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Selective Functionalization of Calix[6]arene

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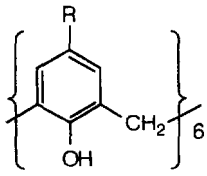
Calix[6]arenes are selectively dialkylated at the lower rim and further functionalized by the aminomethylation and Claisen Rearrangement reactions. Dialkylation was conducted by the reaction of calix[6]arene and alkyl halides such as benzyl bromide, allyl bromide, ethyl bromoacetate, propyl bromide, and methyl iodide under the carefully controlled reaction conditions. Aminomethylation was carried out with the treatment of disubstituted calix[6]arene and secondary amine in the presence of formaldehyde. Claisen rearrangement reaction of the *O*-diallylcalix[6]arene produced the *p*-diallylcalix[6]arene.

Introduction

Calixarenes[1] are cavity-containing macrocyclic compounds which have a tremendous attention recently as an attractive host molecule. Particularly calix[6]arenes have a very suitable cavity for the complexation of various aromatic compounds such as anthracene, pyrene,[2] and fullerene[3] and also the functionalized calix[6]arenes were found to bind certain metal ion[4] selectively. Functionalization of calix[6]arene usually is more complicated than that of calix[4]arene due to several factors including the bad solubility and the variety of conformational isomers. Particularly selective functionalization of calix[6]arene could be difficult task to achieve. So far a few examples[5-7] were reported as a reliable selective functionalization procedure of calix[6]arene.

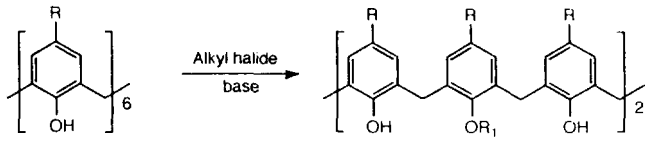
Here we report a selective functionalization of calix[6]arene. We expanded Gutsche's dibenzylation of *p-tert*-butylcalix[6]arene to the general dialkylation procedure of *p-tert*-butylcalix[6]arene as well as calix[6]arene. Also aminomethylation[8] and Claisen rearrangement reactions[9] of dialkylated calix[6]arenes were carried out.



1a R = $C(CH_3)_3$
1b R = H

Results and Discussion

Dialkylation of *p-tert*-Butylcalix[6]arene[10] and Calix[6]arene[11]. Gutsche and Kanamathareddy[6] reported that *p-tert*-butylcalix[6]arene **1a** is selectively dibenzylated with the reaction of *p-tert*-butylcalix[6]arene and benzyl bromide in the presence of Me_3SiOK as a base. We found that **1a** reacted not only with benzyl bromide but with the various alkyl halides such as allyl bromide, ethyl bromoacetate, and propyl bromide in the presence of base to give a corresponding disubstituted calix[6]arenes. Also calix[6]arene **1b** was found to react with the various alkyl halides in the presence of base to yield the dialkylated calix[6]arenes. The various dialkylated calix[6]arenes were prepared in moderate to high yield as shown in Scheme 1.



1a R = $C(CH_3)_3$
1b R = H

2a R = $C(CH_3)_3$, R_1 = $CH_2CH{=}CH_2$
2b R = $C(CH_3)_3$, R_1 = $CH_2CH_2CH_3$
2c R = $C(CH_3)_3$, R_1 = CH_2CO_2Et
2d R = H, R_1 = $CH_2C_6H_5$
2e R = H, R_1 = $CH_2CH{=}CH_2$
2f R = H, R_1 = $CH_2CH_2CH_3$
2g R = H, R_1 = CH_2CO_2Et
2h R = H, R_1 = CH_3

Scheme 1. Dialkylation of Calix[6]arene.

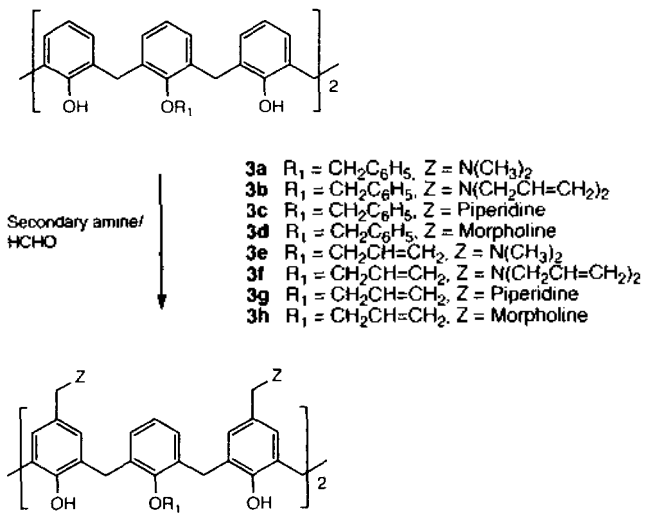
Typical dialkylation procedures are as followed. Treating **1a** with 2.8 equivalents of allyl bromide in the presence of 6 equivalents of Me_3SiOK in THF-DMF for 3.5 h produced the diallylated **2a** in 61% yield after recrystallization from $CHCl_3$-hexane. The ^1H NMR spectrum of **2a** showed a singlet at 8.13 ppm arising from the 4 hydroxy protons, three singlets at 7.07, 7.00, and 6.98 ppm arising from the 12 aromatic protons, 2 : 1 ratio of two singlets at 3.83 and 3.75 ppm arising from the 12 bridge methylene protons, and 2 : 1 ratio of two singlets at 1.20 and 1.10 ppm for the 54 *tert*-butyl

protons and also three multiplets at 5.80, 4.80, and 4.32 ppm arising from three allylic protons. The ^{1}H NMR pattern of **2a** clearly indicated that the alkylation was occurred at the 1,4-dihydroxy position of **1a**. Two sharp singlets of the bridge methylene protons showed that the conformation of **2a** is very flexible as expected from Gutsche's dibenzylated calix[6]arene.[6] Under the similar condition **2b** was obtained in 40% yield after the fractional column chromatography. When ethyl bromoacetate was used for the dialkylation, BaO/Ba(OH)$_2$ was used as a base[12] because Me_3SiOK produced various side products. The ^{1}H NMR of **2b** and **2c** showed the similar spectral pattern as that of **2a** such as two singlets for the *t*-butyl protons, three singlets for the aromatic protons, two singlets for the bridge methylene protons, and one singlet for the hydroxy protons.

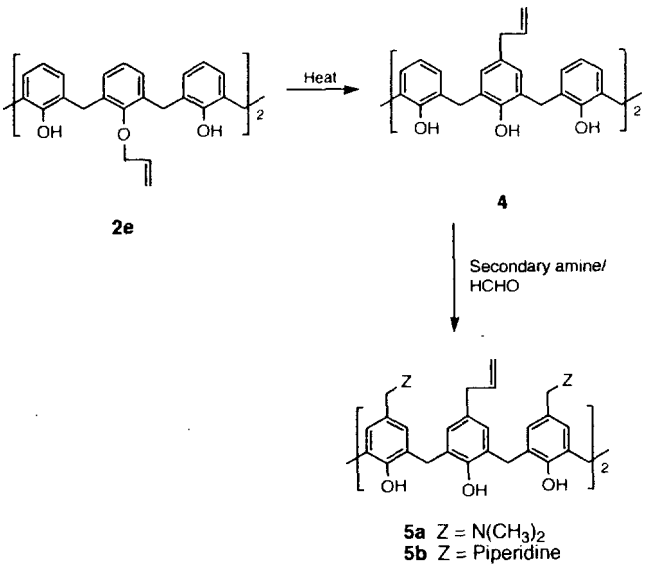
Dialkylation of calix[6]arene **1b** was conducted under the similar reaction conditions described above. **1b** might be more useful host compound because it can be further functionalized after dialkylation as shown later. **2d**, **2e**, **2f**, **2g**, and **2h** were obtained in relatively high yield by the reaction of **1b** and the corresponding alkyl halides such as benzyl bromide, allyl bromide, propyl bromide, ethyl bromo acetate, and methyl iodide in the presence of base. 1,4-Dialkylation of calix[6]arene was confirmed by the ^{1}H NMR spectra of each compound. For example, the ^{1}H NMR spectrum of **2g** showed a singlet at 8.12 ppm for the 4 hydroxy protons, a multiplet at 6.24-7.11 ppm for the 18 aromatic protons, a singlet at 4.51 ppm for the O-methylene protons, 2 : 1 ratio of two singlets at 3.96 and 3.90 for the 12 bridge methylene protons, and a quartet and triplet at 3.80 and 1.05 ppm for the 10 ethoxy protons.

Claisen Rearrangement of Allyl Group. The Claisen Rearrangement[9,13] has been known as a means for introducing a functional group into the *p*-positions of calix[6]arene. In the present work this process was extended to the cyclic hexamer particularly preparing diallylcalix[6]arene. Treatment of **2e** with refluxing N,N-diethyl aniline for **3h** produced a 17,35-diallyl-37,38,39,40,42-hexahydroxycalix[6]arene **4** in 81% yield as shown in Scheme 3. The ^{1}H NMR of **4** showed a doublet at 7.16, a singlet at 6.97, and a triplet at 6.84 ppm arising from the 16 aromatic protons, a broad singlet at 3.89 ppm arising from the 12 bridge methylene protons, two multiplets at 5.90 ppm and 5.10 for the 6 vinylic protons, a doublet at 3.25 ppm arising from the 4 methylene protons between aromatic and vinyl group.

Aminomethylation of Dialkylcalix[6]arene. Aminomethylation[8] has been known to the one of the most useful reactions for the functionalization of calixarene. Various calixarenes such as tetramer, pentamer, hexamer, heptamer, and octamer without substituents at the para positions reacted with secondary amine and formaldehyde to yield the corresponding Mannich bases. But certain aroylated and alkylated calix[4]arenes such as tri- or di- benzoylated calix[6]arene as well as dibenzylated calix[4]arene did not react with secondary amine and formaldehyde even under the vigorous reaction conditions. Disubstituted calix[6]arenes such as **2d** and **2e**, however, reacted with the various secondary amines and formaldehyde in THF to yield the corresponding Mannich bases in high yield without difficulties as shown in Scheme 2. The ^{1}H NMR spectra of **3a** through **3h** showed two sharp singlets for the bridge methylene protons, indica-



Scheme 2. Aminomethylation of Dialkylcalix[6]arene.



Scheme 3. Claisen Rearrangement and Aminomethylation of Diallylcalix[6]arene.

ting that the conformation is very flexible. On the other hand di- or tri- substituted calix[4]arenes have been known to be very rigid and did not react with secondary amine and formaldehyde. Conformational flexibility could effect the acidity of the hydroxy protons of calixarene, so it could be determining factor for the aminomethylation. It was confirmed also by the aminomethylation of calixarene with substituents at the para positions. **4** reacted smoothly with secondary amines and formaldehyde as shown in Scheme 3. Two *p*-allyl groups in **4** do not effect the conformational flexibility on the calixarene and aminomethylation proceeded without difficulties.

Experimental

The melting points of all compounds were taken in sealed and evacuated capillary tubes on a Mel-Temp apparatus. ^{1}H NMR and ^{13}C nuclear magnetic resonance spectra were reco-

rded on a Bruker AMX-300 spectrometer. Chemical shifts are reported as a δ values in parts per million relative to tetramethylsilane. Infrared spectra were determined on a Nicolet 520-FT spectrometer. Column chromatography was carried out with E. Merck silica gel (230-400 mesh ASTM). THF was dried over refluxing with Na-benzophenone.

37,40-Diallyl-5,11,17,23,29,35-hexa-*tert*-butyl-38,39,41,42-tetrahydroxycalix[6]arene (2a). To a solution of 0.49 g (0.5 mmol) of **1a** in 50 mL of THF and 5 mL of DMF was added 0.39 g (3 mmol) of Me_3SiOK and stirred for 15 min under nitrogen atmosphere. 0.13 mL of allyl bromide (1.4 mmol) in 5 mL of THF was added slowly into the reaction mixture and the mixture was stirred for 3.5 h. The solvents were evaporated and the residue was treated with 70 mL of 1 N HCl. After stirring for 2 h the precipitate was collected and dried. Recrystallization from $CHCl_3$-hexane produced 0.32 g (61%) of **2a**: mp 193-197 ℃. ^{1}H NMR ($CDCl_3$) δ 8.13 (br s, 4H, -OH), 7.07 (d, 4H, ArH, J=2.45 Hz due to long range coupling), 7.0 (d, 4H, ArH, J=2.44 Hz), 6.98 (s, 4H, ArH), 5.8 (m, 2H, -CH=), 5.20 (d, 2H, =CH_2, J=16.3 Hz), 4.80 (d, 2H, =CH_2, J=10.6 Hz), 4.32 (d, 4H, -OCH_2-, J=5.46 Hz), 3.83 and 3.75 (two s, 12H, $ArCH_2Ar$), 1.20 and 1.10 (two s, 54H, -$C(CH_3)_3$). ^{13}C NMR ($CDCl_3$) δ 150.4, 149.4, 147.6, 142.4, 132.4, 131.8, 126.8, 126.3, 125.7, 125.5, and 118.3 (Ar and -CH=CH_2), 75.5 (-OCH_2-), 34.2, 33.8, 31.9, 31.5, and 31.2 ($ArCH_2Ar$ and -$C(CH_3)_3$). IR (KBr) 3414 cm^{-1} (OH).

5,11,17,23,29,35-Hexa-*tert*-butyl-38,39,41,42-tetrahydroxy-37,40-dipropyloxy calix[6]arene (2b). Following the procedure described above 0.49 g (0.5 mmol) of **1a** was treated with 0.39 g (3.0 mmol) of Me_3SiOK and 0.31 mL (3.0 mmol) of propyl bromide for 25 h to yield 0.21 g (40%) of **2b** from column chromatography (eluent; $CHCl_3$). mp 226-228 ℃. ^{1}H NMR ($CDCl_3$) δ 8.45 (s, 4H, -OH), 7.10 (d, 4H, ArH, J=2.4 Hz), 7.02 (d, 4H, ArH, J=2.4 Hz), 6.98 (s, 4H, ArH), 3.87 and 3.80 (two s, 12H, $ArCH_2Ar$), 3.75 (t, 4H, -OCH_2-, J=6.8 Hz), 1.65 (m, 4H, -CH_2-), 1.23 and 1.12 (two s, 54H, -$C(CH_3)_3$), 0.64 (t, 6H, -CH_3, J=7.3 Hz). ^{13}C NMR ($CDCl_3$) δ 150.3, 149.4, 147.3, 142.4, 132.2, 126.6, 126.3, 125.7, and 125.5 (Ar), 34.2, 33.6, 32.2, 31.8, 31.5, 31.2, 22.8, and 9.6 ($ArCH_2Ar$, -CH_2CH_3, and -$C(CH_3)_3$). IR (KBr) 3412.5 cm^{-1} (OH).

5,11,17,23,29,35-Hexa-*tert*-butyl-37,40-diethyloxycarbonylmethyloxy-38,39,41,42-tetrahydroxycalix[6]arene (2c). To a solution of 0.49 g (0.5 mmol) of **1a** in 15 mL of DMF, 0.31 g (2.0 mmol) of BaO, 0.33 g (1.0 mmol) of $Ba(OH)_2$, and 0.12 mL (1.05 mmol) of ethyl bromoacetate were added and the mixture was stirred for 5.5 h. Then, 60 mL of water was added and the precipitate was collected. The crude product was dissolved with 20 mL of $CHCl_3$ and washed with 2 N HCl three times. The organic layer was separated and the solvents were evaporated. The solid obtained was purified by recrystallization from $CHCl_3$-hexane to yield 0.37 g (65%) of **2c**. mp 227-228 ℃. ^{1}H NMR ($CDCl_3$) δ 8.21 (br s, 4H, -OH), 7.12 (d, 4H, ArH, J=2.4 Hz), 7.02 (s, 4H, ArH), 6.96 (d, 4H, ArH, J=2.4 Hz), 4.53 (s, 4H, -OCH_2 CO_2-), 4.32-3.50 (br s, 16H, $ArCH_2Ar$ and -OCH_2C-), 1.22 and 1.16 (two s, 54H, -$C(CH_3)_3$), 1.01 (m, 6H, -CH_3), ^{13}C NMR ($CDCl_3$) δ 169.5 (C=O), 151.8, 149.2, 147.7, 142.4, 132.1, 126.9, 125.9, 125.8, and 125.4 (Ar), 70.9 and 61.3 (-OCH_2-, and -CO_2 CH_2-), 34.2, 33.8, 32.3, 31.5, 31.2, and 13.9 ($ArCH_2Ar$, -$C(CH_3)_3$, and -CH_3). IR (KBr) 3335 (OH), 1728 cm^{-1} (CO_2).

37,40-Diallyloxy-38,39,41,42-tetrahydroxycalix[6]arene (2d). To a solution of 0.64 g (1.0 mmol) of **1b** in 100 mL THF and 10 mL DMF, 0.78 g (6.0 mmol) Me_3SiOK was added under nitrogen atmosphere at 0 ℃ and 0.28 mL (2.4 mmol) of benzyl bromide in 10 mL THF was added. After 1.5 h the solvents were evaporated and 100 mL of 1 N HCl was added. The precipitate was collected and recrystallized from $CHCl_3$ to yield 0.65 g (83%) of **2d**. mp 232-233 ℃. ^{1}H NMR (DMSO-d_6) δ 9.16 (br s, 4H, -OH), 7.60-7.28 (m, 14H, ArH), 7.02 (d, 4H, ArH, J=6.0 Hz), 6.82 (t, 4H, ArH, J=6.0 Hz), 6.50 (t, 2H, ArH, J=6.0 Hz), 6.15 (d, 4H, ArH, J=8.0 Hz) 5.05 (br s, 4H, -OCH_2-), 3.99 and 3.86 (two s, 12H, $ArCH_2Ar$). ^{13}C NMR (DMSO-d_6) δ 154.0, 151.4, 137.7, 133.4, 130.2, 129.1, 128.7, 128.4, 127.6, 126.4, 125.4, 123.8, and 120.4 (Ar), 72.8 (-OCH_2Ar), 31.0 and 30.3 ($ArCH_2Ar$). IR (KBr) 3426.1 and 3223.5 cm^{-1} (OH).

37,40-Dibenzyloxy-38,39,41,42-tetrahydroxycalix[6]arene (2e). Treating a 3.2 g (5.0 mmol) of **1b** with 3.9 g (30 mmol) of Me_3SiOK and 1.25 mL (14 mmol) of allyl bromide for 3 h as described for **2d**, 3.42 g (96%) of **2e** was obtained from recrystallization in $CHCl_3$-hexane. mp 188-190 ℃. ^{1}H NMR ($CDCl_3$) δ 8.03 (s, 4H, -OH), 7.09-6.89 (m, 14H, ArH), 6.76 (t, 4H, ArH, J=6.0 Hz), 5.95 (m, 2H, -CH=), 5.40 (d, 2H, =CH_2, J=20.0 Hz), 5.08 (d, 2H, =CH_2, J=12.0 Hz), 4.46 (d, 4H, -OCH_2- J=6.0 Hz), 3.94 and 3.78 (two s, 12H, $ArCH_2Ar$). ^{13}C NMR ($CDCl_3$) δ 162.5, 152.4, 151.8, 133.2, 131.8, 129.1, 128.9, 128.7, 127.5, 127.1, 125.5, 120.2, and 118.5 (Ar and -CH=CH_2), 75.9 (-OCH_2-), 36.4 and 31.5 ($ArCH_2Ar$). IR (KBr) 3329 cm^{-1} (OH).

38,39,41,42-Tetrahydroxy-37,40-dipropyloxycalix[6]arene (2f). Treating a 0.32 g (0.5 mmol) of **1b** in 15 mL of DMF, 0.31 g (2.0 mmol) of BaO, 0.33 g (1.0 mmol) of $Ba(OH)_2$, and 0.27 mL (3.0 mmol) of *n*-propyl bromide for 24 h as described for **2c**, 0.32 g (55%) of **2f** was obtained from recrystallization in $CHCl_3$-hexane. mp 295-298 ℃. ^{1}H NMR ($CDCl_3$) δ 8.18 (br s, 4H, -OH), 7.10-6.73 (m, 18H, ArH), 3.93 and 3.79 (two s, 12H, $ArCH_2Ar$), 3.88 (m, 4H, -OCH_2- J=2.3 Hz), 1.84 (m, 4H, -CH_2-, J=6.0 Hz), 0.88 (t, 6H, -CH_3, J=6.0 Hz). ^{13}C NMR ($CDCl_3$) δ 152.4, 151.9, 133.1, 129.1, 128.9, 128.7, 127.5, 127.1, 125.4, and 120.1 (Ar), 77.4 (-OCH_2-), 31.6 and 31.4 ($ArCH_2Ar$), 23.0 and 10.0 (-CH_2- and -CH_3). IR (KBr) 3271.7 cm^{-1} (OH).

37,40-Diethyloxycarbonylmethyloxy-38,39,41,42-tetrahydroxycalix[6]arene (2g). Treating a 0.32 g (0.5 mmol) of **1b** with 0.39 g (3.0 mmol) Me_3SiOK and 0.18 mL (1.5 mmol) of ethyl bromoacetate for 4 h as described for **2d**, 0.16 g (40%) of **2g** was obtained from fractional column chromatography (eluent; $CHCl_3$: hexane : ethyl acetate = 6.5 : 3.0 : 1.5). mp 247-249 ℃. ^{1}H NMR ($CDCl_3$) δ 8.12 (br s, 4H, -OH), 7.11 (d, 4H, ArH, J=9.0 Hz), 6.96 (m, 10H, ArH), 6.74 (d, 4H, ArH, J=9.0 Hz), 4.51 (s, 4H, -OCH_2-), 3.96 and 3.90 (two s, 12H, $ArCH_2Ar$), 3.80 (q, 4H, -OCH_2-, J=6.0 Hz), 1.05 (t, 6H, -CH_3 J=6.0 Hz). ^{13}C NMR ($CDCl_3$) δ 170.3 (C=O), 154.5, 151.9, 133.5, 129.4, 129.3, 129.0, 128.0, 127.0, 125.7, and 120.7 (Ar), 71.1 and 61.8 (-OCH_2- and -CO_2CH_2-), 31.9 and 31.8 ($ArCH_2Ar$), 14.4 (-CH_3). IR (KBr) 3325 (OH), 1720 cm^{-1} (CO_2).

38,39,41,42-Tetrahydroxy-37,40-dimethyloxycalix[6]arene (2h). Treating **1b** 0.32 g (0.5 mmol) with Me_3 SiOK 0.39 g (3.0 mmol) and 0.11 mL (1.6 mmol) of methyl iodide for 5.5 h as described for **2d**, 0.29 g (88%) of **2h** was

obtained from recrystallization in $CHCl_3$-hexane. mp 270 ℃ dec. ^{1}H NMR (DMSO-d_6) δ 7.08 (d, 4H, ArH, J=6.9 Hz), 6.88 (d, 4H, ArH, J=5.4 Hz), 6.60 (m, 6H, ArH), 6.33 (d, 4H, ArH, J=6.9 Hz), 3.81 and 3.73 (two br s, 12H, $ArCH_2Ar$), 3.43 (br s, 6H, -CH_3). ^{13}C NMR (DMSO-d_6) δ 162.0, 156.0, 134.1, 129.7, 129.2, 128.7, 127.2, 126.9, 123.5, and 118.2 (Ar), 59.5 (-OCH_3), 30.7, and 30.6 ($ArCH_2Ar$). IR (KBr) 3443.4 cm^{-1} (OH).

37,40-Dibenzyloxy-38,39,41,42-tetrahydroxy-5,11,23,29-tetra[(dimethylamino)methyl]calix[6]arene (3a). To a solution of 0.33 g (0.4 mmol) of **2d** in 15 mL of THF was added 0.17 mL (2.1 mmol, 37%) of aqueous formaldehyde and 0.28 mL (2.1 mmol, 50%) of dimethylamine and stirred for 22 h. Then the solvents were removed, and the residue was triturated with methanol. The solid was collected and dried to give 0.38 g (90%) of **3a**. mp 215 ℃ dec. ^{1}H NMR (DMSO-d_6) δ 7.59-6.15 (m, 24H, ArH), 5.03 (br s, 4H, -OCH_2-), 3.93 and 3.77 (two br s, 12H, $ArCH_2Ar$), 3.32 (br s, 8H, $ArCH_2N$-), 2.15 (br s, 24H, -NCH_3). IR (KBr) 3393 cm^{-1} (OH).

5,11,23,29-Tetra[(diallylamino) methyl]-37,40-dibenzyloxy-38,39,41,42-tetrahydroxycalix[6]arene (3b). To a solution of 0.33 g of **2d** in 15 mL of THF was added 0.17 mL (35%) of aqueous formaldehyde and 0.25 mL (99%) of diallylamine and the mixture was stirred for 22 h. The solvents were removed and the residue was dissolved in 10 mL of chloroform and washed with 0.1 N HCl solution. The organic layer was dried over Na_2SO_4, and the solvents were removed under the reduced pressure to leave 0.46 g (92%) of **3b**. ^{1}H NMR ($CDCl_3$) δ 7.45-6.87 (m, 24H, ArH), 5.87 (m, 8H, -CH=), 5.19 (d, 8H, $=CH_2$), 5.10 (br s, 8H, $=CH_2$), 5.02 (br s, 4H, -OCH_2-), 3.91 and 3.70 (two br s, 12H, $ArCH_2Ar$), 3.47 (br s, 8H, -NCH_2-), 3.08 (d, 16H, -NCH_2C=).

37,40-Dibenzyloxy-38,39,41,42-tetrahydroxy-5,11,23,29-tetra[(N-piperidino) methyl]calix[6]arene (3c). Treating a 0.33 g of **2d** with 0.17 mL (35%) of aqueous formaldehyde and 0.21 mL (98%) of piperidine as described for **3a**, 0.36 g (75%) of **3c** was obtained. mp 166-167 ℃. ^{1}H NMR (DMSO-d_6) δ 7.58-6.20 (m, 24H, ArH), 5.03 (br s, 4H, -OCH_2-), 3.94 and 3.76 (two br s, 12H, $ArCH_2Ar$), 3.32 (br s, 16H, $ArCH_2N$-), 2.34 (br s, 16H, -NCH_2-), 1.47 (br s, 16H, -CH_2-), 1.37 (br s, 8H, -CH_2-).

37,40-Dibenzyloxy-38,39,41,42-tetrahydroxy-5,11,23,29-tetra[(N-morpholino) methyl]calix[6]arene (3d). Treating a 0.33 g of **2d** with 0.17 mL (35%) of aqueous formaldehyde and 0.18 mL (99%) of morpholine as described for **3a**, 0.30 g (78%) of **3d** was obtained. mp 184-185 ℃. ^{1}H NMR (DMSO-d_6) δ 7.59-6.21 (m, 24H, ArH), 5.03 (br s, 4H, -OCH_2-), 4.00 and 3.80 (two br s, 12H, $ArCH_2Ar$), 3.54 (br s, 16H, -NCH_2-), 3.30 (br s, 8H, -$ArCH_2N$-), 2.31 (br s, 16H, -NCH_2-).

37,40-Diallyloxy-38,39,41,42-tetrahydroxy-5,11,23,29-tetra[(dimethylamino) methyl]calix[6]arene (3e). Treating a 0.22 g (0.3 mmol) of **2e** with 0.26 mL (3.12 mmol, 35%) of aqueous formaldehyde and 0.42 mL (3.12 mmol, 50%) of dimethylamine for 24 h as described for **3a**, 0.27 g (96%) of **3e** was obtained. mp 191 ℃ dec. ^{1}H NMR (DMSO-d_6) δ 7.18-6.33 (m, 14H, ArH), 6.17 (m, 2H, -CH=), 5.47 (d, 2H, $=CH_2$, J=18 Hz), 5.28 (d, 2H, $=CH_2$, J=8.0 Hz), 4.50 (br s, 4H, -CH_2C=), 3.95 and 3.85 (two br s, 12H, $ArCH_2Ar$), 3.54 (br s, 8H, -NCH_2Ar), 2.20 (s, 24H, -NCH_3).

5,11,23,29-Tetra[(diallylamine) methyl]-37,40-diallyloxy-38,39,41,42-tetrahydroxycalix[6]arene (3f). Treating a 0.22 g of **2e** with 0.26 mL (35%) of aqueous formaldehyde and 0.4 mL (99%) of diallylamine for 24 h as described for **3a**, 0.33 g (96%) of **3f** was obtained. mp 92-95 ℃. ^{1}H NMR ($CDCl_3$) δ 7.03-6.92 (m, 14H, ArH), 5.89 (m, 2H, -CH=), 5.82 (m, 8H, -CH=), 5.46 (d, 2H, $=CH_2$, J=18 Hz), 5.18 (m, 18H, $=CH_2$), 4.46 (d, 4H, -CH_2C=, J=18 Hz), 3.92 and 3.72 (two br s, 12H, $ArCH_2Ar$), 3.45 (s, 8H, $ArCH_2N$-), 3.03 (d, 16H, -NCH_2C=, J=6.0 Hz).

37,40-Diallyloxy-38,39,41,42-tetrahydroxy-5,11,23,29-tetra[(N-piperidino) methyl]calix[6]arene (3g). Treating a 0.22 g of **2e** with 0.39 mL (35%) of aqueous formaldehyde and 0.48 mL for 20 h as described for **3a**, 0.3 g (91%) of **3g** was obtained. mp 129 ℃ dec. ^{1}H NMR (DMSO-d_6) δ 7.00 and 6.79 (two s, 8H, ArH), 6.29-6.14 (m, 8H, ArH and -CH=), 5.49 (d, 2H, $=CH_2$, J=16 Hz), 5.23 (d, 2H, $=CH_2$, J=10 Hz), 4.47 (br s, 4H, -OCH_2C=), 3.79 and 3.53 (two br s, 12H, $ArCH_2Ar$), 3.23 (s, 8H, $ArCH_2N$-), 2.28 (br s, 16H, -NCH_2-), 1.44 and 1.35 (two br s, 24H, -CH_2-).

37,40-Diallyloxy-38,39,41,42-tetrahydroxy-5,11,23,29-tetra[(N-morpholino) methyl]calix[6]arene (3h). Treating a 0.22 g of **2e** with 0.39 mL (35%) of aqueous formaldehyde and 0.42 mL of morpholine for 20 h as described for **3a**, 0.26 g (80%) of **3h** was obtained. mp 142 ℃ dec. ^{1}H NMR ($CDCl_3$) δ 7.04-6.89 (m, 14H, ArH), 6.02 (m, 2H, -CH=), 5.46 (d, 2H, $=CH_2$, J=18.0 Hz), 5.14 (d, 2H, $=CH_2$, J=12.0 Hz), 4.48 (d, 4H, -OCH_2-), 3.92 and 3.73 (br s, 12H, $ArCH_2Ar$), 3.68 (br s, 16H, -NCH_2C-), 3.37 (s, 8H, -NCH_2-), 2.40 (br s, 16H, -OCH_2-). ^{13}C NMR ($CDCl_3$) δ 152.8, 151.4, 133.6, 132.4, 130.6, 130.2, 129.4, 129.2, 127.8, 127.4, 125.5, and 118.8 (Ar and C=C), 76.3 (-OCH_2C=), 67.4 (-OCH_2C-), 63.4 (-NCH_2-), 53.9 (-NCH_2-), 31.9 and 31.8 ($ArCH_2Ar$).

17,35-Diallyl-37,38,39,40,41,42-hexahydroxycalix[6]arene (4). 0.72 g (1.0 mmol) of **2e** in 10 mL of diethyl aniline was refluxed for 3 h, then the solution was cooled and 30 mL of conc. HCl was added. The insoluble solid was collected and dissolved in 15 mL chloroform and washed with 2 N HCl 15 mL to remove the remaining diethyl aniline. Then organic layer separated, dried over Na_2SO_4, and evaporated the solvents. The crude products were purified from recrystallization in $CHCl_3$-hexane to give 0.58 g of **4** (81%). mp 296 ℃ dec. ^{1}H NMR ($CDCl_3$) δ 7.16 (d, 8H, ArH, J=6.0 Hz), 6.97 (s, 4H, ArH), 6.84 (t, 4H, ArH, J=8.0 Hz), 5.90 (m, 2H, -CH=), 5.10 (d, 2H, $=CH_2$, J=4.0 Hz), 5.06 (s, 2H, $=CH_2$), 3.89 (br s, 12H, $ArCH_2Ar$), 3.25 (d, 4H, -CH_2-, J=6.0 Hz). ^{13}C NMR ($CDCl_3$) δ 150.1, 148.2, 138.1, 133.7, 130.0, 129.9, 127.8, 127.7, 127.6, 122.1, and 115.9 (Ar), 39.8 (ArC), 32.6 and 32.0 ($ArCH_2Ar$). IR (KBr) 3165.6 cm^{-1} (OH).

17,35-Diallyl-37,38,39,40,41,42-hexahydroxy-5,11,23,29-tetra[(dimethylamino)methyl]calix[6]arene (5a). Treating a 0.22 g (0.3 mmol) of **4** with 0.39 mL (4.7 mmol, 35%) of aqueous formaldehyde and 0.68 mL (4.7 mmol, 50%) of dimethylamine for 24 h as described for **3a**, 0.23 g (82.1%) of **5a** was obtained. mp 235 ℃ dec. ^{1}H NMR ($CDCl_3$) δ 7.10-6.48 (m, 12H, ArH), 6.11 (m, 2H, -CH=), 4.96 (m, 4H, $=CH_2$), 4.12 (br s, 4H, -CH_2C=), 3.62 (br s, 12H, $ArCH_2$ Ar), 3.12 (br s, 8H, $ArCH_2N$-), 2.28 (br s, 24H, -NCH_3).

17,35-Diallyl-37,38,39,40,41,42-hexahydroxy-5,11,23,29-tetra[(N-piperidino)methyl]calix[6]arene (5b).

Treating a 0.22 g of **4** with 0.39 mL of aqueous formaldehyde and 0.48 mL of piperidine for 24 h as described for **3a**, 0.25 g (75.8%) of **5b** was obtained. mp 172 ℃ dec. ^{1}H NMR (DMSO-d_6) δ 6.90-6.52 (m, 12H, ArH), 5.79 (m, 2H, -CH=), 5.00-4.88 (m, 4H, $=CH_2$), 4.11 (br s, 4H, $-CH_2C=$), 3.53 (br s, 12H, $ArCH_2Ar$), 3.09 (br s, 8H, $ArCH_2N$-), 2.62 (br s, 16H, $-NCH_2$-), 1.50 and 1.38 (two br s, 24H, $-CH_2$-).

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The Adsorption and Decomposition of NO on a Stepped Pt(111) Surface

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The adsorption and decomposition of NO on a stepped Pt(111) surface have been studied using thermal desorption spectroscopy and Auger electron spectroscopy. NO adsorbs molecularly in two different states of the terrace and the step, which are distinguishable in thermal desorption spectra. NO dissociates *via* a bent species at the step sites on the basis of vibrational spectrum data reported previously. The dissociation of NO is an activation process : the activation energy is estimated to be about 2 kcal/mol. Increase in the NO dissociation with adsorption temperature is explained by a process controlled by diffusion of the dissociated atomic nitrogen from the step to the terrace of the surface. In addition to NO and N_2, the desorption peak of N_2O is observed. We conclude that the formation of N_2O is attributed to surface reaction of NO and N adsorbed on the surface.

Introduction

The adsorption and reaction of nitric oxide on metal surface are interesting in both fundamental and technological aspects.[1] The catalytic reduction of nitric oxide plays an important role in control of air pollution. NO and CO are two of the most widely studied adsorbates because of its simplicity. They have similar electronic structures except that NO has an unpaired electron in the antibonding 2π orbital. This causes more complex behaviors in chemisorption and reaction of NO than those of CO. CO adsorbs only molecularly on noble metals. In contrast, as for NO on noble metals there are evidences for dissociative adsorption at low temperatures as well as molecular adsorption with various geometries, including tilt, bent, and linear NO at two-fold and on-top sites.[2-16]

Gorte *et al.*[7] reported that the desorption spectra of NO adsorbed on Pt(111), (110) and (100) show different shapes and different peak temperatures. In their report, the desorption activation energies for major tightly-bound states on the (100), (110) and (111) planes are 36, 33.5 and 25 kcal/mol, respectively, and the fraction of the dissociation is less than 2% on Pt(111) surface. Ertl *et al.*[9] also studied the interaction of NO with Pt(111) surface using molecular beam technique and thermal desorption spectroscopy (TDS), and reported

We dedicate this work to Professor Woon-Sun Ahn on the occasion of his retirement.