR spectra of **3a** and **3b** both show one pair of doublets at 3.5-4.0 ppm for the bridged methylene protons and the methylene carbon peak only appears at around 32 ppm, indicating they exist as a cone conformation. The higher homolog acyl chlorides such as ethyl adipoyl chloride and ethyl glutaryl chloride reacted with calix[4]arene in a same manner desc-

ribed for ethyl succinyl chloride.

Reaction with Ethyl Malonyl Chloride. Two malonyl ester substituted calix[4]arenes **2c** and **4a** were obtained by chance. To obtain a disubstituted ester with ethyl malonyl chloride, calix[4]arene **1a** was treated with 2.5 equivalents of ethyl malonyl chloride in the presence of 2.5 equivalents of pyridine. But the reaction was not completed more than for 24 h from room temperature to reflux and the starting material was observed on the TLC analysis. After additional 2.5 equivalents of ethyl malonyl chloride and pyridine were added, the starting material was disappeared and two spots were observed. The column chromatography separated the major product which could be a tetra-O-substituted calix[4]arene **2c** and the minor trisubstituted calix[4]arene **4a**. Tetra-substituted **2c** exists in 1,3-alternate conformation as observed for **2a**. The ¹H NMR spectrum of **4a** shows a multiplet at 6.8 to 7.2 ppm for the aromatic protons, a singlet at 5.35 ppm for the one hydroxy proton, two pair of doublets at 4.1 to 4.4 ppm for the bridge methylene protons. The interesting ¹H NMR peaks are for the malonyl methylene protons. Three malonyl methylene groups appear as two peaks, one singlet at 2.5 ppm with the integration for 2 hydrogens and one pair of doublets at 3.2 ppm with the integration for 4 hydrogens. If this compound exists as a cone conformation, two singlets with the ratio of 1 : 2 should be appeared. But if **4a** exists as a partial cone conformation or 1,2-alternate, outside two malonyl methylene protons could be diastereotopic, so one singlet from the middle malonyl methylene protons and one pair of doublet from the outside malonyl methylene protons could be appeared. The partial cone conformation of **4a** was confirmed by the ¹³C NMR spectrum. Two bridge carbon peaks appear at 37.4 and 33.0 ppm, indicating that there are two syn and two anti orientation of phenol rings. If it is 1,2-alternate conformation, there are also two syn and two anti oriented bridge carbon, but four peaks for the bridge carbons should be appeared, that is, two anti oriented bridge carbons and two syn oriented carbons. We observed only two bridge carbon peaks at 37.4 and 33.0 ppm, therefore **4a** should be in a partial cone conformation.

Disubstitution with ethyl malonyl chloride was not succeeded, but trisubstitution with partial cone conformation suggests the order of substitution. Second substitution occurs at 1,3-position of opposite hydroxy group, and third substitu-

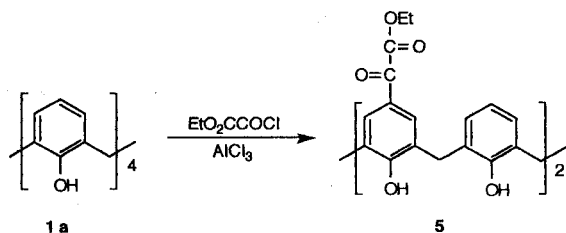


Figure 2. C-Acylation Products by the Reaction of Calix[4]arene and Ethyl Oxalyl Chloride in the presence of AlCl_3 .

tion will be preferred at the stage of one hydroxy group flipped over the other side to prevent the steric crowding of remaining two malonyl units.

Reactions with Ethyl Oxalyl Chloride. Calix[4]arene **1a** reacted with ethyl oxalyl chloride in the presence of pyridine similar to the reaction of ethyl malonyl chloride. In the presence of excess ethyl oxalyl chloride and pyridine calixarene **1a** produced the trisubstituted **4b**. This compound was not stable enough under TLC and column chromatography, but can be purified by recrystallization in carbon tetrachloride. The trisubstituted **4b** exists in a partial cone conformation as observed for **4a**. The ^{13}C NMR spectrum of **4b** shows two bridge methylene carbon peaks at 37.3 and 31.8 ppm, indicating that there are two anti and two syn oriented phenol rings present. Unfortunately we failed to introduce two or four ethyl oxalyl groups at the lower rim of calixarene.

Acylation was sometimes carried out successfully in the presence of aluminum chloride¹⁷ instead of base. Surprisingly calix[4]arene **1a** reacted with ethyl oxalyl chloride to give C-acylated calix[4]arene **5** (at the para position of phenol ring) rather than O-acylation commonly observed as shown in Figure 2. The ^1H NMR spectrum shows a broad singlet at 10.16 ppm for the four hydroxy protons, a singlet at 7.8 ppm for the four aromatic protons with ethyl oxalyl group, a doublet and a triplet at 7.1 and 6.82 ppm for the six aromatic protons, and two broad singlets at 3.5–4.4 ppm for the eight bridge methylene protons, indicating that the reaction occurred at the *p*-position and only two oxalyl units were introduced at the 1,3-position of calix[4]arene. It was known¹⁸ that in the presence of aluminum chloride the treatment of the calixarenes with acyl chloride yielded the O-acylated esters rather than acylation at the *p*-position. On the other hand the calixarene ethers undergo C-acylation at the *p*-position even though the process sometimes is complicated by concomitant dealkylation. We do not have a good explanation for this reaction at this time, but somehow in the presence of aluminum chloride and ethyl oxalyl chloride only 1,3-C-acylated calix[4]arene obtained. This could open up another easy pathway for the selective functionalization of calixarenes.

Conclusion

Several ester group-containing calix[4]arenes were synthesized by the reaction of calix[4]arene and various acyl chlorides. Two or four ethyl succinyl units were introduced into the calix[4]arene lower rim depending on the reaction

conditions. But the mixture of three and four ethyl malonyl substituted calix[4]arenes were obtained and only three ethyl oxalyl units were introduced at the lower rim of calix[4]arene. Interestingly when calix[4]arene was treated with ethyl oxalyl chloride in the presence of aluminum chloride, two ethyl oxalyl units were introduced at the upper rim of calix[4]arene. The trimalonyl and trioxalyl substituted calix[4]arene **4a** and **4b** exist in a partial cone conformation. The tetrasuccinylated **2a** and tetramalonylated **2c** exist in a 1,3-alternate conformation, but **2b** exists in a cone conformation. The disubstituted **3a** and **3b** exist in a cone conformation. The metal binding properties of ester-containing calix[4]arenes and selective C-acylation with oxalyl chloride are under way.

Experimental

Melting points of all compounds were recorded on a Mel Temp apparatus without calibration. Infrared (IR) spectra were determined on a Nicolet 520 FT-IR spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity 300 spectrometer. Chemical shifts were recorded as δ values in part per million relative to tetramethylsilane as an internal standard. Thin layer chromatography (TLC) analyses were carried out on a silica gel plates.

Calixarene 1a¹³ and **1b**¹⁹ were synthesized by the previously reported method.

25,26,27,28-Tetrakis[(ethyl succinyl)oxy]calix[4]arene 2a. To a solution of 0.5 g (1.2 mmol) of calix[4]arene **1a** and 0.77 g (19.3 mmol) of NaH (60% dispersion in oil) in 35 mL THF, 0.97 mL (6.9 mmol) of ethyl succinyl chloride in 10 mL THF was added dropwise over a period of 30 min under ice bath. The reaction mixture was stirred for 2h at room temperature and the solvents were evaporated. The residue was treated with CHCl_3 and aqueous HCl solution. Organic layer was separated and the solvent was removed. The residue was triturated with MeOH and recrystallized from CHCl_3 -MeOH to yield 0.52 g (47%) of **2a**. mp 176–179 °C. IR(KBr) 1750 and 1734 cm^{-1} ($-\text{CO}_2$). ^1H NMR (CDCl_3) δ 7.20–7.00 (m, 12H, ArH), 4.15 (q, 8H, $-\text{OCH}_2-$), 3.75 (s, 8H, ArCH_2Ar), 2.45 and 1.95 (two t, 16H, $-\text{CH}_2\text{CH}_2-$), 1.30 (t, 12H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3) δ 172.1, 169.6 ($-\text{CO}_2$), 148.2, 133.2, 129.2, and 125.4 (Ar), 60.7 ($-\text{OCH}_2-$), 37.4 (ArCH_2Ar), 28.4 and 28.0 ($-\text{CH}_2\text{CH}_2-$), 14.2 ($-\text{CH}_3$).

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis[(ethyl succinyl)oxy]calix[4]arene 2b. To a solution of 0.5 g (0.77 mmol) of *t*-butylcalix[4]arene **1b** and 0.5 g (12.6 mmol) of NaH (60% dispersion in oil) in 35 mL THF, 0.64 mL (4.5 mmol) of ethyl succinyl chloride in 10 mL THF was added dropwise over a period of 30 min under ice bath. The reaction mixture was stirred for 3h at room temperature and the solvents were evaporated. The residue was treated with CHCl_3 and aqueous HCl solution. Organic layer was separated and the solvent was removed. The residue was triturated with MeOH and recrystallized from CHCl_3 -MeOH to yield 0.43 g (48%) of **2b**. mp 154–155 °C. IR(KBr) 1754 and 1735 cm^{-1} ($-\text{CO}_2$). ^1H NMR (CDCl_3) δ 6.94 (s, 8H, ArH), 4.14 (q, 8H, $-\text{OCH}_2-$), 3.92 and 3.23 (pair of d, 8H, ArCH_2Ar), 3.20 and 2.75 (two t, 16H, $-\text{CH}_2\text{CH}_2-$), 1.26 (t, 12H, $-\text{CH}_3$), 1.10 (s, 36H, $-\text{CH}_3$ from *t*-butyl). ^{13}C NMR (CDCl_3) δ 172.8,

and 172.4 (-CO₂), 147.7, 143.4, 132.9, and 125.4 (Ar), 60.5 (-OCH₂-), 34.10, 31.33, 31.25, 31.10, 30.7, 29.1, and 14.2 (ArCH₂Ar, -CH₂CH₂-, and -CH₃).

25,27-Bis[(ethyl succinyl)oxy]-26,28-dihydroxycalix[4]arene 3a. To a solution of 0.3 g (0.71 mmol) of calix[4]arene **1a** and 0.15 mL (1.80 mmol) of pyridine in 25 mL THF, 0.26 mL (1.77 mmol) of ethyl succinyl chloride was added. The reaction mixture was stirred for 1h at room temperature and the solvents were evaporated. The residue was triturated with MeOH and recrystallized from CHCl₃-MeOH to yield 0.29 g (60%) of **3a**. mp 198-200 °C. IR(KBr) 3506 cm⁻¹ (OH), 1763 and 1728 cm⁻¹ (-CO₂). ¹H NMR (CDCl₃) δ 7.14-6.70 (m, 12H, ArH), 5.59 (s, 2H, OH), 4.15 (q, 4H, -OCH₂-), 3.95 and 3.51 (pair of d, 8H, ArCH₂Ar), 3.01 and 2.83 (two t, 8H, -CH₂CH₂-), 1.26 (t, 6H, -CH₃). ¹³C NMR (CDCl₃) δ 172.0 and 170.1 (-CO₂-), 152.7, 145.1, 132.2, 129.2, 128.9, 127.7, 126.8, and 119.8 (Ar), 60.9 (-OCH₂-), 32.8 (ArCH₂Ar), 29.0 and 28.9 (-CH₂CH₂-), 14.2 (-CH₃).

5,11,17,23-Tetra-tert-butyl-25,27-bis[(ethyl succinyl)oxy]-26,28-dihydroxy calix[4]arene 3b. To a solution of 0.5 g (0.77 mmol) of *t*-butylcalix[4]arene **1b** and 0.17 mL (2.00 mmol) of pyridine in 30 mL THF, 0.29 mL (2.00 mmol) of ethyl succinyl chloride was added. The reaction mixture was stirred for 5h at room temperature and the solvents were evaporated. The residue was triturated with MeOH and recrystallized from CHCl₃-MeOH to yield 0.38 g (55%) of **3b**. mp 195-196 °C. IR(KBr) 3483 cm⁻¹ (OH), 1770 and 1728 cm⁻¹ (-CO₂-). ¹H NMR (CDCl₃) δ 7.08 and 6.94 (two s, 8H, ArH), 4.89 (s, 2H, OH), 4.14 (q, 4H, -OCH₂-), 3.84 and 3.50 (pair of d, 8H, ArCH₂Ar), 2.83 and 2.37 (two t, 8H, -CH₂CH₂-), 1.30 and 1.03 (two s, 36H, -CH₃ from *t*-butyl), 12.4 (t, 6H, -CH₃). ¹³C NMR (CDCl₃) δ 171.9 and 170.3 (-CO₂-), 150.4, 148.8, 143.5, 142.2, 131.8, 127.3, 126.2, and 125.4 (Ar), 60.9 (-OCH₂-), 34.1, 34.0, 33.9, 31.6, 31.0, 28.9, 28.8, and 14.2 (ArCH₂Ar, -CH₂CH₂-, *t*-butyl carbons, and -CH₃).

25,26,27,28-Tetrakis[(ethyl malonyl)oxy]calix[4]arene 2c and 25,26,27-Tris[(ethyl malonyl)oxy]-28-hydroxycalix[4]arene 4a. To a solution of 0.3 g (0.71 mmol) of calix[4]arene **1a** and 0.30 mL (3.50 mmol) of pyridine in 25 mL THF, 0.38 mL (3.50 mmol) of ethyl malonyl chloride was added slowly. The reaction mixture was stirred for 2h at room temperature and the solvents were evaporated. The residue was triturated with MeOH and then subjected to column chromatography (eluent; CHCl₃:*n*-Hexane:ethyl acetate=1:1:1) to give 0.19 g of **2c** and 0.10 g of **4a**. Compound **2c**; mp 169-170 °C. IR(KBr) 1769 and 1734 cm⁻¹ (-CO₂-). ¹H NMR (CDCl₃) δ 7.2-7.0 (m, 12H, ArH), 4.30 (q, 8H, -OCH₂-), 3.78 (s, 8H, ArCH₂Ar), 2.70 (s, 8H, -CO₂CH₂CO₂-), 1.38 (t, 12H, -CH₃). ¹³C NMR (CDCl₃) δ 165.8 and 163.7 (-CO₂-), 148.0, 133.1, 129.6, and 126.0 (Ar), 62.0 (-OCH₂-), 40.3 (-COCH₂CO-), 37.3, 14.2 (-CH₃). Compound **4a**; mp 168-170 °C. IR(KBr) 3459 cm⁻¹ (OH), 1769 and 1732 cm⁻¹ (-CO₂-). ¹H NMR (CDCl₃) δ 7.2-6.7 (m, 12H, ArH), 5.35 (s, 1H, OH), 4.4-4.1 (two q, 6H, -OCH₂-), 4.1-3.4 (two pair of d, 8H, ArCH₂Ar), 3.2-2.5 (pair of d and s, 6H, -CH₂- from malonyl), 1.4-1.2 (two t, 9H, -CH₃). ¹³C NMR (CDCl₃) δ 165.9 and 163.8 (-CO₂-), 152.7, 146.6, 133.2, 132.9, 132.4, 129.9, 129.7, 129.2, 128.7, 127.1, 126.4, 125.8, and 119.8 (Ar), 61.9 and 61.5 (-OCH₂-), 41.0 and 40.0 (-COCH₂CO-), 37.4 and 33.0 (ArCH₂Ar), 14.1 and 14.0 (-CH₃).

25,26,27-Tris[(ethyl oxalyl)oxy]-28-hydroxycalix[4]arene 4b. To a solution of 0.5 g (1.18 mmol) of calix[4]arene **1a** and 0.50 mL (5.90 mmol) of pyridine in 25 mL THF, 0.68 mL (5.80 mmol) of ethyl oxalyl chloride was added slowly. The reaction mixture was stirred for 1h at room temperature and the solvents were evaporated. The residue was triturated with *n*-hexane and recrystallized from CCl₄ to yield 0.38 g (45%) of **4b**. mp 203-205 °C. IR(KBr) 3572 cm⁻¹ (OH), 1781, 1772, 1747, and 1740 cm⁻¹ (-CO₂-). ¹H NMR (CDCl₃) δ 7.4-6.6 (m, 12H, ArH), 6.00 (s, 1H, OH), 4.7-4.3 (m, 6H, -OCH₂-), 4.0-3.4 (m, 8H, ArCH₂Ar), 1.50 and 0.60 (two t, 9H, -CH₃). ¹³C NMR (CDCl₃) δ 157.3, 156.0, 155.8, and 152.0 (-CO₂-), 147.6, 145.6, 132.9, 131.8, 131.5, 130.6, 130.1, 129.2, 128.8, 127.3, 126.7, 126.5, and 119.8 (Ar), 63.4 and 63.0 (-OCH₂-), 37.3 and 31.8 (ArCH₂Ar), 14.1 and 13.1 (-CH₃).

5,17-Bis[(ethyl oxalyl)oxy]-25,26,27,28-tetrahydroxycalix[4]arene 5. To a solution of 0.63 g (47 mmol) of AlCl₃ and 1.4 mL (12.5 mmol) of ethyl oxalyl chloride in 10 mL CH₂Cl₂, 0.2 g (0.47 mmol) of calix[4]arene **1a** was added. The reaction mixture was stirred for 2h at room temperature and then poured into ice water. The organic layer was separated and the solvents were removed. The residue was triturated with MeOH and recrystallized from CHCl₃-MeOH to give 0.2 g (69%) of **5**. mp 276-278 °C. IR(KBr) 3216 cm⁻¹ (OH), 1731 and 1670 cm⁻¹ (-CO₂- and -CO-). ¹H NMR (CDCl₃) δ 10.16 (br s, 4H, OH), 7.80, 7.10, and 6.82 (s, d, and t, 10H, ArH), 4.41 (q, 4H, -OCH₂-), 4.2 and 3.7 (two br s, 8H, ArCH₂Ar), 1.40 (t, 6H, -CH₃). ¹³C NMR (CDCl₃) δ 184.3 (-CO-), 163.6 (-CO₂-), 155.2, 148.1, 131.7, 129.5, 128.7, 127.2, 126.8, and 123.0 (Ar), 62.1 (-OCH₂-), 31.4 (ArCH₂Ar), 14.1 (-CH₃).

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References

- (a) Gutsche, C. D.; Muthukrishnan, R. *J. Org. Chem.* **1978**, *43*, 4905. (b) Gutsche, C. D.; Dhawan, B.; No, K. H.; Muthukrishnan, R. *J. Am. Chem. Soc.* **1981**, *103*, 3782.
- Arimura, T.; Kawabata, H.; Matsuda, T.; Muramatsu, T.; Satoh, H.; Fugio, K.; Manabe, P.; Shikai, S. *J. Org. Chem.* **1991**, *56*, 301.
- Han, Sang Yoon; Kang, Myong Hee; Jung, Yeon Eui; Chang, Suk Kyu. *J. Chem. Soc. Perkin. Trans. 2.* **1994**, *4*, 835.
- Takeshita, Michiori; Shinkai, Seiji. *Bull. Chem. Soc. Jpn.* **1995**, *68*(4), 1088.
- Xu, W.; Vital, J. J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 8362.
- Ungaro, R.; Pochini, A.; Andreetti, G. D.; Domiano, P. *J. Inc. Phen.* **1985**, *3*, 35.
- Araki, Koji; Yanagi, Akihiro; Shinkai, Seiji. *Tetrahedron.* **1993**, *49*(31), 6763.
- Gutsche, C. D.; Alam, I. *Tetrahedron* **1988**, *44*, 4689.
- Calestani, G.; Ugozzoli, F.; Ghidini, E.; Ungaro, R. *J. Chem. Soc., Chem. Comm.* **1987**, 344.
- Kubo, Yuji; Hamaguchi; Niimi, Atsuko; Yoshida, Katsuhira; Tokita, Sumio. *J. Chem. Soc., Chem. Commun.* **1933**, *3*, 305.
- Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud,

- F. Fanni, S.; Schwing, M.; Egberink, R. J. M.; Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 2767.
12. Arnaud-Neu, F.; Collins, E. M.; Deasy, M.; Ferguson, G.; Harris, S. J.; Kaitner, B.; Lough, A. J.; Mckervery, M. A.; Marques, E.; Ruhl, B. L.; Schiwig-Weill, M. J.; Seward, E. *J. Am. Chem. Soc.* **1989**, *111*, 8681.
13. The calix[4]arenes can exist four different conformations, cone (all "up"), partial cone (three "up" and one "down"), 1,2-alternate (adjacent two "up" and two "down"), and 1,3-alternate (opposite side two "up" and two "down"). Gutsche, C. D.; Dhawan, B.; Levine, J. A.; No, K. H.; Bauer, L. *Tetrahedron.* **1983**, *39*, 409.
14. Iqbal, M.; Mangiafico, T.; Gutsche, C. D. *Tetrahedron* **1987**, *43*, 4917.
15. Jaime, C.; Mandoza, J. D.; Prados, P.; Nieto, P. M.; Sanchez, C. *J. Org. Chem.* **1991**, *56*, 3372.
16. Shinkai, Seiji. *Tetrahedron.* **1993**, *49*, 8933.
17. (a) Gutsche, C. D.; See, K. A. *J. Org. Chem.* **1992**, *57*, 4527. (b) No, K. H.; Hong, M. *J. Chem. Soc., Chem. Commun.* **1990**, 572.
18. Gutsche, C. D.; Lin, L. G. *Tetrahedron* **1986**, *42*, 1633.
19. Gutsche, C. D.; Iqbal, M. *Org. Syn.* **1990**, *68*, 234.

The Photochemical Reactivities of Benzenes Tethered to Haloarene

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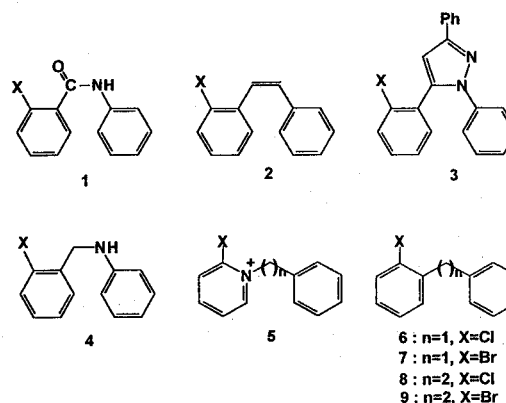
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The syntheses and photoreactions of haloarenes, in which the aryl and haloaryl moieties are tethered by a simple alkyl group, were studied. For 2-benzyl-1-halobenzene, in which two aryl moieties were connected by methylene group, photoreduced product, diphenylmethane, was obtained along with the minor formation of the photocyclized product, fluorene, in acetonitrile solvent. For 1-halo-2-phenethylbenzene, in which two aryl moieties were connected by ethylene group, photocyclized products, 9,10-dihydrophenanthrene and phenanthrene, were obtained along with the minor formation of photoreduced product, bibenzyl, in acetonitrile solvent. The photoreaction selectivities in several solvent systems were studied: In cyclohexane, 2-benzyl-1-chlorobenzene was photoreduced more effectively than 2-benzyl-1-bromobenzene; In the presence of NaOH, 1-halo-2-phenethylbenzenes gave 9,10-dihydrophenanthrene and, in the presence of toluene, they gave phenanthrene. A radical reaction mechanism is proposed for the explanation of the reactions. This study shows that the photoreaction of haloarene, in which haloaryl and aryl moieties are tethered by ethylene group, can be used for ring formation of 9,10-dihydrophenanthrene otherwise difficultly accessible.

Introduction

Photoreactions of haloarenes are of considerable interest in the development of synthetic methods and in the understanding mechanistic pathways. The reactions are of interest for the degradation of the haloarenes which can pollute the environment. Intramolecular photocyclization of haloarenes, in which phenyl and 2-halophenyl moieties are linked by amide¹⁻³ (1), alkenyl^{4,5} (2), 1,6-pyrazole⁶ (3), and aminoalkyl groups⁷⁻⁹ (4) have been studied (Scheme 1). Intramolecular photocyclization of halogenated pyridinium salts (5) also have been studied intensively.¹⁰⁻¹³ However, little is known about the photoreactions of haloarenes in which the aryl and haloaryl moieties are connected by the simple alkyl groups (6-9). The photochemistry of these systems deserves special attention as should be the standard for the intramolecular photocyclization.

We now wish to report the first studies of the photoreactions and selectivities of the 1-halo-2-benzylbenzenes (6 or 7) and 2-halo-1-phenethylbenzenes (8 or 9).



Scheme 1.

Results and Discussion

Synthesis. 2-Benzyl-1-chlorobenzene (6) was prepared