

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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

Kei Goto; Michel Holler; Renji Okazaki

To cite this Article Goto, Kei , Holler, Michel and Okazaki, Renji(1997) 'Synthesis of a Stable Sulfenic Acid by Oxidation of a Thiol Bearing a Novel Bowl-type Substituent and Its Redox Reactions', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 120: 1, 325 — 326

To link to this Article: DOI: 10.1080/10426509708545531

URL: <http://dx.doi.org/10.1080/10426509708545531>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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

KEI GOTO, MICHEL HOLLER, AND RENJI OKAZAKI

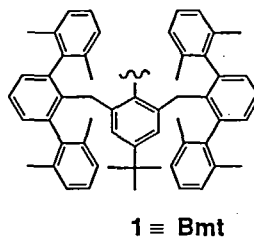
*Department of Chemistry, Graduate School of Science, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan*

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 sulfonic 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

Sulfenic acids are generally assumed to be transient intermediates in the oxidation of thiols both to disulfides and to sulfonic 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 sulfonic 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.

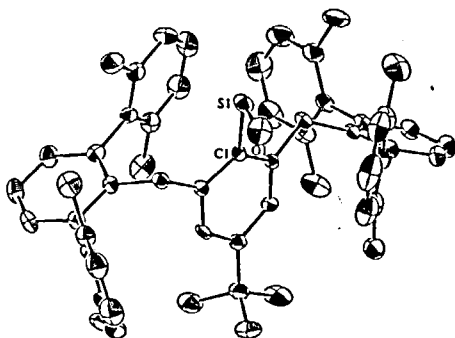
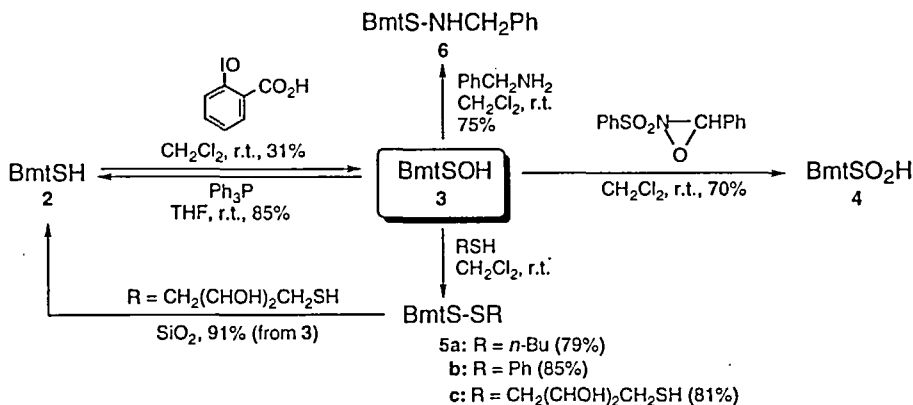


Figure 1. ORTEP drawing of BmtSOH (**3**). Selected bond lengths (Å) and bond angles (deg): S(1)–O(1), 1.679(5); S(1)–C(1), 1.770(5); O(1)–S(1)–C(1), 100.3(3).



REFERENCES

1. D. R. Hogg, in *The Chemistry of Sulfenic Acids and Their Derivatives*, edited by S. Patai (John Wiley & Sons, New York, 1990), pp361-402.
2. (a) W. S. Allison, *Acc. Chem. Res.*, **9**, 293 (1976). (b) A. Claiborne, H. Miller, D. Parsonage, R. P. Ross, *FASEB J.*, **7**, 1483 (1993).
3. (a) K. Goto, N. Tokitoh, R. Okazaki, *Angew. Chem., Int. Ed. Engl.*, **34**, 1124 (1995). (b) T. Saiki, K. Goto, N. Tokitoh, R. Okazaki, *J. Org. Chem.*, **61**, 2924 (1996).
4. K. Goto, M. Holler, R. Okazaki, *Tetrahedron Lett.*, **37**, 3141 (1996).