porator. The crude product was purified by flash column chromatography on silica gel (ethyl acetate/hexane, 1 : 20) to give the desired compound, (*E*)-olefin **1** (404 mg, 48%) as an oil and by-product, (*Z*)-olefin **2** (396 mg, 47%) as an oil. The stereochemistry and ratio (*ca.* 1 : 1) of two isomers, (*E*)-olefin **1** and (*Z*)-olefin **2**, were determined by ^{1}H NMR spectrum analysis: (*E*)-olefin **1**: R_f=0.53 (ethyl acetate/hexane, 1 : 9); ^{1}H NMR ($CDCl_3$) δ 8.31-8.28 (m, 1H), 7.88-7.85 (m, 1H), 7.81-7.78 (m, 1H), 7.54-7.41 (m, 4H), 6.18 (dt, *J*= 15.7, 6.6 Hz, 1H), 5.70 (dt, *J*=15.7, 1.4 Hz, 1H), 3.92 (s, 2H), 3.15 (dd, *J*=6.6, 1.4 Hz, 2H), 2.25 (s, 3H), 1.26 (s, 9H): (*Z*)-olefin **2**: R_f=0.42 (ethyl acetate/hexane, 1 : 9); ^{1}H NMR ($CDCl_3$) δ 8.31-8.28 (m, 1H), 7.88-7.85 (m, 1H), 7.81-7.78 (m, 1H), 7.54-7.41 (m, 4H), 6.05 (dt, *J*=10.2, 6.5 Hz, 1H), 5.69 (dt, *J*=10.2, 1.4 Hz, 1H), 3.95 (s, 2H), 3.39 (dd, *J*=6.5, 1.4 Hz, 2H), 2.28 (s, 3H), 1.29 (s, 9H). Spectrum matches that in *J. Med. Chem.* **1984**, *27*, 1539.

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Synthesis and Conformational Properties of 1,2-Dibenzoester Calix[4]arene

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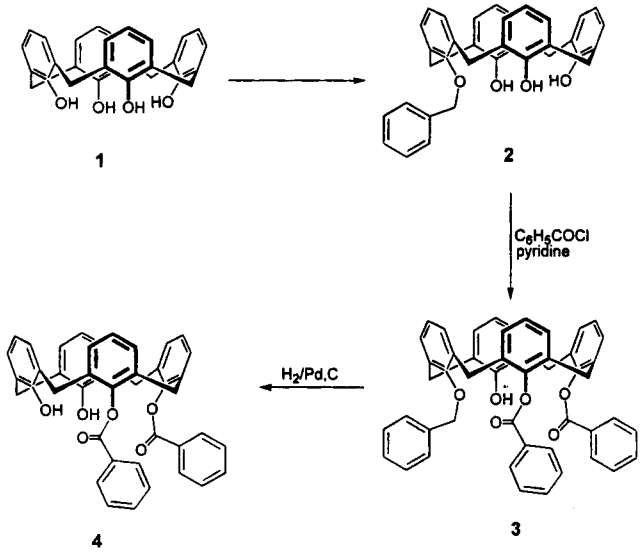
Selective derivatization of calixarene has greatly widened the area of calixarenes in Host-Guest chemistry.[1-3] Several synthetic procedures for selective alkylation have been developed such as 1,3-dialkylation,[4] 1,2-dialkylation,[5] monoalkylation,[6] and trialkylation.[7] Also a few selective acylation techniques has been reported.[8] Unlike alkyl moiety, acyl groups at the lower rim of calixarenes not only can control the reactivity of the *para* position of upper rim, but be utilized as useful protecting groups. Thus selective acylation can provide the quite useful intermediate compounds for the developing of important calixarene host. Gutsche and Lin[8a] found that calix[4]arene is only tribenzoylated when it is treated with excess benzoyl chloride in pyridine. They also reported[8] that when *t*-butylcalix[4]arene was treated with 3,5-dinitrobenzoyl chloride in the presence of bases, various substitution patterns were observed such as triester, 1,3-diester, 1,2-diester, and monoester compounds depending on reaction conditions. But these substitution patterns were only applied to *t*-butylcalix[4]arene with 3,5-dinitrobenzoyl chloride. Here we developed a selective indirect acylation procedure providing specifically 1,2-dibenzoester by removing benzyl group selectively from trisubstituted calix[4] arene. Trisubstituted calix[4]arene was obtained from benzoylation of monobenzylcalix[4]arene in pyridine. 1,2-Dibenzoester of calix[4]arene never has been prepared and it could provide the excellent building block for the useful host calix[4]arenes.

Direct 1,2-substitution of calix[4]arene with benzoyl groups was attempted by varying the reaction conditions, but failed to obtain any significant amounts of 1,2-dibenzoester products. Always 1,3-dibenzoylated calix[4]arene and/or tribenzoylated calix[4]arene was obtained as a major products depending on the reaction conditions.[8] After direct 1,2-dibenzoylation failed, a three step procedure was sought. It is known[8] that calix[4]arene **1** produces only tribenzoylated products in pyridine when treated with excess benzoyl chloride. If this selective benzoylation occurred with monoalkylcalix[4]arenes, it is possible to get 1,2-benzoester from this reaction. Thus, we treated monobenzyl ether calix[4]arene **2** prepared by the reported procedure[6] with excess benzoyl chloride in pyridine to obtain the asymmetrically substituted calix[4]arene **3**. As expected, only two benzoyl groups were introduced exclusively, one at the opposite and the other at the adjacent position relative to the present benzyl group, to give so called ABBH type[10] chiral calix[4]arenes as shown in Scheme 1. Two benzoyl group might end up at both adjacent positions relative to alkyl group, which can be described as a ABHB type, but we observed none of this product. It can be rationalized by the order of benzoylation. If we assume that two benzoylation do not occur simultaneously, first benzoyl group could prefer to be introduced at the opposite side of the existing alkyl group due to steric crowd. Then the second benzoyl group will end up either side to finish a ABBH type calix[4]arene. The ^{1}H NMR spectrum of **3** shows the typical chiral calix[4]arene characteristics such as four pairs of doublet at 3.2-4.1 ppm for the eight bridge methylene protons and the very complicated aromatic signals around 6.2-8.0 ppm. The diastereotopic protons of benzylic methylene appear as a pair of doublets at 4.3 ppm as expected.



Scheme 1. Synthesis of 1,2-dibenzoester calix[4]arene.

Debenzylation with trimethylsilyl iodide[10] only gave unreacted starting materials. But debenzylation was succeeded with hydrogenation. Treatment of **3** with H_2 in the presence of palladium catalysts produced a clean 1,2-dibenzoylated calix[4]arene **4** in 72% yield. The ^{1}H NMR spectrum of **4** showed two triplets at δ 6.59 and 6.45 for the *para* hydrogens of calixarene aromatic rings (each 2H) as characteristic signals[11,12] of 1,2-disubstituted calix[4]arenes, and the bridge methylene protons appear as best interpreted as four singlets at δ 3.88, 3.85, 3.84 and 3.81 with a intensity of 1 : 1 : 1 : 1. The difference in the chemical shifts among four peaks is extremely small (Δδ=0.07 ppm) as shown in Figure 1. According to Gutsche,[7,13] the Δδ becomes smaller when the phenol unit is flattened. But the four singlets for the bridge methylene protons give no clear clues for the conformation. In our best knowledge four singlets signals for the bridge methylene protons have never been observed.

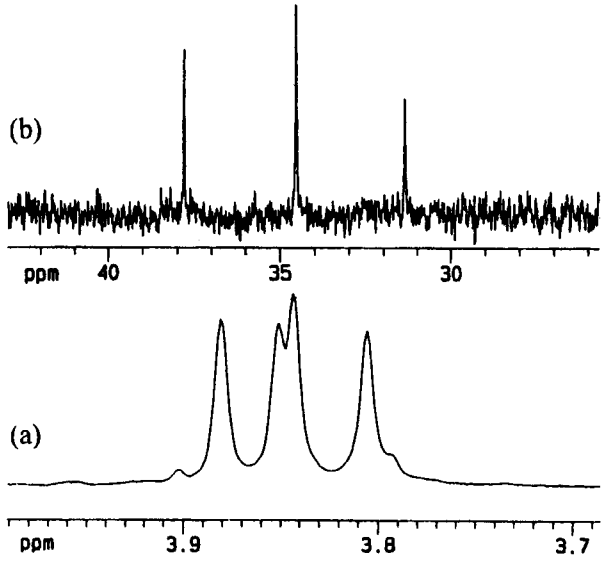


Figure 1. The partial NMR spectra of **4** in $CDCl_3$. (a) the partial ^{1}H NMR spectrum, (b) the partial ^{13}C NMR spectrum.

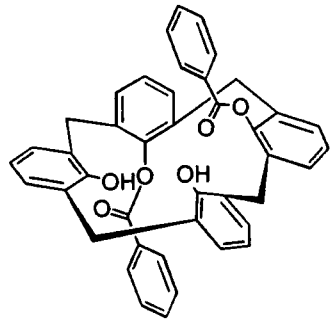


Figure 2. Proposed flattened conformation of **4**.

The IR absorption bands of **4** showed at 3377 cm $^{-1}$ as a broad peak with a shoulder at 3432 cm^{-1} for the OH and two peaks at 1730 cm^{-1} and 1708 cm^{-1} for the ester carbonyl stretching band, indicating that two ester and two OH are not equivalent. This phenomena could be resulted in from the unsymmetrically flatten structure to form intramolecular hydrogen bonds between OH and ester groups.

The conformation of calix[4]arene can be determined by the ^{13}C NMR spectrum. Particularly diagnostic were the chemical shifts for the methylene carbons[14] of calix[4]arene which showed peaks at about δ 32 for the *syn* oriented phenol rings or δ 37 for the *anti* oriented phenol rings. Interestingly the ^{13}C NMR spectrum of **4** showed three signals at δ 37.80, 34.55, and 31.38 for the bridge carbons, that is, one *syn* and one anti carbons, but peak at δ 34.55 could not be assigned as *syn* or *anti* on the basis of previous analysis method,[14] but rather might be interpreted as signal of platten phenol rings. To accommodate these spectral characteristics it is suggested that **4** exist in a "flatten" conformation[7,12] as shown in Figure 2.

In conclusion, the present paper describes the synthetic pathway for the preparation of 1,2-benzoester calix[4]arene. The conformation was suggested as a flatten conformation on the basis of IR, ^{1}H, and ^{13}C NMR analyses.

Experimental

25,26,27,28-Tetrahydroxycalix[4]arene 1 was prepared by the known procedure.[8a] mp 314-316 °C (*lit.*[8a] 313-315 °C).

25-Benzyloxy-26,27,28-trihydroxycalix[4]arene 2 was prepared by the known procedure.[6] mp 224-225 °C (*lit.*[10] 225-226 °C).

25-Benzyloxy-26,27-bisbenzoyloxy-28-hydroxycalix[4]arene 3. To a solution of 0.30 g (0.58 mmol) of **2** in 30 mL of pyridine, 2.0 mL (17 mmol) of benzoyl chloride was added slowly at room temperature. The reaction mixture was stirred for 13 hrs, and then 50 mL $CHCl_3$ and 60 mL H_2O were added. The organic layer was separated and washed with the water three times. After removing the solvents, the residue was triturated with methanol. Recrystallization from chloroform-methanol gave 0.35 g (83%) of colorless crystals **3**. mp 261-264 °C. ^{1}H NMR ($CDCl_3$) δ 8.0-6.20 (m, 27H, ArH and OH), 5.18 and 4.86 (a pair of d, 2H, -OCH_2Ar, J=11.7 Hz), 4.04, 4.11, 3.86, 3.82, 3.77, 3.71, 3.28, and 3.24 (four pairs of d, 8H, $ArCH_2Ar$, J=12.9 Hz, 15.9 Hz, and 15.6 Hz). ^{13}C NMR ($CDCl_3$) δ 164.94, 163.55

(-CO_2-), 153.05, 152.68, 148.12, 146.72, 135.81, 133.16, 133.14, 133.05, 132.81, 132.71, 132.59, 132.47, 131.80, 130.73, 130.36, 130.30, 130.22, 129.66, 129.46, 129.35, 129.30, 129.25, 128.89, 128.68, 128.64, 128.47, 128.41, 128.14, 127.32, 126.32, 125.34, 125.26, 125.18, and 119.18 (Ar), 77.34 (-OCH_2Ar), 38.01, 37.80, 31.70, and 31.11 (ArCH_2Ar). IR (KBr) 3392 cm^{-1} (OH), 1731 and 1714 cm^{-1} (-CO_2-).

25,26-Bisbenzoyloxy-27,28-dihydroxycalix[4]arene 4. A mixture of 1.0 g (1.38 mmol) of **3** and 0.05 g of Pd/C in THF/ethanol (7 : 3) was shaken for 7 hrs under H_2 atmosphere at 50 psi. After filtered off the catalyst, the solvents were removed and the residue was triturated with methanol. Recrystallization from chloroform-methanol produced 0.73 g (72%) of colorless crystals **4**. mp 239-241 °C. ^{1}H NMR ($CDCl_3$) δ 7.42 (t, 2H, ArH), 7.16-7.00 (m, 14H, ArH and OH), 6.84 (d, 2H, ArH, *J*=7.52 Hz), 6.72 (d, 2H, ArH, *J*=7.52 Hz), 6.59 (t, 2H, ArH, *J*=7.52 Hz), 6.45 (t, 2H, ArH, *J*=7.52 Hz), 3.88, 3.85, 3.84, and 3.81 (four s, 8H, ArCH_2Ar). ^{13}C NMR ($CDCl_3$) δ 163.54 (-CO_2-), 151.01, 146.73, 133.18, 133.05, 132.40, 130.06, 129.57, 129.50, 128.96, 128.59, 128.06, 127.94, 127.22, 126.44, and 121.04 (Ar), 37.80, 34.55, and 31.38 (ArCH_2Ar). IR (KBr) 3432 and 3376 cm^{-1} (OH), 1730 and 1706 cm^{-1} (-CO_2-).

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Rhodium Catalyzed Reactions of Cyclic 2-Diazo-1,3-dicarbonyl Compounds with Nitriles

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Various benzoxazole derivatives are found as the sub-unit of the several natural products,[1] drugs[2] and industrial chemicals[3] and of interest for useful intermediates in the area of organic synthesis.[4] In the continuation of our research work on the use of α-diazocarbonyl compounds for the synthesis of heterocycles such as β-furoic acid,[5] γ-pyrone,[6] oxazole,[7] and thiazole,[8] we have investigated efficient method for the preparation of the 4-oxo-4,5,6,7-tetrahydrobenzoxazole. While the rhodium-catalyzed dipolar cycloaddition of cyclic 2-diazo-1,3-dicarbonyl compounds such as 2-diazo-1,3-cyclohexanedione (**1a**), 2-diazo-5-methyl-1,3-cyclohexanedione (**1b**), and diazodimedone (**1c**) to aromatic heterocycles,[9] acetylenes,[10] vinyl ethers,[9b] vinyl acetates,[11] are developed, the utility of these reagents for the synthesis of 4-oxo-4,5,6,7-tetrahydrobenzoxazole has not been exploited. Consequently, we examined the reactions of cyclic 2-diazo-1,3-dicarbonyl compounds with nitriles. We describe herein our results on the synthesis of oxotetrahydrobenzoxazoles *via* 1,3-dipolar cycloadditions of cyclic rhodium carbenoids with nitriles.