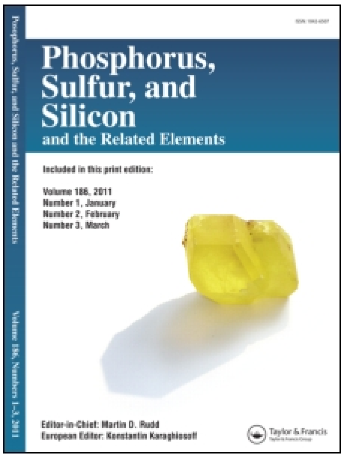

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Synthesis of a Stable Sulfenic Acid by Oxidation of a Thiol Bearing a Novel Bowl-type Substituent and Its Redox Reactions

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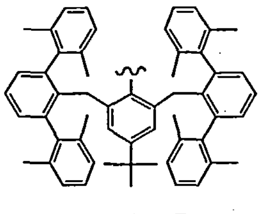
A stable sulfenic acid bearing a novel bowl-type substituent was synthesized by direct oxidation of a thiol, and its structure was determined by X-ray crystallographic analysis. The redox reactions of a sulfenic acid to a thiol and to a sulfinic acid, for which only those of transient species have been reported so far, were also demonstrated conclusively.

KEY WORDS: Sulfenic Acid, Thiol, Oxidation, Steric Protection, X-ray Analysis

INTRODUCTION



1 ≡ **Bmt**

Sulfenic acids are generally assumed to be transient intermediates in the oxidation of thiols both to disulfides and to sulfinic acids.[1] From a biological point of view, redox reactions between thiols and sulfenic acids are of great importance because they are key processes in the redox functions of some enzyme catalysis.[2] However, under non-enzymatic conditions, the evidence for these processes is circumstantial due to the instability of sulfenic acids. We previously reported the synthesis of stable sulfenic acids bearing a bowl-shaped cyclophane skeleton.[3] Recently, we have developed a novel bowl-type substituent **1** (denoted as Bmt hereafter) with a rigid, all-carbon framework.[4] Here we present the first synthesis of a stable sulfenic acid by direct oxidation of a thiol and its redox reactions to the corresponding thiol and the sulfinic acid by taking advantage of this new type of reaction field.

RESULTS AND DISCUSSION

The treatment of thiol **2** with *o*-iodosobenzoic acid in CH_2Cl_2 afforded sulfenic acid **3** as stable crystals in a yield of 31%. The ^1H NMR ($CDCl_3$) spectrum of **3** showed the signal of the hydroxyl proton at $\delta = 1.36$ (readily exchangeable with D_2O), indicating that it is shielded by the xylyl rings of the *m*-terphenyl units. The structure of **3** was established by X-ray crystallographic analysis (Figure 1), which revealed that two rigid *m*-terphenyl units of the Bmt group surround the SOH functionality like a brim of a bowl, thus effectively preventing its self-condensation to the corresponding thiosulfinate. The reactions of sulfenic acid **3** with a reductant or an oxidant presented the conclusive demonstration of redox processes from sulfenic acids to thiols and to sulfinic acids. The treatment of sulfenic acid **3** with triphenylphosphine afforded thiol **2** in a good yield of 85%. Oxidation of sulfenic acid **3** with an equimolar amount of oxaziridine afforded sulfinic acid **4** in 70% yield. The reactions of sulfenic acid **3** with an excess of 1-butanethiol or thiophenol afforded the unsymmetrical disulfides **5a**,**b**, respectively, in good yields (Scheme 2). Dithiothreitol reduced sulfenic acid **3** to thiol **2** via disulfide **5c** in a total yield of 91%. Treatment of sulfenic acid **3** with an excess of benzylamine in CH_2Cl_2 afforded sulfenamide **6** in 75% yield. These reactions of **3** with nucleophiles demonstrate that a sulfenic acid exhibits the electrophilic reactivity, even under basic conditions.

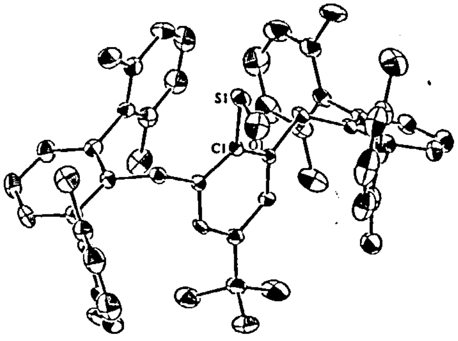
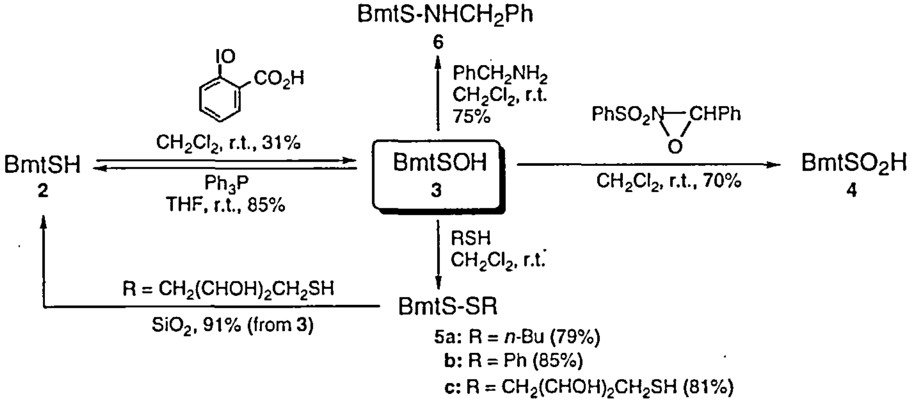


Figure 1. ORTEP drawing of BmtSOH (3). Selected bond lengths (Å) and bond angles (deg): S(1)–O(1), 1.679(5); S(1)–C(1), 1.770(5); O(1)-S(1)–C(1), 100.3(3).



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