Synthesis, Structure, and Some Reactions of (2,4,6-Tri-*t*-butyl)thiobenzaldehyde, the First Stable Aromatic Thioaldehyde

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The title compound **1** was synthesized by the reaction of 2,4,6-tri-*t*-butylphenyllithium with *O*-ethyl thioformate or that of 2,4,6-tri-*t*-butylbenzaldehyde hydrazone with disulfur dichloride in the presence of triethylamine. The thioaldehyde **1** is a purple crystalline compound which is thermally quite stable; only around 200 °C it underwent intramolecular cyclization to give 6,8-di-*t*-butyl-3,4-dihydro-4,4-dimethyl-1*H*-2-benzothiopyran **9**. The X-ray crystallographic analysis of **1** revealed that the thioformyl group is almost perpendicular to the aromatic ring. The reaction of **1** with 1-cyano-1-methylethyl radicals afforded **9**, while that with *t*-butyl radicals gave 1,3,5-tri-*t*-butyl-2-*t*-butylthiomethylbenzene and *t*-butyl 2,2-dimethyl-1-(1,3,5-tri-*t*-butylbicyclo[2.2.0]hexa-2,5-dien-2-yl)propyl sulfide in addition to **9**. Some Grignard reagents and organolithiums reacted with **1** gave carbophilic, thiophilic, double addition products and some others depending on the kind of the organometallic reagents. Hydrazine and butylamine reacted with **1** very readily to give the corresponding hydrazone and imine, respectively.

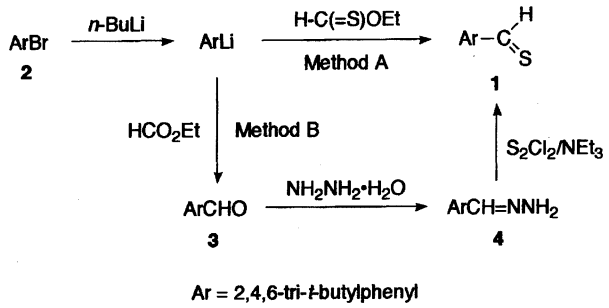
The chemistry of thioketones has been studied extensively in recent years because of their unique and interesting properties, which are sometimes quite different from those of ketones.[1] Conversely, thioaldehydes which are much more reactive than thioketones have eluded isolation until recently. If a thioformyl group is connected, directly or through a conjugate system, with heteroatoms such as nitrogen, oxygen, and sulfur, it is remarkably stabilized by the mesomeric effect of heteroatoms.[2]

During the course of our study on sterically congested molecules,[3] we became interested in the kinetic stabilization of a highly reactive thioformyl group by steric protection due to bulky groups. This paper is a detailed account of the synthesis, structure, and some reactivities of (2,4,6-tri-*t*-butyl)thiobenzaldehyde (**1**), the first kinetically stabilized thiobenzaldehyde.[4] Since our communication on the first stable thioaldehyde **1**,[4] a couple of stable thioaldehydes have been reported.[5]

Results and Discussion

Synthesis. The synthesis of (2,4,6-tri-*t*-butyl)thiobenzaldehyde (**1**) was accomplished by methods A and B shown in Scheme 1, starting from 1-bromo-2,4,6-tri-*t*-butylbenzene (**2**).

The reaction of the bromobenzene **2** with butyllithium, followed by addition of *O*-ethyl thioformate at −78 °C in tetrahydrofuran, afforded thioaldehyde **1** in 56% yield (Method A).



Scheme 1.

A similar reaction using ethyl formate instead of *O*-ethyl thioformate gave 2,4,6-tri-*t*-butylbenzaldehyde (**3**) (47%), which was converted to the corresponding hydrazone **4** in 79% by treatment with hydrazine monohydrate. The reaction of the hydrazone **4** with disulfur dichloride led to the formation **1** in 40% yield (Method B). This method of oxidative sulfurization of a hydrazone into a thiocarbonyl compound is an application of the synthetic methodology for thioketones previously developed by us.[6] It is noteworthy that a highly reactive thioaldehyde can be synthesized by using a reactive organolithium reagent. This is obviously because very bulky ArLi (Ar denotes 2,4,6-tri-*t*-butylphenyl in this paper) cannot attack thioaldehyde **1**, which is also very much congested.

Structure. The X-ray crystallographic analysis was

performed for **1** recrystallized from oxygen free methanol. The ORTEP drawing is shown in Fig. 1. The relevant crystal and structural data are listed in Tables 1, 2, and 3. This represents the first example for the crystallographic analysis of a thioaldehyde.[7]

The thioformyl group is almost perpendicular (89.8(3)°) to the aromatic ring because of steric repulsion caused by two *o*-*t*-butyl groups, being efficiently protected by the bulky substituents.

The length of the C=S bond is 1.602(5) Å, which is between those of **5** (**5a**: 1.588(11) Å, **5b**: 1.602(7) Å)[5d] and *p*,*p*′-dihydroxythiobenzophenone (1.647 Å; X-ray crystallography) (Chart 1).[8] This is most likely interpreted in terms of the conjugation between the C=S bond and the aromatic ring and/or *p*-hydroxyl groups. Thus, the thioformyl group of **1** is almost perpendicular to the aromatic ring as mentioned above, while those of **5** can conjugate with the aromatic ring to some extent, judging from the dihedral angles of their thioformyl groups and the aromatic rings (**5a**: 48.7°, **5b**: 10.6°). In the case of *p*,*p*′-dihydroxythiobenzophenone, a large mesomeric effect involving the *p*-hydroxyl groups is reasonably expected. The calculated C=S bond length (1.599 Å) for thioformaldehyde[9] is close to those of **1** and **5**.

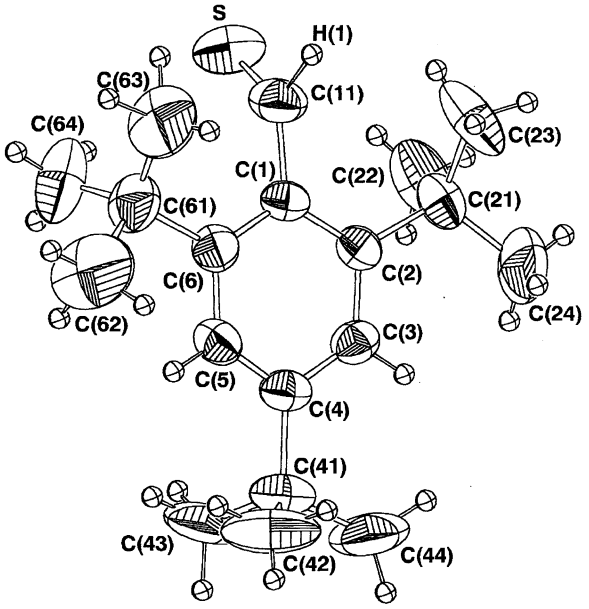


Fig. 1. ORTEP drawing with the atom-numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å.

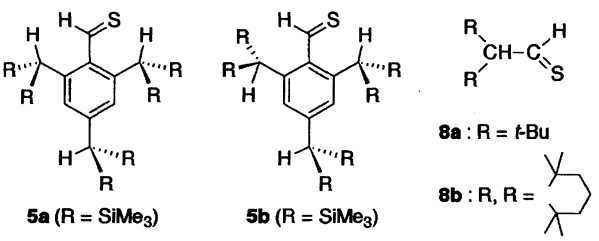


Chart 1.

Table 1. Crystal Data, Details of Data Collection and Structure Refinement

	$C_{19}H_{30}S$
Color	Purple
Crystal shape	Needles
Crystal size /mm	0.3 × 0.3 × 0.2
M_w	290.51
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.948(2)
b/Å	10.356(1)
c/Å	10.559(2)
α/°	90.22(2)
β/°	90.35(2)
γ/°	120.10(1)
V/Å^3	941.1(2)
Z	2
D_X/Mg m^{-3}	1.025
Radiation	Cu $K\alpha$
λ/Å	1.54178
μ/mm^{-1}	1.391
F(000)	320
For cell parameters	
2θ range/°	37.5—78.1
No. of reflections	22
Scan range 2θ/°	2—130
Scan width $\Delta\omega$/°	1.1+0.5tanθ
Scan speed 2θ/° min^{-1}	4
Scan mode	2θ–ω
Monitored reflections (every 50 reflections)	6 −3 0, −1 1 −5, 0 4 0
Variation of intensities	0.971—1.000
Range of h, k, l	−11—11, 0—12, −12—12
Time for background/s	10
No. of reflections	
Measured	3563
Observed ($\|F_o\| > 3\sigma(F)$)	2668
R for 2667 refined refs.[a]	0.086
wR[b]	0.140
R for 2668 observed refs.	0.088
s	1.213
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	−0.517, 0.275
$(\Delta/\sigma)_{max}$	0.046

a) The reflection, −2 1 0, which was considered to be affected by an extinction effect was omitted from refinement.
b) $w=\{\sigma^2(F_o)+0.04529|F_o|+0.00417|F_o|^2\}^{-1}$.

Spectroscopic Properties. NMR and electronic spectral data for stable thioaldehydes **5**—**8** so far reported[5] are listed in Table 4, along with those for **1**.

a) Electronic Spectra. The thioaldehyde **1** is a purple crystalline compound and shows its n→π* absorption in the electronic spectrum at 564 nm (ε 19) in hexane and 552 nm (ε 19) in ethanol. These absorptions are clearly more red-shifted than those of aliphatic thioaldehydes **6**—**8**, but slightly blue-shifted compared with those of aromatic thioaldehydes **5** and thioketones (e.g., thiobenzophenone 600 nm[1a]). The blue shift of **1** can be interpreted in terms of the orthogonality of its thioformyl group to the aromatic ring, as shown in the X-ray structural analysis.

Table 2. Positional Parameters and Equivalent Isotropic Temperature Factors (B_{eq})[c] for Non-H Atoms

Atom	x	y	z	B_{eq}/Å^2
S	−0.1013(1)	0.1382(1)	0.4749(1)	7.27(5)
C(1)	0.1778(3)	0.3656(3)	0.3897(3)	3.70(10)
C(2)	0.2518(3)	0.4942(3)	0.4684(3)	3.64(10)
C(3)	0.3221(4)	0.6327(3)	0.4095(3)	3.98(10)
C(4)	0.3271(4)	0.6499(3)	0.2804(3)	4.05(10)
C(5)	0.2614(4)	0.5209(4)	0.2071(3)	4.25(11)
C(6)	0.1882(4)	0.3784(3)	0.2571(3)	4.03(11)
C(11)	0.0805(5)	0.2140(4)	0.4462(3)	5.28(14)
C(21)	0.2569(4)	0.4897(4)	0.6140(3)	4.84(14)
C(22)	0.1113(6)	0.4784(7)	0.6688(4)	7.59(26)
C(23)	0.2813(8)	0.3650(8)	0.6633(4)	8.47(32)
C(24)	0.3953(8)	0.6351(8)	0.6662(5)	10.14(29)
C(41)	0.4028(5)	0.8039(4)	0.2179(4)	5.49(14)
C(42)[a]	0.5209(10)	0.8176(8)	0.1235(9)	9.36(33)
C(43)[a]	0.2770(8)	0.8220(8)	0.1552(9)	9.23(32)
C(44)[a]	0.4815(14)	0.9305(7)	0.3168(8)	11.40(43)
C(61)	0.1202(5)	0.2443(5)	0.1620(4)	5.75(15)
C(62)	0.2032(10)	0.2968(8)	0.0331(5)	11.34(35)
C(63)	0.1457(9)	0.1192(6)	0.2050(6)	9.39(30)
C(64)	−0.0485(7)	0.1908(8)	0.1375(6)	9.43(28)
C(45)[b]	0.563(3)	0.891(3)	0.259(2)	9.3(6)
C(46)[b]	0.312(3)	0.880(3)	0.248(3)	9.9(6)
C(47)[b]	0.400(3)	0.785(3)	0.064(3)	9.3(6)

Multiplicity: a) 0.75, b) 0.25, c) $B_{eq} = 4/3 \sum_i \sum_j \beta_{ij} \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

b) NMR Spectra. The chemical shift of the thioformyl proton in ^{1}H NMR appears at $\delta = 13.02$; this is the lowest value among thioformaldehydes so far reported. The lower chemical shift of the thioformyl proton of **1** than that of the corresponding aldehyde ArCHO ($\delta = 10.38$) indicates the higher anisotropy of a C=S group than that of a C=O group, which has already been reported in ^{1}H and ^{13}C NMR for some thiocarbonyl compounds.[10] It is interesting that the ^{13}C chemical shift for **1** is closer to those for aliphatic thioaldehydes **6**—**8** rather than to those for aromatic ones **5**. This is again due to the orthogonality of the thioformyl group, which prevents its conjugation with the aromatic ring.

Reactions. a) Thermal and Photochemical Reactions. The thioaldehyde **1** is very stable; it can be stored in the solid state at room temperature for a long time (several years) without any appreciable change. In solution it is stable in refluxing benzene over two weeks in the absence of oxygen, whereas it is slowly converted into the corresponding aldehyde in the presence of oxygen even at room temperature.

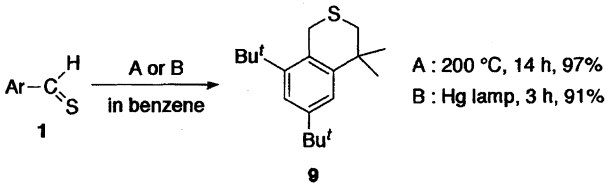
Table 3. Selected Bond Lengths (Å) and Angles (°)

Lengths			
S–C(11)	1.602(5)	C(3)–C(4)	1.373(4)
C(1)–C(2)	1.417(4)	C(4)–C(5)	1.386(4)
C(1)–C(6)	1.406(4)	C(4)–C(41)	1.534(5)
C(1)–C(11)	1.499(4)	C(5)–C(6)	1.385(5)
C(2)–C(3)	1.393(4)	C(6)–C(61)	1.560(5)
C(2)–C(21)	1.539(4)		
Angles			
C(2)–C(1)–C(6)	120.7(3)	C(3)–C(4)–C(41)	122.4(3)
C(2)–C(1)–C(11)	120.5(3)	C(5)–C(4)–C(41)	120.6(3)
C(6)–C(1)–C(11)	118.8(3)	C(4)–C(5)–C(6)	123.7(3)
C(1)–C(2)–C(3)	117.4(3)	C(1)–C(6)–C(5)	117.5(3)
C(1)–C(2)–C(21)	124.1(3)	C(1)–C(6)–C(61)	124.9(3)
C(3)–C(2)–C(21)	118.5(3)	C(5)–C(6)–C(61)	117.6(3)
C(2)–C(3)–C(4)	123.5(3)	S–C(11)–C(1)	124.8(3)
C(3)–C(4)–C(5)	117.0(3)		

Upon heating at higher temperatures (ca. 200 °C) in a degassed benzene solution, **1** undergoes an interesting intramolecular cyclization involving its thioformyl group to give dihydrobenzothiopyran **9** almost quantitatively (Scheme 2). This cyclization most likely proceeds through a radical mechanism, in view of the facile cyclization to the same dihydrobenzothiopyran **9** in the reaction with radicals (see **b**) below). Although the detailed mechanism is not clear, the reaction is considered to proceed via the mechanism shown in Scheme 3a.

The photolysis of **1** also gives **9** in a good yield.

b) Reactions with Radicals.[11a] Thioketones are known to react with radicals at the sulfur atom to give persistent carbon radicals as the initial products, which can be detected by

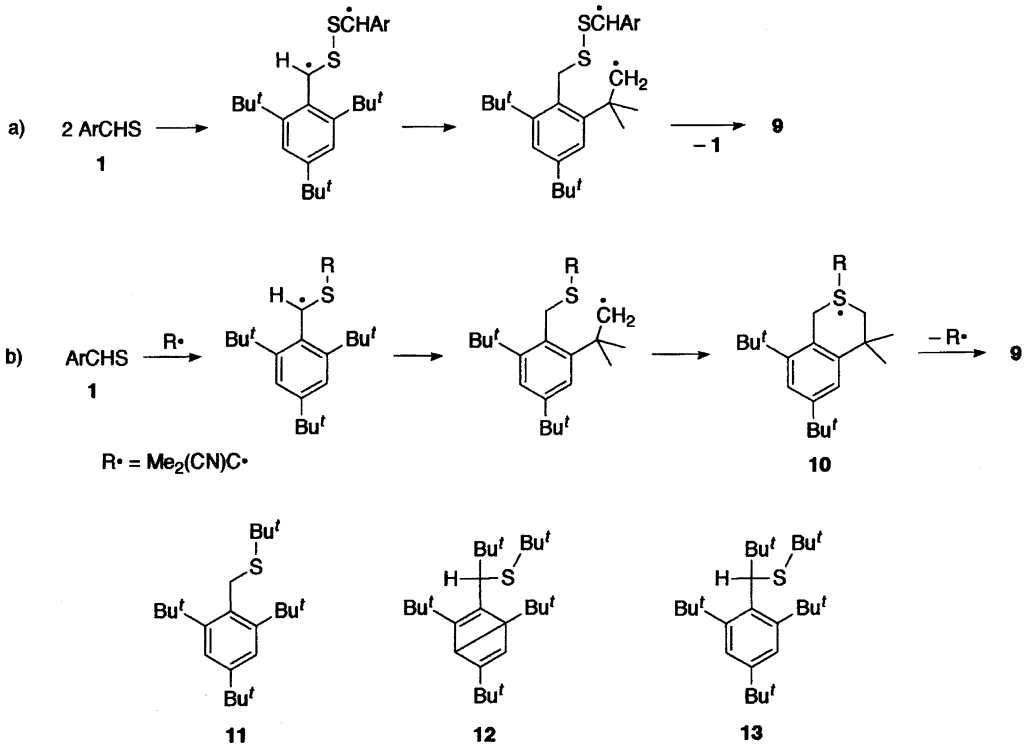


Scheme 2.

Table 4. Spectral Data of **1** and Some Other Stable Thioaldehydes

	^{1}H NMR/δ	^{13}C NMR/δ	VIS/nm	
Thioaldehyde	*H*–C=S	H–*C*=S	(n→π*)	Ref.
1	13.02	250.4	564,[a] 552[b]	This work
5a	12.05	243.1	587[a]	5d
5b	11.77	229.8	604[a]	5d
t-BuCHS (**6**)	11.45	248.4	518,[a] 503[b]	5a
$(Me_3Si)_3CCHS$ (**7**)	11.67	255.6	508[c]	5b
8a	11.58	253.8	536[d]	5c
8b	11.65	255.3	529[d]	5c

a) In hexane. b) In ethanol. c) In acetonitrile. d) Not specified.



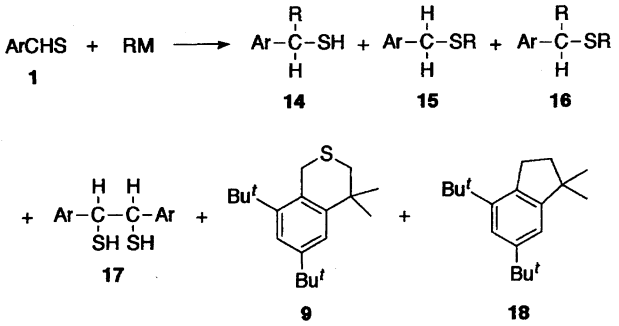
Scheme 3.

ESR spectroscopy (spin-trapping technique).[12] Tsuchihashi and his co-workers reported that the reaction of thiobenzophenone with 1-cyano-1-methylethyl radicals generated from azobisisobutyronitrile (AIBN) gave a C, S double adduct of the radical.[13] In view of these precedents for thioketones, we became interested in the reaction of radicals with the thioaldehyde **1**.

Interestingly, the reaction of **1** with the 1-cyano-1-methylethyl radical afforded the dihydrobenzothiopyran **9**. The mechanism for the formation of **9** in this reaction is considered to begin with an attack of the radical at the sulfur atom (Scheme 3b). Since the 1-cyano-1-methylethyl radical is relatively stable, it is expelled from the intermediate radical **10**. According to this mechanism, the cyclization is a catalytic process in principle, but the reaction actually required a large excess of AIBN, because most of 1-cyano-1-methylethyl radicals generated from AIBN underwent dimerization and disproportionation. In the reaction with *t*-butyl radical, a less stable radical, which was generated by photolysis of 2,2′-dimethyl-2,2′-azopropane, sulfides **11** (17%) and **12** (30%), was formed in addition to **9** (20%). The Dewar benzene **12** is a secondary product derived from **13**, since a separate photoreaction of **13**, obtained by the reaction of **1** with *t*-butylmagnesium chloride (vide infra), resulted in the quantitative formation of **12**. Arenes bearing bulky substituents are known to give Dewar benzene derivatives upon photolysis.[14]

c) Reactions with Grignard and Organolithium Reagents.[11b] Since reactions of thiocarbonyl compounds with organometallic reagents RM (M = Li, MgX; X = halogens) have been reported to give a variety of compounds via a mechanism different from those for carbonyl compounds, thioaldehyde **1** was allowed to react with some Grignard and organolithium reagents. The results are summarized in Scheme 4 and Table 5.

Reactions with ethyl and isopropylmagnesium bromides gave thiophilic products **15**,[16] whereas those with phenyl and benzyl Grignard reagents mainly afforded carbophilic products **14**. It is interesting that reactions with benzyl and *t*-butyl Grignard reagents gave double addition products **16** as well as dithiol **17**. When a very bulky organometallic like $ArCH_2MgBr$ was used, the benzothiopyran **9** was a main product, no addition products like **14**—**16** were formed, most likely for steric reasons. While the reaction of phenylmagnesium bromide in ether afforded both carbophilic and thiophilic products (**14** and **15**), that in THF gave only thiophilic product **15**, probably because of stronger solvation in THF which leads to an increase of steric bulk of the reagent. Although a complete mechanistic interpretation of these reactions for **1** is rather difficult because of the presence of many



Scheme 4.

Table 5. Reactions of **1** with Grignard and Organolithium Reagents

RM			Products/%					
(M = MgX or Li)	Solv	Temp[a)]	**14**	**15**	**16**	**17**	**9**	**18**
MeMgI	Ether	RT		53		21		
EtMgBr	Ether	RT		82				
i-PrMgBr	Ether	RT		80				
PhMgBr	Ether	RT	43	38				
PhMgBr	Ether	Reflux	58	15				
PhMgBr	THF	RT		91				
$PhCH_2MgCl$	Ether	RT	50		12	21		
t-BuMgCl	Ether	0 °C		27	13	31		
t-BuMgCl	Ether	RT		32	12	35	5	
t-BuMgCl	Ether	Reflux		18	14	26	10	
t-BuMgCl	THF	0 °C		25	7	19		
$ArCH_2MgBr$	Ether	RT					65	
MeLi	Ether	RT		46		39		
t-BuLi	Ether	RT	7	23	11	12		24[b)]
Me_3SiLi	THF	−78 °C	85					
PhLi	Ether	RT		97				

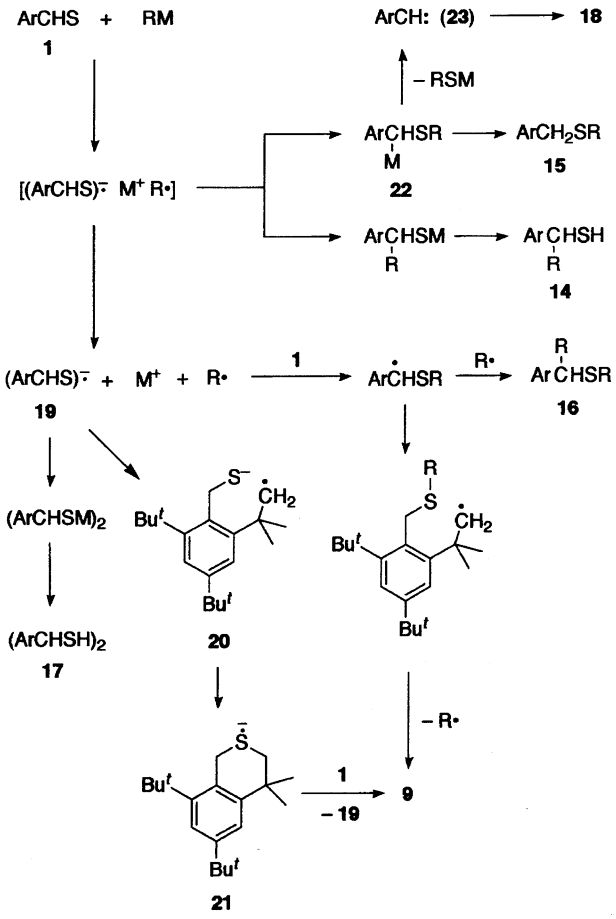
a) RT denotes room temperature. b) The structure of **18** was identified by comparison of the spectroscopic data with those of the literature.[15)]

factors affecting the mechanism, the formation of these reaction products is reasonably explicable in terms of a single electron transfer (SET) mechanism, as depicted in Scheme 5. A similar SET mechanism was proposed for the reactions of thioketones with organometallic compounds.[17)]

Anion radical **19** formed by SET from the organometallics recombines with a radical R· in the solvent cage to give **14** or **15** in the cases of common organometallic reagents, although the reason for the preferential formation of carbophilic products in the reactions with benzyl and phenyl reagents is not clear at present. In the reactions with benzyl and *t*-butyl reagents, however, radicals R· formed from RM are stable enough to escape from the solvent cage, leaving the anion radical $ArCHS^{-\cdot}$ (**19**). The radicals R· thus formed react with **1** to afford a double-addition product **16**, while the anion radical **19** dimerizes to give **17** after work up. It is noteworthy that the present dimerization of **19** represents the first example of the dimerization of thioketyl radicals.

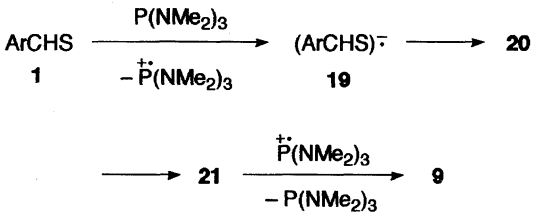
The fact that **9** and **18** were formed only in the reactions with bulky reagents RM (R=*t*-Bu, $ArCH_2$) can be interpreted as follows. The coupling of **19** with a bulky radical R· is so slow that **19** undergoes intramolecular cyclization via **20** and **21**, the latter of which is oxidized by **1** to give **9**, with **19** being regenerated. The formation of **18** is reasonably explained in terms of intramolecular cyclization of carbene **23** produced by α-elimination of bulky *t*-BuSLi from a thiophilic intermediate **22**. There has been reported a similar α-elimination leading to a carbene in the reaction of bulky di-*t*-butyl thioketone.[17c)]

In connection with the SET mechanism for the formation of **9** in the above reactions with organometallics, it is of great interest that the reaction of the thioaldehyde **1** in the presence of a catalytic amount of hexamethylphosphorous triamide also gave **9** in 87% yield. This catalytic transformation is most reasonably interpreted in terms of an SET mechanism very similar to that described above for the reactions with organometallics (Scheme 6).

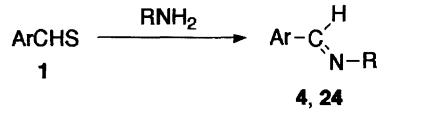


Scheme 5.

d) Reactions with Amino Compounds. In view of well known reactivities of aldehydes with a variety of amino compounds, it is interesting to study the reactivity of **1** with such compounds. The results are summarized in Scheme 7.



Scheme 6.



R = NH_2	EtOH, 0 °C, 5 min	**4**, 88%
R = *n*-Bu	PhH, 70 °C, 1 h	**24**, 96%
R = Ph	Xylene, reflux, 9 h	no reaction

Scheme 7.

Reaction of hydrazine monohydrate with **1** was completed at 0 °C within several minutes to give the corresponding hydrazone **4**, whereas that with the corresponding aldehyde ArCHO required heating at 180 °C for 5 d. Similarly, the reaction of butylamine with ArCHO did not occur at all in refluxing benzene, while that with **1** proceeded at 70 °C within 1 h to give imine **24**. These facts clearly indicate that the reactivity of a thioformyl group is much more enhanced than that of a formyl group, in keeping with much lower LUMO level for the former group.[18]

The reaction of **1** with aniline did not proceed even under more forced conditions (xylene reflux, 9 h).

e) Reduction. Thiobenzaldehyde **1** was easily reduced with lithium aluminum hydride to give the corresponding thiol, $ArCH_2SH$ (92%).

Experimental

^{1}H NMR spectra were measured with a Hitachi R-24B, JEOL FX-90Q, JEOL GX-270, or Bruker AM-500 spectrometer, using tetramethylsilane as an internal standard. ^{13}C NMR spectra were measured with a JEOL FX-90Q or Bruker AM-500 spectrometer using tetramethylsilane as an internal standard. These spectra were taken in $CDCl_3$ unless otherwise noted. Infrared spectra were measured with a Hitachi 260-30 spectrometer. Ultraviolet and visible spectra were taken on a Hitachi 340 spectrometer. Mass and high resolution mass spectra were measured with a JEOL JMS-D300 or JEOL DX-303 mass spectrometer. Preparative liquid chromatography (HPLC) was carried out using LC-08 with JAIGEL 1H+2H columns (Japan Analytical Industry) with chloroform as solvent. Dry column chromatography (DCC) was carried out with ICN silica DCC 60A. For flash chromatography Merck Kieselgel 60 Art 9385 was used. Preparative thin layer chromatography (PTLC) was carried out using Merck Kieselgel 60 PF254 Art 7747. THF and ether were purified by distillation from sodium diphenyl ketyl under an argon atmosphere. Benzene and dichloromethane used in the reactions as solvents were purified by reflux and distillation from calcium hydride. All the reactions were carried out under an argon atmosphere.

Synthesis of (2,4,6-Tri-*t*-butyl)thiobenzaldehyde (1). Method A. 1-Bromo-2,4,6-tri-*t*-butylbenzene[19] (13.0 g, 40 mmol) in 150 ml of THF was allowed to react with *n*-BuLi (52 mmol, 1.2 molar amount in hexane) at −78 °C for 30 min, and to this solution was added *O*-ethyl thioformate (4.5 ml, 52 mmol) during 50 min. The temperature was gradually raised to room temperature; after being stirred for an additional hour, the solution was quenched with saturated aq ammonium chloride. After the solvent was removed, the residue was subjected to DCC (SiO_2, hexane–ether 20 : 1) to give a purple fraction, which was crystallized from degassed methanol to afford thioaldehyde **1** as purple crystals. Mp 146.0—147.0 °C; ^{1}H NMR (CCl_4) δ = 1.30 (s, 9H), 1.32 (s, 18H), 7.22 (s, 2H), and 13.02 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 31.3, 32.9, 34.8, 37.0, 121.8, 145.1, 145.6, 149.5, and 250.4; UV/vis (EtOH) 340 (ε 1690) and 552 nm (19); UV/vis (hexane) 338 (ε 1850) and 564 nm (19). Calcd for $C_{19}H_{30}S$: C, 78.55; H, 10.41; S, 11.04%. Found: C, 78.76; H, 10.45; S, 11.19%.

Method B.

(a) Synthesis of 2,4,6-Tri-*t*-butylbenzaldehyde (3). The benzaldehyde **3** was synthesized in a way similar to **1** from 1-bromo-2,4,6-tri-*t*-butylbenzene (8.12 g, 25.0 mmol), butyllithium (30 mmol), and ethyl formate (5.6 ml, 69 mmol). The crude products were purified by DCC (SiO_2, ether–hexane 30 : 1) to give the aldehyde (3.23 g, 47%). Mp 197.5—198.5 °C (from methanol); ^{1}H NMR ($CDCl_3$) δ = 1.32 (s, 9H), 1.36 (s, 18H), 7.37 (s, 2H), and 11.11 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 31.3, 32.6, 35.1, 36.6, 121.4, 137.2, 147.4, 150.8, and 202.7. Calcd for $C_{19}H_{30}O$: C, 83.14; H, 11.03%. Found: C, 83.02; H, 11.20%.

(b) Synthesis of 2,4,6-Tri-*t*-butylbenzaldehyde hydrazone (4). The benzaldehyde **3** (1.00 g, 3.67 mmol) and hydrazine hydrate (5.68 g, 114 mmol) were dissolved in a mixture of ethanol (8 ml) and diethylene glycol (20 ml). After the solution was heated at 180 °C for 5 d, it was poured into ice water to give white precipitates, which were filtered off. The filtrate was extracted with dichloromethane three times. The precipitates were dissolved into the extract and the solution thus obtained was dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was purified by DCC (SiO_2, dichloromethane) to give the hydrazone **4** (0.967 g, 91%), which was further purified by crystallization from aq ethanol to give white needles (0.838 g, 79%). Mp 122.0—125.0 °C; ^{1}H NMR ($CDCl_3$) δ = 1.32 (s, 9H), 1.37 (s, 18H), 4.9 (br s, 2H), 7.39 (s, 2H), and 8.04 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 31.4, 32.5, 35.0, 37.1, 121.5, 131.0, 147.0, 149.3, and 149.6. Calcd for $C_{19}H_{32}N_2$: C, 79.09; H, 11.19; N, 9.72%. Found: C, 78.92; H, 11.29; N, 9.95%.

(c) Synthesis of 1. To a toluene solution (5 ml) of triethylamine (0.33 ml, 2.4 mmol) was added dropwise at −78 °C toluene solutions (3 ml each) of hydrazone **4** (289 mg, 1.0 mmol) and disulfur dichloride (80 μl, 1 mmol) simultaneously over 15 min. After completion of the addition, the solution was stirred for 30 min and then quenched with water. Ether was added to the solution and the purple ether extract was dried over anhydrous magnesium sulfate. The ether was evaporated and the residue was subjected to DCC (SiO_2, hexane) to give **1** (116 mg, 40%) and **3** (22.3 mg, 8%).

Thermal Reaction of 1. A benzene solution (5 ml) of **1** (870 mg, 3.0 mmol), which was degassed by three freeze-thaw cycles, was heated in a sealed tube at 200 °C for 12 h, after which time the solution turned slightly brown. After removal of the solvent, the reaction products were recrystallized from methanol to afford 6,8-di-*t*-butyl-3,4-dihydro-4,4-dimethyl-1*H*-2-benzothiopyran (**9**) (890 mg, 95%). Mp 174.0—174.5 °C; ^{1}H NMR (CCl_4) δ = 1.27 (s, 9H), 1.41 (s, 15H), 2.61 (s, 2H), 3.82 (s, 2H), 7.10 (s, 2H); MS *m/z* 290 (M^+; 22), 275 (22), 229 (23), and 57 (100). Calcd for $C_{19}H_{30}S$: C, 78.55, H, 10.41; S, 11.04%. Found: C, 78.15; H, 10.18; S, 11.03%.

Photolysis of 1. (a) A degassed benzene solution (15 ml) of

1 (441 mg, 1.52 mmol) in a sealed Pyrex tube was irradiated by a 100 W medium pressure Hg lamp at about 10 °C for 8 h, during which time the purple solution became colorless. After removal of the solvent, the residue was chromatographed over silica gel (hexane–ether 20 : 1) to give **9** (401 mg, 1.38 mmol, 91%).

(b) A degassed benzene solution (15 ml) of **1** (444 mg, 1.53 mmol) was irradiated by sodium lamps (16 W×4) for 24 h at room temperature. Treatment of the reaction mixture in a way similar to the above photoreaction gave **9** (428 mg, 1.87 mmol, 96%).

Reaction of 1 with Radicals. (a) A degassed benzene solution (20 ml) of **1** (582 mg, 2.01 mmol) was refluxed under argon, and to this solution was added 2,2′-azobisisobutyronitrile in four fractions during 4 h, the total amount being 578 mg (3.52 mmol). The benzene was evaporated from the colorless reaction mixture, and the residue was heated under reduced pressure (ca. 15 mmHg, 1 mmHg = 133.322 Pa) at about 80 °C to sublime most of the 2,3-dicyano-2,3-dimethylbutane. The reaction products were purified by DCC (SiO_2, hexane–ether 10 : 1) to give **9** (454 mg, 81.3%).

(b) Benzene (80 ml) was refluxed while nitrogen was being bubbled and then the mixture was cooled to room temperature. 2,2′-Dimethyl-2,2′-azopropane (2.15 g, 15.1 mmol) was added to the solution, which was irradiated by a 100 W Hg lamp at about 10 °C for 3 h. After the solvent was removed, the residue was purified by DCC (SiO_2, hexane–ether 10 : 1) to give **9** (118 mg, 20.3%), 1, 3,5-tri-*t*-butyl-2-(*t*-butylthiomethyl)benzene (**11**) (117 mg, 16.7%), and *t*-butyl 2,2-dimethyl-1-(1,3,5-tri-*t*-butylbicyclo[2.2.0]hexa-2,5-dien-2-yl)propyl sulfide (**12**) (243 mg, 30.0%).

11: Mp 113.5—115.5 °C; ^{1}H NMR (CCl_4) δ = 1.26 (s, 9H), 1.34 (s, 9H), 1.50 (s, 18H), 4.13 (s, 2H), and 7.14 (s, 2H). MS *m/z* 348 (M^+; 2), 259 (16), and 57 (100). Calcd for $C_{23}H_{40}S$: C, 79.04; H, 11.67; S, 9.28%. Found: C, 79.25; H, 11.72; S, 9.02%.

12: Mp 78.0—79.0 °C; ^{1}H NMR (CCl_4) δ = 0.96 (s, 9H), 1.02 (s, 9H), 1.06 (s, 9H), 1.17 (s, 9H), 1.31 (s, 9H), 3.11 (d, J = 1.5 Hz, 1H), 3.57 (s, 1H), and 6.03 (d, J = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 27.3 (q), 29.2 (q), 29.4 (q), 30.5 (q), 32.0 (q), 32.6 (s), 32.8 (s), 34.4 (s), 36.5 (s), 43.5 (s), 45.8 (d), 51.1 (d), 60.9 (s), 133.9 (d), 144.2 (s), 151.5 (s), and 160.2 (s); MS *m/z* 347 ($M^+ - t$-Bu; 10), 235 (39), and 57 (100). Calcd for $C_{27}H_{48}S$: C, 80.11; H, 11.98, S, 7.93%. Found: C, 80.29; H, 12.07; S, 7.71%.

Reaction of 1 with Grignard and Organolithium Reagents. The reactions were conducted in ether or THF under the reaction conditions listed in Table 5. Grignard reagents were prepared from the corresponding halides just before use. Methyl-, *t*-butyl-, and phenyllithiums were commercial products and were used as purchased. 2,4,6-Tri-*t*-butylphenyllithium was prepared by the reaction of 1-bromo-2,4,6-tri-*t*-butylbenzene with butyllithium, while trimethylsilyllithium was synthesized by a literature method.[20]

The reaction with ethylmagnesium bromide is described as a typical example. To an ethereal solution (10 ml) of ethylmagnesium bromide prepared from bromoethane (0.37 ml, 5 mmol) and magnesium (0.12 g, 6 mmol) was added an ether solution (10 ml) of **1** (293 mg, 1.0 mmol) at room temperature over 1 h. After an additional 1 h, the reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl. The organic layer was washed with water three times, dried over anhydrous $MgSO_4$, and the solvent was removed. The crude reaction products were purified with DCC (SiO_2, hexane) and then PTLC (SiO_2, hexane) to give **15** (R = Et) (218 mg, 0.68 mmol, 82%).

15 (R = CH_3): Mp 90—91 °C; ^{1}H NMR δ = 1.29 (s, 9H), 1.55 (s, 18H), 2.05 (s, 3H), 4.23 (s, 2H), and 7.34 (s, 2H); ^{13}C NMR δ = 16.4, 31.4, 33.4, 34.8, 36.5, 37.7, 122.9, 131.7, 147.8, and 149.2; IR 1360, 1640, and 2950 cm^{-1}; MS *m/z* 306 (M^+; 8), 259 (30), and 57 (100). Calcd for $C_{20}H_{34}S$: C, 78.36; H, 11.18; S, 10.46%. Found: C, 78.40; H, 11.13; S, 10.71%.

15 (R = Et): Mp 69—70 °C; ^{1}H NMR δ = 1.28 (t, J = 7.4 Hz, 3H), 1.29 (s, 9H), 1.55 (s, 18H), 2.56 (q, J = 7.4 Hz, 2H), 4.27 (s, 2H), 7.34 (s, 2H); ^{13}C NMR δ = 14.4, 27.7, 31.4, 33.5, 34.4, 34.8, 37.8, 123.0, 131.6, 147.6, and 149.0; IR (KBr) 880, 1360, and 2960 cm^{-1}; MS *m/z* 320 (M^+; 1), 259 (5), and 57 (100). Calcd for $C_{21}H_{36}S$: C, 78.68; H, 11.32; S, 10.00%. Found: C, 78.84; H, 11.46; S, 10.00%.

15 (R = *i* − Pr): Mp 75—76 °C; ^{1}H NMR δ = 1.29 (s, 9H), 1.30 (d, J = 6.8 Hz, 6H), 1.56 (s, 18H), 2.95 (septet, J = 6.8 Hz, 1H), 4.28 (s, 2H), and 7.34 (s, 2H); ^{13}C NMR δ = 23.2, 31.4, 33.4, 33.5, 34.8, 37.3, 37.8, 123.0, 131.4, 147.5, and 149.0; IR (KBr) 880, 1365, and 2960 cm^{-1}; MS *m/z* 334 (M^+; 1), 259 (8), and 57 (100). Calcd for $C_{22}H_{38}S$: C, 78.97; H, 11.45; S, 9.58%. Found: C, 78.92; H, 11.43; S, 9.95%

14 (R = Ph): Mp 128—130 °C; ^{1}H NMR δ = 1.08 (br s, 9H), 1.22 (s, 9H), 1.42 (br s, 9H), 2.68 (d, J = 7.9 Hz, 9H), 6.43 (d, J = 7.9 Hz, 1H), 7.1—7.3 (m, 5H), 7.4 (br s, 1H), and 7.6 (br s, 1H); ^{13}C NMR δ = 31.4, 33.3 (br), 34.9, 35.0 (br), 37.7 (br), 39.1 (br), 41.6, 121.3, 122.0, 125.8, 127.7, 128.3, 136.6, 145.5, 147.5 (br), 148.1, and 149.8 (br); IR (KBr) 710, 1370, 1495, and 2960 cm^{-1}; MS *m/z* 368 (M^+; 5), 335 (12), and 57 (100). Calcd for $C_{25}H_{36}S$: C, 81.46; H, 9.84; S, 8.70%. Found: C, 81.38; H, 9.87; S, 9.20%.

15 (R = Ph): Mp 146—147 °C: ^{1}H NMR δ = 1.31 (s, 9H), 1.55 (s, 18H), 4.73 (s, 2H), 7.3 (m, 5H), and 7.39 (s, 2H); ^{13}C NMR δ = 31.4, 33.5, 34.9, 36.0, 37.8, 123.2, 125.4, 127.7, 128.9, 129.9, 138.7, 148.3, and 149.5; IR (KBr) 690, 740, 1480, and 2970 cm^{-1}; MS *m/z* 368 (M^+; 3), 259 (40), and 57 (100). Calcd for $C_{25}H_{36}S$: C, 81.46; H, 9.84; S, 8.70%. Found: C, 81.33; H, 9.83; S, 8.96%.

14 (R = CH_2Ph): Mp 105—106 °C; ^{1}H NMR δ = 1.32 (s, 9H), 1.60 (br s, 18H), 1.93 (d, J = 7.3 Hz, 1H) 3.15 (dd, J = 5.9, 14 Hz, 1H), 3.68 (dd, J = 11, 14 Hz, 1H), 5.2—5.5 (m, 1H), 7.2—7.3 (m, 5H), and 7.5 (br s, 2H); ^{13}C NMR δ = 31.3, 33.9 (br), 34.7, 35.2 (br), 38.1 (br), 40.3, 44.2, 122.5 (br), 126.1 (br), 126.4, 128.2, 129.4, 138.1, 139.8, 147.6, and 149.1; IR (KBr) 695, 1360, and 2950 cm^{-1}; MS *m/z* 382 (M^+; 1), 348 (55), 57 (100). Calcd for $C_{26}H_{38}S$: C, 81.61; H, 10.01; S, 8.38%. Found: C, 81.31; H, 9.77; S, 8.74%.

16 (R = CH_2Ph): Mp 103—104 °C; ^{1}H NMR δ = 1.33 (s, 9H), 1.35 (br s, 9H), 1.66 (br s, 9H), 3.33 (d, J = 7.5 Hz, 2H), 3.34 (d, J = 11 Hz, 1H), 3.62 (d, J = 11 Hz, 1H), 4.79 (t, J = 7.5 Hz, 1H), and 6.7—7.6 (m, 12H); ^{13}C NMR δ = 31.4, 33.3, 34.7, 35.4, 37.3, 38.9, 40.2, 45.1, 49.8, 121.9, 125.5, 126.2, 126.9, 127.9, 128.3, 129.2, 129.7, 137.7, 139.9, 147.3, and 150.1; MS *m/z* 472 (M^+; 0.2), 415 (1), and 91 (100). Calcd for $C_{33}H_{44}S$: C, 83.84; H, 9.38; S, 6.78%. Found: C, 83.67; H, 9.28; S, 6.79%.

14 (R = *t*-Bu): ^{1}H NMR δ = 0.66 (s, 9H), 1.27 (s, 9H), 1.46 (s, 9H), 1.52 (s, 9H), 2.07 (d, J = 8.5 Hz, 1H), 4.72 (d, J = 8.5 Hz, 1H), 7.18 (d, J = 2.3 Hz, 1H), and 7.30 (d, J = 2.3 Hz, 1H); ^{13}C NMR δ = 28.5, 31.3, 34.3, 34.9, 35.3, 38.7, 39.2, 40.2, 49.1, 121.0, 124.1, 136.4, 146.3, 150.7, and 153.1; IR (KBr) 1360, 1640, and 2950 cm^{-1}; MS *m/z* 347 ($M^+ - 1$; 0.5), 316 (1.2), and 57 (100). High resolution MS: Calcd for $C_{23}H_{40}{}^{32}S$: M, 348.2849. Found: *m/z* 348.2833.

17: Mp 155.0—156.0 °C; ^{1}H NMR (CCl_4) δ = 1.17 (s, 18H), 1.25 (s, 18H), 1.76 (s, 18H), 2.70 (m, 2H, SH), 5.05 (m, 2H), 7.01 (d, 2H), and 7.45 (d, 2H); MS *m/z* 548 ($M^+ - H_2S$; 1), 516 (1), and 57 (100). Calcd for $C_{38}H_{62}S$: C, 78.28; H, 10.72; S, 11.00%. Found: C, 78.18; H, 10.66; S, 11.21%.

14 (R = $SiMe_3$): ^{1}H NMR δ = 0.14 (s, 9H), 1.28 (s, 9H), 1.52 (s, 18H), 2.04 (d, J = 8.8 Hz, 1H), 4.52 (d, J = 8.8 Hz, 1H), 7.32 (d,

J = 2.2 Hz, 1H), and 7.41 (d, J = 2.2 Hz, 1H); ^{13}C NMR δ = 0.99, 25.8, 31.4, 34.2, 37.7, 38.3, 122.2, 125.0, 137.7, 146.5, and 149.8; MS *m/z* 364 (M^+; 0.3), 363 (0.7), 332 (0.4), 307 (100), 73 (43), and 57 (58). High resolution MS: Calcd for $C_{22}H_{40}SSi$: M, 364.2618. Found: *m/z* 364.2587.

Reaction of 1 with Hexamethylphosphorous Triamide. To a degassed benzene solution (10 ml) of **1** (293 mg, 1 mmol) was added hexamethylphosphorous triamide (32 mg, 0.2 mmol); then the solution was heated at reflux for 3 h. After removal of the solvent, the residue was subjected to DCC (SiO_2, hexane–ether 20 : 1) to give **9** (255 mg, 87%).

Reaction of 1 with Butylamine. To a degassed benzene solution (10 ml) of **1** (293 mg, 1 mmol) was added butylamine (365 mg, 5 mmol) and the solution was heated at 70 °C for 1h. Chromatographic separation (DCC, SiO_2, hexane) of the crude products gave the imine **24**[21] (315 mg, 96%).

Reaction of 1 with Hydrazine Monohydrate. A degassed ethanol solution (5 ml) of hydrazine monohydrate (672 mg, 13.4 mmol) was added to a degassed ethanol solution (10 ml) of **1** (749 mg, 2.58 mmol) at 0 °C. The reaction was completed after about 5 min, as indicated by the disappearance of the purple color of **1**. After stirring for a further 15 min, the solvent was evaporated and the residue was extracted with dichloromethane. The crude products were purified by chromatography (DDC, SiO_2, CH_2Cl_2) to give hydrazone **4** (654 mg, 88%).

Reduction of 1 with Lithium Aluminum Hydride. A THF (5 ml) solution of **1** (453 mg, 1.56 mmol) was added to a suspension of lithium aluminum hydride (33.1 mg, 0.87 mmol) in THF (7 ml) at room temperature. After stirring for 2 h, the purple color due to **1** disappeared. To the reaction solution was added saturated aq NH_4Cl and then 2 M HCl (M = mol dm^{-3}). The solution was extracted with CH_2Cl_2, the extract dried over anhydrous $MgSO_4$, and CH_2Cl_2 was evaporated to give white crystals, which were recrystallized from methanol, affording 2,4,6-tri-*t*-butylphenylmethanethiol (420 mg, 92.2%); mp 100—102 °C; ^{1}H NMR (CCl_4) δ = 1.27 (s, 9H), 1.50 (s, 18H), 4.22 (d, J = 6 Hz, 2H), and 7.11 (s, 2H); MS *m/z* 292 (M^+; 20) and 243 (100). Found: C, 78.21; H, 11.27, S, 10.92%. Calcd for $C_{19}H_{32}S$: C, 78.01; H, 11.03; S, 10.96%.

Single-Crystal X-Ray Diffraction Analysis of 1. Purple crystals were obtained from oxygen free methanol solution. Examination of the crystals revealed twinning along the needle axis. Every effort to obtain non-twinning crystals from the recrystallization failed. A specimen for X-ray works was obtained to be splitted into two fragments, one of which no longer showed evidence of twinning. The crystal data, as well as details concerning the data collection and the structure refinement are listed in Table 1. Intensity data were collected using a Rigaku diffractometer (AFC-4) with a graphite monochromator. No absorption corrections were applied. The structure was solved by the direct method with the program MULTAN78.[22] During the refinements, one of the *t*-butyl groups was found to be rotationally disordered around the C(4)–C(41) axis. The occupancy factors of disordered atoms were estimated from the peak heights of the D-maps to be 0.75 : 0.25. The positions of most of the H atoms were found from the D-maps. The positions of the remaining H atoms were obtained from the calculation. The structure was refined by the block-diagonal least-squares with anisotropic temperature factors for non-H atoms and isotropic ones for C atoms with the occupancy factor of 0.25 and H atoms. The function $\sum w(|F_o| - k|F_c|)^2$ was minimized, where $w = \{\sigma^2(F_o) + 0.04529|F_o| + 0.00417|F_o|^2\}^{-1}$. The final R value is 0.088 for 2668 observed reflections. Atomic scattering factors were used from International Tables for X-Ray Crystallography.[23] All computations were performed with the programs MULTAN78, UNICS III,[24] and ORTEP II.[25] The final atomic parameters are given in Table 2.[26]

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