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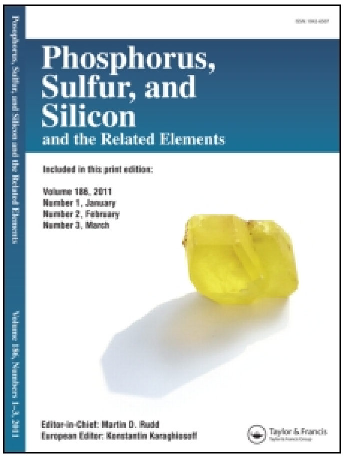

## Phosphorus, Sulfur, and Silicon and the Related Elements

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# SYNTHESIS, STRUCTURE, AND REACTIONS OF STABLE SELENENIC ACIDS BEARING NOVEL BRIDGED CALIX[6]ARENE FRAMEWORKS

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Isolable selenenic acids were synthesized for the first time by taking advantage of the bridged calix[6]arene frameworks. X-ray crystallographic analysis established the structure of the compound with a cone conformation, where the SeOH functionality is deeply buried in the cavity of the *p-tert*-butylcalix[6]arene macrocycle. Its thermal stability was so remarkable that no decomposition was observed even after heating at 120 °C for 5 h in $CDCl_2CDCl_2$.

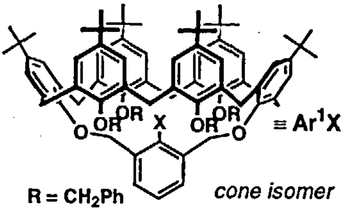
Keywords: selenenic acid, calix[6]arene, steric protection, X-ray analysis, conformational isomer

## INTRODUCTION

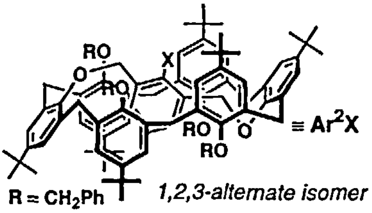
Although selenenic acids (RSeOH) have been well-recognized as important intermediates in organic and biochemical reactions of selenium compounds, the elucidation of their chemistry has been hampered by the absence of the methodology to get a stable compound of this species.[1] Recently, we have developed a new type of reaction environment based on the 1,4-bridged calix[6]arene frameworks and applied it to the stabilization of a sulfenic acid (RSOH).[2] Here we report the first synthesis and structural elucidation of isolable selenenic acids by taking advantage of the frameworks.

## RESULTS AND DISCUSSION

Oxidation of selenide **1a** bearing a 1,4-bridged calix[6]arene framework with a cone conformation followed by thermolysis in toluene at 80 °C afforded selenenic acid **2a**, which was isolated by silica gel chromatography as colorless crystals (74%). Selenenic acid **2b** with a 1,2,3-alternate conformation, a conformational isomer of **2a**, was synthesized from the corresponding selenide **1b** by a similar method in 44% yield.



**1a** (X = SeBu$^n$)
**2a** (X = SeOH)



**1b** (X = SeBu$^n$)
**2b** (X = SeOH)

The structure of **2a** was established by X-ray crystallographic analysis (Figure 1), representing the first example of X-ray analysis of a selenenic acid. The SeOH functionality was found to be deeply buried in the cavity of the *p-tert*-butylcalix[6]arene macrocycle, and thus it resides in an environment apparently unfavorable for the intermolecular processes leading to its decomposition. A nonbonded interaction between the oxygen atom of the ortho position and the selenium atom was observed in this crystal structure (Se1-O3, 2.64 Å).

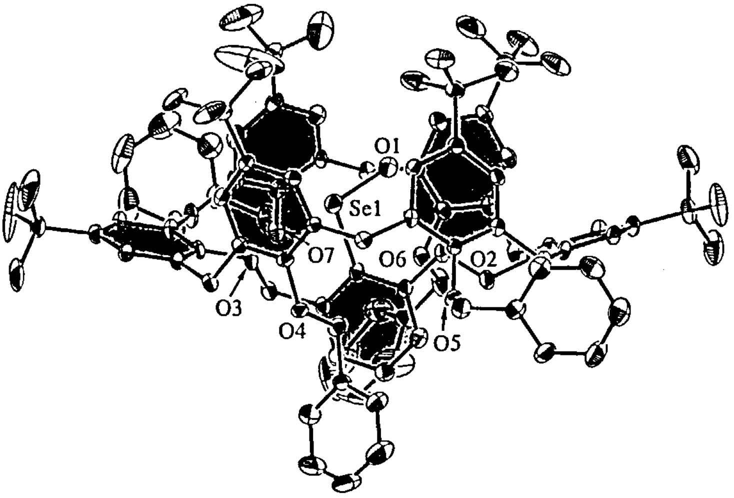


FIGURE 1 ORTEP drawing of **2a** (20% probability).

In $CDCl_3$ the $^{77}Se$ NMR signals of **2a** and **2b** appeared at $\delta$ = 1134 and 1098, respectively. The $^1H$ NMR spectrum of **2a** showed the signal of the hydroxyl proton at $\delta = -0.05$, indicating that it is highly shielded by the calix[6]arene macrocycle also in solution. The OH absorptions of **2a** and **2b** in the IR spectra were observed at 3523 and 3392 $cm^{-1}$, respectively, suggesting that there are intramolecular hydrogen bonding interactions in the latter while no significant interaction of such kind in the former. This interpretation is supported by the resonance of the hydroxyl proton of **2b** ($\delta$ = 4.34) at a rather lower field than that of **2a**. Apparently, in these two kinds of isomers, the calix[6]arene macrocycle of each conformation provides a considerably different environment for the SeOH functionality, although both of them stabilize the unstable species effectively.

Selenenic acids **2a** and **2b** showed high stability both in crystalline state and in solution. Even after heating at 120 °C for 5 h in $CDCl_2CDCl_2$, **2b** underwent only slight decomposition, and no decomposition was observed for **2a**. Considering the reported fact that even 2,4,6-tri-*tert*-butylbenzeneselenenic acid disproportionates completely within 2 h in 4% $D_2O/CD_3CN$ at 25 °C,[3] such high stability of these selenenic acids is remarkable.

Both conformational isomers **2a** and **2b** reacted with mCPBA to afford the corresponding seleninic acids **3a** and **3b**, respectively. On the other hand, they showed different reactivities towards a thiol. While the cone isomer **2a** reacted with excess amount of 1-butanethiol at room temperature to give selenenyl sulfide **4a**, the 1,2,3-alternate isomer **2b** underwent no reaction even at 50 °C. These results demonstrate that the reactivity of the endohedral functionality can be regulated by the conformation of the molecule.

$$\mathrm{ArSeOH} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{mCPBA,\ 0°C}} \mathrm{ArSeO_2H}$$

**2a**: Ar = $Ar^1$ **3a**: Ar = $Ar^1$ (88%)
**2b**: Ar = $Ar^2$ **3b**: Ar = $Ar^2$ (94%)

$$\underset{\mathbf{2a}}{\mathrm{Ar^1SeOH}} \xrightarrow[\mathrm{CDCl_3,\ 25°C,\ 4\ h}]{\mathrm{10\ eq}\ n\text{-}\mathrm{BuSH}} \underset{\mathbf{4a}\ (78\%)}{\mathrm{Ar^1SeSBu}^n}$$

$$\underset{\mathbf{2b}}{\mathrm{Ar^2SeOH}} \overset{\mathrm{10\ eq}\ n\text{-}\mathrm{BuSH}}{\underset{\mathrm{CDCl_3,\ 50°C,\ 12\ h}}{-\!\!/\!\!/\!\!\longrightarrow}} \mathrm{Ar^2SeSBu}^n$$

## Acknowledgments

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