SELECTIVE DEALKYLATION OF TETRA-*O*-PROPYL-*p-tert*-BUTYL CALIX[4]ARENE AT THE LOWER RIM BY $AlCl_3$

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Abstract

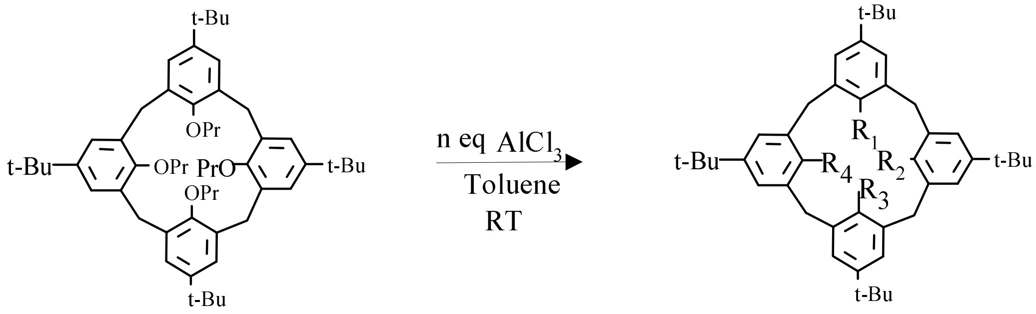
As a result of experimental studies on the dealkylation of tetra-*O*-propyl-*p-tert*-butyl calix[4]arene **1**, we have found that by treating **1** with the stoichiometric amount of $AlCl_3$, the tri, di and mono-*O*-propyl-*p-tert*-butyl calix[4]arene are obtained in good yield. In these reactions *tert*-butyl groups at the upper rim are uchanged.

Introduction

The extensive use of calixarenes and in particular calix[4]arenas, in supramolecular chemistry[1] justifies the efforts of several research groups to find synthetic methodologies for their selective functionalization both at the upper and lower rim. Several useful synthetic methodologies have been reported which allow the synthesis of tetra substituted calix[4]arenas at the lower rim.[2] Apart from one example by Gutsche who reported the synthesis of monoallyloxy calix[4]arene,[3] no general methodology is available for the synthesis of calix[4]arene mono alkyl ethers. Several attempts to obtain these compounds by direct alkylation of *p-tert* calix[4]arene failed, this reaction giving tetra[1] and dialkylated [4-6] products or mixture of compounds.

Results and discussion

An alternative to direct alkylation for generating partially alkylated calix[4]arenas involves selective dealkylation of the readily available tetra-O- propyl-*p-tert*-butyl calix[4]arene by means of stiochiometric amounts of $AlCl_3$. By this procedure, 75-83% yields of tri, di and mono-O-propyl-*p-tert*-butyl calix[4]arene have been obtained.



1

2a: n=1 R1=OH, R2=R3=R4=OPr
2b: n=2 R1=R3=OH, R2=R4=OPr
2c: n=3 R1=OPr, R2=R3=R4=OH

Scheme

The cavity of the upper rim can be modified by introducing substituents at the para positions of the phenol rings of calix[4]arene. Gutsche et al. have described the modification via a Claisen rearrangement.[7] They prepared calix[4]arene by aluminium chloride-catalyzed debutylation of *p-tert*-butyl calix[4]arene at the upper rim. The comparison between this two reaction show that the dealkylation of O-Pr groups at the lower rim take place before dealkylation of *tert*-butyl at the upper rim.

The calix[4]arene tetrapropylether **1** is produced in quantitative yield by simple alkylation procedure.[8] The compound **1** is used for dealkylation step (Scheme) and tri, di, and mono propylethers are obtained in 83, 79 and 75% yield, respectively.

All products show a cone conformation.[1] In compounds **2a** and **2c** the ^{1}H NMR spectra show a typical pattern represent by two doublets for the equatorial and two doublets for the axial protons of the bridging methylene ($ArCH_2Ar$). Compound **2c** interestingly shows two sharp signals for the three OH groups, one at 10.15 ppm (2H) and one at 9.57 ppm (1H). The high chemical shift for two OH groups indicates that these two H bonds are weaker than the other one and are those probably formed by the two opposite phenolic OH groups with the neighbour alkoxy oxygen atom with according to molecular mechanics calculations, bears less negative charge than a hydroxyl oxygen atom.[9] (Scheme 2)

Experimental

Melting points are taken on a Büchi SMP-20 apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a Bruker AM-400 MHz in $CDCl_3$ with Me_4Si as an internal standard. IR spectra were recorded on Bruker IFS 25 spectrophotometer. Compounds **2a-2c** have bee reported. for microanalytical and spectral data, see ref. 8.

General Procedure for the preparation of 2a-2c:

Calix[4]arene tetrapropylether **1** (1.0 mmol) and $AlCl_3$ (1.04 mmol for preparation of **2a**, 2.08 mmol for **2b** and 3.12 mmol for **2c**) in 50 ml of dried and distilled toluene, were stirred for 6 h at room temperature. The reaction mixture was diluted with 10% HCl solution (100 ml). The organic layer was separated and dried over $MgSO_4$. After filtration, the filtrate was concentrated to dryness. The residue was recrystalized from CH_2Cl_2-CH_3OH.

2a: mp 191-193 °C yield 83%; IR (KBr/cm^{-1}) ν_{OH} 3530; ^{1}H NMR (400 MHz; $CDCl_3$) δ 0.81 (s, 18H, t-Bu), 0.96 (t, 3H, CH_3), 1.10 (t, 3H, CH_3), 1.30 (s, 9H, t-Bu), 1.32 (s, 9H, t-Bu), 1.82-2.00 (m, 2H, CH_2), 2.28-2.38 (m, 4H, CH_2), 3.15, 4.29 (2d, 4H, $ArCH_2Ar$), 3.22, 4.33 (2d, 4H, $ArCH_2Ar$), 5.54 (s, 1H, OH), 6.47 (d, 2H, ArH), 6.48 (d, 2H, ArH), 7.03 (s, 2H, ArH), 6.94 (s, 2H, ArH).

2b: mp 246-249 °C yield 79%; IR (KBr/cm^{-1}) ν_{OH} 3375; ^{1}H NMR (400 MHz; $CDCl_3$) δ 0.94 (s, 18H, t-Bu), 1.26 (t, 6H, CH_3), 1.29 (s, 18H, t-Bu), 1.96-2.05 (m, 4H, CH_2), 3.29, 4.25 (2d, 8H, $ArCH_2Ar$), 3.93 (t, 4H, CH2), 6.75 (s, 4H, ArH), 7.04 (s, 4H, ArH), 7.75 (s, 2H, OH).

2c: mp 236-238 °C yield 75%; IR (KBr/ cm^{-1}) ν_{OH} 3180, 3300; ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.18 (s, 9H, t-Bu), 1.20 (s, 18H, t-Bu), 1.21 (s, 9H, t-Bu), 1.24 (t, 3H, CH_3), 2.13-2.22 (m, 2H, CH_2), 3.41, 4.27 (2d, 4H, $ArCH_2Ar$), 3.43, 4.36 (2d, 4H, $ArCH_2Ar$), 4.10 (t, 2H, OCH2), 6.99 (d, 2H, ArH), 7.04 (s, 2H, ArH), 7.06 (d, 2H, ArH), 7.09 (s, 2H, ArH), 9.57 (s, 1H, OH), 10.15 (s, 2H, OH).

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References

1. *Clixarenes a versatile class of macrocyclic compounds*, Vicenc, J. and Bohmer, V. Eds., Kluwer Academic publishers, Dordrecht, the Netherlands, **1990**.
2. C.D. Gutsche, *Calixarenes, monograph in supramolecular chemistry*, Vol. 1; Stoddart, F. J. Ed. The Royal Society of Chemistry: Cambridge, **1989**.
3. C.D. Gutsche, and K. C. Nam, *J. Am. Chem. Soc.* **1988**, *110*, 6153-6162.
4. P. J. Dijkstra, J. A. Brunink, K. E. Bugge, D. N. Reinhoudt, S. Harkema, R. Ungaro, F. Ugozzoli, E. Ghidini, *J. Am. Chem. Soc.* **1988**, 7567-7575.
5. J. D. Van loon, A. Arduini, L. Coppi, W. Werboom, A. Pochini, R. Ungaro, S. Harkema, and D. N. Reinhoudt, *J. Org. Chem.* **1990**, 5639-5646.
6. E. M. Collins, M. A. Mckervey, S. J. Harris, *J. Chem. Soc. Perkin Trans.1*, **1989**, 372-375.
7. C. D. Gutsche, J. A. Levine, P. K. Sujeeth, *J. Org. Chem.* **1985**, *50*, 5802-5806.
8. K. Iwamoto, K. Araki, S. Shinkai, *J. Org. Chem*. **1991**, *56*, 4955-4962.
9. P. D. J. Grootenhuis, P. A. Kollman, L. P. Groenen, D. N. Reinhoudt, G. J. Van Hummel, F. Ugozzoli, C. D. Andreetti, *J. Am. Chem. Soc.* **1990**, 4165-4176.

Povzetek

Opazili smo, da z obdelavo tetra-*O*-propil-*p*-*tert*-butilkaliks[4]arena s stehiometrično množino $AlCl_3$ lahko pripravimo tri, di in mono-tetra-*O*-propil-*p*-*tert*-butilkaliks[4]arene. Pri the pretvorbah ostanejo *terc*-butilne skupine na gornejm robu nedotaknjene.