

## Synthesis and X-Ray Structure of 25-Acetoxy-26,27,28-trimethoxycalix[4]arene

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25-Acetoxy-26,27,28-trimethoxycalix[4]arene was synthesized by the treatment of calix[4]arene trimethyl ether with acetyl chloride in the presence of NaH. The solution conformation was inferred as a partial cone conformation based on the  $^1\text{H}$ - and  $^{13}\text{C}$  NMR spectra. The crystal structure has been determined by X-ray diffraction method. The crystals are monoclinic, space group  $P2_1/n$ ,  $a=8.186$  (1),  $b=17.137$  (2),  $c=19.878$  (3) Å,  $\beta=95.67$  (1)°,  $Z=4$ ,  $V=2774.90$  Å<sup>3</sup>,  $D_c=1.22$  g cm<sup>-3</sup>,  $D_m=1.23$  g cm<sup>-3</sup>. The intensity data were collected on an Enraf-Nonius CAD-4 Diffractometer with a graphite monochromated Cu-K $\alpha$  radiation. The structure was solved by direct method and refined by full-matrix least-squares methods to a final  $R$  value of 0.054 for 3675 observed reflections. The molecule possesses a partial cone conformation with one flattened phenyl unit, in which one anisole ring, distal to the ester ring, is inverted. The acetoxyphenyl ring is flattened.

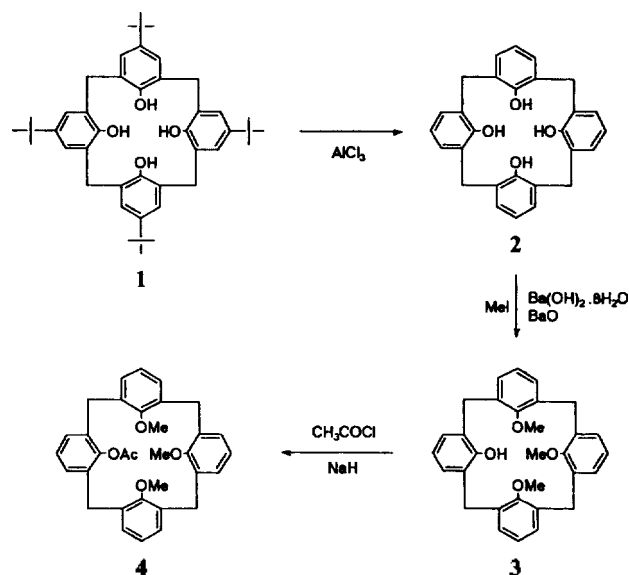
### Introduction

Calixarenes, which are accessible from base-catalyzed condensation of *para*-substituted phenols with formaldehyde, have attracted considerable attention because of their basket shape and their ability to be functionalized in various ways.<sup>1,2</sup> All the calix[4]arenes containing free intraannular OH groups are conformationally mobile in solution at room temperature<sup>3</sup> and exist four possible conformational isomers: cone, partial cone, 1,2-alternate and 1,3-alternate. All four of the conformers for a calix[4]arene are interchangeable by rotations of the aryl groups around the axis that passes through the *meta* carbon atoms bonded to the bridging methylene groups. Upon replacement of the phenolic hydrogens with various alkyl or acyl substituents, the calix[4]arene becomes conformationally immobilized, existing as a discrete conformational isomer.<sup>4,5</sup>

Shaping the cavity plays a potentially vital role in the design of calixarenes as enzyme mimics, for host-guest interactions depend on complementarity in shape as well as functionality. In study of the arylmethylation<sup>6</sup> and aroylation<sup>7</sup> of calix[4]arene, Gutsche showed that the particular conformation in which a calix[4]arene is fixed upon derivatization is dependent on the reaction conditions. The products of arylmethylation partition principally between the cone and partial cone conformers, while those of aroylation partition principally between the cone and 1,3-alternate conformers. Shinkai<sup>8</sup> also reported the similar result from the alkylation of calix[4]arene. We<sup>9,10</sup> also reported the conformational outcomes in the acylation of calix[4]arenes and calix[4]arenes 1,3-dialkyl ethers. The present investigation is an extension of these earlier works and involves the determination of the conformation of the product obtained in the acetylation of the calix[4]arenes trimethyl ether.

**Synthesis.** The acetate of calix[4]arenes trimethyl ether was synthesized as shown in Scheme 1.

The regioselective introductions of alkyl or acyl groups into the lower rim of calix[4]arene were reported by Gutsche,<sup>4</sup> Shinkai,<sup>8</sup> Reinhoudt<sup>11</sup> Pappalardo<sup>12</sup> and our laboratory.<sup>13</sup> Gutsche<sup>14</sup> reported the synthesis of trimethyl ether 3 in 60%



Scheme 1.

yield by the treatment calix[4]arene 2 with dimethyl sulfate in the presence of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and BaO in DMF. It was reported by Shinkai<sup>15</sup> that the alkylation reaction in the presence of excess  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and BaO in DMF afforded only trialkylated calix[4]arene in cone conformation. However, when calix[4]arenes 2 was treated with methyl iodide under the Gutsche or Shinkai's conditions, tetramethyl ether was obtained as the only isolable product with no indication of the desired product. Treatment of compound 2 in DMF with methyl iodide in the presence of equivalent amount of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  affords the trimethylated calix[4]arene 3 in 71% yield. The conformation of a derivatized calix[4]arene can be readily established on the bases of its  $^1\text{H}$  NMR spectrum, particularly from the patterns arising from the methylene protons joining the aromatic rings of the cyclic array. The  $^{13}\text{C}$  NMR spectrum, which can be utilized for the conformational assignment of calix[4]arene<sup>16</sup> shows resonances at around  $\delta$  37 and 31 for the bridge methylene

carbons. The down field resonance is characteristic of a methylene carbon carrying adjacent aromatic moieties 'anti' to one another, and the upfield one is characteristic of a methylene carbon carrying these groups 'syn' to each other. The  $^1\text{H}$  NMR spectrum of compound 3 shows three sets of doublets in the ratio 1:2:1 for the methylene protons and two sharp singlets in the ratio 1:2 for the OMe protons. However, a choice between the cone and partial cone conformations cannot be made; as a result of the reduced symmetry of the compound 3, both would be expected to show two OMe resonances and two pairs of doublets for methylene protons. The conformation was assigned as cone conformation based on the  $^{13}\text{C}$  NMR spectrum, which shows twelve peaks from aromatic carbons, two peaks from methoxy carbons, two peaks at  $\delta$  30.73 and 30.64 from the methylene bridge carbons. The absence of peak at around  $\delta$  37 supports the cone conformation of 3. Compound 4 was prepared in 91% yield by treatment of 3 with acetyl chloride and NaH in THF.  $^1\text{H}$  NMR spectrum of 4 shows three sets of doublet in the ratio of 1:2:1 for methylene hydrogens, two singlets for OMe hydrogens and a singlet for methyl hydrogens adjacent to carbonyl group, which is commensurate with either of cone or partial cone conformation. The  $^{13}\text{C}$  NMR spectrum shows single peak of carbonyl carbon, twelve peaks from aromatic carbons, two peaks from OMe carbons and two peaks at  $\delta$  36.86 and 30.17 from methylene carbons, which indicate the partial cone conformation. Compound 4 can exist in three partial cone conformations, OAc-inverted partial cone, proximal-OMe-inverted partial cone, and distal-OMe-inverted partial cone. The proximal-OMe-inverted partial cone, which is the lowest symmetry of the three, is not compatible with the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. A choice between OAc-inverted partial cone and distal-OMe-inverted partial cone cannot be made based on the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra.

**X-Ray Structure Analysis.** The crystal of compound 3 was obtained by slow evaporation of a solution 3 in a mixture of dichloromethane and acetone. The crystal system is monoclinic with space group  $P2_1/n$ . X-ray intensity data were measured on an Enraf-Nonius CAD-4 diffractometer using graphite monochromatized Cu-K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation by using  $\omega/2\theta$  mode with a  $\omega$ -scan width of  $0.08^\circ + 0.14^\circ \tan\theta$ . Three standard reflections (0  $\bar{6}$  0), (4 0 0), (1 0  $\bar{7}$ ) were monitored for intensity and the crystal orientation. There was no significant intensity variation during the data collection. Among the 4243 independent reflections measured in the range of  $2^\circ \leq \theta \leq 65^\circ$ , the 3675 reflections with the  $|F_o| > 4\sigma|F_c|$  were used in the structure determination and refinements. Accurate cell constants were obtained by least-squares analysis of 25 reflections, with  $\theta$  in the range of 14–22 $^\circ$ .

Data were corrected for Lorentz and polarization effects, but absorption was ignored. All of the crystal data are summarized in Table 1.

The structure was solved by direct method of the program Shelxs-86<sup>17</sup> using 776 reflections whose  $|E|$  values were greater than 1.4. All the nonhydrogen atoms were located on the E-map.

The structure was refined by the full-matrix least-squares using the program Shelxl-93.<sup>17</sup> After three cycles of isotropic full-matrix least-squares refinements,  $R$  value ( $R = \sum |F_o - F_c|$

**Table 1.** Summary of Crystal Data

Formular	$\text{C}_{33}\text{H}_{32}\text{O}_5$
Mw, amu	508.6
Crystal system	monoclinic
Space group	$P2_1/n$
$a$ , $\text{\AA}$	8.186 (1)
$b$ , $\text{\AA}$	17.137 (2)
$c$ , $\text{\AA}$	19.878 (3)
$\beta$ , deg	95.67 (1)
$Z$	4
$V$ , $\text{\AA}^3$	2774.90
$\mu$ (Cu-K $\alpha$ ), $\text{cm}^{-1}$	6.5
Density, $\text{gcm}^{-3}$	1.22 (calc.)
	1.23 (meas, by flotation in $\text{CCl}_4$ and $\text{CH}_3\text{OH}$ )
Diffractometer	Enraf-Nonius CAD-4
Radiation	Cu-K $\alpha$ ( $\lambda = 1.5418 \text{ \AA}$ ) graphite monochromator
Crystal size, mm	0.3 $\times$ 0.2 $\times$ 0.6
$\theta$ limits, deg	65
Scan type	$\omega/2\theta$
Scan range, deg	$0.80 + 0.14 \tan\theta$
no. of observed reflections	3675 $ F_o  > 4\sigma F_c $
$R$	0.054

**Table 2.** Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Thermal Parameters for Non-hydrogen Atoms.\* The e. s. d.'s are in parentheses.  $U_{eq} = 1/3 \sum_j U_{ij} a_j^2$ ,  $a_j^2$  ( $\text{\AA}^2$ )

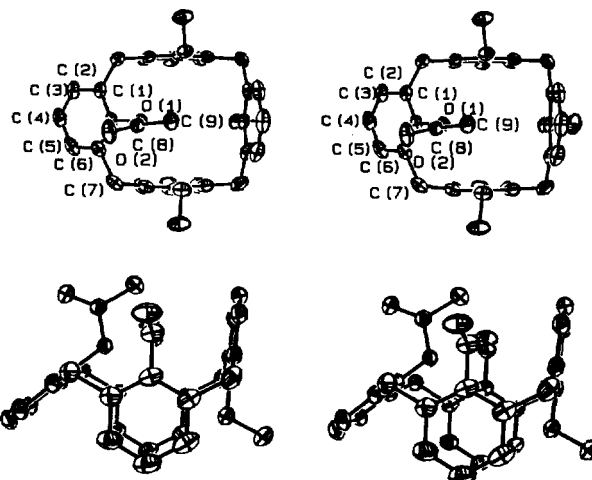
Atom	$x$	$y$	$z$	$U_{eq}$
O (1A)	-263 (2)	3189 (1)	5487 (1)	.050
O (2A)	-2226 (2)	3487 (1)	4664 (1)	.088
C (1A)	947 (2)	3483 (1)	5095 (1)	.052
C (2A)	1600 (3)	4212 (1)	5271 (1)	.055
C (3A)	2832 (3)	4497 (2)	4904 (1)	.070
C (4A)	3388 (3)	4065 (2)	4389 (1)	.082
C (5A)	2737 (3)	3345 (2)	4236 (1)	.081
C (6A)	1491 (3)	3028 (1)	4593 (1)	.063
C (7A)	852 (3)	2209 (2)	4467 (1)	.069
C (8A)	-1852 (3)	3256 (1)	5225 (1)	.054
C (9A)	-3004 (3)	3012 (2)	5716 (1)	.066
O (1B)	-814 (2)	4049 (1)	6915 (1)	.054
C (1B)	879 (2)	3961 (1)	6996 (1)	.047
C (2B)	1576 (3)	3530 (1)	7550 (1)	.054
C (3B)	3278 (3)	3478 (1)	7641 (1)	.067
C (4B)	4238 (3)	3818 (1)	7197 (1)	.071
C (5B)	3524 (3)	4199 (1)	6638 (1)	.062
C (6B)	1825 (2)	4274 (1)	6521 (1)	.049
C (7B)	1068 (3)	4646 (1)	5872 (1)	.055
C (8B)	-1338 (4)	4773 (2)	7169 (2)	.078
O (1C)	1950 (2)	1771 (1)	7415 (1)	.062
C (1C)	249 (3)	1825 (1)	7342 (1)	.057
C (2C)	-651 (3)	1263 (1)	6955 (1)	.067
C (3C)	-2354 (3)	1320 (2)	6908 (2)	.081
C (4C)	-3128 (4)	1915 (2)	7218 (1)	.085
C (5C)	-2206 (3)	2479 (2)	7574 (1)	.076

C (6C)	-492 (3)	2455 (1)	7638 (1)	.060
C (7C)	513 (3)	3094 (2)	8003 (1)	.068
C (8C)	2591 (5)	1357 (2)	8007 (2)	.091
O (1D)	-1126 (2)	1402 (1)	5378 (1)	.065
C (1D)	568 (3)	1323 (1)	5485 (1)	.061
C (2D)	1550 (3)	1666 (1)	5025 (1)	.064
C (3D)	3227 (3)	1539 (2)	5126 (2)	.086
C (4D)	3906 (4)	1111 (2)	5665 (2)	.098
C (5D)	2937 (4)	817 (2)	6130 (2)	.088
C (6D)	1234 (3)	924 (1)	6057 (1)	.067
C (7D)	184 (4)	629 (1)	6581 (2)	.081
C (8D)	-1857 (4)	847 (2)	4900 (2)	.088

\*Tables for anisotropic thermal parameters of the non-hydrogen atoms, coordinates of hydrogen atoms and structure factors are available from the author (YJP).

**Table 3.** Bond Distances (Å) and Angles (°). The e. s. d.'s are in parentheses

	A	B	C	D
C(1)-C(2)	1.390 (3)	1.399 (3)	1.396 (3)	1.405 (3)
C(2)-C(3)	1.391 (3)	1.390 (3)	1.391 (3)	1.386 (3)
C(3)-C(4)	1.376 (4)	1.380 (3)	1.377 (5)	1.369 (5)
C(4)-C(5)	1.366 (5)	1.368 (3)	1.378 (4)	1.373 (5)
C(5)-C(6)	1.408 (3)	1.393 (3)	1.397 (3)	1.400 (4)
C(1)-C(6)	1.376 (3)	1.385 (3)	1.396 (3)	1.391 (3)
C(6)-C(7)	1.509 (4)	1.516 (3)	1.511 (4)	1.502 (4)
C(8)-C(9)	1.482 (3)			
O(1)-C(1)	1.411 (3)	1.388 (2)	1.389 (3)	1.388 (3)
O(1)-C(8)	1.358 (3)	1.422 (4)	1.430 (4)	1.432 (4)
O(2)-C(8)	1.195 (3)			
C(2A)-C(7B)	1.508 (3)	C(2B)-C(7C)	1.511 (3)	
C(2C)-C(7D)	1.518 (3)	C(2D)-C(7A)	1.516 (3)	
C(3)-C(2)-C(1)	117.7 (2)	117.5 (2)	117.4 (2)	117.5 (2)
C(4)-C(3)-C(2)	120.8 (3)	121.3 (2)	121.6 (3)	121.2 (3)
C(5)-C(4)-C(3)	120.0 (2)	120.0 (2)	119.7 (3)	120.4 (3)
C(6)-C(5)-C(4)	121.5 (2)	121.2 (2)	121.4 (3)	121.2 (3)
C(5)-C(6)-C(1)	116.7 (2)	117.9 (2)	117.3 (2)	117.1 (2)
C(6)-C(1)-C(2)	123.2 (2)	121.9 (2)	122.5 (2)	122.3 (2)
C(7)-C(6)-C(1)	121.0 (2)	122.2 (2)	121.7 (2)	122.8 (2)
C(7)-C(6)-C(5)	122.2 (2)	119.9 (2)	121.1 (2)	121.2 (2)
O(1)-C(1)-C(2)	117.1 (2)	118.3 (2)	118.7 (2)	119.0 (2)
O(1)-C(1)-C(6)	119.6 (2)	119.8 (2)	118.7 (2)	118.6 (2)
C(1)-O(1)-C(8)	117.2 (2)	112.8 (2)	113.7 (2)	112.5 (2)
O(1)-C(8)-O(2)	122.2 (2)			
O(1)-C(8)-C(9)	111.8 (2)			
O(2)-C(8)-C(9)	125.9 (2)			
C(2D)-C(7A)-C(6A)	110.5 (2)			
C(2A)-C(7B)-C(6B)	110.0 (2)			
C(2B)-C(7C)-C(6C)	112.9 (2)			
C(2C)-C(7D)-C(6D)	114.5 (2)			
C(1A)-C(2A)-C(7B)	120.5 (2)	C(3A)-C(2A)-C(7B)	121.6 (2)	
C(1B)-C(2B)-C(7C)	121.2 (2)	C(3B)-C(2B)-C(7C)	121.3 (2)	
C(1C)-C(2C)-C(7D)	121.7 (2)	C(3C)-C(2C)-C(7D)	120.9 (2)	
C(1D)-C(2D)-C(7A)	122.4 (2)	C(3D)-C(2D)-C(7A)	120.0 (2)	



**Figure 1.** Conformation and Atomic Numbering. Acetoxyphenyl ring is labeled A and three methoxyphenyl rings are labeled B, C and D, clockwise.

$|E|/F_0$ ) was 0.26 for 3673 reflections. After four cycles of partially anisotropic and two cycles of fully anisotropic refinements of the nonhydrogen atoms,  $R$  values decreased to 0.11 and all of the hydrogen atoms were obtained on the difference Fourier map.

In the final refinement, the positional parameters of all atoms, anisotropic temperature factors of the carbon and oxygen atoms and isotropic thermal parameters for the hydrogen atoms were refined. Mean  $(\Delta/\sigma)$  was 0.28 and maximum and minimum peak height on final difference Fourier map were  $\Delta\rho_{\max}=0.30$  and  $\Delta\rho_{\min}=-0.35$   $\text{e}\text{\AA}^{-3}$  respectively. All the atomic scattering factors are obtained from the International Table of X-ray Crystallography.<sup>18</sup> The final positional and thermal parameters of nonhydrogen atoms are listed in Table 2.

**Description of the Structure.** The bond distances and angles are listed in Table 3. These are mainly as expected for the type of bonds involved.

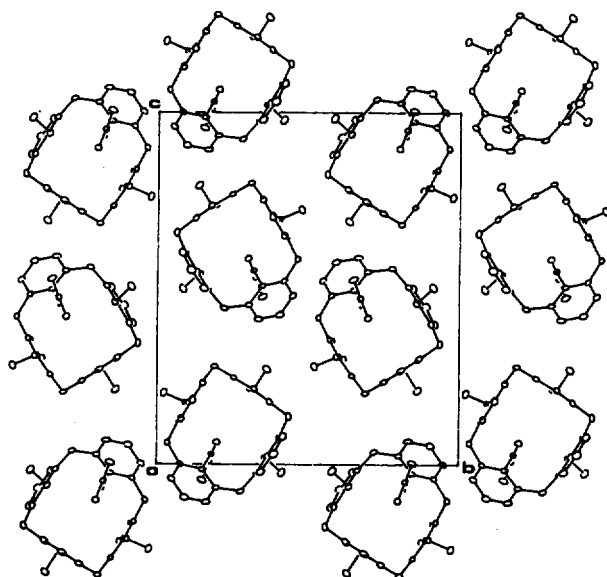
The molecule adopts a partial cone conformation, in which three of the phenyl groups (A, B and D) are down and one phenyl (C) is up. (See Figure 1) The dihedral angles between the four aromatic rings and the mean plane of the macrocyclic ring CH<sub>2</sub> groups are 139.3°, 90.0°, 85.4° and 93.1°. The inversed phenyl unit (C) is more flattened than the other two adjacent rings (B, D) and the acetoxy phenyl unit (A) opposed to inversed phenyl unit is most flattened.

The orientation of the functional groups with respect to its benzene ring can be described by the  $\angle C(4)\cdots C(1)-O(1)-C(8)$  torsion angles of 152.2°, 29.7°, -3.4° and -5.7° for units A to D, respectively. Therefore all the methoxy groups point outwards. The acetoxy group points inwards the macrocyclic ring, and it partly fills the cavity of the molecule. We carefully checked several spatial atomic distances where interactions involving acetoxy group may take place. There are 15 intramolecular interactions less than 3.6 Å. Among them, the C(9A)H<sub>3</sub>...C(4C)H interactions can also play a major part in this self-complexation of an acetoxy group in the cavity of the molecule as well as in flattened acetoxy phenyl unit.

The crystal structure is illustrated in Figure 2. There are

**Table 4.** Selected Torsion Angles( $^{\circ}$ ). The e. s. d.'s are in parentheses

C(1A)-C(2A)-C(7B)-C(6B)	74.0 (2)
C(1B)-C(2B)-C(7C)-C(6C)	63.1 (2)
C(1C)-C(2C)-C(7D)-C(6D)	-61.0 (2)
C(1D)-C(2D)-C(7A)-C(6A)	112.7 (3)
C(1A)-O(1A)-C(8A)-O(2A)	6.5 (2)
C(1A)-O(1A)-C(8A)-C(9A)	-173.4 (3)
C(4A)···C(1A)-O(1A)-C(8A)	152.2 (2)
C(4B)···C(1B)-O(1B)-C(8B)	29.7 (2)
C(4C)···C(1C)-O(1C)-C(8C)	-3.4 (3)
C(4D)···C(1D)-O(1D)-C(8D)	-5.7 (3)

**Figure 2.** Crystal Structure viewed down a axis.

several intermolecular distances shorter than 3.6 Å, of which the shortest is O(2A)···C(8C), at symmetry position  $x-0.5$ ,  $-y+0.5$ ,  $z-0.5$  of 3.293 Å. The molecules are packed by van der Waals forces.

## 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 in a Nicolet Impact 400 FT-IR spectrometer as KBr pellet.  $^1\text{H}$ - and  $^{13}\text{C}$  NMR spectra were recorded on Varian Gemini 300 (300 and 75 MHz) instrument. Chemical shifts are recorded as  $\delta$  values in parts per million relative to TMS ( $\delta$  0.0) as an internal standard. TLC analyses were carried out on silica gel plates (absorbent thickness 250  $\mu\text{m}$ ).

**5,11,17,23-Tetra-*t*-butyl-25,26,27,28-tetrahydroxycalix[3]arene 1.** was prepared in 52% yield from *p*-*tert*-butylphenol and formaldehyde as described elsewhere<sup>4</sup>; mp. 344-346  $^{\circ}\text{C}$  (lit<sup>4</sup>, 344-346  $^{\circ}\text{C}$ ).

**25,26,27,28-Tetrahydroxycalix[4]arene 2.** was prepared in 74% yield by  $\text{AlCl}_3$ -catalyzed removal of the *tert*-

butyl groups from the compound 1 following the literature procedure<sup>19</sup>; mp. 315-317  $^{\circ}\text{C}$  (lit.<sup>19</sup> 314-318  $^{\circ}\text{C}$ ).

**25-Hydroxy-26,27,28-trimethoxycalix[4]arene 3.** To a stirred suspension of calix[4]arenes (1.40 g, 2.69 mmole) and  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  (1.29 g, 4.09 mmole) in DMF (24 mL), was added  $\text{CH}_3\text{I}$  (5 mL) dropwise. The mixture was stirred for 7 hr at room temperature, and conc.  $\text{NH}_4\text{OH}$  (5 mL) was added followed by water (25 mL). The product was extracted with chloroform and the organic layer was washed with water, dried over  $\text{Na}_2\text{SO}_4$ , and evaporated. The crude product was stirred with a small amount of hexane and the precipitate was collected by filtration. A recrystallization from a mixture of chloroform and methanol afforded 890 mg (71%) of the title compound 3 as a colorless crystalline solid; mp. 213-215  $^{\circ}\text{C}$  (lit.<sup>14</sup> 212.5-214.5  $^{\circ}\text{C}$ ) IR (KBr) 3450  $\text{cm}^{-1}$  (OH);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.37-6.47 (m, 12, ArH), 5.77 (s, 1, OH), 4.39 (d, 4,  $\text{CH}_2$ ,  $J=13.5$  Hz), 4.00 (s, 3,  $\text{OCH}_3$ ), 3.86 (s, 6,  $\text{OCH}_3$ ), 3.37 (d, 2,  $\text{CH}_2$ ,  $J=13.5$  Hz), 3.30 (d, 2,  $\text{CH}_2$ ,  $J=13.5$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  155.83, 136.73, 133.36, 132.61, 130.56, 130.52, 129.49, 129.31, 129.14, 128.56, 128.29, 123.67, 123.48, 119.46 (Ar), 62.81, 60.53 ( $\text{OCH}_3$ ), 30.73, 30.64 ( $\text{CH}_2$ ).

**25-Acetoxy-26,27,28-trimethoxycalix[4]arene 4.** To a solution of compound 3 (940 mg, 2.0 mmole) and NaH (200 mg, 60% oil dispersion) in THF (60 mL), was added a solution of acetyl chloride (0.5 mL) in THF (30 mL) dropwise, followed by stirring the mixture for 3 hr at room temperature. After solvent was evaporated, the resulting residue was treated with water (100 mL), and extracted with chloroform (100 mL). The organic layer was washed with water, dried over  $\text{Na}_2\text{SO}_4$ , and evaporated. The resulting solid was recrystallized from a mixture of chloroform and methanol to give 930mg (91%) of the titled compound 4 as a colorless crystalline solid; mp. 238-240  $^{\circ}\text{C}$ ; IR (KBr) 1747  $\text{cm}^{-1}$  (C=O);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.28-6.64 (m, 12, ArH), 3.86 (d, 2,  $\text{CH}_2$ ,  $J=13.2$  Hz), 3.79 (d, 4,  $\text{CH}_2$ ,  $J=3$  Hz), 3.65 (s, 6,  $\text{OCH}_3$ ), 3.30 (s, 3,  $\text{OCH}_3$ ), 3.22 (d, 2,  $\text{CH}_2$ ,  $J=13.2$  Hz), 1.59 (s, 3,  $\text{COCH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  172.46 (C=O), 158.75, 156.29, 148.16, 135.85, 135.18, 133.24, 132.86, 130.59, 129.87, 129.25, 129.01, 128.53, 125.66, 122.80 (Ar), 60.38, 58.00 ( $\text{OCH}_3$ ), 36.86, 30.17 ( $\text{CH}_2$ ), 20.92 ( $\text{CH}_3$ ).

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## Epoxidation of Olefins by Iodosylbenzene Catalyzed by Non-Porphyrin Metal Complexes

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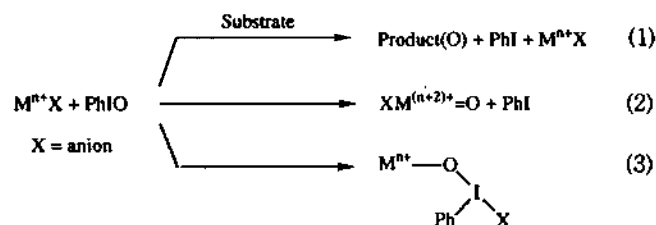
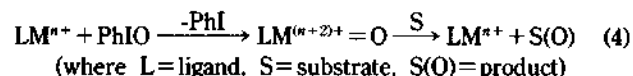
Epoxidation of olefins has been studied using iodosylbenzene (PhIO) as the terminal oxidant and binuclear and mononuclear complexes of Mn<sup>2+</sup>, Co<sup>2+</sup>, and Cu<sup>2+</sup> as catalysts. Epoxides were the predominant products with trace amounts of allylic oxidation products, and the metal complexes were found to be effective catalysts in the epoxidation reactions. The reactivity of binuclear copper complexes was greater than that of the mononuclear copper complexes, whereas the binuclear and mononuclear complexes of Mn<sup>2+</sup> and Co<sup>2+</sup> showed similar reactivities. The nature of the ligands bound to copper did not influence the reactivity of the binuclear copper complexes so long as copper ions were held in close proximity. A metal-iodosylbenzene complex, such as suggested previously for Lewis acidic metal complex-catalyzed epoxidation by iodosylbenzene, is proposed as the active epoxidizing species. Some mechanistic aspects are discussed as well.

### Introduction

Iodosylbenzene, PhIO, has been widely used as a source of oxygen atom in functionalization of hydrocarbons catalyzed by metal complexes, usually with the intention of understanding the mechanism of oxygen atom transfer reactions.<sup>1</sup> The general reactions by iodosylbenzene in the presence of metal complexes are shown in Scheme 1. Iodosylbenzene can transfer its oxygen to organic substrates in metal-catalyzed reactions (Eq. 1)<sup>2</sup> or to metal complexes to generate high-valent metal oxo species (Eq. 2).<sup>3</sup> Iodosylbenzene also reacts with

metal complexes to form metal-iodosylbenzene adducts (Eq. 3).<sup>4</sup>

Since Groves and coworkers showed that high-valent iron oxo porphyrin cation radical, (TMP)<sup>+</sup>Fe<sup>IV</sup>=O, was generated in the reaction of Fe(TMP)Cl and iodosylbenzene,<sup>5</sup> it has generally been asserted that oxygen transfer from iodosylbenzene to organic substrates occurs *via* high-valent metal oxo intermediates in metal-catalyzed oxygen atom transfer reactions (Eq. 4).



Scheme 1.

In addition to the metalloporphyrin systems, it has been shown that simple metal salts are capable of transferring an oxygen atom from iodosylbenzene to organic substrates in catalytic epoxidation reactions.<sup>6</sup> Metal complexes containing non-porphyrin ligands have also been used in iodosylbenzene reactions in order to prove the intermediacy of high-valent metal oxo species and/or to make efficient catalysts.<sup>7</sup> The intermediacy of high-valent metal oxo complexes as rea-