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Contributions to the chemistry of silicon–sulphur compounds

LV *. Isosteric isobutyl(isopropoxy)silanethiols. Preparation and spectroscopic properties

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Abstract

The reactions of isobutyl(isopropoxy)silyl bromides i-Bu$_n$(i-PrO)$_{3-n}$SiBr (n = 0–3) with H_2S in the presence of Et_3N yield the corresponding silanethiols, i-Bu$_n$(i-PrO)$_{3-n}$SiSH. The transition energy $\sigma \rightarrow \sigma^*$ and the IP of Si–S bond, as well as the first IP of sulphur lone pairs do not change significantly as the number of electronegative i-PrO groups is varied. The geminal anomeric effects seems to be the reason for the increased reactivity of i-Bu(i-PrO)$_2$SiSH and i-Bu(i-PrO)$_2$SiH.

Introduction

For some years we have been interested in the synthesis and properties of silicon–sulphur compounds [1]. Although there have been a number of reports on the synthesis and properties of trialkoxysilanethiols (R′O)$_3$SiSH [2] and triorganosilanethiols R$_3$SiSH [3], compounds such as R$_n$(R′O)$_{3-n}$SiSH appear to have been almost neglected [4].

The only report on the relationships between the structure of silanethiols and their reactivity concerns compounds of the types (R′O)$_3$SiSH or R$_3$SiSH [5]. We thus decided to undertake a systematic investigation of compounds of the series i-Bu$_n$(i-PrO)$_{3-n}$SiSH (n = 0–3). This set of compounds was chosen in order to find out how replacement of an oxygen atom in RO group for a more electropositive but presumably approximately isosteric methylene group influences the properties of silanethiols. We describe below the synthesis of these silanethiols and some of their spectroscopic properties.

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* For part LIV see ref. 1.

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Preparation

Pure $(\text{i-PrO})_3\text{SH}$ (IVa) was prepared by treatment of $(\text{i-PrO})_3\text{SiSNa}$ [2] with aqueous NH_4Cl followed by immediate workup and removal of traces of water. The other isosteric silanethiols $\text{i-Bu}_n(\text{i-PrO})_{3-n}\text{SiSH}$ (IVb,c,d, Table 4) were prepared by the following reaction sequence, which was found to be the best.

$$\text{HSiCl}_3 + n\ \text{i-BuMgBr} \longrightarrow \text{i-Bu}_n\text{Cl}_{3-n}\text{SiH} + n\text{MgBrCl} \tag{1}$$

$$\text{i-Bu}_n\text{Cl}_{3-n}\text{SiH} + (3-n)\text{i-PrOH} \longrightarrow \text{i-Bu}_n(\text{i-PrO})_{3-n}\text{SiH} + (3-n)\text{HCl} \tag{2}$$

$$\text{i-Bu}_n(\text{i-PrO})_{3-n}\text{SiH} + \text{C}_3\text{H}_5\text{Br} \xrightarrow{\text{H}_2\text{PtCl}_6} \text{i-Bu}_n(\text{i-PrO})_{3-n}\text{SiBr} + \text{C}_3\text{H}_6 \tag{3}$$

$$\text{i-Bu}_n(\text{i-PrO})_{3-n}\text{SiBr} + \text{H}_2\text{S} + \text{NEt}_3 \longrightarrow \text{i-Bu}_n(\text{i-PrO})_{3-n}\text{SiSH} + \text{NEt}_3\text{HBr} \tag{4}$$

Synthesis of silanes I $\text{i-Bu}_n\text{Cl}_{3-n}\text{SiH}$ ($n = 1$–3)

The silanes Ib,c,d (Table 1) were prepared by addition of a solution of i-BuMgBr in ether to a solution of Cl_3SiH in ether. For silane Id ca. 24 h refluxing in heptane was needed after removal of the ether.

Alcoholysis of silanes I

Slow addition of isopropanol to a solution of Cl_3SiH, Ib, or Ic in chloroform gave the corresponding $\text{i-Bu}_n(\text{i-PrO})_{3-n}\text{SiH}$ (IIa,b,c Table 2) in good yield. The Si–H bond was not cleaved under such conditions and only traces of higher boiling siloxanes were observed.

Bromination of silanes IIa,b,c and Id with allyl bromide

Our attempts to prepare $\text{i-Bu}_n(\text{i-PrO})_{3-n}\text{SiBr}$ (IIIa,b,c,d Table 3) by commonly used bromination procedures [6,7] were unsuccessful. The system $AlCl_3$–n-BuBr [6] proved to be completely ineffective and an attempt to force the conversion of IIb and IIc into IIIb and IIIc, respectively, resulted in the formation of higher-boiling siloxanes. The use of a n-BuBr–H_2PtCl_6 mixture for the synthesis of III from II was also unsuccessful.

Allyl chloride and allyl bromide are known to react in the presence of H_2PtCl_6 with less hindered silanes, mainly via a hydrosilylation route [8]. This process is

Table 1

Synthesis of the silanes $\text{i-Bu}_n\text{Cl}_{3-n}\text{SiH}$ ($n = 1$–3) (I)

Compound	Cl_3SiH (mol) Et_2O (ml)	i-BuMgBr (mol) [a] Et_2O (ml)	Refl. (h)	Yield of dist. (%)	B.p. (°C/torr)
$\text{i-BuCl}_2\text{SiH}$ (Ib)	1.19 600	1.28 600	1	47 [b]	116–118
$\text{i-Bu}_2\text{ClSiH}$ (Ic)	0.58 400	1.19 400	10	73 [b]	69/20
$\text{i-Bu}_3\text{SiH}$ (Id)	0.67 250	2.10 700	24 [c]	72	82/20

[a] The Grignard reagent was assumed to have been formed quantitatively from the i-BuBr taken. [b] Use of an efficient distillation column (glass helixes packed) is important. [c] See Experimental.

Table 2

Syntheses of the silanes i-Bu_n(i-PrO)$_{3-n}$(SiH (n = 0–2) (II)

Compound	Silane (mol)	i-PrOH (mol)	$CHCl_3$ (ml)	Dropping time (h)	Yield (%)	B.p. (°C/torr)
(i-PrO)$_3$SiH (IIa)	Cl_3SiH (0.43)	1.42	350	3 [a]	89	44/15
i-Bu(i-PrO)$_2$SiH (IIb)	Ib (0.42)	0.87	250	3 [a]	79	65/20
i-Bu_2(i-PrO)SiH (IIc)	Ic (0.16)	0.18	100	1 [b]	84	75/15

[a] After the addition of i-PrOH the mixture was refluxed for ca. 2 h. [b] After addition of i-PrOH the mixture was refluxed for ca. 10 h.

Table 3

Synthesis of the bromosilanes i-Bu_n(i-PrO)$_{3-n}$SiBr (n = 0–3) (III)

III Compound	Silane (mol)	C_3H_7Br (mol)	H_2PtCl_6 ($\times 10^{-5}$ mol)	Refl. (h)	Yield (%)	B.p. (°C/torr)
(i-PrO)$_3$SiBr (IIIa)	IIa (0.13)	0.29	3.7	0.5	86	86/25
i-Bu(i-PrO)$_2$SiBr (IIIb)	IIb (0.20)	0.45	4.6	0.5	92	65/4
i-Bu_2(i-PrO)SiBr (IIIc)	IIc (0.034)	0.06	1.2	0.5	98	78/2
i-Bu_3SiBr (IIId)	IId (0.055)	0.13	1.8	1.0	97	82/0.1

accompanied by exchange reactions Cl/H or Br/H. We found that for the silanes IIa, b, c and Id, the exothermic Br/H exchange was, under certain conditions, the sole process [9]. During the syntheses of IIIa,b,c we did not observe any redistributions.

Thiolysis of bromosilanes IIIb,c,d

The required silanethiols i-Bu_n(i-PrO)$_{3-n}$SiSH (IVb,c,d) were prepared by the reaction of IIIb,c,d with H_2S in the presence of Et_3N [4] with precautions (see Experimental) to minimize disilthiane formation. IVb,c,d were carefully breed from Et_3N contamination. IVa,c,d are relatively stable and can be isolated by slow column distillation under moderate vacuum from the crude product (after water work-up) to which some SiS_2 (as a drying agent) had been added. The only

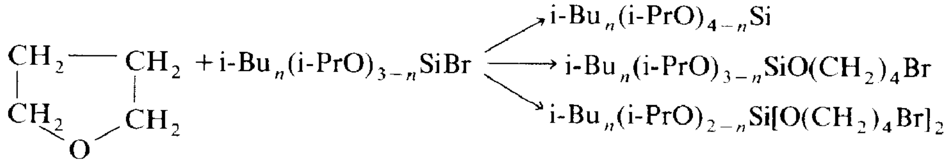
Table 4

Synthesis of the silanethiols i-Bu_n(i-PrO)$_{3-n}$SiSH (n = 0–3) (IV)

IV Compound	Bromosilane (mol)	Et_3N (mol)	Et_2O (ml)	Time (h)	Yield (%)	B.p. (°C/torr)
(i-PrO)$_3$SiSH (IVa)					41	78/15
i-Bu(i-PrO)$_2$SiSH (IVb)	IIIb (0.028)	0.031	70	6	71 [a,b]	53/0.1
i-Bu_2(i-PrO)SiSH (IVc)	IIIc (0.034)	0.037	70	6	56 [c,d]	71/0.1
i-Bu_3SiSH (IVd)	IIId (0.13)	0.14	200	12	72 [e,f]	82/0.1

[a] 3.1% i-Bu(i-PrO)$_3$Si, 2.0% i-Bu(i-PrO)$_2$SiOH (GLC mol-%). [b] 0.003 mol of [i-Bu(i-PrO)$_2$Si]$_2$S was isolated by Kugelrohr distillation (130 °C/0.05 torr).

[c] 3.8% i-Bu_2(i-PrO)$_2$Si, 2.4% i-Bu_2(i-PrO)SiOH (GLC). [d] 0.007 mol of [i-Bu_2(i-PrO)Si]$_2$S was isolated by Kugelrohr distillation (135 °C/0.05 torr). [e] 3.7% i-Bu_3SiOH (GLC). [f] 0.007 mol of (i-Bu_3Si)$_2$S was isolated by Kugelrohr distillation (115 °C/0.01 torr).



Scheme 1

Table 5

Cleavage of THF by bromosilanes IIIb and IIIc

III (mol)	THF (ml)	NaSH (mol)	Reflux (h)	Products (mol)	B.p. (°C/torr)
IIIb (0.068)	50	0.087	4	i-Bu(i-PrO)$_3$Si (Vb) (0.043)	54/0.2
				i-Bu(i-PrO)$_2$SiO(CH$_2$)$_4$Br (VIb) (0.009)	135/0.1
IIIc (0.1)	70	0.12	7	i-Bu$_2$(i-PrO)$_2$Si (Vc) (0.021)	61/1
				i-Bu$_2$(i-PrO)$_2$SiO(CH$_2$)$_4$Br (VIc) (0.04)	110/0.1
				i-Bu$_2$Si[O(CH$_2$)$_4$Br]$_2$ (VIIc) (0.022)	160/0.1 [a]

[a] Kugelrohr distillation.

exception was IVb, which is air sensitive (oxidation occurring to give sulphur and silanol), and during prolonged heating at 90 °C in the presence of SiS_2 undergoes redistribution. After 3 h under these conditions Kugelrohr distillation (50 °C, 0.05 Torr) gave a product containing 57% of i-Bu(i-PrO)$_2$SiSH, 41% of i-Bu(i-PrO)$_3$Si and 2% of i-Bu(i-PrO)$_2$SiOH (detected by GLC).

Attempted synthesis of IV by the use of NaSH – cleavage of THF with IIIb and IIIc

Attempts to prepare IVb and IVc by reaction of IIIb and IIIc with NaSH in the presence of dibenzo-18-crown-6 resulted only in redistribution and cleavage of a C–O bond of THF.

The results listed in Table 5 reveal that the cleavage of THF is considerably faster than the reaction of NaSH with III, but it was possible to obtain IVd by reaction of NaSH with i-Bu$_3$SiCl in the presence of crown ether in THF. (Details of this procedure will be published elsewhere.)

Cleavage of THF in the presence of bromosilanes has been observed previously [11], although without a catalyst the reaction was very slow.

Results and discussion

The spectroscopic data are summarized in Table 6 and 7. Our main objective in our spectroscopic studies was to determine the relative energy levels of the HOMO and LUMO frontier orbitals for isosteric silanethiols IVa–IVd by electron spectroscopy. The IR spectra were also recorded in order to reveal the influence of substituents on the acidity of silanethiols (IV), which can be of importance in kinetic investigations of solvolyses which are strongly catalyzed by nucleophilic bases and inhibited by aliphatic amines [12]. The IR spectra of the compounds IIa,b,c and Id were determined in order to establish the influence of substituents on the silicon atoms on the force constants of Si–H bonds. The ^1H, ^{13}C and ^{29}Si NMR

Table 6

VIS absorption data for CT-complexes and UV-absorption data for the silanethiols i-$Bu_n(i\text{-}PrO)_{3-n}SiSH$ ($n = 0$–3) (IV)

Compound	CT		UV (σ–σ^*)	
	ν_{CT} (cm^{-1})	IP (eV)	ν(cm^{-1})	ϵ
(i-PrO)$_3$SiSH (IVa)	16460 S_n	7.57 [a]	48500 [d]	229
	21000 σ	8.19 [b]		
i-Bu(i-PrO)$_2$SiSH (IVb)	16460 S_n [c]	7.57 [a]	49230 [d]	230
	20000 σ [c]	8.04 [b]		
i-Bu$_2$(i-PrO)SiSH (IVc)	17230 S_n	7.78 [a]	49380 [d]	287
	20730 σ	8.15 [b]		
i-Bu$_3$SiSH (IVd)	16150 S_n	7.49 [a]	48770 [d]	514
	20390 σ	8.10 [b]		

[a] ν_{CT} (cm^{-1}) = 3960 IP − 11491 [14]. [b] ν_{CT} (eV) = 0.771 IP − 3.716 [15]. [c] Only for i-Bu(i-PrO)$_2$SiSH there is a very strong CT absorption. [d] Asymmetric band.

and mass spectra were recorded in all cases to confirm the identities and purities of the prepared compounds.

Electronic spectra of IVa,b,c,d and their CT complexes with TCNE

Compounds IVa–IVd can be used to analyse the influence of replacing the i-Bu groups by the more electronegative OPr-i groups which have almost the same steric effect on the electronic properties of Si–S bond and the sulphur lone pairs. (The electronic spectra of some silicon–sulphur catenates were considered previously [13].)

The results (Table 6) show that the introduction of electronegative i-PrO groups in place of i-Bu groups does not significantly change the $\sigma \rightarrow \sigma^*$ transition energy or the IP of the Si–S bond or that of the sulphur lone pairs (HOMO). This means that the nature of the Si–S bonds remains essentially constant in IVa–IVd and that the σ^*(Si–S) orbitals (LUMO) in IVa–IVd are of comparable energy. Thus when this series of compounds is used in kinetic investigations differences in the HOMO–LUMO energies can be neglected in discussions of kinetic effects.

IR spectroscopic investigations of IVa–IVd, IIa–IIc and Id

The compounds IVa–IVd can be used for a study of the influence of the number of alkoxy substituents on the acidity of isosteric silanethiols. The difference between

Table 7

ν(S–H) (CCl_4), ν(S–H) (THF), $\Delta\nu$(S–H) for the silanethiols i-$Bu_n(i\text{-}PrO)_{3-n}SiSH$ ($n = 0$–3) (IV) and ν(Si–H) for the silanes i-$Bu_n(i\text{-}PrO)_{3-n}SiH$ ($n = 0$–3) (III)

Compound	ν(S–H) (cm^{-1}) [a]		$\Delta\nu$	Compound	ν(Si–H) (CCl_4) [b] (cm^{-1})
	CCl_4	THF			
(i-PrO)$_3$SiSH (IVa)	2585	2507	78	(i-PrO)$_3$SiH (IIa)	2197
i-Bu(i-PrO)$_2$SiSH (IVb)	2585	2507	76	i-Bu(i-PrO)$_2$SiH (IIb)	2155, 2115
i-Bu$_2$(i-PrO)SiSH (IVc)	2582	2518	64	i-Bu$_2$(i-PrO)SiH (IIc)	2104
i-Bu$_3$SiSH (IVd)	2585	2528	57	i-Bu$_3$SiH (Id)	2115

[a] 2598 cm^{-1} (indene) as reference. [b] 1944 cm^{-1} (polystyrol) as reference.

the stretching vibrations frequency of the SH bond recorded in THF (hydrogen bond acceptor), ν(SH–THF), and that in CCl_4, ν(SH–CCl_4), can be used as a measure of relative acidity [16]. The results are summarized in Table 7. The acidities of the silanethiol increase with increase in the number of electronegative i-PrO groups, but $(i\text{-}PrO)_3SiSH$ and $i\text{-}Bu(i\text{-}PrO)_2SiSH$ are almost equally acidic, and this can be accounted for in terms of variable polar effect of alkoxy groups [17]. The strong CT band as well as the increased acidity and reactivity of IVb can be interpreted as a manifestation of the geminal anomeric effect [18] which, by interaction of the oxygen electron lone pairs with the σ^* orbitals of the Si–O bond can greatly hinder rotation around Si–O bonds and thus reduce the effective steric hindrance of $i\text{-}Bu(i\text{-}PrO)_2Si$ moiety. The similarly enhanced reactivity of $i\text{-}Bu(i\text{-}PrO)_2SiH$ in reaction (3) [9] and the higher reactivity of $n\text{-}Pr(EtO)_2SiH$ than of other compounds of the series $n\text{-}Pr_nEtO)_{3-n}SiH$ ($n = 0$–3) in solvolytic cleavage of the Si–H bond [19] and in hydrosilylation of hexene-1 [20] suggest that in these cases also the geminal anomeric effect operates.

We determined the Si–H stretching vibrations for the isosteric silicon hydrides. There is no simple relationship between the Si–H stretching frequency and the number of alkoxy groups, but it is noteworthy that for IIb a splitting of the Si–H band is observed. Such splitting was previously observed for a few dialkoxysilanes [21] and tetraphenyldisiloxane [22], and its origin is not clear. In our opinion this splitting cannot be caused by conformational isomerism arising from hindered rotation as has been suggested [21]. Instead, as discussed previously [22,23], it probably arises from intramolecular interaction between the H and O atoms.

Experimental

All reactions were performed under argon. The reagents i-PrOH, C_3H_5Br, $i\text{-}C_4H_9Br$, and Et_3N were distilled over CaH_2, diethyl ether over sodium/benzophenone, and $CHCl_3$ over P_2O_5.

Preparation of Ib

The Grignard reagent prepared from 177.2 g (1.29 mol) of i-BuBr and 31.1 g (1.28 mol) of Mg in 600 ml of ether was added dropwise to a solution of 160.7 g (1.19 mol) of Cl_3SiH in ether (300 ml). The mixture was then refluxed for 1 h. The solution was filtered, the solvent was removed, and the residue distilled twice through a heated 30 cm glass-helix packed column to yield 80.3 g (43%) of Ib, b.p. 116–118 °C.

Analysis for $C_4H_{10}Cl_2Si$ found (calc.)(%): C, 30.7 (30.59); H, 6.6 (6.42); Si, 18.0 (17.88); ^1H NMR (δ): 1.02–1.08(d,6H), 1.15–1.27(2d,2H), 1.65–2.20(m,1H), 5.53–5.59(t,1H); MS m/e: 141(71%)[$M - CH_3$], 99(62)[$M - C_4H_9$], 43(100)[C_3H_7].

Preparation of Ic

Compound Ic was obtained similarly. Analysis for $C_8H_{19}ClSi$ found (calc.)(%): C, 54.0 (53.75); H, 10.9 (10.71); Si, 15.8 (15.71); ^1H NMR (δ): 0.73–0.93(2d,4H), 0.93–1.17(d,12H), 1.60–2.27(m,2H), 4.65–4.93(m,1H).

Preparation of Id

A solution of 90.5 g (0.67 mol) of Cl_3SiH in 250 ml of ether was added dropwise to a solution of the Grignard reagent prepared from 288.2 g (2.10 mol) of i-BuBr and 50.6 (2.1 mol) of Mg in ether (700 ml). The mixture was refluxed for 6 h then the solution was filtered and the precipitate was washed with 100 ml of ether. The combined filtrate and washing was diluted with 600 ml of heptane, the ether was distilled off, and the residue was heated at reflux for ca. 24 h. The solution was filtered and the residue washed with ether. The combined filtrate and washings were evaporated under reduced pressure and a little $LiAlH_4$ was added to the liquid residue, which was then heated at about 70 °C for 3 h. Finally vacuum distillation (30 cm Vigreux column) gave 97.1 g (72%) of Id, b.p. 82–83 °C (20 Torr).

Analysis for $C_{12}H_{28}Si$ found (calc.)(%): C, 71.9 (71.91); H, 14.1 (14.08); Si, 14.2 (14.01); ^{1}H NMR (δ): 0.95–1.05(d,18H), 0.5–0.7(d,6H), 1.4–2.05(m,3H), 3.75–4.0(m,1H); MS. *m/e*: 198(10%)[$M - H_2$], 143(62)[$M - C_4H_9 - C_3H_6$], 101(35)[$M - C_4H_9 - C_3H_6$], 87(50)[$M - C_4H_9 - C_4H_8$], 59(100).

Preparation of IIa and IIb

These were prepared in the same way as IIc.

IIa: Analysis for $C_9H_{22}O_3Si$ found (calc.)(%): C, 52.5 (52.38); H, 10.9 (10.75); Si, 13.9 (13.61); ^{1}H NMR (δ): 1.15–1.25(d,18H), 4.0–4.5(m,3H), 4.36(s,1H); MS. *m/e*: 205(7%)[$M - H$], 191(98)[$M - CH_3$], 149(100)[$M - CH_3 - C_3H_6$], 107(66)[$M - CH_3 - 2C_3H_6$], 105(68)[$M - C_3H_7O - C_3H_6$], 63(100)[$M - C_3H_7O - 2C_3H_6$].

IIb: Analysis for $C_{10}H_{24}O_2Si$ found (calc.)(%): C, 59.1 (58.76); H, 11.9 (11.84); Si, 14.1 (13.74); ^{1}H NMR (δ): 0.55–0.72(2d,2H), 0.93–1.02(d,6H), 1.16–1.24(d,12H), 1.62–2.15(m,1H), 3.91–4.41(m,2H), 4.55–4.60(t,1H); MS. *m/e*: 203(5%)[$M - H$], 189(7)[$M - CH_3$], 147(47)[$M - CH_3 - C_3H_6$], 133(22)[$M - CH_3 - C_4H_8$], 105(49)[$M - CH_3 - 2C_3H_6$], 63(100)[$SiH(OH)_2$].

Preparation of IIc

i-Propanol (11.0 g; 0.18 mol) was added dropwise to a solution of 28.1 g (0.16 mol) of Ic in 100 ml of $CHCl_3$, a stream of argon being passed through the solution. When addition was complete, the solution was heated under reflux for about 10 h and the solvent then distilled off. The residue was twice distilled under reduced pressure (Vigreux column 30 cm) to give 27.1 g (84%) of pure IIc, b.p. 75–76 °C (15 Torr).

Analysis for $C_{11}H_{26}OSi$ found (calc.)(%): C, 65.4 (65.27); H, 12.8 (12.95); Si, 14.1 (13.88); ^{1}H NMR (δ): 0.53–0.78(m*,4H), 0.95–1.02(d,12H), 1.16–1.21(d,6H), 1.75–1.96(m,2H), 3.92–4.08(m,1H), 4.61–4.65(m,1H); MS. *m/e*: 202(2%)[M^+], 187(4)[$M - CH_3$], 145(100)[$M - CH_3 - C_3H_6$], 103(36)[$M - CH_3 - 2C_3H_6$], 61(86)[$M - CH_3 - 3C_3H_6$].

Preparation of IIIa, IIIb, and IIIc

These were prepared as described for IIId.

IIIa: Analysis for $C_9H_{21}O_3SiBr$ found (calc.)(%): C, 37.7 (37.89); H, 7.5 (7.42); Si, 9.8 (9.85); ^{1}H NMR (δ): 1.2–1.3(d,6H), 4.1–4.6(m,1H); MS. *m/e*: 269(54%)[$M - CH_3$], 227(54)[$M - C_4H_9$], 141(58)[$M - C_3H_7O - 2C_3H_6$], 79(55)[$Si(OH)_3$], 43(100)[C_3H_7].

IIIb: Analysis for $C_{10}H_{23}O_2SiBr$ found (calc.)(%): C, 42.2 (42.40); H, 8.2 (8.18); Si, 10.1 (9.92); ^{1}H NMR (δ): 0.87–0.91(d,2H), 0.97–1.02(d,6H), 1.20–1.25(d,6H),

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* Spin system ABX.

1.88–2.02(m,1H), 4.28–4.38(m,2H); MS. *m/e* (abundance): 282(1)$[M^+]$, 267(20)$[M - CH_3]$, 225(31)$[M - C_4H_9]$, 211(20)$[M - CH_3 - C_4H_8]$, 183(39)$[M - C_4H_9 - C_3H_6]$, 169(28)$[M - CH_3 - C_4H_8 - C_3H_6]$, 141(100)$[M - C_4H_9 - 2C_3H_6]$.

IIIc: Analysis for $C_{11}H_{25}OSiBr$ found (calc.)(%): C, 47.2 (46.96); H, 9.1 (8.96); Si, 10.2 (9.99); ^1H NMR (δ): 0.95–1.05(d), 0.93–1.05(d), 1.14–1.25(d,6H), 1.62–2.25(m,2H), 4.02–4.45(m,1H); MS. *m/e* (abundance): 223(100)$[M - C_4H_9]$, 181(65)$[M - C_4H_9 - C_3H_6]$, 139(78)$[M - C_4H_9 - 2C_3H_6]$.

Preparation of IIId

A solution of 0.0095 g (0.018 mmol) of $H_2PtCl_6 \cdot 6H_2O$ in 0.04 ml of i-PrOH was added to a stirred solution of 11.0 g (0.055 mol) of Id in 16.1 g (0.13 mol) of allyl bromide. The mixture was heated under reflux and an exothermic reaction raised the temperature to 135 °C. The mixture was refluxed for 1 h at ca. 100 °C. After removal of unchanged C_3H_5Br, the residue was distilled under vacuum (15 cm Vigreux column) to give 14.2 g (93%) of IIId, b.p. 82–83 °C (0.1 Torr).

Analysis for $C_{12}H_{27}SiBr$ found (calc.)(%): C, 51.9 (51.60); H, 9.9 (9.74); Si, 10.4 (10.06); ^1H NMR (δ): 0.9–1.0(d,2H), 0.95–1.05(d,6H), 1.7–2.2(m,1H); MS: 278(6%)$[M^+]$, 221(100)$[M - C_4H_9]$, 179(50)$[M - C_4H_9 - C_3H_6]$, 165(82)$[M - C_4H_9 - C_4H_8]$.

Preparation of IVa

A mixture (116 g) of (i-[PrO)$_3$SiSH (45 mol-%) and (i-PrO)$_4$Si (55 mol-%) was heated with 4.1 g (0.18 mol) of Na [2,10] at 95 °C for 12 h. The slurry was shaken with hexane then the precipitate was filtered off under argon, washed three times with hexane and breed from solvent to give 45.6 g (0.17 mol) of (i-PrO)$_3$SiSNa, which was shaken in a separatory funnel with Et_2O (300 ml) and 10% aqueous NH_4Cl (200 ml). The ethereal layer was separated, washed twice with H_2O (50 ml), dried with $MgSO_4$ and then with SiS_2, and finally the Et_2O was distilled off. The residue was distilled through a 15 cm Vigreux column from a little SiS_2 to yield 17.1 g (41%) of IVa.

Preparation of IVb

A stream of H_2S was bubbled slowly for 1.5 h through a solution of 3.2 g (0.032 mol) of Et_3N in 50 ml of ether and 7.9 g (0.028 mol) of IIIb in 20 ml of ether was then slowly added dropwise (4 h) with H_2S still bubbling through. The mixture was left overnight, then the solution was filtered and the ether removed. Kugelrohr distillation of the residue gave 5.6 g of crude IVb, b.p. 50 °C/0.1 Torr and 1.3 g (0.003 mol) of [i-Bu(i-PrO)$_2$Si]$_2$S b.p. 130 °C/0.05 Torr. A solution of the crude IVb in 25 ml of hexane was shaken twice in a separatory funnel with 20 ml of H_2O. The hexane layer was separated and dried over CaH_2, and the hexane was taken off. Kugelrohr distillation then gave 4.7 g (71%) of IVb b.p. 53–55 °C (0.1 Torr).

Analysis for $C_{10}H_{24}O_2SiS$ found (calc.)(%): C, 51.1 (50.80); H, 10.4 (10.23); Si, 12.2 (11.88); ^1H NMR (δ): 0.90–0.97(d,2H), 0.97–1.01(d,6H), 1.24–1.79(d,12H), 1.84–1.96(m,1H), 4.25–4.33(m,2H); MS. *m/e*: 236(1%)$[M^+]$, 221(5)$[M - CH_3]$, 202(65)$[M - H_2S]$, 179(53)$[M - C_4H_9]$, 165(44)$[M - CH_3 - H_2S]$, 137(70)$[M - C_4H_9 - C_3H_6]$, 95(100)$[M - C_4H_9 - 2C_3H_6]$.

Preparation of IVc

This was prepared as described for IVb, but SiS_2 was used in place of CaH_2 for drying.

Analysis for $C_{11}H_{26}OSiS$ found (calc.)(%): C, 56.8 (56.35); H, 11.3 (11.18); Si, 12.2 (11.98); ^{1}H NMR (δ): 0.79–0.84(d,4H), 0.96–1.01(2d*,12H), 1.16–1.20(d,6H), 1.80–1.20(m,2H), 4.01–4.45(m,1H), −0.35(s,1H); MS. *m/e*: 234(1%)$[M^+]$, 200(54)$[M - H_2S]$, 177(100)$[M - C_4H_9]$, 135(46)$[M - C_4H_9 - C_3H_6]$.

Preparation of IVd

This was prepared as described for IVc.

Analysis for $C_{12}H_{28}SiS$ found (calc.)(%): C, 61.9 (61.99); H, 12.1 (12.14); Si, 12.3 (12.08); ^{1}H NMR (δ): 0.90–1.00(d), 0.95–1.05(d), 1.70–2.22(m,3H), −0.34(s,1H); MS. *m/e*: 232(1%)$[M^+]$, 198(36)$[M - H_2S]$, 175(68)$[M - C_4H_9]$, 142(22)$[M - H_2S - C_4H_8]$, 119(100)$[M - C_4H_9 - C_4H_8]$.

Attempted preparation of IVb by reaction of IIIb with NaSH in THF

A slurry of 4.8 g (0.087 mol) of NaSH and a solution of 19.2 g (0.068 mol) of IIIb in 50 ml of THF was heated with a catalytic amount of dibenzo-18-crown under reflux for about 7 h. The solution was filtered and the THF distilled off. Vacuum distillation (15 cm Vigreux column) gave 11.3 g (0.043 mol) Vb b.p. 45–47 °C/0.2 Torr. The residue was subjected to Kugelrohr distillation to give 3.2 g (0.009 mol) of VIb, b.p. 135 °C/0.1 Torr.

Vb: Analysis for $C_{13}H_{30}O_3Si$ found (calc.)(%): C, 59.5 (59.49); H, 11.4 (11.52); Si, 11.1 (10.70); ^{1}H NMR (δ): 0.51–0.59(d,2H), 0.92–1.00(d,6H), 1.14–1.22(d,18H), 1.61–2.10(m,1H), 3.95–4.45(m,3H); MS. *m/e*: 247(8%)$[M - CH_3]$; 205(82)$[M - C_4H_9]$, 191(30)$[M - CH_3 - C_4H_8]$, 163(22)$[M - C_4H_9 - C_3H_6]$, 121(50)$[M - C_4H_9 - 2C_3H_6]$, 79(100)$[Si(OH)_3]$.

VIb: Analysis for $C_{14}H_{31}O_3SiBr$ found (calc.)(%): C, 47.6 (47.31); H, 8.7 (8.79); Si, 8.1 (7.90); ^{1}H NMR (δ): 0.51–0.61(d,2H), 0.95–1.05(d,6H), 1.22–1.31(d,12H), 1.50–2.20(m,5H), 3.37–3.55(t,2H), 3.68–3.83(t,2H), 4.00–4.55(m,2H); MS. *m/e* (abundance): 297(10)$[M - C_4H_9]$, 255(24)$[M - C_4H_9 - C_3H_6]$, 213(52)$[M - C_4H_9 - 2C_3H_6]$, 55(100).

Attempted preparation of IVc by reaction of IIIc with NaSH in THF

A similar procedure starting from IIc gave Vc, VIc, and VIIc.

Vc: Analysis for $C_{14}H_{32}O_2Si$ found (calc.)(%): C, 64.8 (64.55); H, 12.7 (12.38); Si, 10.9 (10.78); ^{1}H NMR (δ): 0.50–0.62(d,2H), 1.01–1.12(d,6H), 1.15–1.22(d,6H), 1.50–2.12(m,2H), 3.81–4.38(m,1H); MS. *m/e*: 203(98%)$[M - C_4H_9]$, 189(32)$[M - CH_3 - C_4H_8]$, 161(78)$[M - C_4H_9 - C_3H_6]$, 147(100)$[M - C_4H_9 - C_4H_8]$, 119(100)$[M - C_4H_9 - 2C_3H_6]$, 77(98)$[M - C_4H_9 - 3C_3H_6]$.

VIc: Analysis for $C_{15}H_{33}O_2SiBr$ found (calc.)(%): C, 51.1 (50.98); H, 9.2 (9.41); Si, 8.1 (7.95); ^{1}H NMR (δ): 0.56–0.61(d,4H), 0.92–1.00(d,12H), 1.15–1.25(d,6H), 1.60–2.11(m,6H), 3.40–3.50(t,2H), 3.65–3.75(t,2H), 4.05–4.25(m,1H); MS. *m/e* (abundance): 295(36)$[M - C_4H_9]$, 253(51)$[M - C_4H_9 - C_3H_6]$, 211(52)$[M - C_4H_9 - 2C_3H_6]$, 55(100).

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* Anisochronism of methyl groups.

VIIc: Analysis for $C_{16}H_{34}O_2SiBr_2$ found (calc.)(%): C, 43.3 (43.05); H, 7.5 (7.48); Si, 6.5 (6.29); ^{1}H NMR (δ): 0.5–0.7(d,2H), 0.9–1.1(d,6H), 1.5–2.4(m,3H), 3.3–3.6(t,1H), 3.6–3.9(t,1H).

Gas-chromatographic analyses (FID) were performed on 1 m ∅ 4 mm SE-30 column (7.5% on Chromosorb W-NAW, 80–100 mesh) with Ar as a flow gas. The temperature was programmed in the range 100–250 °C (6 °C/min).

^{1}H-NMR spectra were recorded in CCl_4 with TMS as internal standard, on Bruker WP 80SY, Bruker AM 250, or Varian 360A spectrometer.

Mass spectra (70 eV) were obtained with a Finnigan-MAT 8230 spectrometer. For bromo compounds the *m/e* values refer to ^{79}Br.

IR spectra were recorded for CCl_4 solutions in 0.22 mm NaCl cells on a Carl Zeiss "Specord 75 IR" spectrophotometer.

UV-Vis spectra were recorded on a Carl Zeiss "Specord UV-Vis" spectrometer. CT spectra were measured at room temperature in 1 cm quartz cells containing an 0.15–0.44 *M* solution in $CHCl_3$ saturated with TCNE. The UV spectra were recorded at room temperature in 1 cm quartz cells containing 10^{-5} *M* solutions in hexane.

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