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

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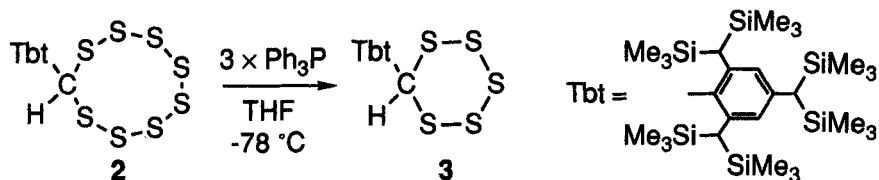
SYNTHESIS, STRUCTURE, AND REACTIVITIES OF 2,4,6-TRIS[BIS-(TRIMETHYLSILYL)METHYL]THIOBENZALDEHYDES: FIRST ISOLATION OF ROTATIONAL ISOMERS OF THIOBENZALDEHYDES

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Abstract The first example of rotational isomers of thiobenzaldehydes $\text{TbtCH}=\text{S}$ (**1a** and **1b**; $\text{Tbt}=\text{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}$) 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

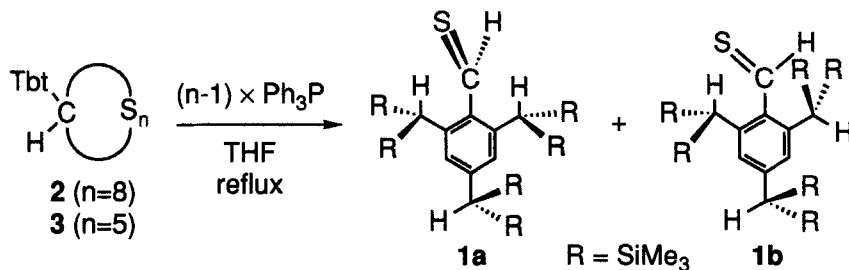
Recently, we have succeeded in the synthesis of novel metallanethiones of group 14 metals, $\text{Tbt(Tip)M}=\text{S}$ ($\text{M}=\text{Si, Ge, or Sn}$; $\text{Tip}=\text{2,4,6-trisopropylphenyl}$) as stable compounds via the desulfurization of the corresponding cyclic tetrasulfides, Tbt(Tip)MS_4 , by 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.



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 $\times$ 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 geometries 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 [$\delta_{\text{H}}(\text{CHS})$ 12.05 and 11.77, δ_{C} (CHS) 234.1 and 229.8, $^1J_{\text{CH}}(\text{CHS})$ 162.4 and 156.9 Hz, $\lambda_{\text{max}}(\text{C}=\text{S})$ 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** $\rightarrow$ **1b**) (50.0–80.0 $^{\circ}\text{C}$) and its equilibrium constants (50.0–140.0 $^{\circ}\text{C}$) at several temperatures lead to the following kinetic and thermodynamic parameters: $\Delta H^{\ddagger} = 21.5 \pm 0.4 \text{ kcal mol}^{-1}$, $\Delta S^{\ddagger} = -13 \pm 1 \text{ cal mol}^{-1} \text{K}^{-1}$, $\Delta H^{\circ} = 0.27 \pm 0.02 \text{ kcal mol}^{-1}$, and $\Delta S^{\circ} = -1.77 \pm 0.07 \text{ cal mol}^{-1} \text{K}^{-1}$.

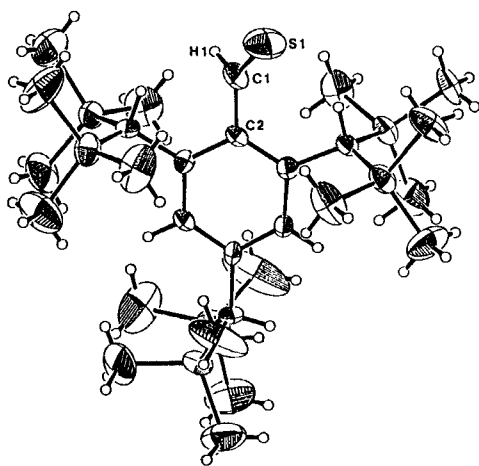


Fig 1. ORTEP drawing of **1a**.

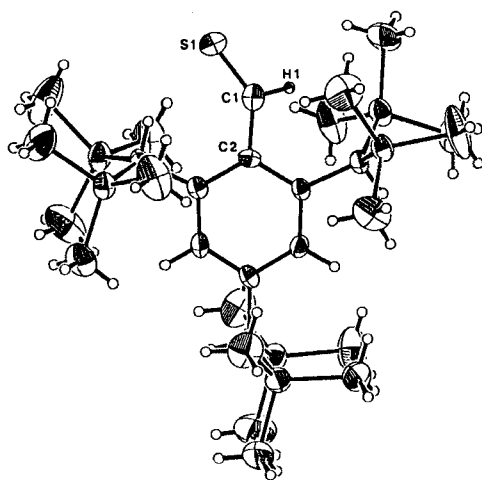


Fig 2. ORTEP drawing of **1b**.

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2. Tokitoh, N.; Takeda, N.; Imakubo, T.; Goto, M.; Okazaki, R. *Chem. Lett.*, **1992**, 1599.