Synthesis of a Sulfur-bridged Calixarene

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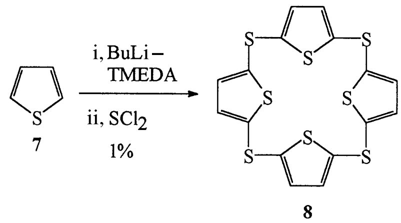
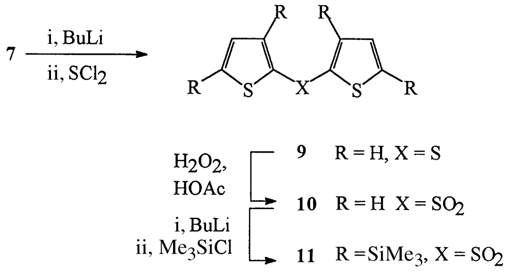
A thiacalix[4]arene was obtained by the reaction of the 2,5-thiophene dianion with SCl_2; the analogous reactions of dianions of diaryl thioethers did not yield macrocyclic structures and under the applied conditions diaryl sulfones were further deprotonated and the structure of the fourfold Me_3Si-adduct **11** determined by X-ray crystallography.

The first thiacalix[4]arene **8** was isolated in small amounts from the reaction of the 2,5-thiophene dianion with SCl_2. Thiophene was deprotonated to the 2,5-dianion by treatment with BuLi–TMEDA.[6] Slow addition of the biselectrophile SCl_2 to a cold solution of the thiophene dianion gave, after work-up, a white solid. From the crude product a small amount of the thiacalix[4]arene **8** could be isolated. The thiophene moieties of the compound rotate freely on the NMR timescale in solution, as shown by simple NMR spectra.



Scheme 3

To increase the yield of the thiacalix[4]arene **8** a stepwise synthesis was investigated. However, the reaction was improved neither by the use of the thioether **9**[6] nor the sulfone **10**.[5] In the latter case the regioselectivity of the deprotonation was lost, as illustrated by the formation of the tetrasilylated compound **11** upon treatment of the anion solution with Me_3SiCl. The structure of **11** was confirmed by X-ray analysis.[7] The thiophene units show an *anti* arrangement in the solid state and the geometry of the central sulfur atom is nearly ideal tetrahedral.



Scheme 4

Crystal Data.—$C_{20}H_{38}O_2S_3Si_4$, monoclinic, $a = 1663.0(2)$, $b = 1055.0(0)$, $c = 1736.8(1)$ pm, $\beta = 103.89(1)°$, $V = 2.958(2)$ nm^3, space group $P2_1/n$, $Z = 4$. The structure was solved by direct methods and refined anisotropically on F^2, using the program SHELXL-93.[7] Hydrogen atoms were included as rigid methyl groups or with a riding model. Final refinement with 274 parameters led to a final w$R(F^2)$ for all reflections of 0.084, $S = 0.934$, with a conventional $R(F)$ of 0.034; max. $\Delta\rho$ 393 e nm^{-3}. A colourless prism *ca*. 0.64 × 0.44 × 0.42 mm was mounted on a glass fibre in inert oil. Measurements were performed on a Siemens P4 diffractometer with an LT-2 low-temperature attachment at 173 K using graphite-monochromated Mo-Kα radiation ($\lambda = 71.073$ Å). 5196 independent reflections below $2\theta = 50°$ were measured with the ω-scan method. 3794 reflections with $F_0 > 4\sigma(F_0)$ were used in the structure solution and refinement.†

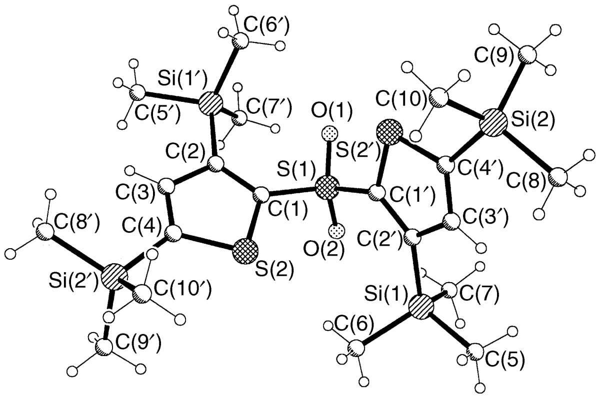


Fig. 1 Crystal structure of **11**

We conclude that the reaction of dianions with SCl_2 is less suitable for the synthesis of heteroatom-bridged macrocycles. Compared to Me_2SiCl_2,[1] the reaction is less selective because of the high reactivity of the biselectrophile SCl_2, yielding only small amounts of macrocycles. However, from the reaction of the 2,5-thiophene dianion and SCl_2 the first thiacalix[4]arene **8** was isolated.

Techniques used: ^{1}H NMR, ^{13}C NMR, MS, UV, IR, combustion analysis, X-ray diffraction

References: 7

Schemes: 4

Table 1: Crystal data and structure refinement for **11**

Table 2: Atomic coordinates and equivalent isotropic displacement parameters for **11**

Table 3: Intramolecular bond distances and angles for **11**

Appendix: ^{1}H and ^{13}C NMR spectra for compound **8**

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†Atomic coordinates, bond lengths and angles, and thermal parameters are given in the full text and have also been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number 423/3.