cohol), 141375-17-9; **1e** (isomer 1), 141375-18-0; **1e** (isomer 2), 141375-19-1; **1f** (isomer 1), 141375-21-5; **1f** (isomer 2), 141434-76-6; **1f** (alcohol), 141375-23-7; **1g** (isomer 1), 141375-24-8; **1g** (isomer 2), 141375-25-9; **1g** (alcohol), 141375-27-1; **1h**, 141375-28-2; **1i**, 141375-30-6; **2** (Ar = *p*-chlorophenyl), 141375-32-8; **3a**, 141375-06-6; **3b**, 141375-10-2; **3c**, 141375-13-5; **3d**, 141375-16-8; **3e**, 141375-20-4; **3f**, 141375-22-6; **3g**, 141375-26-0; **3h**, 141375-29-3; **3i**, 141375-31-7; **4** (Ar = *p*-chlorophenyl), 141375-33-9; $4\text{-}ClC_6H_4CHO$, 104-88-1; $4\text{-}ClC_6H_4SO_2NH_2$, 98-64-6; $PhCH_2O(CH_2)_4Ts$, 141375-34-0; $Ts\text{-}(CH_2)_2CH(CH_3)_2$, 91485-21-1; methyl furoate, 611-13-2.

Supplementary Material Available: Proton and carbon NMR spectra for products (15 pages). Ordering information is given on any current masthead page.

Synthesis and Alkali Metal Binding Properties of "Upper Rim" Functionalized Calix[4]arenes[1]

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Introduction

The calixarenes are receiving considerable attention as starting materials for the preparation of novel hosts, ligands, and pores.[3-6] Of special interest, in this regard, has been the use of the *cone*-conformer of calix[4]arenes. Previous studies have shown that certain lower rim (phenolic side) ester and amide derivatives of calix[4]arene cones are effective in extracting alkali metal picrates from water into chloroform and that sodium salts are strongly favored.[3,4,7-9] To date, no effort has been made to examine the extracting behavior of upper-rim analogs. Because of the splay that is inherent in the calix[4]arene framework, one might expect that placement of ligands on the upper rim could result in stronger binding toward larger metal ions and that extraction of potassium or cesium salts might be favored. The fact that calix[4]arenes have moderate flexibility, however, makes it difficult to predict their precise complexation and selectivity features.[10] In order to probe this issue, we have synthesized calixarenes **I-III**, and have compared their extracting behavior with those previously reported for a lower-rim functionalized ester (**IV**).[7] This paper reports our principal findings.

Scheme I

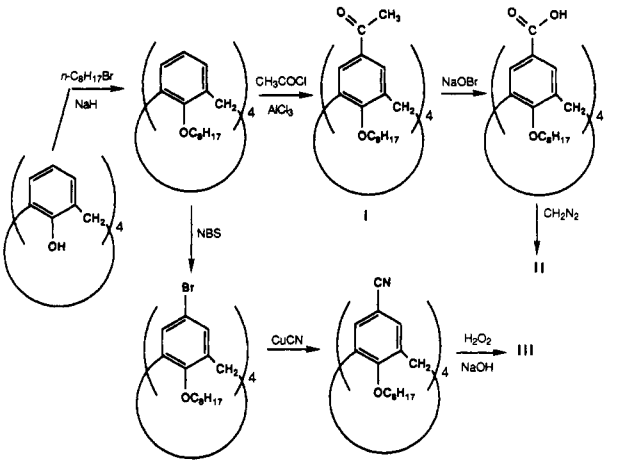
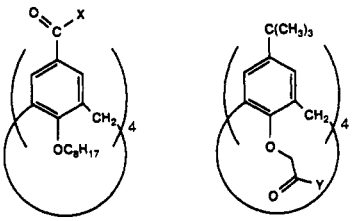


Table I. Extraction Equilibrium Constants for Picrate Salts by I-III

	$10^{-5} K_e$[a]			
calixarene	Li^+	Na^+	K^+	Cs^+
I	0.122 ± 0.011	1.411 ± 0.088	0.686 ± 0.054	0.109 ± 0.008
II	0.152 ± 0.007	0.842 ± 0.078	1.295 ± 0.142	0.102 ± 0.014
III	0.062 ± 0.007	1.463 ± 0.029	1.084 ± 0.139	0.489 ± 0.066
IV[b]	0.056	11.3	0.1	0.11

[a] Average of three to five independent experiments, using [calixarene] = 1×10^{-3} M; $[Li^+] = 8.4 \times 10^{-3}$; $[Na^+] = [K^+] = 1.0 \times 10^{-3}$; $[Cs^+] = 4.8 \times 10^{-3}$; error values represent one standard deviation of the mean. [b] See ref 7.



Results and Discussion

Alkylation of 25,26,27,28-tetrahydroxycalix[4]arene[11] with 1-bromooctane afforded the corresponding tetrakis(*n*-octyloxy) ether, which was readily isolated as the cone isomer. Friedel-Crafts acylation (CH_3COCl) of this tetraether afforded **I**; subsequent haloform oxidation, and esterification (CH_2N_2), yielded **II**. Calixarene **III** was prepared by bromination of the starting tetrakis(*n*-octyloxy) ether (NBS), followed by sequential displacement with cyanide and hydrolysis (Scheme I).

Specific methods that we have used for extracting alkali metal picrates from water into chloroform were similar to those previously described.[7,12] Extraction constants (K_e), which define the equilibrium shown in eq 1, were calculated using eq 2. Here, M^+_{aq} and Pi^-_{aq} represent the alkali cation and picrate anion that is present in the aqueous phase, and L_{org} and $\{LM^+,PI^-_{org}\}$ are the ligand and ligand-metal picrate complex in chloroform, respectively; the activity coefficients, γ^2, that have been used to calculate K_e values were 0.88 and 0.95, when employing 5×10^{-3} and 1×10^{-3} M picrate solutions, respectively.[12]

(1) Supported by the Division of Basic Energy Sciences of the Department of Energy (DE-FG02-85ER-13403) and by Air Products and Chemicals, Trexlertown, PA.
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$$M^+_{aq} + Pi^-_{aq} + L_{org} \overset{K_e}{\rightleftharpoons} \{LM^+,Pi^-_{org}\} \quad (1)$$

$$K_e = \frac{[\{LM^+,Pi^-_{org}\}]}{\gamma^2[M^+_{aq}][Pi^-_{aq}]([L_{org}]_0 - [\{LM^+,Pi^-_{org}\}])} \quad (2)$$

Calix[4]arenes **I–III** proved to be very effective in extracting Li^+, Na^+, K^+, and Cs^+ picrates (Table I).[13] Unlike the lower-rim analog (**IV**), however, each showed similar extractability of sodium and potassium picrates, but significantly reduced efficacy toward lithium and cesium salts. Also in contrast to **IV**, which yields a well-defined 1:1 symmetrical "cone"-complex with sodium thiocyanate that is observable by ^1H NMR spectroscopy,[7] calixarene **III** exhibits very complicated binding and/or conformational behavior in the presence of this salt (not shown). Specifically, the aromatic and bridging (plus oxy-) methylenes of the pure calixarene, which appeared as broad signals at δ 6–8 and 3–5 ppm ($CDCl_3$, 23 °C), respectively, sharpened to multiple absorbances (>12 peaks in each region) on going from 0 to 1 equiv of sodium thiocyanate. The low degree of ion selectivity that is associated with **I–III**, and the complicated spectral behavior of **III**, found in the presence of sodium thiocyanate, are likely consequences of greater spatial mobility and reduced preorganization on the upper rim of the calix[4]arene framework.

Experimental Section

Unless stated otherwise, all chemicals and reagents were obtained commercially and used without further purification. Water was purified using a Milli-Q system consisting of one-carbon, two-ion exchange and one Organex-Q cartridge. Mass spectral analyses were performed at the Midwest Center for Mass Spectrometry, University of Nebraska, Lincoln, NE. All reactions were routinely carried out under a nitrogen atmosphere.

Cone Conformer of 25,26,27,28-Tetrakis(octyloxy)calix[4]arene. To a suspension of 1.18 g of NaH (29.5 mmol; washed with 3 × 30 mL of hexane) in 90 mL of anhydrous DMF was added 1.48 g of tetrahydroxycalix[4]arene (3.50 mmol). After the mixture was stirred for 10 min at 70 °C, 1-bromooctane (5.79 g, 30 mmol) was added. The reaction mixture was stirred for an additional 1 h at 70 °C, cooled to room temperature, and then quenched by the dropwise addition of 2 mL of CH_3OH. After removal of solvent under reduced pressure, 100 mL of water was added followed by additional stirring (5 min). The solid organic product was then washed with CH_3OH (2 × 50 mL) and recrystallized from acetone, affording 1.97 g (65%) of pure cone conformer having mp 80.5–81 °C, R_f = 0.60 [silica, $CHCl_3$/hexanes (1/3) (v/v)]: ^1H NMR (90 MHz, $CDCl_3$) 0.90 (t, 12 H, CH_3), 1.30 (m, 40 H, CH_2), 1.90 (m, 8 H, OCH_2CH_2), 3.15 (d, J = 13.5 Hz, 4 H, exo-ArC*H*), 3.90 (t, 8 H, CH_2O), 4.45 (d, J = 13.5 Hz, 4 H, endo-ArC*H*), 6.60 (m, 12 H, Ar*H*). Anal. Calcd for $C_{60}H_{88}O_4$: C, 82.51; H, 9.98. Found: C, 82.54; H, 10.16.

Cone Conformer of 5,11,17,23-Tetraacetyl-25,26,27,28-tetrakis(1-*n*-octyloxy)calix[4]arene (I). To a 300-mL round-bottomed flask, which was charged with 3.7 g (27.7 mmol) of aluminum chloride, was added 100 mL of CH_2Cl_2 followed by acetyl chloride (18.0 g, 78.5 mmol). The cone conformer of 25,26,27,28-tetrakis(octyloxy)calix[4]arene (4.4 g, 5.05 mmol), dissolved in 50 mL CH_2Cl_2, was then added dropwise with stirring and the mixture stirred for 5 h at 25 °C. Subsequent addition of 20 mL of water followed by 25 mL of 1 N HCl, extraction with 100 mL of CH_2Cl_2, and column chromatography (300 g silica, gradient of $CHCl_3$/acetone (20/1 to 3/1)) afforded 2.8 g (48%) of **I** as a white solid having mp 109–110 °C, R_f = 0.38 [silica, $CHCl_3$/acetone (10/1) (v/v)]: ^1H NMR (500 MHz, $CDCl_3$) 0.89 (t, 12 H, CH_3), 1.29–1.37 (brm, 40 H, CH_2); 1.88 (m, 8 H, OCH_2CH_2), 2.33 (s, 12 H, $COCH_3$), 3.29 (d, J = 13.7 Hz, 4 H, exo-ArC*H*), 3.94 (t, 8 H, OCH_2), 4.46 (d, J = 13.6 Hz, 4 H, endo-ArC*H*), 7.27 (s, 8 H, Ar*H*). Anal. Calcd for $C_{68}H_{96}O_8$: C, 78.42; H, 9.29. Found: C, 78.40; H, 9.20.

Cone Conformer of 5,11,17,23-Tetracarboxy-25,26,27,28-tetrakis(1-*n*-octyloxy)calix[4]arene. A cooled solution (0 °C) of sodium hypobromite [formed by adding 589 mg (3.7 mmol Br_2) to 1.5 mL 23% (w/w) aqueous NaOH] was added to a solution of calix[4]arene **I** (60 mg, 0.058 mmol) in 7 mL of DMF. Subsequent addition of 3 mL of DMF, followed by heating (80 °C) for 18 h, cooling to rt, quenching with 10 mL of 1 M HCl, extracting with 2 × 15 mL of $CHCl_3$, concentrating under reduced pressure, washing of the residue with 2 × 10 mL (OCH_2), water, and purifying the product by preparative TLC (silica, $CHCl_3$/MeOH/H_2O (65/25/4), R_f para), 0.64), afforded 20 mg (33%) of colorless product having the following characteristic data: ^1H NMR (500 MHz, DMSO-d_6) 0.85 (t, 12 H, CH_3), 1.3–1.4 (brm, 40 H, CH_2), 1.86 (m, 8 H, OCH_2CH_2), 3.37 (d, J = 13.3 Hz, 4 H, exo-ArC*H*), 3.89 (t, 8 H, OCH_2), 4.31 (d, J = 13.1 Hz, 4 H, endo-ArC*H*), 7.30 (s, 8 H, Ar*H*), 12.26 (brs, 4 H, CO_2H); ^{13}C NMR (125.76 MHz, DMSO-d_6) δ 14.58 (CH_3), 22.9, 26.6, 29.8, 30.2, 30.6, 30.7, 32.2 ($(CH_2)_6$ + $ArCH_2$), 75.8 (OCH_2, aromatic C, relative to acid), (125.4 ipso, 130.4, 135.0 ortho, meta; 160.5 para), 167.5 (CO_2H); exact mass calcd for $C_{64}H_{88}O_{12}$ M^+Na 1071.6173, found 1071.6310; error 13 ppm.

Cone Conformer of 5,11,17,23-Tetrakis(carboxymethyl)-25,26,27,28-tetrakis(1-*n*-octyloxy)calix[4]arene (II). To a solution of 18 mg (0.017 mmol) of the cone conformer of 5,11,17,23-tetracarboxy-25,26,27,28-tetrakis(1-*n*-octyloxy)calix[4]arene in 0.8 mL of THF was added 0.720 mL (0.7 mmol) of a 1 M etheral solution of diazomethane. The solution was then stirred for 18 h and quenched with two drops of concentrated HOAc. Preparative TLC [silica, $CHCl_3$/acetone (10/1) (v/v), R_f = 0.60] afforded 12 mg (67%) of **II** as a white solid having mp 145–147 °C: ^1H NMR (500 MHz, $C_2D_2Cl_4$) 0.85 (t, J = 6.7 Hz, 12 H, CH_3) 1.2–1.4 [brm, 40 H, (CH_2)], 1.82 (m, 8 H, OCH_2CH_2), 3.22 (d, J = 13.8 Hz, 4 H, exo-ArCH), 3.74 (s, 12 H, CO_2CH_3), 3.87 (t, J = 7.3 Hz, 8 H, OCH_2), 4.38 (d, J = 13.6 Hz, 4 H, endo-ArC*H*), 7.27 (s, 8 H, Ar*H*). Anal. Calcd for $C_{68}H_{96}O_{12}$: C, 73.88; H, 8.75. Found: C, 73.68; H, 8.73.

Cone Conformer of 5,11,17,23-Tetrabromo-25,26,27,28-tetrakis(1-*n*-octyloxy)calix[4]arene. A solution of 0.48 g (0.55 mmol) of the cone conformer of 25,26,27,28-tetrakis(octyloxy)-calix[4]arene and 0.65 g (3.54 mmol) of *N*-bromosuccinimide in 10 mL of 2-butanone was stirred at rt for 48 h (open to the atmosphere and exposed to laboratory light). A 10% aqueous $NaHSO_3$ solution (25 mL) was then added, and the mixture stirred for an additional 15 min at rt. Extraction with CH_2Cl_2 (3 × 25 mL) followed by concentration under reduced pressure and two recrystallizations [using 10 mL of acetone/methanol (10:1), v/v] afforded 0.46 g (70%) of product having R_f = 0.56 ($CHCl_3$/hexane (1:3), v/v): mp 145–6 °C; ^1H NMR (90 MHz, $CDCl_3$) 0.90 (t, 12 H, CH_3), 1.20–1.35 (bs, 40 H, CH_2), 1.35–1.90 (m, 8 H, OCH_2CH_2), 3.00 (d, 13.5 Hz, 4 H, exo-C*H*Ar), 3.85 (t, 8 H, CH_2O), 4.35 (d, J = 13.5 Hz, 4 H, endo-C*H*Ar), 6.85 (s, 8 H, Ar*H*). Anal. Calcd for $C_{60}H_{84}O_4Br_4$: C, 60.61; H, 7.12; Br, 26.89. Found: C, 61.01; H, 7.42; Br, 26.45.

Cone Conformer of 5,11,17,23-Tetracyano-25,26,27,28-tetrakis(octyloxy)calix[4]arene. A solution of 0.672 g (0.141 mmol) of the cone conformer of 5,11,17,23-tetrabromo-25,26,27,28-tetrakis(1-*n*-octyloxy)calix[4]arene and 1.79 g (20 mmol) of CuCN in 6 mL of anhydrous *N*-methylpyrrolidone was refluxed for 5 h. The temperature of the mixture was then lowered to 100 °C, and a solution made from 5.41 g (20 mmol) of $FeCl_3 \cdot 6H_2O$ dissolved in 90 mL of 1.7 M HCl was added. The resulting mixture was then stirred for 0.5 h at 100 °C, followed by additional stirring for 16 h at rt. The organic product which precipitated was separated, washed 3 × 20 mL of 1 M HCl, 3 × 20 mL of H_2O, and then dissolved in 60 mL of acetone/$CHCl_3$ (5/1). The solution was treated with 2 g of activated charcoal, filtered, and concentrated under reduced pressure. Recrystallization from acetone–methanol (3/2, v/v) afforded 0.268 g (49%) of product having mp 209–10 °C, R_f = 0.33 [silica, hexane/$CHCl_3$/acetone (10/20/1)]; ^1H NMR (90 MHz, $CDCl_3$) 0.90 (t, 12 H, CH_3), 1.25 (s, 40 H, CH_2), 1.6–2.0 (m, 8 H, OCH_2CH_2), 3.25, 4.45 (2d, 8 H, exo + endo-ArC*H*, respectively), 3.90 (t, 8 H, CH_2O), 7.00 (s, 8 H, Ar*H*). Anal. Calcd for $C_{64}H_{84}N_4O_4$: C, 78.95; H, 8.64;

(13) In a control experiment, negligible extraction of potassium picrate was observed by 25,26,27,28-tetrakis(octyloxy)calix[4]arene (cone conformer) ($K_e < 2 \times 10^2$).

N, 5.76. Found: C, 78.49; H, 8.56; N, 5.73.

Cone Conformer of 5,11,17,23-Tetracarbamoyl-25,26,27,28-tetrakis(octyloxy)calix[4]arene (III). A mixture of 0.206 g (0.211 mmol) of cone conformer of 5,11,17,23-tetracyano-25,26,27,28-tetrakis(octyloxy)calix[4]arene, 0.100 g (0.295 mmol) of $Bu_4N{\cdot}HSO_4$, 0.8 mL of 30% H_2O_2, 0.8 mL of 20% NaOH, and 1.0 mL of CH_2Cl_2 was stirred at rt for 48 h. The product mixture was then concentrated under reduced pressure and the organic residue dissolved in 1 mL of CH_2Cl_2 and subjected to identical hydrolysis conditions for an additional 16 h. Addition of 13 mL of 1 N HCl, followed by concentration under reduced pressure, washing of the solid product with 3 × 30 mL of water, and recrystallization from 30 mL of MeOH afforded 0.163 g of white solid which consisted of four components having R_f = 0.78 (w), 0.55 (s), 0.42 (w), and 0.33 (m) (silica, $CHCl_3/MeOH/H_2O$ (75:20:3), v/v). Purification of that component having R_f = 0.55 via preparative TLC and recrystallization (3 × from CH_3OH) afforded 0.111 g (51%) of **III**, having mp 302-4 °C dec: ^1H NMR (500 MHz, $CDCl_2CDCl_2$, 100 °C) 0.95 (t, 12 H, CH_3), 1.35 (m, 40 H, CH_2), 1.90 (m, 8 H, OCH_2CH_2), 4.49-4.52, 3.28-3.30 (2 d, J = 14.0 Hz, 8 H, endo, exo-CHAr); 3.99 (t, 8 H, CH_2O), 5.57 (s, 8 H, NH_2), 7.15 (s, 8 H, ArH). Anal. Calcd for $C_{64}H_{92}N_4O_8$: C, 73.52; H, 8.87; N, 5.36. Anal. Calcd for $C_{64}H_{92}N_4O_8{\cdot}2CH_3OH$: C, 71.45; H, 9.08; N, 5.50. Found: C, 71.60; H, 8.81; N, 5.54.

Registry No. I, 141344-71-0; II, 141344-72-1; III, 141434-03-9; 25,26,27,28-tetrakis(octyloxy)calix[4]arene, 141344-73-2; tetrahydroxycalix[4]arene, 74568-07-3; bromooctane, 111-83-1; 5,11,17,23-tetracarboxy-25,26,27,28-tetrakis(1-*n*-octyl)calix[4]arene, 141434-74-4; 5,11,17,23-tetrabromo-25,26,27,28-tetrakis(1-*n*-octyl)calix[4]arene, 141344-74-3; 5,11,17,23-tetracyano-25,26,27,28-tetrakis(octyloxy)calix[4]arene, 141344-75-4.

Supplementary Material Available: ^1H NMR (500-MHz) spectrum of **III** (1 page). Ordering information is given on any current masthead page.

Synthesis of Nitropolycyclic Aromatic Hydrocarbons with the Substituent at the Longest Axis[1]

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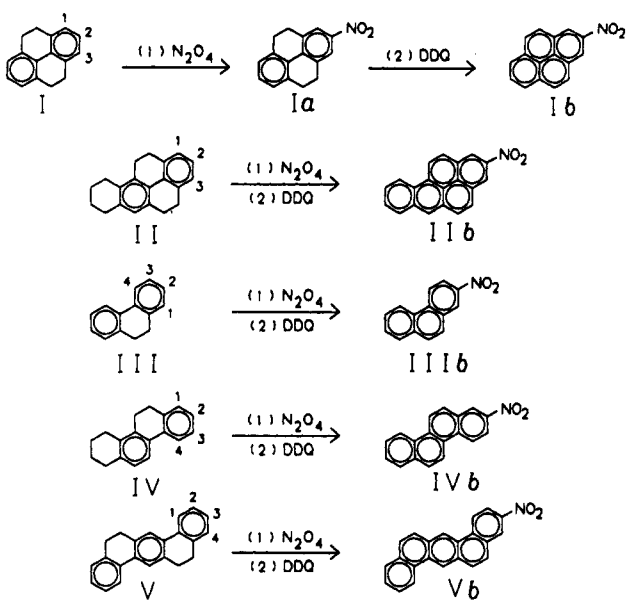
Received December 16, 1991

Introduction

Nitropolycyclic aromatic hyrocarbons (nitro-PAHs) are environmental contaminants and are present in the food chain.[2-5] Since many nitro-PAHs are metabolized to highly mutagenic and tumorigenic metabolites by mammalian and/or bacterial enzymes, there is concern regarding possible adverse human health effects from exposure to these compounds. We have been interested in structure–activity relationships as a means of utilizing the structural and electronic features of nitro-PAHs for the interpretation and/or prediction of their metabolism and their biological activities, including mutagenicity and tumorigenicity.[4-10] Recent studies by several groups have demonstrated that the geometric location and the orientation of the nitro substituent[6-11] and the first half-wave

Scheme I



reduction potential[8,10,12] are all important features that may affect the mutagenic potency of nitro-PAHs. As a continuation of our interest in the biological studies of nitro-PAHs, we need to prepare the nitro-PAHs with the nitro substituent situated at the longest axis of the molecule. Because carbons on the longest axis of a PAH are not the most reactive positions for electrophilic aromatic substitution reactions, direct nitration will not produce the nitro-PAHs with the nitro group in these positions.[13] As a consequence, alternative approaches are required for the synthesis of nitro-PAHs of this type. We report here a general synthetic method for the synthesis of ten nitro-PAHs with the nitro substituent located on the longest axis of the molecule. The nitro-PAH compounds synthesized include 2-nitro-4,5,9,10-tetrahydropyrene (Ia), 2-nitro-4,5,7,8,9,10,11,12-octahydrobenzo[*a*]pyrene (IIa), 2-nitro-9,10-dihydrophenanthrene (IIIa), 2-nitro-7,8,9,10,11,12-hexahydrochrysene (IVa), 3-nitro-5,6,12,13-tetrahydrobenz[*a*,*h*]anthracene (Va), 2-nitropyrene (Ib), 2-nitrobenzo[*a*]pyrene (IIb), 2-nitrophenanthrene (IIIb), 2-nitrochrysene (IVb), and 3-nitrodibenz[*a*,*h*]anthracene (Vb).

Results and Discussion

Synthesis of nitro-PAHs with the substituent situated on the longest axis of the molecules started with the partially saturated PAHs I–V, all of which contained a biphenyl moiety (Scheme I). This strategy is based on the prediction by molecular orbital calculations that nitration of biphenyl occurs at the 2- and 4-positions,[13] the reported nitration of 4,5,9,10-tetrahydropyrene (I) to 2-

(1) Presented in part at the 200th National Meeting of the American Chemical Society, Boston, MA, April, 1990.

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