Synthesis of Symmetrical and Unsymmetrical 2,5-Bis(trialkylsilyl)furans and 2,6-Bis(trialkylsilyl)-4*H*-pyrans from 1,4- and 1,5-Bis(acylsilanes)

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Received 26 September 1999; revised 21 February 2000

Abstract: 2,5-Bis(trialkylsilyl)furans and 2,6-bis(trialkylsilyl)-4*H*-pyrans have been synthesized by cyclodehydration of 1,4- and 1,5-bis(acylsilanes) under *p*-toluenesulfonic acid catalysis. The 1,4-bis(acylsilanes) have been prepared from 1,2-bis(1,3-dithian-2-yl)ethane according to the reaction sequence metallation-silylation-dethioketalization. The 1,5-bis(acylsilanes) have been prepared from 1,3-bis(1,3-dithian-2-yl)propane by a similar strategy or from a S_N reaction of 1,3-dihalopropanes with 2-trialkylsilyl-2-lithio-1,3-dithiane and deprotection. The method allows efficient preparation of symmetrical as well as unsymmetrical bis(silylated) heterocycles.

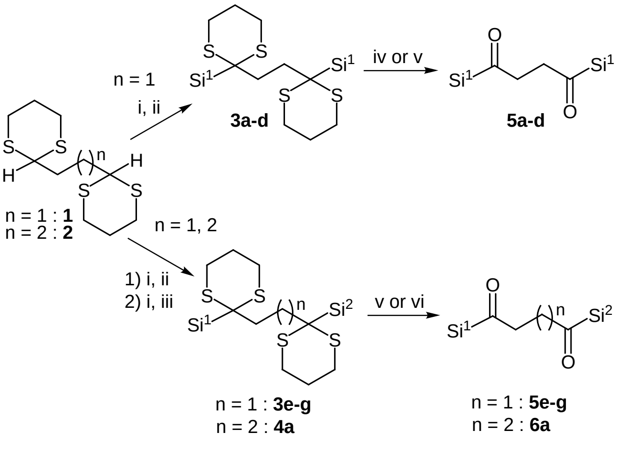
Key words: furans, 4*H*-pyrans, acylsilanes, cyclizations, dithianes, heterocycles

Silylated furans have been a topic of continuing interest in organic chemistry. Indeed, the peracid oxidation of substituted 2-trimethylsilylfurans to but-2-en-4-olides is the pivotal step in the synthesis of many natural products, namely hispanolone, prehispanolone and sphydrofuran.[1] Moreover, the judicious placement of a silyl group on the furan ring can be used to control the position of new groups around the furan or the silane can be directly replaced by electrophile via an *ipso*-substitution.[2] Only few examples of 2,5-bis(trialkylsilyl)furans have been reported. The 2,5-bis(trimethylsilyl)furan and analogs have been studied by NMR or were involved in redox reactions.[3] The 1,3-bis(trimethylsilyl)-isobenzofuran[4] and naphtho[1,2-*c*]furan[5] were used with arynes in cycloaddition. Silylated polyfurans (tetrasila[2.2]paracyclophane,[6] silacalix[4]arenes[7]) have been studied for their coordination and photoelectron properties. All of these furans have been prepared by silylation of dilithio derivatives with trialkylsilyl chlorides in low to moderate yields. More recently, an interesting electroreductive silylation of 2,5-dibromofuran has been reported,[8] but only symmetrical 2,5-bis(silyl)furans have been prepared by this method. On the other hand, 2,6-bis(trialkylsilyl)-4*H*-pyrans were unprecedented before our study. Metallation-silylation of the corresponding 4*H*-pyrans was applied only to the preparation of 2-trimethylsilyl-4*H*-pyrans,[9a] and to derivatives in the related family of 2-trialkylsilyldihydropyrans,[9b] the latter have been prepared by various cyclization procedures.[10]

Acylsilanes, a class of compounds with interesting reactivity, have been widely employed in organic synthesis.[11] In contrast, the chemistry of bis(acylsilanes) have been little studied,[12] despite the high potential of transformations one can expect from such dicarbonyl compounds. We have recently undertaken a research programme on the synthesis of bis(acylsilanes) and their application to new silylated heterocycles. The first example dealt with the preparation of 3,4-dihydroxybis(acylsilane) which cyclized spontaneously into (5-trimethylsilylfuran-2-yl)acetyltrimethylsilane.[13]

A general methodology to have an access to symmetrical as well as unsymmetrical 2,5-bis(trialkylsilyl)furans and 2,6-bis(trialkylsilyl)-4*H*-pyrans remains a challenge which could be resolved by a simple cyclodehydration of the corresponding bis(acylsilanes). Such a strategy should have at one's disposal an easy access to symmetrical and unsymmetrical 1,4- and 1,5-bis(acylsilanes). This paper is a full account of this investigation,[14] and reports on both aspects of the methodology: the synthesis and characterization of the bis(acylsilanes) precursors and of the corresponding bis(silylated) furans and 4*H*-pyrans.

The more general approach to the synthesis of simple linear symmetical and unsymmetrical bis(acylsilanes) is depicted in Scheme 1. It consists of lithiation followed by silylation of the bis(dithianes) **1** or **2**, in a reaction using 2.4 equivalents of reagents for symmetrical compounds, or in a two-step sequence for the unsymmetrical ones. Oxidative removal of the dithiane moiety led to the expected bis(acylsilanes).



Reagents and conditions: i) BuLi; ii) Cl–Si^1; iii) Cl–Si^2; iv) MeI/$CaCO_3$; v) $Hg(ClO_4)_2/CaCO_3$; vi) $I_2/CaCO_3$

Scheme 1

Table 1 Synthesis of Bis(acylsilanes) **5a–g** and **6a** According to Scheme 1

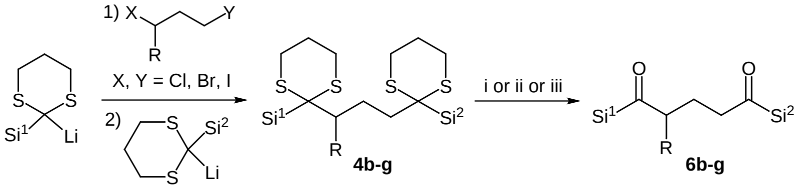
Entry	n	Si^1	Si^2	Bis(dithiane)	Yield (%)	Hydrolysis Method[a]	Bis(acylsilane)	Yield (%)
1	1	$SiMe_3$	–	**3a**	78	iv	**5a**	90
2	1	$SiEt_3$	–	**3b**	86	v	**5b**	80
3	1	$SiMe_2Bu$-*t*	–	**3c**	47	v	**5c**	86
4	1	Si(Pr-*i*)$_3$	–	**3d**	81	v	**5d**	61
5	1	$SiMe_3$	$SiEt_3$	**3e**	88	v	**5e**	72
6	1	$SiMe_3$	$SiMe_2Bu$-*t*	**3f**	75	v	**5f**	63
7	1	$SiMe_3$	Si(Pr-*i*)$_3$	**3g**	91	v	**5g**	74
8a	2	$SiMe_3$	Si(Pr-*i*)$_3$	**4a**	78	v	**6a**	53
8b						vi	**6a**	87

[a] iv) MeI/$CaCO_3$; v) $Hg(ClO_4)_2/CaCO_3$; vi) $I_2/CaCO_3$.

1,2-Bis(1,3-dithian-2-yl)ethane **1**[15] was obtained by treatment of dimethoxytetrahydrofuran with propane-1,3-dithiol and hydrogen chloride (90%), whereas the analog **2**[16] was derived from 3,4-dihydro-2-methoxy-2*H*-pyran. It is worth noting that the preparation of **2** with gaseous hydrogen chloride (95%) gives better yield than with BF_3•OEt_2 (55%).[16b] Symmetrical 1,4-bis(dithianes) **3a–d** were prepared in good yields (78–86%), even for hindered silyl groups, except for the TBDMS derivative **3c** (47%) (Scheme 1, Table 1). New unsymmetrical bis(dithianes) **3e–g** and **4a** were also synthesized in good yields (75–91%) by a two steps procedure via the trimethylsilylated intermediate (94% for n = 1, 85% for n = 2) which, after purification by recrystallization from petroleum ether, was reacted with various trialkylsilyl chlorides (Scheme 1, Table 1). The conversion of the bis(dithianes) into the corresponding bis(acylsilanes) **5a–g** and **6a** was performed using methyl iodide, mercuric perchlorate, or iodine in the presence of calcium carbonate (Scheme 1, Table 1).[14b]

1,5-Bis(acylsilanes) **6b–g** were prepared according to the reaction path depicted in Scheme 2, via the corresponding 1,5-bis(trialkylsilyl) dithianes **4b–g** derived from a S_N reaction of 1,3-dihalopropanes with 2-trialkylsilyl-2-lithio-1,3-dithiane. The results are summarized in Table 2. Except for **4g** whose yield (36%) was reduced by a competing elimination reaction, the intermediate 1,5-bis(trialkylsilyl)dithianes were obtained in excellent yields (66–91%), even for hindered and/or unsymmetrical derivatives. Similarly, the deprotection step gave good yields of the corresponding 1,5-bis(acylsilanes) **6b–g** (59–100%). Recent results (for example: compounds **6a**, **6c** and **6g**) show that dethioketalization with iodine gave high yield of bis(acylsilanes) without the drawback of using heavy metal salts.

The 2,5-bis(trialkylsilyl)furans **8a–g** were prepared by cyclodehydration (Paal–Knorr type synthesis) of 1,4-bis(acylsilanes) **5a–g** under acid catalysis. A mixture of **5** and a catalytic amount of *p*-toluenesulfonic acid (PTSA) was thermolysed under reduced pressure, using a Kugelrohr apparatus to furnish silylated furans **8** (Scheme 3, Table 3, Entries 1–7). This reaction was general and gave good yields (61–71%) even for hindered silyl groups such as TBDMS and TIPS. Unfortunately, this cyclodehydration seemed to be very sensitive to substituent in position 2 of the bis(acylsilane). Indeed, the thermolysis of α-methyl 1,4-bis(acylsilane) failed (degradation of the starting material).[14b] It is worth noting that furans **8b–g** have not been described yet in the literature.



Reagents and conditions: i) MeI/$CaCO_3$; ii) $Hg(ClO_4)_2/CaCO_3$; iii) $I_2/CaCO_3$

Scheme 2

Table 2 Synthesis of Bis(acylsilanes) **6b–g** According to Scheme 2

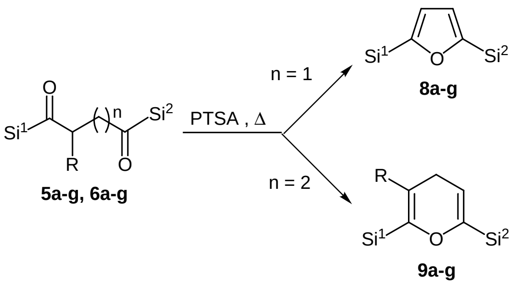
Entry	R	Si^1	Si^2	Bis(dithiane)	Yield (%)	Hydrolysis Method[a]	Bis(acylsilane)	Yield (%)
1	H	SiMe$_3$	SiMe$_3$	**4b**	91[16b]	i	**6b**	75[16b]
2a	H	SiMe$_2$Bu-*t*	SiMe$_2$Bu-*t*	**4c**	86	ii	**6c**	~100
2b						iii	**6c**	97
3	H	SiMe$_3$	SiMePh$_2$	**4d**	82	ii	**6d**	59
4	H	SiEt$_3$	SiMe$_2$Bu-*t*	**4e**	66	ii	**6e**	77
5	Me	SiMe$_3$	SiMe$_3$	**4f**	85	ii	**6f**	79
6a	Me	SiMe$_2$Bu-*t*	SiMe$_2$Bu-*t*	**4g**	36[b]	ii	**6g**	84
6b						iii	**6g**	90

[a] i) MeI/CaCO$_3$; ii) Hg(ClO$_4$)$_2$/CaCO$_3$; iii) I$_2$/CaCO$_3$.

[b] Bis(dithiane) **4g** was accompanied by 2-(but-3-enyl)-2-(*tert*-butyldimethylsilyl)-1,3-dithiane **7** (57%).

A similar Kugelrohr treatment of 1,5-bis(acylsilanes) **6a–g** under *p*-toluenesulfonic acid catalysis furnished easily the 2,6-bis(trialkysilyl)-4*H*-pyrans **9a–g** (Scheme 3, Table 3, Entries 8–14). In contrast to the furan series, α-methyl bis(acylsilanes) **6f** and **6g** were effectively cyclized, giving the corresponding 3-methyl-2,6-bis(trialkysilyl)-4*H*-pyrans **9f** and **9g** (Table 3, Entries 13, 14).

The cyclodehydration of 1,4- and 1,5-bis(acylsilanes) is an excellent and general method to prepare 2,5-bis(trialkylsilyl)furans **8a–g** and 2,6-bis(trialkylsilyl)-4*H*-pyrans **9a–g**, interesting compounds for various applications. The main interest of this method is the possible access to



Scheme 3

Table 3 Synthesis of Furans **8a–g** and 4*H*-Pyrans **9a–g** According to Scheme 3

Entry	Bis(acylsilane)	n	R	Si^1	Si^2	Furan or 4*H*-Pyran	Yield (%)
1	**5a**	1	H	SiMe$_3$	SiMe$_3$	**8a**	68[8]
2	**5b**	1	H	SiEt$_3$	SiEt$_3$	**8b**	67
3	**5c**	1	H	SiMe$_2$Bu-*t*	SiMe$_2$Bu-*t*	**8c**	71
4	**5d**	1	H	Si(Pr-*i*)$_3$	Si(Pr-*i*)$_3$	**8d**	68
5	**5e**	1	H	SiMe$_3$	SiEt$_3$	**8e**	67
6	**5f**	1	H	SiMe$_3$	SiMe$_2$Bu-*t*	**8f**	61
7	**5g**	1	H	SiMe$_3$	Si(Pr-*i*)$_3$	**8g**	69
8	**6a**	2	H	SiMe$_3$	Si(Pr-*i*)$_3$	**9a**	85
9	**6b**	2	H	SiMe$_3$	SiMe$_3$	**9b**	80
10	**6c**	2	H	SiMe$_2$Bu-*t*	SiMe$_2$Bu-*t*	**9c**	89
11	**6d**	2	H	SiMe$_3$	SiMePh$_2$	**9d**	53
12	**6e**	2	H	SiEt$_3$	SiMe$_2$Bu-*t*	**9e**	94
13	**6f**	2	Me	SiMe$_3$	SiMe$_3$	**9f**	50
14	**6g**	2	Me	SiMe$_2$Bu-*t*	SiMe$_2$Bu-*t*	**9g**	91

unsymmetrical bis(silylated) derivatives, with variable hindered silyl groups, which would allow differentiation of the 2,5- or 2,6-positions, for example in silyl group substitution reactions.

Melting points are uncorrected. FT-IR spectra were run on a MIDAS Corporation apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a BRUCKER AC-250 spectrometer. TMS (δ = 0.00) or $CHCl_3$ (δ = 7.27) were used as internal standards, and $CDCl_3$ was used as the solvent. MS data were obtained on a FISON VG AUTOSPEC apparatus at 70 eV in the electron impact mode. Elemental analyses were performed with a Perkin-Elmer CHN 2400 apparatus. All reactions were monitored by TLC (Merck F 254). Silicagel Merck 9385 (40−63 µm) was used for flash chromatography. All anhydrous reactions were performed under a blanket of argon. THF was distilled under argon from sodium benzophenone ketyl. The purity of the commercially available BuLi was checked according to Gilman.[17] Trialkylsilyl chlorides were stirred with triphenylamine and distilled before use (except TBDMS-Cl).

Bis(trialkylated) Symmetrical Bis(dithianes) 3a-d; General One-Step Procedure

To a solution of **1**[15] (18.8 mmol, 1.0 equiv) in THF (40 mL) cooled in an ice-water bath was added a solution of BuLi in hexane (45.1 mmol, 2.4 equiv). After stirring for 30 min at 0 °C, trialkylsilyl chloride (45.1 mmol, 2.4 equiv) was added dropwise. The mixture was then stirred for 1 h at 0 °C. The same procedure was repeat-

Table 4 Spectroscopic Data of Bis(dithianes) **3a**,**d**,**f**,**g** and **4c**,**d**,**f**

Product[a]	R_f (solvent)[b]	Mp[c] (°C)	IR (KBr) ν (cm^{-1})	MS *m/z*	^{1}H NMR ($CDCl_3$) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$) δ
3a	0.35 petroleum ether/ Et_2O (98:2)	152−154	2946, 1458, 1422, 1238	410 (M^+), 231, 191, 179	0.23 (s, 18 H), 1.8−2.1 (m, 4 H), 2.4−2.5 (m, 8 H), 3.14 (td, 4 H, *J* = 14.5, 2.3)	−2.5 [$Si(CH_3)_3$], 23.2 (CH_2), 25.2 (CH_2) , 35.4 (CH_2), 39.2 (C_4)
3d	0.51 petroleum ether/ Et_2O (99:1)	112−114	2948, 2865, 1460, 1271	578 (M^+), 535, 157, 115	1.27 (d, 36 H, *J* = 7.3), 1.51 (sept, 6 H, *J* = 7.3), 1.8−2.1 (m, 4 H), 2.48 (ddd, 4 H, *J* = 14.1, 3.8, 3.5), 2.73 (s, 4 H), 3.15 (ddd, 4 H, *J* = 13.2, 13.0, 2.7)	12.4 (SiCH), 20.1 (CH_3), 24.4 (CH_2), 25.4 (CH_2), 39.7 (CH_2), 41.4 (C_4)
3f	0.30 petroleum ether/ Et_2O (99:1)	112−114	2936, 2855, 1422, 1248	452 (M^+), 337, 221, 179	0.24 (s, 15 H), 1.08 (s, 9 H), 1.8−2.1 (m, 4 H), 2.4−2.5 (m, 4 H), 2.53 (m, 4 H), 3.1−3.2 (m, 4 H)	−5.3 [$Si(CH_3)_2$], −2.4 [$Si(CH_3)_3$], 19.8 (C_4), 23.3 (CH_2), 23.5 (CH_2) , 25.0 (CH_2), 25.1 (CH_2), 28.4 (CH_3), 35.8 (CH_2), 36.7 (CH_2), 39.3 (C_4), 41.2 (C_4)
3g	0.37 petroleum ether/ Et_2O (99:1)	106−107	2948, 2865, 1458, 1244	494 (M^+), 263, 191, 157	0.25 (s, 9 H), 1.27 (d, 18 H, *J* = 7.3), 1.49 (sept, 3 H, *J* = 7.3), 1.9−2.1 (m, 4 H), 2.3−2.7 (m, 8 H), 3.13 (ddd, 2 H, *J* = 13.9, 12.4, 2.7), 3.18 (ddd, 2 H, *J* = 13.7, 12.4, 2.7)	−2.4 [$Si(CH_3)_3$], 12.4 (SiCH), 20.2 (CH_3), 23.6 (CH_2), 24.6 (CH_2), 24.8 (CH_2), 25.1 (CH_2), 36.2 (CH_2), 38.6 (CH_2), 39.3 (C_4), 41.7 (C_4)
4c	Petroleum ether[d]	121−123	2957, 2853, 1419, 1253	508 (M^+), 261, 203, 145	0.24 (s, 12 H), 1.06 (s, 18 H), 1.8−2.1 (m, 6 H), 2.3−2.4 (m, 8 H), 3.05 (ddd, 4 H, *J* = 13.5, 13.1, 2.7)	−5.3 [$Si(CH_3)_2$], 19.9 (C_4), 23.3 (CH_2), 25.0 (CH_2), 26.9 (CH_2), 28.3 (CH_3), 38.1 (CH_2), 41.0 (C_4)
4d	Petroleum ether[d]	142−144	3069, 2951, 1428, 1250	548 (M^+), 351, 197, 145	0.12 (s, 9 H), 0.81 (s, 3 H), 1.5-1.7 (m, 2 H), 1.8-2.1 (m, 6 H), 2.2-2.3 (m, 2 H), 2.3-2.5 (m, 4 H), 2.84 (ddd, 2 H, *J* 13.5, 13.2, 2.7), 3.03 (ddd, 2 H, *J* 12.8, 12.4, 3.4), 7.3-7.5 (m, 6 H), 7.84 (d, 4 H, *J* 6.5)	−3.8 ($SiCH_3$), −2.7 [$Si(CH_3)_3$], 23.2 (CH_2), 23.8 (CH_2), 24.7 (CH_2), 25.0 (CH_2), 25.7 (CH_2), 36.7 (C_4), 37.6 (CH_2), 38.4 (CH_2), 39.1 (C_4), 127.5 (CH), 129.5 (CH), 134.1 (C_4), 135.8 (CH)
4f	0.38 petroleum ether/ EtOAc (99:1)	124−127	2948, 2897, 1424, 1273	438 (M^+), 205, 191, 159	0.22 (s, 9 H), 0.25 (s, 9 H), 1.30 (d, 3 H, *J* 6.9), 1.8−2.2 (m, 6 H), 2.3−2.6 (m, 7 H), 2.9-3.2 (m, 4 H)	−2.6 [$Si(CH_3)_3$], −0.2 [$Si(CH_3)_3$], 18.3 (CH_3), 23.3 (CH_2), 23.5 (CH_2), 23.6 (CH_2), 24.7 (CH_2), 25.2 (CH_2), 33.0 (CH_2), 37.4 (CH_2), 38.8 (C_4), 40.6 (CH), 45.0 (C_4)

[a] Satisfactory microanalyses for all crystallized compounds: C ± 0.4; H ± 0.4.

[b] Solvents used for TLC and chromatographic separation.

[c] White crystals.

[d] Recrystallization

ed with BuLi (11.3 mmol, 0.6 equiv) and trialkylsilyl chloride (11.3 mmol, 0.6 equiv). After another 1 h at 0 °C, the reaction was quenched with H_2O (100 mL). The crude mixture was extracted with Et_2O (4 × 50 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The residue was chromatographed on silica gel using mixture of petroleum ether/Et_2O (Tables 1 and 4).

Mono Trimethylsilylated Intermediates for Two-Step Reactions; 1-(1,3-Dithian-2-yl)-2-(2-trimethylsilyl-1,3-dithian-2-yl)ethane; Typical Procedure

Monosilylation of **1** (5.0 g, 18.8 mmol) with BuLi in hexane (10.1 mL, 19.7 mmol) and trimethylsilyl chloride (2.5 ml, 19.7 mmol), by a procedure similar to that reported for **3a**–**d**, gave after recrystallization from petroleum ether the mono trimethylsilylated bis(dithiane) intermediate (5.9 g, 94%) as a white solid; mp 91−92 °C; R_f 0.33 (petroleum ether/EtOAc, 96:4).

^{1}H NMR: δ = 0.20 (s, 9 H), 1.8−2.2 (m, 6 H), 2.4−2.5 (m, 4 H), 2.8−2.9 (m, 4 H), 3.08 (ddd, J = 13.6, 13.1, 2.7 Hz, 2 H), 4.08 (dd, J = 6.9, 6.5 Hz, 1 H).

^{13}C NMR: δ = −2.7 [$Si(CH_3)_3$], 23.1 (CH_2), 25.0 (CH_2), 25.9 (CH_2), 30.3 (CH_2), 33.5 (CH_2), 33.8 (CH_2), 38.2 (C_4), 47.7 (CH).

IR (KBr):ν = 2903, 2857, 1453, 1410, 1250 cm^{-1}.

MS: m/z = 338 (M^+), 265, 206, 159, 132, 107.

Anal. calcd for $C_{13}H_{26}SiS_4$: C 46.10, H 7.74; found: C 46.28, H 8.04.

1-(1,3-Dithian-2-yl)-3-(2-trimethylsilyl-1,3-dithian-2-yl)propane

The same procedure of monoalkylation with trimethylsilyl chloride applied to **2** (6.7 g, 24.0 mmol) gave after two successive recrystallizations from petroleum ether the corresponding bis(silylated) compound (1.2 g, 11%)[16b] and the mono trimethylsilylated bis(dithiane) intermediate (7.2 g, 85%) as a yellow oil.

Mono Trimethylsilylated Bis(dithiane) Intermediate Corresponding to n = 2, Si^1 = SiMe$_3$ (cf. Scheme 1)

R_f 0.26 (petroleum ether/Et_2O, 99:1).

^{1}H NMR: δ = 0.21 (s, 9 H), 1.6−2.0 (m, 6 H), 2.0−2.3 (m, 4 H), 2.4−2.5 (m, 2 H), 2.8−2.9 (m, 4 H), 3.04 (m, 2 H), 4.10 (dd, J = 6.9, 6.5 Hz, 1 H).

^{13}C NMR: δ = −2.7 [$Si(CH_3)_3$], 23.3 (CH_2), 24.6 (CH_2), 25.0 (CH_2), 25.9 (CH_2), 30.3 (CH_2), 35.6 (CH_2), 36.6 (CH_2), 38.4 (C_4), 47.1 (CH).

IR (film): ν = 2897, 2847, 1422, 1248, 911 cm^{-1}.

MS: m/z = 352 (M^+), 279, 179, 145, 113.

Anal. calcd for $C_{14}H_{28}SiS_4$: C 47.68, H 8.00; found: C 47.89, H 8.32.

Unsymmetrical Bis(dithianes) 3e−g and 4a; General Two-Step Procedure

Silylation of mono trimethylsilylated bis(dithiane) intermediate (7.4 mmol, 1.0 equiv) with BuLi in hexane (8.2 mmol, 1.1 equiv) and trialkylsilyl chloride (8.2 mmol, 1.1 equiv), by a procedure similar to that reported for **3a**−**d**, gave after chromatography on silica

Table 5 Spectroscopic Data of Bis(acylsilanes) **5a,d,f,g** and **6c,d,f**

Product[a,b]	R_f (solvent)[c]	IR (film) ν (cm^{-1})	MS m/z	^{1}H NMR ($CDCl_3$) δ, J (Hz)	^{13}C NMR ($CDCl_3$) δ
5a	0.49 petroleum ether/ EtOAc (96:4)	2961, 1644, 1250, 843	230 (M^+), 220, 205, 147	0.18 (s, 18 H), 2.80 (s, 4 H)	−3.3 [$Si(CH_3)_3$], 40.0 (CH_2), 245.3 (CO)
5d	0.49 petroleum ether/ EtOAc (99:1)	2946, 2869, 1634, 1387	398 (M^+), 355, 157, 115	1.11 (d, 36 H, J = 7.2), 1.29 (sept, 6 H, J = 7.2), 2.84 (s, 4 H)	10.7 (SiCH), 18.5 (CH_3), 43.0 (CH_2), 244.2 (CO)
5f	0.35 petroleum ether/ EtOAc (98:2)	2957, 2861, 1642, 1250	272 (M^+), 215, 147, 115	0.21 (s, 6 H), 0.23 (s, 9 H), 0.94 (s, 9 H), 2.84 (m, 4 H)	−7.1 [$Si(CH_3)_2$], −3.3 [$Si(CH_3)_3$], 16.4 (C_4), 26.3 (CH_3), 40.0 (CH_2), 42.3 (CH_2), 244.6 (CO), 245.5 (CO)
5g	0.55 petroleum ether/ EtOAc (96:4)	2946, 2869, 1638, 1250	314 (M^+), 299, 157, 115	0.23 (s, 9 H), 1.11 (d, 18 H, J 6.9), 1.28 (sept, 3 H, J = 6.9), 2.84 (m, 4 H)	−3.3 [$Si(CH_3)_3$], 10.6 (SiCH), 18.4 (CH_3), 39.5 (CH_2), 43.6 (CH_2), 244.1 (CO), 245.4 (CO)
6c	0.35 petroleum ether/ EtOAc (97:3)	2930, 2859, 1640, 1250	328 (M^+), 189, 159, 147	0.16 (s, 12 H), 0.91 (s, 18 H), 1.72 (quint, 2 H, J = 6.9), 2.59 (t, 4 H, J = 6.9)	-7.0 ($SiMe_2$), 14.4 (CH_2), 16.5 (C_4), 26.4 (CH_3), 49.3 (CH_2), 247.1 (CO)
6d	0.32 petroleum ether/ EtOAc (96:4)	3052, 2957, 1642, 1250	368 (M^+), 209, 197, 149	0.15 (s, 9 H), 0.77 (s, 3 H), 1.73 (quint, 2 H, J = 6.9), 2.52 (t, 2 H, J = 6.9), 2.67 (t, 2 H, J = 6.9), 7.35−7.50 (m, 6 H), 7.55−7.65 (m, 4 H)	−5.5 ($SiCH_3$), −3.3 [$Si(CH_3)_3$], 14.8 (CH_2), 47.3 (CH_2), 48.7 (CH_2), 128.2 (CH), 130.1 (CH), 132.6 (C_4), 134.9 (CH), 244.0 (CO), 247.6 (CO)
6f	0.33 petroleum ether/ ETOAc (96:4)	2961, 2903, 1642, 1250	258 (M^+), 185, 147, 131	0.20 (s, 9 H), 0.22 (s, 9 H), 0.97 (d, 3H, J = 6.9), 1.4−1.6 (m, 1 H), 1.90 (dddd, 1 H, J = 14.5, 7.6, 7.3, 6.9), 2.54 (m, 2 H), 2.89 (hex, 1 H, J = 6.9)	−3.3 [$Si(CH_3)_3$], −2.7 [$Si(CH_3)_3$], 14.4 (CH_3), 23.0 (CH_2), 45.5 (CH_2), 49.4 (CH), 247.4 (CO), 250.3 (CO)

[a] Oil.

[b] Satisfactory microanalyses obtained.

[c] Solvents used for TLC and chromatographic separation.

Table 6 Spectroscopic Data of Furans **8b**–**g** and 4*H*-Pyrans **9a**–**g**

Products[a,b]	Thermolysis (°C)	IR (film) ν (cm^{-1})	MS *m/z*	^1H NMR ($CDCl_3$) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$) δ
8b	80−90	2955, 2878, 1537, 1460	296 (M^+), 267, 189, 115	0.77 (q, 12 H, *J* = 8.0), 1.01 (t, 18H, *J* = 7.6), 6.64 (s, 2 H)	3.4 ($SiCH_2$), 7.3 (CH_3), 119.9 (CH), 162.6 (C_4)
8c	83−85	2955, 2859, 1539, 1472	296 (M^+), 239, 167, 147	0.23 (s, 12 H), 0.92 (s, 18 H), 6.63 (s, 2 H)	−6.3 [$Si(CH_3)_2$], 16.8 (C_4), 26.3 (CH_3), 120.1 (CH), 163.1 (C_4)
8d	120−135	2946, 2867, 1537, 1464	380 (M^+), 337, 295, 119	1.09 (d, 36 H, *J* = 6.9), 1.31 (sept, 6 H, *J* = 6.9), 6.68 (s, 2 H)	11.2 (SiCH), 18.6 (CH_3), 120.9 (CH), 160.9 (C_4)
8e	65−70	2957, 2878, 1539, 1460	254 (M^+), 225, 147, 130	0.27 (s, 9 H), 0.77 (q, 6 H, *J* = 8.0), 1.00 (t, 9 H, *J* = 8.0), 6.62 (m, 2 H)	−1.6 [$Si(CH_3)_3$], 3.4 ($SiCH_2$), 7.3 (CH_3), 118.9 (CH), 120.0 (CH), 162.7 (C_4), 164.5 (C_4)
8f	75−85	2957, 2859, 1539, 1472	254 (M^+), 239, 197, 147	0.24 (s, 6 H), 0.27 (s, 9 H), 0.93 (s, 9 H), 6.62 (m, 2 H)	−6.2 [$Si(CH_3)_2$], −1.6 [$Si(CH_3)_3$], 16.9 (C_4), 26.3 (CH_3), 118.9 (CH), 120.3 (CH), 163.0 (C_4), 164.6 (C_4)
8g	80−90	2946, 2869, 1539, 1464	296 (M^+), 253, 211, 115	0.26 (s, 9 H), 1.10 (d, 18 H, *J* = 6.9), 1.27 (sept, 3 H, *J* = 6.9), 6.62 (d, 1 H, *J* = 3.1), 6.66 (d, 1 H, *J* = 3.1)	−1.6 [$Si(CH_3)_3$], 11.2 (SiCH), 18.6 (CH_3), 118.7 (CH), 120.9 (CH), 161.3 (C_4), 164.2 (C_4)
9a	80−90	2942, 2865, 1609, 1246	310 (M^+), 237, 153	0.09 (s, 9 H), 1.0−1.2 (m, 21 H), 2.66 (dd, 2 H, *J* = 3.4, 3.1), 5.00 (dd, 2 H, *J* = 3.4, 3.1)	−2.7 [$Si(CH_3)_3$], 10.5 (SiCH), 18.6 (CH_3), 19.2 (CH_2), 109.3 (CH), 111.7 (CH), 154.0 (C_4), 157.5 (C_4)
9b	75−85	2959, 2899, 1608, 1249	226 (M^+), 168, 153, 147	0.10 (s, 18 H), 2.61 (t, 2 H, *J* = 3.3), 5.00 (t, 2 H, *J* = 3.3)	−2.8 [$Si(CH_3)_3$], 19.3 (CH_2), 109.4 (CH), 157.9 (C_4)
9c	85−90	2953, 2930, 1607,1248	310 (M^+), 195, 115	0.05 (s, 12 H), 0.93 (s, 18 H), 2.65 (t, 2 H, *J* = 3.4), 4.98 (t, 2 H, *J* = 3.4)	−7.0 [$Si(CH_3)_2$], 16.4 (C_4), 19.3 (CH_2), 26.6 (CH_3), 110.9 (CH), 156.1 (C_4)
9d	80−90	3069, 2959, 1609, 1248	350 (M^+), 277, 153	0.08 (s, 9 H), 0.68 (s, 3 H), 2.67 (t, 2H, *J* = 3.1), 5.00−5.15 (m, 2 H), 7.3−7.4 (m, 6 H), 7.6−7.7 (m, 4 H)	−5.1 ($SiCH_3$), −2.8 [$Si(CH_3)_3$], 19.5 (CH_2), 109.5 (CH), 113.7 (CH), 127.7 (CH), 129.4 (CH), C_4 (not observed), 135.1 (CH), 154.7 (C_4), 157.9 (C_4)
9e	85−95	2953, 2928, 1607, 1246	310 (M^+), 195, 115	0.04 (s, 6 H), 0.60 (q, 6 H, *J* = 8.0), 0.92 (s, 9 H), 0.96 (t, 9 H, *J* = 8.0), 2.63 (m, 2 H), 4.9−5.0 (m, 2 H)	−7.1 [$Si(CH_3)_2$], 2.3 ($SiCH_2$), 7.3 (CH_3), 16.4 (C_4), 19.2 (CH_2), 26.6 (CH_3), 110.7 (CH), 110.9 (CH), 155.4 (C_4), 156.2 (C_4)
9f	75−85	2959, 2924, 1620, 1248	240 (M^+), 182, 167, 147	0.11 (s, 9 H), 0.20 (s, 9 H), 1.61 (s, 3 H), 2.54 (d, 2 H, *J* = 2.7), 5.05 (dd, 1 H, *J* = 3.4, 3.1)	−2.6 [$Si(CH_3)_3$], −0.7 [$Si(CH_3)_3$], 19.2 (CH_3), 25.9 (CH_2), 108.7 (CH), 118.1 (C_4), 149.3 (C_4), 156.8 (C_4)
9g	85−95	2928, 2857, 1617, 1250	324 (M^+), 267, 167, 147	0.05 (s, 6 H), 0.17 (s, 6 H), 0.92 (s, 9 H), 0.93 (s, 9 H), 1.59 (s, 3 H), 2.57 (dd, 2 H, *J* = 3.4, 1.1), 5.02 (t, 1 H, *J* = 3.4)	−6.9 [$Si(CH_3)_2$], −4.2 [$Si(CH_3)_2$], 16.5 (C_4), 17.9 (C_4), 20.2 (CH_3), 26.2 (CH_2), 26.7 (CH_3), 26.8 (CH_3), 110.2 (CH), 119.1 (C_4), 147.9 (C_4), 154.9 (C_4)

[a] Oil.
[b] Satisfactory microanalyses obtained.

gel using a mixture of petroleum ether/Et_2O the unsymmetrical bis(dithianes) **3e**−**g** and **4a** (Tables 1 and 4).

Dethioketalization with Methyl Iodide; General Procedure

The dethioketalization of **3** and **4** with MeI was carried out according to the procedure reported by us in Ref. 12 (Tables 1, 2, 5).

Dethioketalization with Mercury(II) Perchlorate; General Procedure

To a solution of bis(dithiane) **3** or **4** (5.0 mmol, 1.0 equiv) in a mixture THF/H_2O (80:20, 30 mL) were added $CaCO_3$ (30.5 mmol, 6.1 equiv), $Hg(ClO_4)_2$ (30.0 mmol, 6.0 equiv). The mixture was stirred at r.t. until total conversion (overnight), and was then partitioned between CH_2Cl_2 (150 mL) and brine (100 mL). After filtration through Celite, the filtrate was extracted with CH_2Cl_2 (5 × 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was chromatographed over silica gel using petroleum ether/EtOAc as eluent (Tables 1, 2, 5).

Dethioketalization with Iodine; General Procedure

To a solution of the bis(dithiane) **3** or **4** (7.7 mmol, 1.0 equiv) in THF/H_2O (80:20, 40 mL), at r.t., were added $CaCO_3$ (92.4 mmol, 12.0 equiv) and I_2 (69.3 mmol, 9.0 equiv). The mixture was stirred at the same temperature until total conversion (overnight), then partitioned between Et_2O (100 mL) and satd aq $Na_2S_2O_3$ solution (60 mL). After stirring for 10 min, the crude was filtered over Celite and extracted with Et_2O (5 × 50 mL). The organic phase was dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was chromatographed over silica gel using petroleum ether/EtOAc as eluent (Tables 1, 2, 5).

Bis(dithianes) 4b,c,f,g; General Procedure

The bis(dithianes) were prepared according to the procedure reported by us in Ref. 12 (Tables 2 and 4).

Unsymmetrical Bis(dithianes) 4d−e; General Procedure (Scheme 2)

To a solution of the 2-trialkylsilyl-1,3-dithiane (10.0 mmol, 1.1 equiv) in THF (30 mL) cooled to −25 °C was added dropwise a solution of BuLi hexane (10.0 mmol, 1.1 equiv) over a period of 5 min. After stirring for 2.5 h at −25 °C, a solution of 1-chloro-3-iodopropane (9.1 mmol, 1.0 equiv) in THF (10 mL) was added at 0 °C. The mixture was stirred for a further 2 h at 0 °C, and then a solution of another 2-trialkylsilyl-2-lithio-1,3-dithiane (10.9 mmol, 1.2 equiv, prepared by the same procedure) was added dropwise over a period of 5 min. After stirring overnight at 0 °C, the reaction was quenched by the addition of satd aq NH_4Cl solution (50 mL). The crude mixture was extracted with Et_2O (3 × 50 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was recrystallized from petroleum ether (Tables 2 and 4). The bis(dithiane) **4g** was accompanied by 2-(but-3-enyl)-2-(*tert*-butyldimethylsilyl)-1,3-dithiane **7**.

Compound 7

Yield: 57%; oil.

^1H NMR: $\delta = 0.22$ (s, 6 H), 1.04 (s, 9 H), 1.8−2.1 (m, 2 H), 2.3−2.5 (m, 6 H), 3.06 (ddd, $J = 13.5, 13.2, 2.7$ Hz, 2 H), 4.9-5.1 (m, 2 H), 5.8−6.0 (m, 1 H).

^{13}C NMR: $\delta = -5.3$ [$Si(CH_3)_2$], 19.7 (C_4), 23.4 (CH_2), 24.9 (CH_2), 28.2 (CH_3), 32.4 (CH_2), 36.9 (CH_2), 40.7 (C_4), 114.6 (CH_2), 138.3 (CH).

IR (film): $\nu = 3082, 2937, 2853, 1637, 1469, 1253$ cm^{-1}.

MS: $m/z = 289$ (M^+), 273, 247, 189, 173.

HRMS: m/z calcd for $C_{14}H_{28}SiS_2$ 288.1402; found 288.1420.

Furans 8a−g and 4*H*-Pyrans 9a−g; General Procedure

A mixture of 1,4- or 1,5-bis(acylsilane) **5** or **6** (5.0 mmol, 1.0 eq.) and *p*-toluenesulfonic acid (0.5 mmol, 0.1 equiv) was thermolysed under reduced pressure (0.05 mbar), using a Büchi Kugelrohr apparatus, to give 2,5-bis(trialkylsilyl)furans **8a**−**g** or 2,6-bis(trialkylsilyl)-4*H*-pyrans **9a**−**g**, respectively (Tables 3 and 6).

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Article Identifier:
1437-210X,E;2000,0,06,0843,0849,ftx,en;Z00500SS.pdf