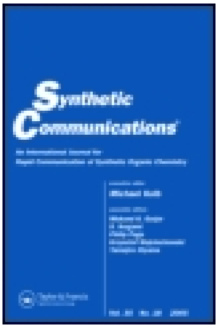

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New Synthetic Method of p-Nitrocalixarenes

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NEW SYNTHETIC METHOD OF *p*-NITROCALIXARENES

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Abstract: Calixarenes **1** were directly nitrated with potassium nitrate and aluminum chloride to give *p*-nitrocalixarenes **2** in good yields. Formation of *p*-nitrocalix[4]arene (**2a**) from reaction of *p*-bromomethylcalix[4]arene (**3**) with silver nitrate is also described.

Calixarenes are cavity-containing macrocyclic compounds which are attracting increasing interest because of their potential for forming host-guest complexes and acting as enzyme mimics, especially if appropriately functionalized.[1,2] In order to functionalize calixarenes, nitrocalixarenes could play an important role as potential synthetic intermediates. However, problems have been encountered in the use of general procedures for the nitration of aromatic compounds when applied to the synthesis of nitrocalixarenes. Shinkai et al. reported the synthesis of *p*-nitrocalixarenes via the *p*-sulfonatocalixarenes, but the overall yields were low.[3,4] Direct nitration has been reported for calix[4]arenes.[5] Ipso nitration of *p*-*tert*-butylcalix[4]arene methyl ether has been reported using fuming nitric acid,[6] but failed when applied to the parent *p*-*tert*-butylcalix[4]arene. Herein, we wish to report a new synthetic method for *p*-nitrocalixarenes.

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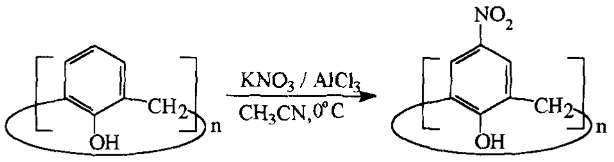
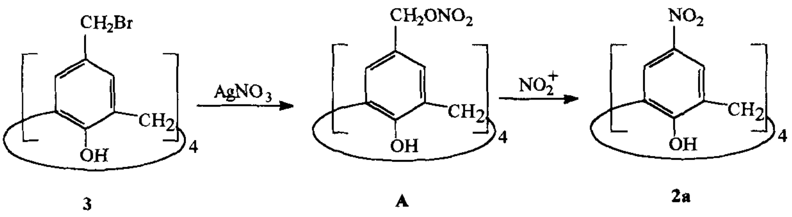
The reason for failure of direct nitration to give *p*-nitrocalixarenes is the drastic reaction conditions, and decomposition products, probably resulting from partial oxidation of the calixarene ring, were the main products.[4] Shinkai et al. found that direct nitration of calixarene at 0 °C gave carbonyl compounds which were not removed by repeated recrytallization.[4] Therefore, we developed a new method of direct nitration of calixarenes by using potassium nitrate and aluminum chloride as a mild nitrating agent.[7]

When calixarenes **1** were partially suspended in dry acetonitrile, nitration proceeded smoothly with potassium nitrate and anhydrous aluminum chloride at 0 °C. The reaction mixture turned to yellow and nitration was completed within two hours. The *p*-nitrocalixarenes **2** can be easily isolated in good yields (75-89 %).



a, n = 4; **b**, n = 6; **c**, n = 8

The formation of *p*-nitrocalix[4]arene (**2a**) were also found in the reaction of *p*-bromomethylcalix[4]arene (**3**) with silver nitrate. The pathway of the reaction may be formation of nitrate ester **A** first, followed by an *ipso* aromatic nitration.



EXPERIMENTAL

Melting points are uncorrected. ^1H NMR spectra were recorded with a Varian Unity 200 spectrometer. IR spectra were recorded on a Perkin-Elmer 782 spectrometer. Mass spectra were measured on Finnigan MAT 90 and AEI MS-50/PS30 instrument. Elemental analyses were performed by the Analytical Laboratory of the Institute. Calixarenes **1** were prepared by debutylation of *p*-*t*-butylcalixarnes.[8,9]

Synthesis of p-Nitrocalix[n]arene (**2**); *General Procedure*:

To a mixture of 0.5 g (3.3 milliequiv. of phenol methylene unit) of **1** in 20 ml of dry acetonitrile, 0.5 g (5 mmol) of potassium nitrate and 1.0 g (7.5 mmol) of anhydrous aluminium chloride were added at 0 °C. The reaction mixture was stirred at 0 °C for two hours, and the solution turned to yellow. Then the reaction mixture was poured into 200 ml of 5 % hydrochloric acid solution, and the precipitate was filtered. The crude product was recrystallized from acetone/chloroform to give pure **2** as a pale yellow solid.

p-Tetranitrocalix[4]arene (**2a**).[4]

Yield: 84 %. m. p. > 300 °C (decomp.). IR (KBr): $\nu = 3400$ (OH), 1585, 1485 and 1330 cm^{-1} (NO_2). ^1H NMR (DMSO-d6): $\delta = 3.68$ and 4.22 (b, 8H, $ArCH_2Ar$), 8.19 (s, 8H, ArH) ppm. MS-FAB: *m/z* = 603 $(M-1)^+$. Anal. calcd. for $C_{28}H_{20}N_4O_{12} \cdot 3H_2O$ (658.5): C 51.07, H 3.98, N 8.51; found C 51.10, H 3.52, N 8.39.

p-Hexanitrocalix[6]arene (**2b**).[3,4]

Yield: 89 %. m. p. > 300 °C (decomp.). IR (KBr): $\nu = 3410$ (OH), 1585, 1490 and 1330 cm^{-1} (NO_2). ^1H NMR (DMSO-d_6): $\delta = 4.02$ (s, 12H, $ArCH_2Ar$), 8.02 ppm (s, 12H, ArH). MS-FAB: *m/z* = 905 $(M-1)^+$. Anal.

calcd. for $C_{42}H_{30}N_6O_{18} \cdot 3H_2O$ (960.8): C 52.50, H 3.78, N 8.75; found C 52.14, H 3.82, N 8.77.

p-Octanitrocalix[8]arene (**2c**).[4]

Yield: 84 %. m. p. > 300 °C (decomp.). IR (KBr): ν = 3380 (OH), 1580, 1510 and 1335 cm^{-1} (NO_2). ^1H NMR (DMSO-d_6): δ = 4.86 (s, 16H, $ArCH_2Ar$), 7.99 (s, 16H, ArH). MS-FAB: m/z = 1207 $(M-1)^+$. Anal. calcd. for $C_{56}H_{40}N_8O_{24} \cdot 2H_2O$ (1245.0): C 54.02, H 3.56, N 9.00; found C 53.88, H 3.76, N 8.98.

Formation of p-Tetranitrocalix[4]arene (**2a**) *from p-Tetrakis(bromomethyl)-calix[4]arene* (**3**).

To a solution of 200 mg (0.25 mmol) of **3** in 10 ml of chloroform was dropped a solution of 340 mg (2 mmol) of silver nitrate in 10 ml of acetonitrile. After completion of the addition the mixture was filtered, and the filtrate was refluxed for 1.5 hours. The solution was evaporated to dryness, then 15 ml of acetone was added and the insoluble material was filtered off. The filtrate was concentrated to ca. 2 ml and poured to 15 ml of chloroform. **2a** was obtained as yellow precipitate weighing 110 mg (73 %). The IR, ^1H NMR and MS spectra are same as above.

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