

Table I. Relevant Distances (Å) and Angles (deg) in  $[\text{Fe}_3(4\text{-Ettr})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ 

	temp, K	
	300	105
Fe1...Fe2	3.840 (1)	3.795 (2)
Fe1-N1	2.174 (4)	2.031 (6)
Fe2-N2	2.157 (4)	2.176 (6)
Fe2-Ow	2.156 (4)	2.166 (6)
N1-Fe1-N1'	90.6 (2)	92.4 (2)
N1-Fe1-N1''	88.5 (3)	87.7 (4)
N1-Fe1-N1'''	178.7 (3)	179.8 (4)
N1'-Fe1-N1'''	90.4 (3)	87.5 (4)
N2-Fe2-Ow	89.3 (2)	89.7 (2)
N2-Fe2-Ow'	92.9 (2)	95.2 (3)
Ow-Fe2-Ow'	86.5 (2)	86.6 (2)

<sup>a</sup> A prime indicates a symmetry operation  $1 - y, 1 + x - y, z$ ; A double prime indicates a symmetry operation  $y - x, y, 3/2 - z$ ; A triple prime indicates a symmetry operation  $1 - y, 1 - x, 1/2 - z$ .

1. The change in the susceptibility near 203 K corresponds with a change to the low-spin state for one-third of the iron ions. Mössbauer spectra<sup>13</sup> show a similar phase transition. At 300 K two quadrupole doublets are observed in the ratio 1:2, corresponding to high-spin Fe(II) (isomer shifts 1.41 and 1.35 mm/s respectively; quadrupole splittings 1.73 and 2.68 mm/s, respectively). At 150 K the low-intensity doublet has changed into a singlet (isomer shift 0.78 m/s) corresponding to low-spin iron(II). Two spectra are shown in Figure 2. The transition to the low-spin state is found at  $203 \pm 3$  K.

To study the details of this very unusual phase transition and the connected HS-LS change, we decided to determine the crystal structure at both 300 and 105 K.<sup>14-16</sup> An illustration of the cation geometry (at 300 K only) is shown in Figure 3, together with some information about the numbering. The low-temperature structure is essentially the same, except for a significant shortening of the band involving the central iron ion. Some relevant structural parameters are compared in Table I. The observed decrease in the Fe-N bond length for the central iron ion clearly reflects the strengthening of these bonds in the low-spin state. The change of about 0.14 Å is close to the value found for the few known monomeric iron-phenanthroline compounds.<sup>1,3</sup> The structure type described in this paper is interesting from several points of view. In the first place the different chemical environments of the outer two metal ions, compared with the central one, opens the route to mixed-metal species, which allows for the detailed study of the magnetic exchange through the triazole ligand. Secondly, by choosing a diamagnetic central metal ion (e.g., low-spin iron or cadmium), the study of the weak exchange between the two outside metal ions becomes possible. This will permit the study of the often disputed  $J_{13}$  exchange in linear trinuclear compounds.<sup>18</sup> Studies of these types are ongoing in our laboratories.

(12) Magnetic susceptibilities were obtained in the 80-300 K region by using a Faraday balance (data obtained by B. van der Griendt).  $\text{Hg}[\text{Co}(\text{NCS})_4]$  was used as a calibrant.

(13) Mössbauer spectra were obtained in the temperature region 2-300 K (data obtained by A. M. van der Kraan and P. C. M. Gubbens, IRI, Delft). Disodium pentacyanonitrosyliron was used as a calibrant.

(14) Crystal data at 300 K: trigonal;  $a = 14.488$  (5) Å,  $c = 19.858$  (5) Å;  $\gamma = 120^\circ$ ;  $Z = 2$ ; space group  $P31c$ ; Mo  $K\alpha$  radiation; 992 independent nonzero [ $I < 2\sigma(I)$ ] reflections with  $2\theta$  between 4 and  $46^\circ$ ;  $R = 0.0462$ ;  $R_w = 0.0413$ . Iron atoms positions were located by a Patterson map; other atoms came from Fourier maps. Hydrogens were placed at calculated positions; non-hydrogen atoms were refined anisotropically.

(15) Crystal data at 105 K:  $a = 14.265$  (7) Å,  $c = 19.632$  (2) Å; 1112 independent nonzero reflections with  $2\theta$  between 4 and  $44^\circ$ ;  $R = 0.0638$ ;  $R_w = 0.0753$ ; other data are the same as at 300 K. Refinements started with the atomic positions of the 300 K structure.

(16) Atomic coordinates and thermal parameters are available as supplementary material. Full details of both crystal structures will be reported in a later paper,<sup>17</sup> together with a detailed analysis of the Mössbauer spectra.

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**Supplementary Material Available:** Listing of the atomic coordinates and thermal parameters (6 pages). Ordering information is given on any current masthead page.

## 2,2-Dimethylpropanethial: A Long-Lived Aliphatic Thioaldehyde

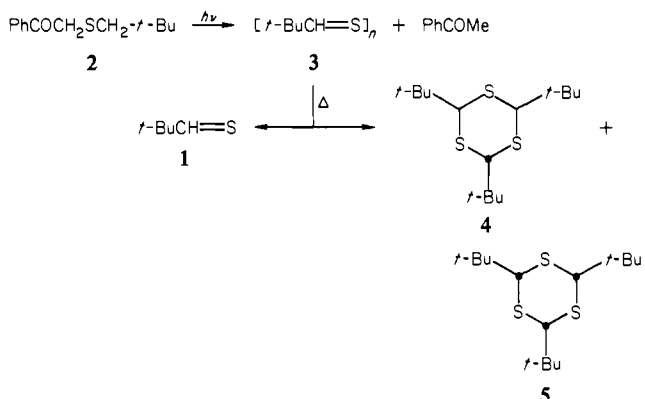
E. Vedejs\* and D. A. Perry

S. M. McElvain Laboratory of Organic Chemistry  
Chemistry Department, University of Wisconsin  
Madison, Wisconsin 53706

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Simple aliphatic thioaldehydes  $\text{RCH}=\text{S}$  have not previously been isolated or observed on the laboratory time scale due to rapid formation of trimers or polymers.<sup>1</sup> Experience gained in synthetic projects caused us to suspect that these decomposition pathways may require catalysis and that intrinsic thioaldehyde lifetimes might be greater than has been supposed. Experiments described below support this hypothesis. The surprisingly stable title compound **1** is the first aliphatic thioaldehyde known to survive in solution.

Photolysis<sup>1e</sup> of phenacyl neopentyl sulfide **2** affords an insoluble



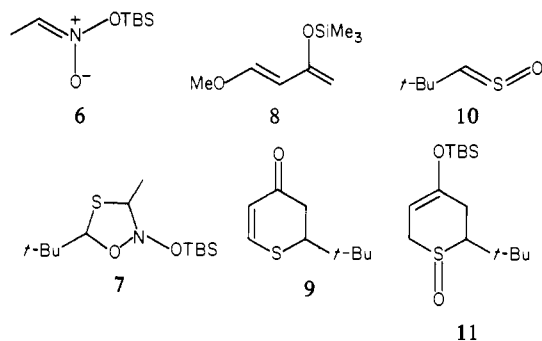
white polymer **3** together with complex minor products, but little if any thioaldehyde trimer.<sup>2</sup> Heating **3** in a simple vacuum distillation apparatus (approximately  $\geq 250^\circ\text{C}$ ) results in 2,2-dimethylpropanethial (**1**, >50% yield distilled)<sup>3</sup> together with

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(2) Neopentylmagnesium chloride in ether was treated with 1 equiv of sulfur to give 40% 2,2-dimethylpropanethiol after acid workup. Reaction with phenacyl chloride +  $\text{Et}_3\text{N}$  (THF) gave **2**, 97%. Photolysis in benzene + 5% 2,3-dimethylbutadiene gave 60% polymer **3**. Photolysis gave only 30% polymer in benzene alone and approximately 5% in THF.

(3) A simple cold trap at  $-196^\circ\text{C}$  was connected via a two-way vacuum stopcock to a container of  $\text{CHCl}_3$  or  $\text{CDCl}_3$  and a second container of polymer **3** under a plug of glass wool. Enough  $\text{CHCl}_3$  was transferred under vacuum to coat the cold trap with a film of frozen  $\text{CHCl}_3$ . The polymer was then heated with a small Bunsen flame until pink distillate appeared in the cold trap (approximately 1-2 min). Warming the distillate to  $20^\circ\text{C}$  gave a characteristic pink solution of **1**. To define the temperature for appearance of **1**, **3** was stirred with diphenyl ether and heated. A pink color appeared at approximately  $250^\circ\text{C}$ . Alternatively, a solution containing **1** (together with ethanol and some  $(\text{CH}_3)_3\text{CH}(\text{SH})\text{OC}_2\text{H}_5$ ) codistilled with xylene from  $\text{TsOH}$  catalyzed decomposition of  $(\text{CH}_3)_3\text{CH}(\text{SH})\text{OC}_2\text{H}_5$  in xylene at approximately  $140^\circ\text{C}$ . The starting material was made from  $t\text{-BuLi} + \text{S}=\text{CHOC}_2\text{H}_5$  and purified by bulb-to-bulb vacuum distillation at room temperature. This solution gives 30-40% of trapping products such as **7** or **9**.

Chart I

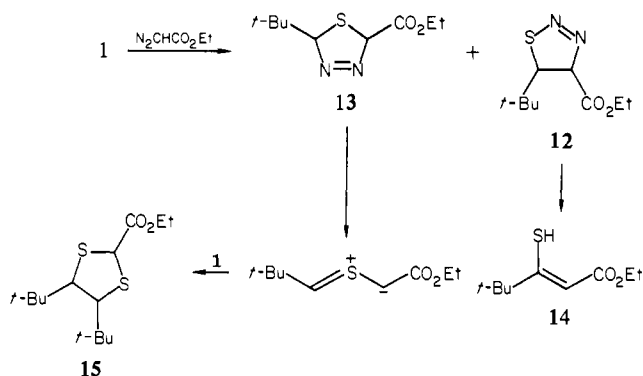


variable amounts of trimers<sup>4</sup> **4** and **5** (**4**:**5** approximately 10:1). Contrary to what might be expected from more than 100 years of unsuccessful attempts to prepare monomeric aliphatic thioaldehydes,<sup>1</sup> the pink color of **1** persists in  $\text{CHCl}_3$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CH}_2\text{Cl}_2$ , ether, etc., for as long as 16 h at 20 °C! Decomposition is accelerated approximately 5-fold by exposure to a sun lamp. Instantaneous polymerization results upon swirling a  $\text{CHCl}_3$  solution of **1** with a trace of anhydrous  $\text{ZnBr}_2$ . The lifetime of **1** in  $\text{CHCl}_3$ -ethanol (approximately 15 min) is reduced to approximately 5 min by adding  $\text{Et}_3\text{N}$  or to a few seconds by adding  $\text{HCl}$ . However, **1** is not highly air-sensitive, and solutions can be transferred without special precautions.

The spectral characteristics of **1** are in accord with expectations. Thus, a visible  $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$  508 nm ( $\epsilon$  approximately 16)<sup>5</sup> is observed in the same range as for aliphatic thioketones,<sup>6</sup> and a strong thiocarbonyl IR stretching frequency is present at  $1085\text{ cm}^{-1}$ .<sup>7</sup> The NMR spectrum has a *tert*-butyl singlet at 1.23 ppm, and the thioaldehyde proton appears at 11.67 ppm. By comparison, vinylogous dithioformates or vinylogous thioformamides have the " $-\text{CH}=\text{S}$ " signal at 10.1–11.65 ppm.<sup>8</sup> These latter compounds are often depicted with use of thioaldehyde resonance forms, but they are strongly perturbed by delocalization involving conjugated nitrogen or sulfur. The recently reported 2,4,6-tri-*tert*-butylthiobenzaldehyde has its  $-\text{CH}=\text{S}$  proton at 13.02 ppm, a chemical shift that suggests substantial deshielding by the aromatic ring.<sup>9</sup> No NMR data have been published for the parent thiobenzaldehyde<sup>10a</sup> so far, and earlier reports of possible isolation of  $\text{ArCH}=\text{S}$  ( $\text{Ar} = 2$ -ethoxy-1-naphthyl) predate methods of spectroscopic characterization.<sup>10b</sup>

Characteristic thiocarbonyl reactions are easily demonstrated by using solutions of **1**. Thus, borohydride reduction affords 2,2-dimethylpropanethiol (<1 min, 20 °C), 1,3 dipolar addition with nitronate ester **6**<sup>11</sup> gives **7**<sup>12</sup> (<1 min, 20 °C), and Diels-Alder addition with diene **8** (approximately 90 min, 20 °C) produces a single major adduct **9** after acid workup. Oxidation at -60 °C with MCPBA results in the previously characterized (*E*)-sulfine **10**,<sup>13</sup> which reacts with excess 2-(*tert*-butyldimethylsilyloxy)-1,3-

Scheme I



butadiene at 65 °C to give Diels-Alder adduct **11**.<sup>12</sup>

Reaction with ethyl diazoacetate at 20 °C (approximately 5 min) results in equal amounts of **14**<sup>12</sup> (Scheme I) and an inseparable mixture of diastereomers tentatively assigned structure **15**. Thiocarbonyl compounds are known to give either or both possible 2 + 3 cycloadduct regioisomers with diazoalkanes.<sup>14,15</sup> Assuming that both **12** and **13** are formed initially, isolation of **14** can be explained by S-N heterolysis of **12** and subsequent hydride transfer. The other products would arise by well-precedented steps via thiocarbonyl ylide formation from **13**.<sup>15,16</sup>

Finally, treatment of **1** in ether with  $\text{C}_6\text{H}_5\text{Li}$  affords neopentyl phenyl sulfide, the product of thiophilic addition, and traces of mercaptan. Thioketones are known to react with organolithium reagents at both carbon and sulfur,<sup>1</sup> and one previous report mentions predominant carbon attack on less hindered aliphatic thioaldehydes generated *in situ*.<sup>17</sup>

Simple thioaldehydes are well-known as transient products from flash photolysis or pyrolysis in the gas phase or in matrix isolation experiments.<sup>1,18</sup> Thioformaldehyde can even be regarded as a product of nature since it persists in interstellar space.<sup>19</sup> Many other thioaldehydes have been proposed as short-lived intermediates in chemical reactions.<sup>20</sup> In view of the stability of **1**, it seems likely that many of the transient species will be found to have reasonable solution lifetimes if decomposition catalysts can be excluded.

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**Supplementary Material Available:** Spectral data for **7**, **9**, **11**, and **14** (1 page). Ordering information if given on any current masthead page.

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(5) To estimate the concentration of **1** in solution, nitronate ester **6** was added and the excess **6** estimated by NMR spectroscopy. Values of  $\epsilon$  were calculated by assuming a quantitative yield for  $\mathbf{1} \rightarrow \mathbf{7}$ . This is reasonable since photolysis of **2** with **6** present gives **7** in >90% yield.

(6) Reference 1c, p 376.

(7) Assignment based on decrease of  $1085\text{-cm}^{-1}$  peak intensity with time.

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(11) Prepared by the method of Calvin et al. (Calvin, E. W.; Beck, A. K.; Bastani, B.; Seebach, D.; Kai, Y.; Dunitz, J. D. *Helv. Chim. Acta* **1980**, *63*, 697), bp 50–60 °C, bulb-to-bulb distillation at 0.4 mmHg.

(12) Structure based on NMR, IR, and exact mass spectra; see supplementary material for data; no other significant products detected if not specified in text.

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(16) A trace of ethyl 4,4-dimethylpen-2-enoate, the expected episulfide decomposition product, is also formed.

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