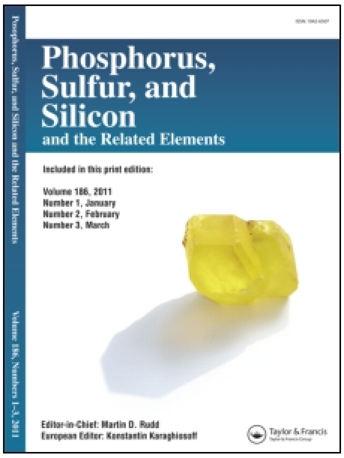

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Syntheses and Reactions of Stable Arenesulfenic Acids Bearing Bowl-Shaped Macrobicyclic Cyclophane Skeletons

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SYNTHESES AND REACTIONS OF STABLE ARENESULFENIC ACIDS BEARING BOWL-SHAPED MACROBICYCLIC CYCLOPHANE SKELETONS

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Abstract Stable arenesulfenic acids were synthesized by solid state pyrolysis of the corresponding *n*-butyl sulfoxides bearing bicyclic cyclophane skeletons with moderate size and rigidity. Their high stability demonstrates that the bowl-shaped cavity of the cyclophane works as an efficient steric protection field. The quantitative disulfide formation by the reaction of a sulfenic acid and a thiol is also described.

INTRODUCTION

Although sulfenic acids are well recognized as important intermediates in biological and mechanistic organosulfur chemistry, their high reactivity, especially their easy dimerization, has hindered the synthesis of a stable compound of this series. For arenesulfenic acids, no kinetically stabilized one has been isolated so far despite numerous attempts using various bulky substituents[1]. In this paper, we wish to report the syntheses and reactions of stable arenesulfenic acids bearing a macrobicyclic cyclophane skeleton as a steric protection group.

RESULTS AND DISCUSSION

A bowl-shaped reaction field schematically depicted in Figure 1 is expected to inhibit the approach of the functional group X of two molecules to one another while not to prevent other molecules from reacting with it. As leading compounds with a rigid bowl-shaped

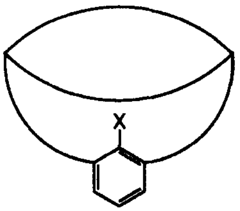
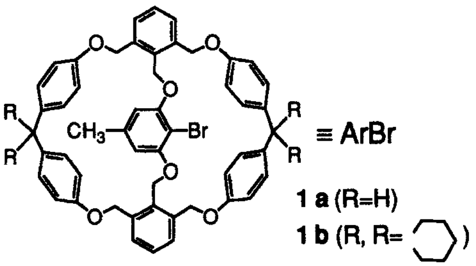


Figure 1 Schematic drawing of *"reaction bowl"*

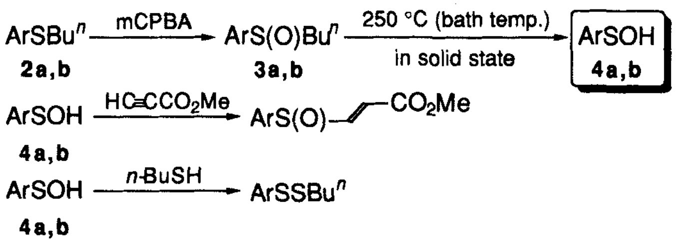


≡ ArBr

1 a (R=H)

1 b (R, R=)

cavity of moderate size, we designed bicyclic cyclophanes **1a,b**[2]. These cyclophanes were synthesized by initial construction of the central bridge followed by cyclization. X-ray crystallographic analysis of **1b** revealed that it is a shallow bowl-shaped molecule, its diameter being *ca.*13 Å. Bromides **1a,b** were able to be functionalized via lithiation. Quenching the lithiated compounds with dibutyl disulfide afforded sulfides **2a,b**, which were readily oxidized by mCPBA to give sulfoxides **3a,b**. Solid state pyrolysis of **3a,b** at 250 °C for *ca.*10 s afforded sulfenic acids **4a,b** in a conversion yield of more than 85%. They were isolated by silica gel chromatography as a crystalline solid. These sulfenic acids are stable in air for more than several weeks. As for thermal stability, **4a,b** decomposed only a little upon heating at 80 °C for an hour in toluene. The ^{1}H NMR ($CDCl_3$) spectrum showed the signal of the hydroxyl proton at δ 3.10 for **4a** and δ 3.26 for **4b**, which are very close to the reported values for the isolated alkanesulfenic acids[3]. In the IR spectrum (CH_2Cl_2) of **4a**, the hydroxyl absorptions at 3690, 3600, and 3510 cm^{-1} were observed and **4b** showed a similar spectrum. The last band suggests the intramolecular hydrogen bonding between the OH group and the oxygen atoms at ortho positions. It is not likely, however, that the effects of the ortho-substituents are responsible for the stability of **4a,b**. First, it is reported that *o*-methoxybenzenesulfenic acid is far less stable than to be isolated[4]. Moreover, electron-donating property of the substituents has been recognized to diminish the stability of a sulfenic acid[4]. The high stability of these sulfenic acids is most reasonably explained in terms of the steric inhibition of the self-condensation by the bicyclic cyclophane skeleton. Sulfenic acids **4a,b** reacted with methyl propiolate to afford the corresponding vinyl sulfoxides in good yields. Their reaction with 1-butanethiol gave the aryl butyl disulfide quantitatively, which is the first direct demonstration of disulfide formation by the reaction of a sulfenic acid with a thiol.



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