Chinese Chemical Letters Vol. 13, No. 3, pp 205 – 206 2002
http://www.imm.ac.cn/journal/ccl.html

An Interesting Approach to Bis-calix[5]arene Analogue from Calix[6]arene

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Abstract: By 1,4-bridging of *p-tert*-butylcalix [6] arene with 2,6-bis (bromomethyl)-4-methyl-anisole, a new type of bis-calix [5] arene analogue was obtained in high yield..

Keywords: Bis-calix [5] arene, calyx [6] arene, bridging.

Calix [n] arenas {n = 4, 6 or 8} are easily prepared from formaldehyde and *para*-substituted phenols *via* cyclic condensation under alkaline conditions in one step. It is not surprising that the calyx [n] arene (n = 4, 6, 8) chemistry has been developing very rapidly during the latest 20 years[1]. However, it is not the case for calixarenes with odd benzene rings (for example, n = 5). The yield of *p-tert*-butylcalix [5] arene synthesized in one-step from *p-tert*-butylphenol and formaldehyde was as low as 15% in the Gutsche′s improved procedure with difficulty[2]. Only one example of bis-calix [5] arenes was reported by Fukazawa *et al.* in 1998 as compared with plenty of the papers concerning bis-calix [4] arene. The bis-calix [5] arene exhibited outstanding coordinated ability toward [60] fullerene[3].

Here, we wish to report an interesting route to synthesize a new type of bis-calix [5] arene analogue **2** from easily obtained *p-tert*-butylcalix [6] arene **1** and 2, 6-bis (bromomethyl)-4-methylanisole (BBA). To the DMF solution of **1**, 5 equivs NaH was added at room temperature, followed by 1.1 equivs of BBA[4]**,** the mixture was stirred at 70°C for 16 h. The excess of NaH was quenched by addition of a minimal quantity of methanol (**caution!**). Distilling off the solvent, the residue was treated with HCl (10%, v/v) and then extracted with $CHCl_3$. After recrystallization from CH_2Cl_2/CH_3OH, compound **2** was obtained as white solid in 75% yield, mp 217-220°C. Its conformation was shown in **Figure 1**. Compound **2** could be also obtained with the system of K_2CO_3/benzene, but the yield was down to 55% and column chromatography was needed.

Compound **2** gave satisfactory elemental analysis results and exhibited the expected molecular ion peak in MS. In the ^1H NMR spectrum, two singlets for the *tert*-butyl groups (2:1), two pairs of doublets (1:2) for the methylene protons and a broad singlet for the oxymethylene groups of the bridge and a singlet for the hydroxyl protons can be assigned. The C_{2v} symmetrical (**u, u, u, u, u, u**) conformation of **2** at room temperature

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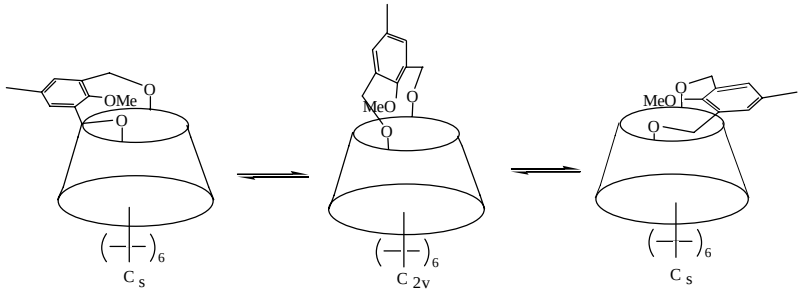
is easily deduced from the methylene protons in calixarene skeleton showing two pairs of doublets in a ratio of 1:2. It is interesting to note that the signals were changed below 0^oC. There are three singlets for the *tert*-butyl hydrogen atoms (1:1:1), four pairs of doublets (1:2:2:1) in the diaryl-methylene region, two doublets for the oxymethylene groups of the bridge (1:1), and two singlets (1:1) for the hydroxyl groups indicating existence of a C_s symmetrical conformation. This phenomenon can be explained by different orientations of the phenyl ring in the bridge (**Figure 1**). The similar phenomenon was observed by U. Lüning *et al.*[5].

Figure 1 C_s and C_{2v} conformations for a (**u, u, u, u, u, u**)-A, D-bridged *p-tert*-butylcalix [6] arene **2**



Acknowledgment

Financial supports from the National Natural Science Foundation of China and Hubei province are gratefully acknowledged.

References and Note

1. (a) C. D. Gusche, *Calixarenes*, Royal Society of Chemistry, Cambridge, U.K., **1989.** (b) J. Vicens, V. Bohmer, Eds., *Calixarenes*: *A Versatile Class of Macrocyclic Compounds*, Kluwer Academic, Dordrecht, **1991.** (c) S. Shinkai, *Tetrahedron*, **1993**, *49*, 8003. (d) V. Bohmer, *Angew. Chem., Int. Ed. Engl.*, **1995**, *34*,713.
2. D. R. Stewart, C. D. Gutsche, *Org. Prep. Proceed. Int.*, **1993**, *25*, 137.
3. T. Haino, M. Yanase, Y. Fukazawa. *Angew. Chem. Int. Ed. Engl.*, **1998**, *37*, 997.
4. K. E. Koenig, G. M. Lein, P. Stuchler, T. Kaneda, D. J. Cram, *J. Am. Chem. Soc.*, **1979**, *101*, 3552.
5. U. Lüning, H. Ross, I. Thondorf, *J. Chem. Soc., Perkin Trans. 2*, **1998**, 1313.
6. Analytic data of compound **2** ^{1}H NMR (300 MHz, $CDCl_3$, 298 K δ): 1.21 (s, 36H, $C(CH_3)_3$), 1.24 (s, 18H, $C(CH_3)_3$), 2.35 (s, 3H, $ArCH_3$), 3.42 (d, 4H, J = 13.5 Hz, $ArCH_2Ar$), 3.56 (d, 2H, J = 12.0 Hz, $ArCH_2Ar$), 3.70 (s, 3H, $ArOCH_3$), 4.14 (d, 4H, J = 13.5 Hz, $ArCH_2Ar$), 4.70 (d, 2H, J = 12.0 Hz, $ArCH_2Ar$), 5.74 (bs, 4 H, CH_2O), 6.94 (bs, 4H, ArH), 7.09 (bs, 4H, ArH), 7.16 (s, 4H, ArH), 7.21 (s, 2H, ArH), 8.02 (s, 4H, ArOH). ^{1}H NMR (300 MHz, $CDCl_3$, 270 K δ) 1.16 (s, 18H, $C(CH_3)_3$), 1.22 (s, 18H, $C(CH_3)_3$), 1.26 (s, 18H, $C(CH_3)_3$), 2.43 (s, 3H, $ArCH_3$), 3.82 (d, 1H, J = 10.2 Hz, $ArCH_2Ar$), 3.90 (d, 1H, J = 12.9 Hz, $ArCH_2Ar$), 4.03 (d, 2H, J = 16.2 Hz, $ArCH_2Ar$), 4.14 (d, 2H, J = 14.1 Hz, $ArCH_2Ar$), 4.19 (d, 1H, J = 10.2 Hz, $ArCH_2Ar$), 4.24 - 4.63 (m, 10H, $ArOCH_3$ and $ArCH_2Ar$ and CH_2O), 5.62 (d, 2H, J = 9.6 Hz, CH_2O), 6.43, 6.62, 6.85, 6.92, 7.09, 7.18 (s each, 2H each, ArH), 7.42 (d, 2H, bridge ArH), 8.25, 8.36 (s each, 2H each, ArOH). MS (FAB): *m/z* 1,118 (M^+). Anal. calcd. for $C_{76}H_{94}O_7$ (%): C, 81.53; H, 8.46; found: C, 81.55; H, 8.42.

Received 20 June, 2001