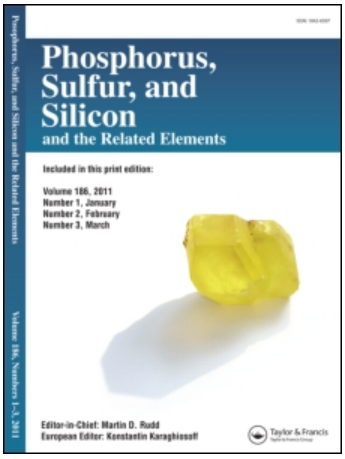


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis, Structure, and Reactivities of 2,4,6-Tris[Bis-(Trimethylsilyl)Methyl]Thiobenzaldehydes: First Isolation of Rotational Isomers of Thiobenzaldehydes

Norihiro Tokitoh[a]; Nobuhiro Takeda[a]; Renji Okazaki[a]
[a] Department of Chemistry, Graduate School of Science, The University of Tokyo, Tokyo, Japan

To cite this Article Tokitoh, Norihiro , Takeda, Nobuhiro and Okazaki, Renji(1994) 'Synthesis, Structure, and Reactivities of 2,4,6-Tris[Bis-(Trimethylsilyl)Methyl]Thiobenzaldehydes: First Isolation of Rotational Isomers of Thiobenzaldehydes', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 389 — 390
To link to this Article: DOI: 10.1080/10426509408034247
URL: http://dx.doi.org/10.1080/10426509408034247

Phosphorus, Sulfur, and Silicon, 1994, Vol. 95–96, pp. 389–390
Reprints available directly from the publisher
Photocopying permitted by license only

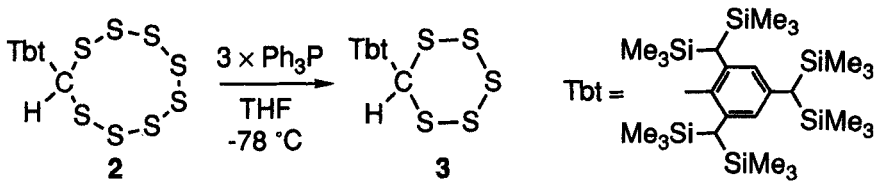
SYNTHESIS, STRUCTURE, AND REACTIVITIES OF 2,4,6-TRIS[BIS-(TRIMETHYLSILYL)METHYL]THIOBENZALDEHYDES: FIRST ISOLATION OF ROTATIONAL ISOMERS OF THIOBENZALDEHYDES

NORIHIRO TOKITOH, NOBUHIRO TAKEDA, AND RENJI OKAZAKI*
Department of Chemistry, Graduate School of Science, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Abstract The first example of rotational isomers of thiobenzaldehydes TbtCH=S (**1a** and **1b**; Tbt=2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) were synthesized and isolated as stable crystalline compounds by the desulfurization of the corresponding overcrowded cyclic polysulfides $TbtCHS_n$ (n=5 or 8). Molecular structures of **1a** and **1b** in the solid state were determined by X-ray crystallographic analysis. Kinetic studies on the thermal interconversion between **1a** and **1b** are also described.

INTRODUCTION

Recently, we have succeeded in the synthesis of novel metallanethiones of group 14 metals, Tbt(Tip)M=S (M=Si, Ge, or Sn; Tip=2,4,6-triisopropylphenyl) as stable compounds via the desulfurization of the corresponding cyclic tetrasulfides, $Tbt(Tip)MS_4$, by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter).[1] In this paper, we present the first example of rotational isomers of thiobenzaldehydes **1a** and **1b** derived from the cyclic polysulfides, **2** and **3**, bearing Tbt group.

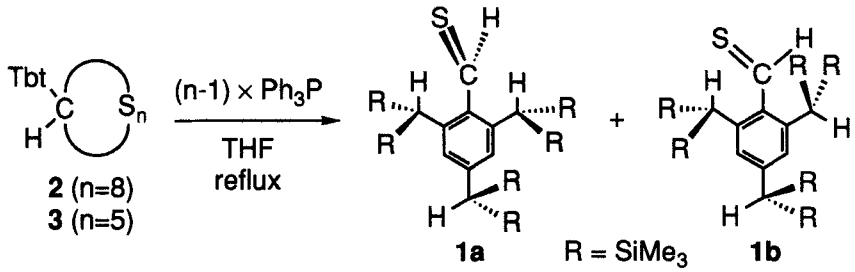


2 **3**

RESULTS AND DISCUSSION

When the Tbt-substituted octathionane **2**, which was readily synthesized by the thermal reaction of $TbtCHN_2$ with elemental sulfur,[2] was treated with Ph_3P (1 equiv × three times) in THF at -78 °C, the ring contracted pentathiane **3** was obtained in 64% yield. On the other hand, desulfurization of **2** with Ph_3P (7 equiv) in refluxing THF resulted in the formation of two types of isomeric thiobenzaldehydes **1a** and **1b** in 65 and 17% yields, respectively. Pentathiane **3** was also desulfurized under similar reaction conditions to

give **1a** and **1b** (72 and 17%). X-Ray crystallographic analysis definitively revealed the molecular geometories of **1a** and **1b** in the solid state (**Figures 1** and **2**), which were consistent with their molecular structures in solution suggested by $^1H\{^1H\}$ nuclear Overhauser effect (NOE) experiment and UV-vis spectroscopy. Both **1a** and **1b** showed satisfactory spectral data characteristic of thiobenzaldehydes [δ_H(CHS) 12.05 and 11.77, δ_C (CHS) 234.1 and 229.8, $^1J_{CH}$(CHS) 162.4 and 156.9 Hz, λ_{max}(C=S) 587 (ε 30) and 604 (30) nm, for **1a** and **1b**, respectively].



Of particular note among the chemical properties of these newly obtained thiobenzaldehydes is their thermal interconversion. Kinetic studies based on the rate constants for isomerization (**1a** → **1b**) (50.0–80.0 °C) and its equilibrium constants (50.0–140.0 °C) at several temperatures lead to the following kinetic and thermodynamic parameters: $\Delta H^{\neq}$ = 21.5±0.4 kcal mol^{-1}, $\Delta S^{\neq}$ = -13±1 cal mol^{-1}K^{-1}, $\Delta H°$ = 0.27±0.02 kcal mol^{-1}, and $\Delta S°$ = -1.77±0.07 cal mol^{-1}K^{-1}.

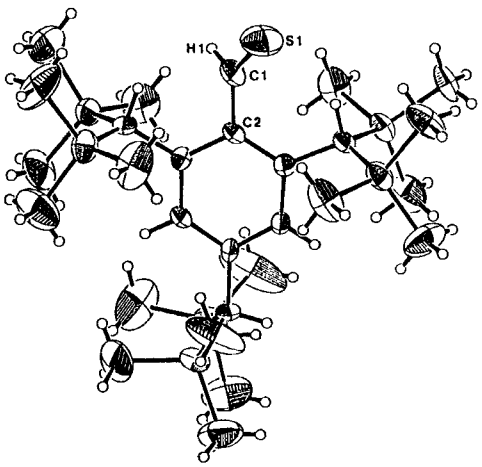


Fig 1. ORTEP drawing of **1a**.

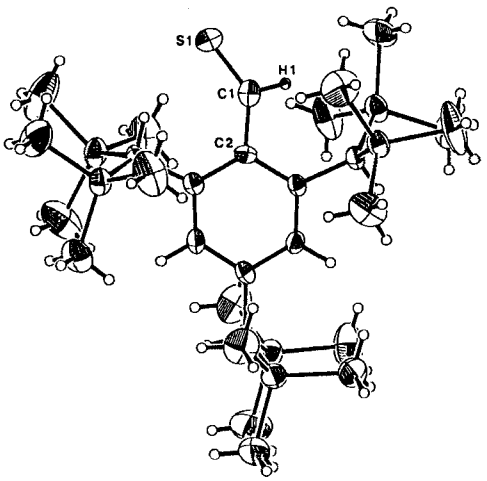


Fig 2. ORTEP drawing of **1b**.

REFERENCES

1. Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.*, **115**, 8855 (1993).
2. Tokitoh, N.; Takeda, N.; Imakubo, T.; Goto, M.; Okazaki, R. *Chem. Lett.*, **1992**, 1599.