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Note

Synthesis of *p-tert*-butylcalix[8]arene ether derivatives

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Octaalkylethers **2a-g** (alkyl: *n*-CH_3, *n*-C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *n*-C_5H_{11}, *n*-C_6H_{13}, *n*-C_8H_{17}) of *p-tert*-butylcalix[8]arene were prepared by the etheration with NaH as base. The structures of the new compouds were determined by IR, ^{1}H NMR, elemental analysis and MS spectra. and the study for their application is under way.

Keywords: *p-tert*-Butylcalix[8]arene, *p-tert*-butylcalix[8]arene ether derivatives, etheration, synthesis, characterization

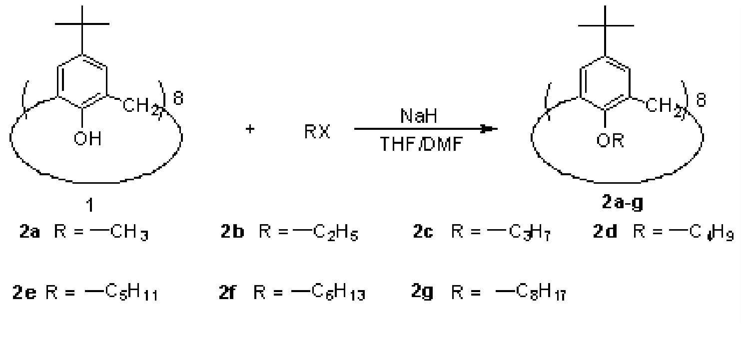
Calixarene, which is assembled by the base-catalyzed condensation of *p*-alkyphenols with formaldehyde[1], was the third generation in supermolecular chemistry after crown ethers and cyclodextrins. Calixarenes are useful building block for the selective recognition of ions or neutral organic molecular. To date, many calix[4]arene derivatives have been developed for the purpose of creating new hosts for guest ions or molecular because the relative small cavity of the macrocycle restrains its role to be a platform where the binding groups are attached and oriented for recognition[2-5].

Interests for these macrocycles like calix[8]arene have grown due to the report on the nature of the purification of fullerenes (C_{60} and C_{70}) by selective complexation[6]. Until now some derivatives of calix[8]arene, which possess ester, carboxylic acid or other functional groups, have been synthesized in order to enhance the selectivity and efficiency of their complexation and improve their solubilities[7,8]. But relatively little attention has been paid to the synthesis of octaalkylethers of *p-tert*-butylcalix[8]arene with different alkyl chain length, which may be the new host molecules potentially useful in supramolecular chemistry.

In this work, a series of octaalkylethers of *p-tert*-butyl calix[8]arene were synthesized by the etheration with NaH as base and halogenated hydrocarbon as alkylating reagent in DMF and THF (**Scheme I**), and the study for relative molecular recognition performance is under way.

Experimental Section

Melting points were recorded on a digital microscope and are uncorrected. TLC analyses were carried out on silica gel plates, using ethyl acetate-petroleum ether (3/10 v/v). IR (KBr) spectra (V cm^{-1}) were obtained on a Nicolet AVATAR 370 spectrometer, ^{1}H NMR spectra were taken in $CDCl_3$ on a Varian INOVA-300NMR spectrometer, using TMS as internal standard. MS were taken on Thermo-Finnigan LCQ-Advantage mass spectrometer. The Model PE 2400 element analyzer was used to determine C and H elements in compound. *p-tert*-butylcalix[8]arene **1** was synthe



Scheme I —Synthetic route of *p-tert*-butylcalix[8]arene ether derivatives and **1** represents *p-tert*-butylcalix[8]arene, NaH as base and halogenated hydrocarbon as alkylating reagent, DMF and THF as solvent.

Table I — Melting points and R_f of **2a-g**

Compd	m. p.[a] /(°C)	R_f[b]
2a	292-94	0.53
2b	288-90	0.63
2c	282-84	0.69
2d	277-79	0.74
2e	269-71	0.78
2f	256-58	0.83
2g	219-21	0.85

[a] Melting points were recorded on a digital microscope and are uncorrected.
[b] TLC analyses were carried out on silica gel plates, using ethyl acetate : petroleum ether (3:10 V/V).

sized according to the procedure described in the previous paper[8].

Procedure for the synthesis of 2a-g:

A solution of *p-tert*-butylcalix[8]arene (0.38 mmole) in THF/DMF(10:1 V/V, 110 mL) was stirred at 60ºC until a clear solution was obtained (10 min), NaH (41.6 mmole) was added, and stirring under nitrogen was continued for an additional 30 min. A solution of RX (2380 mmole) in THF was added, and the mixture was refluxed. TLC followed the track of reaction, evaporated the solvents after reaction, and

Table II — ^{1}H NMR spectra of compounds **2a-g**

Compd	^{1}H NMR, δ, ppm
2a	6.923 (s, 16H, ArH), 4.038 (s, 16H, $ArCH_2Ar$), 3.414 (s, 24H, OCH_3), 1.070 (s, 72H, $C(CH_3)_3$)
2b	6.943(s, 16H, ArH), 4.028 (s, 16H, $ArCH_2Ar$), 3.467-3.514 (m, *J*=14.1Hz, 16H, OCH_2),1.08 (s, 72H, $C(CH_3)_3$), 1.048-1.071 (t, 24H, CH_3)
2c	6.973 (s, 16H, ArH), 4.032 (s, 16H, $ArCH_2Ar$), 3.405-3.448 (t, *J*=12.9Hz,16H, OCH_2), 1.483-1.507 (m, 16H, $\mathrm{OCH_2C}\mathit{H}_2$), 1.09 (s, 72H, $C(CH_3)_3$), 0.668-0.717 (t, 24H, CH_3)
2d	6.961 (s, 16H, ArH), 4.040 (s, 16H, $ArCH_2Ar$), 3.484-3.526 (t, *J*=12.6Hz,16H, OCH_2), 1.496-1.542 (m, 16H, $\mathrm{OCH_2C}\mathit{H}_2$), 1.224-1.293 (m, 16H, $\mathrm{OCH_2CH_2C}\mathit{H}_2$), 1.083 (s, 72H, $C(CH_3)_3$), 0.650-0.699 (t, 24H, CH_3)
2e	6.951 (s, 16H, ArH), 4.049 (s, 16H, $ArCH_2Ar$), 3.480-3.488 (t, *J*=2.4Hz,16H, OCH_2), 1.528-1.542 (m,16H, $\mathrm{OCH_2C}\mathit{H}_2$), 1.302 (m, 16H, $\mathrm{OCH_2CH_2C}\mathit{H}_2$), 1.079 (s, 72H, $C(CH_3)_3$), 1.010-1.189 (m, 16H, $\mathrm{OCH_2CH_2CH_2C}\mathit{H}_2$), 0.692-0.740 (t, 24H, CH_3)
2f	6.948 (s,16H, ArH), 4.044 (s, 16H, $ArCH_2Ar$), 3.519-3.538 (t, *J*=5.7Hz, 16H, OCH_2), 1.513-1.613 (m, 16H, $\mathrm{OCH_2C}\mathit{H}_2$), 1.235-1.352(m, 16H, $\mathrm{OCH_2CH_2C}\mathit{H}_2$), 1.074(s, 72H, $C(CH_3)_3$), 0.957-1.161 (m, 32H, $\mathrm{OCH_2CH_2CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2$), 0.693-0.738 (t, 24H, CH_3)
2g	6.905 (s, 16H, ArH), 4.040(s, 16H, $ArCH_2Ar$), 3.560-3.600 (t, *J*=12Hz,16H, OCH_2), 1.639-1.689 (m, 16H, $\mathrm{OCH_2C}\mathit{H}_2$), 1.463 (m, 16H,$\mathrm{OCH_2CH_2C}\mathit{H}_2$), 1.267 (m, 64H, $\mathrm{OCH_2CH_2CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2$), 1.034(s, 72H, $C(CH_3)_3$), 0.832-0.877 (t, 24H, CH_3)

^{1}H NMR spectra were taken in $CDCl_3$, using TMS as internal standard.

Table III — Elemental analysis and MS spectra for compounds **2a-g**

Compd	Mol formula	Calcd (Found) %		MS *m/z* (%)
		C	H	
2a	$C_{96}H_{128}O_8$	81.71 (81.77	9.20 9.15)	MS(APCI) *m/z* (%):1409.1 (M^+,100)
2b	$C_{104}H_{144}O_8$	(82.06 82.12	9.48 9.53)	MS(APCI) *m/z* (%):1521.3 (M^+,100)
2c	$C_{112}H_{160}O_8$	82.35 (82.30	9.79 9.87)	MS(APCI) *m/z* (%):1633.2 (M^+,100)
2d	$C_{120}H_{176}O_8$	82.56 (82.52	10.11 10.16)	MS(APCI) *m/z* (%):1746.1 (M^+,100)
2e	$C_{128}H_{192}O_8$	82.76 (82.70	10.36 10.41)	MS (ESI) *m/z* (%): 1857.6 (M^+,100)
2f	$C_{136}H_{208}O_8$	82.80 (82.87	10.71 10.64)	MS (ESI) *m/z* (%): 1970.1 (M^+,100)
2g	$C_{152}H_{240}O_8$	83.21 (83.15	10.93 11.02)	MS (ESI) *m/z* (%): 2194.3 (M^+,100)

the residue was taken up in CH_2Cl_2 and washed with HCl (0.1 $mol·L^{-1}$). The organic phase was dried and recrystallized to afford the products.

Results and Discussion

The etheration of calixarene was generally achieved by the Williamson reaction, but the strength of the base may govern the reactions. Neri P reported[9] that the treatment of *p*-*tert*-butylcalyx[8]-arene with *p*-substituted benzyl bromides using K_2CO_3 gives 1,3,5,7-tetraethers, but the use of CsF as base also can not obtain the octaalkylethers of *p*-*tert*-butylcalix[8]arene because fluoride anions are not able to attain complete deprotonation of phenolic OH, and it can form strong hydrogen bonds with acidic protons[10]. In this paper, a series of octaalkylethers of *p*-*tert*-butylcalix[8]arene were synthesized by the etheration with NaH as base in DMF and THF(**Table I**).

Compounds **2a-g** in IR showed absroption at 1110 cm^{-1} (C-O-C), but no absorption at 3210 cm^{-1} (–OH) showed that *p*-*tert*-butylcalix[8]arene **1** was formed. In ^{1}H NMR compounds **2a-g** showed singlets for the methylene resonances (**Table II** and **III**), but *p*-*tert*-butylcalix[8]arene **1** showed double peak for the methylene resonances, which may mean the conformational inversion after etheration, and the systematic studies utilizing these derivatives for the recognition is conducting.

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