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Selective Nitration of Calix[4]arene

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Mono and 1,3-dinitrocalix[4]arene **4** and **7** were prepared by the selective benzoylation followed by nitration. Benzoylation of calix[4]arene with benzoyl chloride in the presence of pyridine produced the tribenzoyl and 1,3-dibenzoylcalix[4]arene selectively depending on the reaction conditions. Nitration of tribenzoyl and 1,3-dibenzoyl-calix[4]arene was conducted with nitric acid in the presence of acetic acid to produce mono and 1,3-dinitrocalix[4]arene. Removal of benzoyl groups was carried out with NaOH in ethanol to give **4** and **7**.

Introduction

Calixarenes[1] are cavity containing metacyclophanes which can complex with various guest compounds. Functional groups can be introduced by the utilization of upper rim[2,3] and lower rim[4] of calix[4]arene. Nitro groups can be introduced on the upper rim of calix[4]arene developed by Shinkai[5] and K. H. No method[6]. Nitrocalixarenes show a very strong acidic protons[7] which may be utilized on the catalytic reaction as well as a proton sensor. But they introduced the nitro groups to the all four para position of calixarene.

Selective nitration of calixarene was reported by Bohmer[8] and Reinhoudt[9]. Bohmer's group synthesized mononitrocalix[4]arene *via* step-wise methods. Reinhoudt group reported the synthesis of 1,3-dinitrocalix[4]arene but succeeded only on O-dimethylated calix[4]arene which could not show the strong acidity.

We report here the synthesis of two nitro-calix[4]arenes including mononitrocalix[4]arene **4**, and 1,3-dinitrocalix[4] arene **7**. Direct nitration of calix[4]arene with nitric acid fail to introduce the selective nitro groups to the para position of calix[4]arene. To introduce the nitro groups to the calix[4]arene selectively we utilized the differences of reactivity for the nitration of phenol ring depending on the substituents on hydroxy group with benzoylation. Selective benzoylation of calix[4]arene developed by Gutsche[10], and Nam[11] groups could provide the best candidate for the synthesis of selective nitrocalix[4]arene. Benzoyl group not only can deactivate the nitration reaction of calix[4]arene but also can be easily removed by the hydrolysis with base[10].

Mononitrocalix[4]arene **4** was prepared from tribenzoylcalix[4]arene[10] **2** by the reaction of nitration followed by hydrolysis as shown in Figure 1. Calix[4]arene **1** was treated
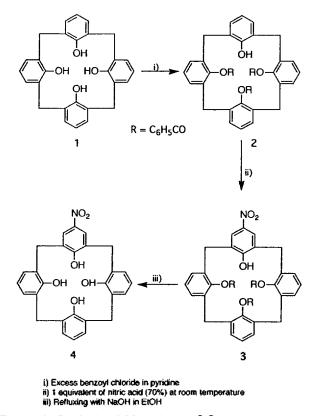

R = C6H5CO

Figure 1. Synthesis of Mononitrocalix[4]arene.

i) Excess benzoyl chloride in pyridine
ii) 1 equivalent of nitric acid (70%) at room temperature
iii) Refluxing with NaOH in EtOH

with excess benzoyl chloride in pyridine under ice bath to yield the tribenzoylated calix[4]arene **2**. Nitration was conducted with the treatment with 70% nitric acid in the pres-
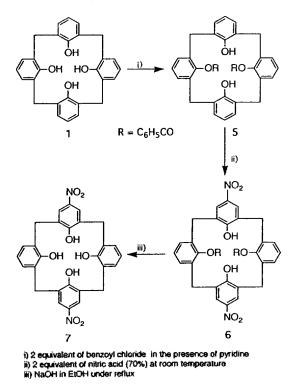
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Figure 2. Synthesis of 1,3-Dinitrocalix[4]arene.

i) 2 equivalent of benzoyl chloride in the presence of pyridine
ii) 2 equivalent of nitric acid (70%) at room temperature
iii) NaOH in EtOH under reflux

ence of acetic acid at ambient temperature. Only one nitro group was introduced at the para position of phenol ring of calix[4]arene without benzolyl group. ^{1}H-NMR spectrum of mononitro-tribenzoylcalix[4]arene 3 shows a characteristic sharp singlet at 8.0 ppm for the aromatic protons containing nitro group. Benzoyl groups were removed with NaOH in aqueous alcohol solution. ^{1}H-NMR spectrum of 4 shows a singlet at 8.0 ppm for the aromatic protons containing nitro group, multiplets at 6.6-7.2 ppm for the aromatic protons, a broad singlet at 8.7 ppm for the hydroxyl protons, and two singlets at 3.95 and 3.85 ppm for the bridge methylene protons. Two singlets at about 3.9 ppm for the methylene protons suggest that the conformation of the mononitrocalix [4]arene is mobile.

Dinitrocalix[4]arene 7 was synthesized using the same technique applied above as shown in Figure 2. Calix[4]arene 1 was treated with 2 equivalents of benzoyl chloride in the presence of pyridine to yield a 1,3-dibenzoylcalix[4]arene[11] 5. Treatment of 5 with 70% nitric acid in the presence of acetic acid at ambient temperature in chloroform yielded a clean yellow product which turned out to be dibenzoyloxy-1,3-dinitrocalix[4]arene 6. Hydrolysis of benzoyl groups [10] provided a 1,3-dinitro-calix[4]arene 7. ^{1}H-NMR spectrum shows a broad singlet at 9.8 ppm for the hydroxyl protons, a characteristic sharp singlet at 8.05 ppm for the aromatic protons containing nitro group, a triplet at 6.62 ppm and a doublet at 7.13 ppm for the aromatic protons as expected.

Benzoylation technique was attempted for the preparation of trinitrocalix[4]arene but it failed. For the selective trinitration of calixarene, monobenzoylcalix[4]arene has to be prepared. Under the various conditions applied for the selective benzoylation, only mixture of di-, tri-, and starting mate-

rials was found without sign of monobenzoylcalix[4]arene. Even though monobenzoylation of calix[4]arene was achieved from the reaction of 3,5-dinitrobenzoyl chloride and calix [4]arene, the following nitration reaction produced mixtures of products which could not be characterized.

Experimental

Melting points of all compounds were measured 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 Bruker 300 AMX spectrometer. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane (δ 0.00) as an internal standard. Thin layer chromatography (TLC) analyses were carried out on silica gel plates. Column chromatography was carried out with E. Merck silica gel (230-400 mesh ASTM).

Calix[4]arene 1. was prepared using the previously described procedure[10] in 70% yield. mp. 314-317°C.

25,26,27-Tribenzoyloxy-28-hydroxycalix[4]arene[10] 2. was prepared in 80% yield from 1 and benzoyl chloride in pyridine. mp. 275-277°C.

5-Nitro-25,26,27-tribenzoyloxy-28-hydroxycalix[4] arene 3. To a solution of 0.74 g of 2 in 15 m*l* of CH_2Cl_2 and 5 m*l* of acetic acid, 0.12 m*l* of 70% nitric acid was slowly added at room temperature. The solution turned to yellow when nitric acid was added and the reaction was complete after 25 min. Solvents were removed under the reduced pressure and the remaining residue extracted with 30 m*l* of water and chloroform. Organic layer was separated and dried over sodium sulfate. Removal of solvent gave 0.70 g (90% yield) of crude yellow solids. mp. 267-268°C (dec.) ^{1}H-NMR (CDCl₃) δ 6.2-8.3 (m, 24H, ArH), 8.0 (s, 2H, ArH containg nitro group), 3.5-3.9 (two pair of d and two s, 8H, ArCH₂-Ar); IR (KBr) 3206 cm⁻¹ (OH) 1725 cm⁻¹ (-COO-), 1520 and 1340 cm⁻¹ (-NO₂).

5-Nitro-25,26,27,28-hydroxycalix[4]arene 4. To a solution of 0.70 g of 3 in 50 m*l* of THF, 30 m*l* of ethanol, and 20 m*l* of water, 3 g of NaOH was added and the whole solution was refluxed for 15 h. Solvents were removed under reduced pressure and the residue was acidified with 2 N HCl and the precipitate was collected and air dried overnight. The crude product was triturated with MeOH and recrystallized from chloroform-methanol to yield 0.26 g of dark gray fine crystals: mp. 247-249°C (dec.) IR (KBr) 3206 cm⁻¹ (OH), 1530 and 1340 cm⁻¹ (-NO₂). ^{1}H-NMR (DMSO-d₆) δ 8.7 (br s, 4H, OH), 8.0 (s, 2H, ArH with nitro group), 6.6-7.2 (m, 9H, ArH), 3.8-4.0 (two s, 8H, ArCH₂Ar). ^{13}C-NMR (DMSO-d₆) δ 159.66, 150.99, 149.92, 138.96, 129.64, 128.95, 128.88, 128.83, 128.69, 128.49, 127.73, 124.29, 120.95, and 120.76 (Ar), 30.62 and 30.44 (-CH₂-).

25,27-Dibenzoyloxy-26,28-dihydroxycalix[4]arene 5 was prepared as previously described[11] by the reaction of 1 and benzoyl chloride and was obtained as white crystals: mp. 269-271°C.

5,17-Dinitro-25,27-dibenzoyloxy-26,28-dihydroxycalix[4]arene 6. To a solution of 1.8 g of 5 in 40 m*l* of chloroform and 16 m*l* of acetic acid, 0.5 m*l* of 70% nitric acid was added at collected and washed with sodium bicar-

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bonate solution. The crude product was recrystallized from chloroform to yield 1.2 g of yellow crystals. mp. 288-289℃ (dec.). IR (KBr) 3490 cm⁻¹ (OH), 1725 cm⁻¹ (-COO-), 1520 and 1340 cm⁻¹ (−NO₂). ¹H-NMR (CDCl₃) δ 7.99 (s, 4H, ArH with nitro group), 7.0-8.3 (m, 16H, ArH), 3.6-4.2 (pair of d, 8H, ArCH₂Ar).

5,17-Dinitro-25,26,27,28-tetrahydroxycalix[4] arene 7. To a solution of 0.72 g of **6** in 50 m*l* of THF, 15 m*l* of water, and 30 m*l* fo EtOH, 2.48 g of NaOH was added and refluxed for 15 h. Solvents were removed under reduced pressure and the residue was acidified with 2N HCl.

Precipitate was collected and washed with MeOH.

Recrystallization from chloroform-MeOH yields 0.3 g of gray crystals. mp. 296-298℃ (dec.). IR (KBr) 3210 cm⁻¹ (OH), 1520 and 1330 cm⁻¹ (-NO₂). ¹H-NMR (DMSO-d₆) δ 9.82 (br s, 4H, OH), 8.05 (s, 4H, ArH containing nitro groups), 7.13 (d, 4H, ArH, *J*=7.5 Hz), 6.62 (t, 2H, ArH, *J*=7.5 Hz), 3.94 (br s, 8H, ArCH₂Ar). ¹³C-NMR (DMSO-d₆) δ 161.44, 150.40, 138.26, 130.19, 128.73, 128.40, 124.09, and 120.53 (Ar), 30.77 (-CH₂-).

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Photodecomposition Mechanism of Diazoindanones by Laser Photolysis and Lamp Photolysis

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The mechanism for the photodecomposition reactions of 2-diazoindan-1-one and 1,3-bis(diazo)indan-2-one have been studied in benzene, toluene, methanol, cyclohexane and acetonitrile solvents using laser photolysis and lamp photolysis. A triplet ketocarbene is observed from the photolysis of bis diazo compounds by the loss of nitrogen molecule from the carbene precursors. It is concluded that the Wolff rearrangement, which involves the formation of a ketene intermediate, can be regarded as a concerted process in nanosecond time scale. The photolytic reactions of diazoindanones in methanol give Wolff rearrangement products, but those in benzene do not involve in the Wolff rearrangement.

Introduction

The photochemical extrusion reaction of aromatic α-diazo ketones into the corresponding aromatic carboxylic acid *via* the Wolff rearrangement has been widely studied by photoresist methods[1]. The Wolff rearrangement in those photodecomposition reactions proceeds through an intermediate ketene. It is well known that the phototransformation of 2-diazo-1,2-naphthoquinones gives a product of 3-indenecarbo-

xylic acid, where the photodecomposition produces an intermediate ketene[2]. It has been suggested that, in some cases, a long-lived intermediate ketene absorb another photon, leading to the photoresist chemistry.

Generally, the conversion of aromatic α-diazo ketones into aromatic ketenes involves an 1,2-migration of a carbon atom, which is known as the Wolff rearrangement. Despite many investigations, the mechanism involving aromatic bis (diazo) ketone and diazo indanone is yet uncertain. That is, it is not clear in those reactions whether a concerted process occurs at the step of the loss of nitrogen or at the step of simultaneous migration of the 1,2-carbon atoms. The other

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This work is a part of "Reactive Intermediate of Bis Diazo Compounds".