Counterattack Reagent: Hexamethyldisilane in a Direct Synthesis of Ketene Dithioacetals and 2-Trimethylsilyl-1,3-dithiane Derivatives from 1,3-Dithiane

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A novel method has been developed for the direct synthesis of ketene dithioacetals and 2-trimethylsilyl-1,3-dithiane derivatives from 1,3-dithiane. Treatment of 1,3-dithiane (1.0 mol equiv.) with BuLi (1.1 mol equiv.), HMPA (4.0 mol equiv.), and $Me_3SiSiMe_3$ (1.1 mol equiv.) produced 2-lithio-2-trimethylsilyl-1,3-dithiane. To this solution was added an aldehyde, ketone, enone, 1-nitroalkene, or organic bromide (1.1–1.2 mol equiv.) in THF to give the desired products (i.e., 7–16) at room temperature in 54–98% yield. In this newly developed 'one-flask' method, $Me_3SiSiMe_3$ acts as a 'counterattack reagent'.

The concept of a 'counterattack reagent'[1] has been applied to the development of various chemical transformations. Examples include oxidative desulfonylation,[2] conversion of allyl alcohols and carbonyl compounds into allyltrimethylsilanes,[3] protection[4] and deprotection[5] of hydroxy groups, polysilylation of hydrazines,[6] as well as formation of thiohydroxamic acids and thiohydroximates from nitro compounds.[7] One of the advantages of the utilization of counterattack reagents is to simplify chemical transformations that require more than one step. We considered using the 'counterattack strategy'[1] to facilitate the syntheses of ketene dithioacetals and 2-trimethyl-silyl-1,3-dithiane derivatives.

Ketene dithioacetals are useful synthetic intermediates,[8–13] which can be produced by treatment of carbonyl compounds with dithiane ylide[9,10] or 2-lithio-2-trimethylsilyl-1,3-dithiane.[14,15] These dithiane reagents are prepared from 1,3-dithiane.[16] We report herein an efficient reaction that allowed the generation of ketene dithioacetals and 2-trimethylsilyl-1,3-dithiane derivatives from 1,3-dithiane in one flask by an intriguing use of $Me_3SiSiMe_3$.
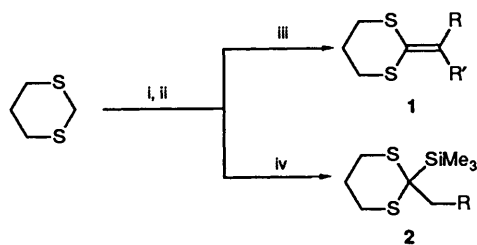
Scheme 1 *Reagents and conditions:* i, BuLi, THF; ii, $Me_3SiSiMe_3$, HMPA, $-25\,°C$; iii, RR'CO; iv, RCH_2X, $-78\,°C$

Results

Scheme 1 shows our new method for a direct synthesis of 1,3-dithiane derivatives 1 and 2. We treated a tetrahydrofuran (THF) solution of 1,3-dithiane with BuLi (1.1 mol equiv.) and a mixture of $Me_3SiSiMe_3$ (1.1 mol equiv.) and hexamethylphosphoramide (HMPA, 4.0 mol equiv.) in sequence. After 2 h, an aldehyde or ketone (1.0–1.2 mol equiv.) was added to the

resultant dark yellow solution. The desired product was obtained at room temperature in 12–24 h. When the substrate was an α,β-unsaturated ketone, nitroalkene, alkyl, allyl, or benzyl bromide, the addition was done at $-78\,°C$ and the reaction was complete in 20 min.

By this new method, we converted benzaldehyde and several ketones into the corresponding ketene dithioacetals 7–10 in 65–92% yield (Table 1). Cyclohex-2-enone and 1-nitrocyclohexene each reacted as a Michael acceptor to give adducts 11 (94%) and 12 (57%), respectively; no adduct from non-conjugate addition was detected by ^1H NMR spectrometry. Alkyl, allyl and benzyl bromides underwent substitution to give products 13–16 in 54–98% yield. Also, Me_3Si-containing 1,3-dithiane derivatives 11 and 16 could be hydrolysed to the corresponding acylsilanes 17 (85%) and 18 (75%), respectively, with $HgCl_2$, $CdCO_3$, and acetone in the presence of water.[17]

Discussion

Design of the 'One-Flask' Method for the Formation of Dithiane Derivatives.—Scheme 2 shows our design for the 'one-flask' synthesis of ketene dithioacetals and 2-trimethylsilyl-1,3-dithiane derivatives from 1,3-dithiane. We first used BuLi to remove a C-2 proton from 1,3-dithiane to give anion 3, which attacked $Me_3SiSiMe_3$ to produce 2-trimethylsilyl-1,3-dithiane 4 and Me_3Si^-. This silyl anionic leaving group then counter-attacked compound 4 to generate the Me_3Si-stabilized anion 5. Thus $Me_3SiSiMe_3$ can be regarded as a 'counterattack reagent'.[1]

Seebach,[13,14] Carey,[15] and their co-workers reported that metalated (trimethylsilyl)formaldehyde dithioacetals react with carbonyl compounds to give ketene dithioacetals by the Peterson olefination. In our method, we first generated 2-lithio-2-trimethylsilyl-1,3-dithiane from 1,3-dithiane without isolating any intermediates. We then adopted the established procedure[13–15] by treating 2-lithio-2-trimethylsilyl-1,3-dithiane with carbonyl compounds *in situ*. This 'one-flask' process gave the desired products 7–11 in good to excellent yield (65–92%). On the other hand, the traditional 'two-step' process requires the isolation of intermediate 4 (71% yield)[16] in the first step; various carbonyl compounds then react with compound 4 to give products 7–11 (62–80% yield)[12,15,18] in the second step. The overall yields are 40–57%. Therefore the newly developed 'one-flask' process is more efficient than the traditional 'two-step' process.

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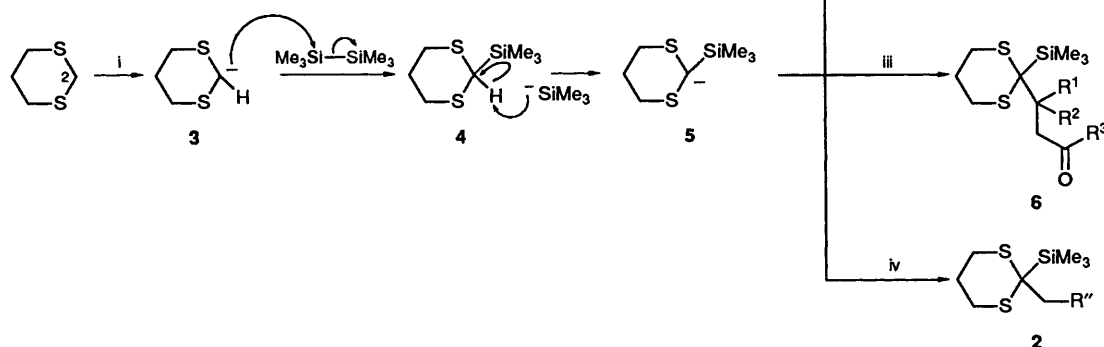
Scheme 2 *Reagents:* i, BuLi; ii, RR'CO; iii, $R^1R^2C=CHCOR^3$; iv, $R''CH_2X$

Using the same strategy of the 'one-flask' process, we were able to get the dithiane anion **5** to react successfully with an α,β-unsaturated ketone (to give products of type **6**), a nitroalkene, and various organic bromides *in situ*. The results are summarized in Table 1 (also see Scheme 2).

Control of the Reaction Conditions.—We found that it was crucial to mix solvent HMPA with reagent $Me_3SiSiMe_3$ *before* they were injected into the THF solution of dithiane anion **3**. If this procedure was not followed, low yields were obtained for the desired products **1** and **2**.

In the reaction with cyclohex-2-en-1-one as the substrate, we obtained the Michael adduct only by using HMPA as the co-solvent; the corresponding adducts from non-conjugate addition were not observed. Our results are consistent with those reported by Brown and Yamaichi.[18]

It is essential to control the time interval between the injections of $HMPA/Me_3SiSiMe_3$ mixture and the substrates (*i.e.*, carbonyl compounds, organic bromides, *etc.*). With an interval larger than 2 h, the reaction mixture became dark red and resulted in the decomposition of 2-lithio-2-trimethylsilyl-1,3-dithiane.

In order to obtain the 1,3-dithiane products possessing the Me_3Si group, we had to add the substrates to the solution of anion **5** at low temperature (*e.g.*, $-78\ ^\circ C$). At room temperature, the reactions produced the desilylated dithiane derivatives as the major products. In addition, the labile Me_3Si group at the C-2 position was removed to a lesser extent by use of organic bromides as the substrate rather than organic chlorides. For example, reaction of benzyl bromide with anion **5** gave silylated dithiane **16** in 54% yield, along with the corresponding desilylated dithiane in 25% yield. Use of benzyl chloride, however, produced the desired dithiane **16** in 25% yield only; the corresponding desilylated dithiane was isolated in 50% yield.

Conclusions.—Reagent $Me_3SiSiMe_3$ was used to facilitate the reaction of 1,3-dithiane with various organic compounds, including an aldehyde, ketone, enone, nitroalkene, alkyl, allyl and benzyl bromide. The desired products, ketene dithioacetals and 2-trimethylsilyl-1,3-dithiane derivatives, were obtained in

good to excellent yield. In these 'one-flask' reactions, Me_3Si-$SiMe_3$ acted as a counterattack reagent.
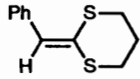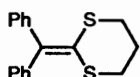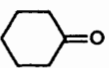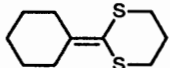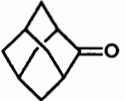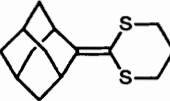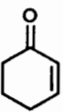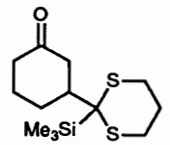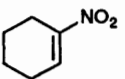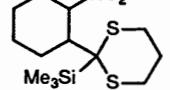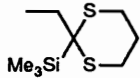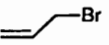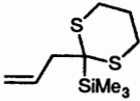
Experimental

General.—Gas chromatographic analyses were performed with a 12.5 m cross-linked methyl silicone gum capillary column (0.2 mm i.d.). The retention time t_R was measured under the following conditions: injector temperature 260 °C, the initial temperature for column 55 °C, duration 2.00 min, increment rate 10 °C/min, and the final temperature for column 250 °C. Analytical TLC was performed on precoated plates (silica gel GHLF), purchased from Analtech Inc. Purification by gravity column chromatography was carried out by use of E. Merck Silica Gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM). Separations by radial TLC were performed on a model 7924T Chromatotron from Harrison Research. Plates of 4 mm thickness were coated with E. Merck Silica Gel 60 PF_{254} containing gypsum. Proton NMR spectra were obtained on a Brüker AC-200 spectrometer with $CDCl_3$ as solvent. Infrared spectra were measured on a Perkin-Elmer 882 spectrometer.

Standard Procedure for the Syntheses of Ketene Dithioacetals and 2-Trimethylsilyl-1,3-dithiane Derivatives.—To a solution of 1,3-dithiane (1.0 mol equiv.) in dry THF (0.2–0.4 mol dm^{-3}) at $-25\ ^\circ C$ under nitrogen was added BuLi (1.54 mol dm^{-3} in hexanes; 1.1 mol 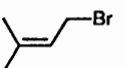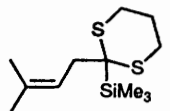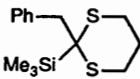equiv.). After being stirred for 30 min the solution was treated with a mixture of HMPA (4.0 mol equiv.) and hexamethyldisilane (1.1 mol equiv.) in one portion. The reaction mixture was slowly warmed to room temperature during 2 h. To this solution was added an aldehyde or ketone (1.0–1.2 mol equiv.) and the mixture was stirred for 12–24 h. When an α,β-unsaturated ketone, nitroalkene, alkyl, allyl, or benzyl halide (1.0–1.2 mol equiv.) was used as the substrate, it was added after the solution was cooled to $-78\ ^\circ C$. After being stirred for 20 min at $-78\ ^\circ C$, the reaction mixture was warmed to room temperature, quenched with saturated aq. NH_4Cl, and extracted with hexanes (25 cm^3 × 4). The combined organic solutions were washed with saturated aq. NH_4Cl, dried over $MgSO_4(s)$, filtered, and concentrated under reduced pressure. The residue was chromatographed or recrystallized to give pure ketene dithioacetals or 2-trimethylsilyl-1,3-dithiane derivatives.

2-Benzylidene-1,3-dithiane **7**. The standard procedure was followed by use of 1,3-dithiane (365 mg, 2.94 mmol, 1.0 mol equiv.), BuLi (2.14 cm^3, 3.30 mmol, 1.1 mol equiv.), hexamethyldisilane (438 mg, 3.30 mmol, 1.1 mol equiv.), HMPA (2.16 g, 12.1 mmol, 4.0 mol equiv.), benzaldehyde (350 mg, 3.30 mmol, 1.1 mol equiv.), and THF (14 cm^3). After work-up and

Table 1 Preparation of ketene dithioacetals and 2-trimethylsilyl-1,3-dithiane derivatives from 1,3-dithiane, hexamethyldisilane, and various organic substrates

Substrate	Product		Yield (%)
		7	80
		8	81
		9	65
		10	92
		11	94
		12	57 9% (cis) + 91% (trans)
		13	98
		14	67
		15	65
		16	54

purification by use of the chromatotron (2% EtOAc in hexanes as eluent), the dithiane **7** was obtained as a yellow oil in 80% yield (493 mg, 2.35 mmol): GLC t_R 16.30 min; TLC R_f 0.40 (5% EtOAc in hexanes); δ_H(CDCl$_3$; 80 MHz) 1.80 (2 H, m, SCCH$_2$CS), 2.70 (4 H, m, 2 × SCH$_2$), 6.75 (1 H, s, C=CH) and 7.00–7.42 (5 H, m, C$_6$H$_5$); ν_{max}(film)/cm^{-1} 3036w, 3000w, 2919s, 1596m (C=C), 1578m (C=C), 1554m (C=C), 1490m, 1437m, 1420m, 1300m, 1240m, 1079w, 1026w, 932m, 914m, 840m, 740s and 690s. The physical properties and spectroscopic characteristics are consistent with those reported.[14]

2,2-Diphenylmethylene-1,3-*dithiane* **8**. The standard procedure was followed by use of 1,3-dithiane (501 mg, 4.03 mmol, 1.0 mol equiv.), BuLi (2.92 cm^3, 4.50 mmol, 1.1 mol equiv.), hexamethyldisilane (644 mg, 4.40 mmol, 1.1 mol equiv.), HMPA (4.06 g, 16.1 mmol, 4.0 mol equiv.), benzophenone (760 mg, 4.20 mmol, 1.1 mol equiv.), and THF (21 cm^3). After work-up, and recrystallization of the crude product with ethanol, the dithiane **8** was obtained in 81% yield (890 mg, 3.24 mmol) as a solid, m.p. 135.0–135.5 °C (lit.,[2] 134.5–135 °C); t_R 20.84 min; R_f 0.46 (5% EtOAc in hexanes); δ_H(CDCl$_3$; 80 MHz) 1.95–2.05 (2 H, m, SCCH$_2$CS), 2.75–2.95 (4 H, m, 2 × SCH$_2$) and 7.18–7.29 (10 H, m, 2 × C$_6$H$_5$); ν_{max}(film)/cm^{-1} 3046w, 3010w, 2919s, 1598m (C=C), 1535m (C=C), 1492m, 1440m, 1415m, 1297m, 1274m, 1072w, 1030w, 932m, 916m, 855m, 740s and 700s. The physical properties and spectroscopic characteristics are consistent with those reported.[14,15]

2-Cyclohexylidene-1,3-*dithiane* **9**. The standard procedure was followed by use of 1,3-dithiane (390 mg, 3.14 mmol, 1.0 mol equiv.), BuLi (2.27 cm^3, 3.50 mmol, 1.1 mol equiv.), hexamethyldisilane (505 mg, 3.45 mmol, 1.1 mol equiv.), HMPA (2.37 g, 13.1 mmol, 4.1 mol equiv.), cyclohexanone (340 mg, 3.45 mmol, 1.1 mol equiv.), and THF (15 cm^3). After work-up, and purification by use of the chromatotron (hexanes as eluent), the dithiane **9** was obtained in 65% yield (410 mg, 1.95 mmol) as a solid, m.p. 90.5–91.5 °C (lit.,[3] 91.5–93.5 °C); t_R 14.07 min; R_f 0.55 (5% EtOAc in hexanes); δ_H(CDCl$_3$; 80 MHz) 1.54 (6 H, m, C[CH$_2$]$_3$C), 2.02–2.22 (2 H, m, SCCH$_2$CS), 2.40–2.50 (4 H, m, 2 × =CCH$_2$) and 2.79–2.93 (4 H, m, 2 × SCH$_2$); ν_{max}(KBr)/cm^{-1} 2949s, 2919s, 1578w (C=C), 1443m, 1420m, 1343w, 1302w, 1270m, 1226m, 990w, 908w, 861w and 840w. The physical properties and spectroscopic characteristics are consistent with those reported.[14,15]

2-[2-(1,3-Dithianylidene)]adamantane **10**. The standard procedure was followed by use of 1,3-dithiane (355 mg, 2.95 mmol, 1.0 mol equiv.), BuLi (2.11 cm^3, 3.25 mmol, 1.1 mol equiv.), hexamethyldisilane (475 mg, 3.25 mmol, 1.1 mol equiv.), HMPA (2.06 g, 11.5 mmol, 3.8 mol equiv.), adamantan-2-one (460 mg, 3.06 mmol, 1.0 mol equiv.), and THF (11 cm^3). After work-up, and purification by use of the chromatotron (2.0% EtOAc in hexanes as eluent), the dithiane **10** was obtained as a light yellow oil in 92% yield (690 mg, 2.70 mmol); t_R 18.21 min; R_f 0.57 (5% EtOAc in hexanes); δ_H(CDCl$_3$; 80 MHz) 1.50–2.20 (14 H, m, 6 × CH$_2$ + 2 × CH), 2.60–2.80 (4 H, m, 2 × SCH$_2$) and 3.10–3.30 (2 H, br, 2 × =CCH); ν_{max}(film)/cm^{-1} 2908s, 2837s, 1448m (C=C), 1420w, 1267m, 1237m, 1090m and 950w. The physical properties and spectroscopic characteristics are consistent with those reported.[15]

3-(2-Trimethylsilyl-1,3-dithian-2-yl)cyclohexanone **11**. The standard procedure was followed by use of 1,3-dithiane (710 mg, 5.72 mmol, 1.0 mol equiv.), BuLi (4.13 cm^3, 6.36 mmol, 1.1 mol equiv.), hexamethyldisilane (924 mg, 6.30 mmol, 1.1 mol equiv.), HMPA (4.07 g, 22.8 mmol, 4.0 mol equiv.), cyclohex-2-en-1-one (550 mg, 5.71 mmol, 1.0 mol equiv.), and THF (20 cm^3). After work-up, and purification by use of the chromatotron (hexanes as eluent), the *dithiane* **11** was obtained as an oil in 94% yield (1.56 g, 5.38 mmol); t_R 18.44 min; R_f 0.13 (5% EtOAc in hexanes); δ_H(CDCl$_3$; 200 MHz) 0.20 (9 H, s, SiMe$_3$), 1.55–1.85 (4 H, m, CCH$_2$CH$_2$C), 1.95–2.20 (3 H, m, SCCH$_2$CS + SCCHC), 2.30–2.50 (4 H, m, CH$_2$COCH$_2$) and 2.55–2.90 (4 H, m, 2 × SCH$_2$); ν_{max}(film)/cm^{-1} 2943s, 2873m, 1708s (C=O), 1449w, 1420m (S–CH$_2$), 1343w, 1308w, 1243s (Si–CH$_3$), 1220m, 1049w, 914w and 844s (Si–CH$_3$) (Found: C, 54.25; H, 8.6. C$_{13}$H$_{24}$OS$_2$Si requires C, 54.12; H, 8.38%).

2-(2-Nitrocyclohexyl)-2-trimethylsilyl-1,3-dithiane **12**. The standard procedure was followed by use of 1,3-dithiane (450 mg, 3.60 mmol, 1.0 mol equiv.), BuLi (2.47 cm^3, 3.80 mmol, 1.1 mol equiv.), hexamethyldisilane (540 mg, 3.70 mmol, 1.03 mol equiv.), HMPA (2.58 g, 14.4 mmol, 4.0 mol equiv.), 1-nitro-

cyclohexene (485 mg, 3.80 mmol, 1.1 mol equiv.), and THF (16 cm^3). After work-up, and purification by use of the chromatotron (5% EtOAc in hexanes as eluent), a 6:1 mixture of diastereoisomers of the dithiane 12 was obtained as a light yellow oil in 57% yield (total weight 650 mg, 2.35 mmol). This mixture was separated by use of the chromatotron (hexanes as eluent) to give light yellow crystals.

First isomer of compound 12: m.p. 73.0–74.5 °C; t_R 19.98 min; R_f 0.58 (20% EtOAc in hexanes); δ_H(CDCl$_3$; 200 MHz) 0.29 (9 H, s, SiMe$_3$), 1.15–2.65 (11 H, m), 2.85–3.20 (4 H, m) and 4.62–4.80 (1 H, dt, J 5.97, 12.1, CHNO$_2$); ν_{max}(film)/cm^{-1} 2942s, 2901m, 2862m, 1548s (NO$_2$), 1517w, 1451m, 1424m, 1370m (NO$_2$), 1262w, 1249s (Si–CH$_3$), 845s (Si–CH$_3$), 787s, 735m and 690m (Found: M$^+$, 319.1097; C, 49.0; H, 7.8%. C$_{13}$H$_{25}$NO$_2$S$_2$Si requires M, 319.1096; C, 48.89; H, 7.90%).

Second isomer of compound 12: m.p. 80.5–82.5 °C; t_R 19.70 min; R_f 0.53 (20% EtOAc in hexanes); δ_H(CDCl$_3$; 400 MHz) 0.21 (9 H, s, SiMe$_3$), 1.20–2.55 (11 H, m), 2.65–3.20 (4 H, m), 5.05–5.20 (1 H, t, J 8.95, CHNO$_2$); its IR spectroscopic characteristics were identical with those listed above (Found: M$^+$, 319.1101; C, 48.8; H, 8.0%).

2-Ethyl-2-trimethylsilyl-1,3-dithiane 13. The standard procedure was followed by use of 1,3-dithiane (403 mg, 3.25 mmol, 1.0 mol equiv.), BuLi (2.34 cm^3, 3.60 mmol, 1.1 mol equiv.), hexamethyldisilane (530 mg, 3.62 mmol, 1.1 mol equiv.), HMPA (2.29 g, 12.8 mmol, 4.0 mol equiv.), ethyl bromide (438 mg, 4.02 mmol, 1.2 mol equiv.), and THF (15 cm^3). After work-up, and purification by use of the chromatotron (hexanes as eluent), the dithiane 13 was obtained as an oil in 98% yield (698 mg, 3.17 mmol); t_R 11.54 min; R_f 0.63 (10% EtOAc in hexanes); δ_H(CDCl$_3$; 200 MHz) 0.15 (9 H, s, SiMe$_3$), 1.05 (3 H, t, CMe), 1.75–2.08 (2 H, m, SCCH$_2$CS), 2.33 (2 H, q, CCH$_2$C), 2.35–2.47 (2 H, m, 2 × SCH equatorial) and 2.90–3.10 (2 H, m, 2 × SCH axial); ν_{max}(film)/cm^{-1} 2960s, 2925s, 2840w, 1450m, 1420m, 1375w, 1247s (Si–CH$_3$), 1115w, 1078w, 920w, 848s (Si–CH$_3$), 757m, 740w, 707m and 698m (Found: M$^+$, 220.0775; C, 48.9; H, 9.2%. C$_9$H$_{20}$S$_2$Si requires M, 220.0776; C, 49.03; H, 9.14%).

2-Allyl-2-trimethylsilyl-1,3-dithiane 14. The standard procedure was followed by use of 1,3-dithiane (560 mg, 4.51 mmol, 1.0 mol equiv.), BuLi (3.16 cm^3, 4.86 mmol, 1.1 mol equiv.), hexamethyldisilane (680 mg, 4.64 mmol, 1.1 mol equiv.), HMPA (3.19 g, 17.8 mmol, 4.0 mol equiv.), allyl bromide (623 mg, 5.15 mmol, 1.1 mol equiv.), and THF (15 cm^3). After work-up, and purification by use of the chromatotron (hexanes as eluent), the dithiane 14 was obtained as an oil in 67% yield (684 mg, 3.02 mmol); R_f 0.60 (5% EtOAc in hexanes); δ_H(CDCl$_3$; 200 MHz) 0.14 (9 H, s, SiMe$_3$), 1.70–2.10 (2 H, m, SCCH$_2$CS), 2.35–2.50 (2 H, m, 2 × SCH equatorial), 2.90–3.00 (2 H, m, CCH$_2$C=), 3.00–3.15 (2 H, m, 2 × SCH axial), 5.00–5.20 (2 H, m, =CH$_2$) and 5.80–6.10 (1 H, m, CH=C); ν_{max}(film)/cm^{-1} 3074w (=CH$_2$), 2952m, 2903m, 1636m (C=C), 1424m, 1248s, (Si–CH$_3$), 1027w, 1000w, 914m, 846s (Si–CH$_3$), 786m (=CH) and 760m (Found: M$^+$, 232.0771; C, 51.6; H, 9.0%. C$_{10}$H$_{20}$S$_2$Si requires M, 232.0776; C, 51.67; H, 8.67%).

2-(2-Methylbut-2-enyl)-2-trimethylsilyl-1,3-dithiane 15. The standard procedure was followed by use of 1,3-dithiane (620 mg, 5.01 mmol, 1.0 mol equiv.), BuLi (3.55 cm^3, 5.47 mmol, 1.1 mol equiv.), hexamethyldisilane (780 mg, 5.33 mmol, 1.1 mol equiv.), HMPA (3.58 g, 20.0 mmol, 4.0 mol equiv.), 1-bromo-3-methylbut-2-ene (690 mg, 4.63 mmol, 0.92 mol equiv.), and THF (16 cm^3). After work-up, and purification by use of the chromatotron (hexanes as eluent), the dithiane 15 was obtained in 65% yield (845 mg, 3.25 mmol) as a crystalline solid, m.p. 42.0–43.5 °C; t_R 14.13 min; R_f 0.71 (5% EtOAc in hexanes); δ_H(CDCl$_3$; 200 MHz) 0.13 (9 H, s, SiMe$_3$), 1.64–1.74 (6 H, 2 s, 2 × CMe), 1.96–2.10 (2 H, m, SCCH$_2$CS), 2.35–2.55 (2 H, m, 2 × SCH equatorial), 2.85–2.95 (2 H, m, CCH$_2$C=), 3.00–3.15 (2 H, m, 2 × SCH axial) and 5.31–5.33 (1 H, m, CH=C);

ν_{max}(KBr)/cm^{-1} 2953m, 2907s, 1670w (C=C), 1439m, 1423m, 1375m, 1247s (Si–CH$_3$), 1111w, 1040w, 908w, 844s (Si–CH$_3$), 787m (=CH) and 758m (Found: M$^+$, 260.1082; C, 55.45; H, 9.2%. C$_{12}$H$_{24}$S$_2$Si requires M, 260.1089; C, 55.36; H, 9.30%).

2-Benzyl-2-trimethylsilyl-1,3-dithiane 16. The standard procedure was followed by use of 1,3-dithiane (492 mg, 3.97 mmol, 1.0 mol equiv.), BuLi (2.88 mg, 4.44 mmol, 1.1 mol equiv.), hexamethyldisilane (645 mg, 4.41 mmol, 1.1 mol equiv.), HMPA (2.86 g, 16.0 mmol, 4.0 mol equiv.), benzyl bromide (719 mg, 4.20 mmol, 1.1 mol equiv.), and THF (20 cm^3). After work-up, and recrystallization of the crude product with ethanol, the dithiane 16 was obtained in 54% yield (610 mg, 2.16 mmol) as a crystalline solid with m.p. 100.5–101.5 °C; t_R 17.49 min; R_f 0.47 (5% EtOAc in hexanes); δ_H(CDCl$_3$; 200 MHz) 0.13 (9 H, s, SiMe$_3$), 1.80–2.00 (2 H, m, SCCH$_2$CS), 2.40–2.50 (2 H, m, 2 × SCH equatorial), 2.75–2.85 (2 H, m, 2 × SCH axial), 3.48 (2 H, s, CCH$_2$Ph) and 7.30–7.58 (5 H, m, C$_6$H$_5$); ν_{max}(film)/cm^{-1} 3062w (C$_6$H$_5$), 3028w (C$_6$H$_5$), 2952m, 2911m, 1584w, 1493m, 1453m, 1417w, 1390w, 1248s (Si–CH$_3$), 1070w, 845s (Si–CH$_3$), 786m, 765m and 698s (Found: M$^+$, 282.0934; C, 59.4; H, 8.0%. C$_{14}$H$_{22}$S$_2$Si requires M, 282.0932; C, 59.52; H, 7.85%).

The dithiane 16 was also synthesized in 25% yield by replacement of benzyl bromide with benzyl chloride. The by-product, 2-benzyl-1,3-dithiane, was isolated in 50% yield as a crystalline solid with m.p. 34–35 °C (lit.,[19] 34–35 °C); δ_H-(CDCl$_3$; 200 MHz) 1.78–1.97 (2 H, m, SCCH$_2$CS), 2.45–2.58 (2 H, m, 2 × SCH equatorial), 2.76–2.86 (2 H, m, 2 × SCH axial), 3.01 (2 H, d, J 7.1, CH$_2$Ph), 4.18 (1 H, t, J 7.1, PhCCH) and 7.23–7.41 (5 H, m, C$_6$H$_5$); ν_{max}(film)/cm^{-1} 3061w (C$_6$H$_5$), 3025w (C$_6$H$_5$), 2952m, 2911m, 1608w, 1492m, 1451m, 735m and 699s (Found: M$^+$, 210.0549. C$_{11}$H$_{14}$S$_2$ requires M, 210.0537). The physical properties and spectroscopic characteristics are consistent with those reported.[19]

3-(Trimethylsilylcarbonyl)cyclohexanone 17. The procedure developed by Brook *et al.*[17] was followed by use of the silane 11 (188 mg, 0.62 mmol, 1.0 mol equiv.), HgCl$_2$ (2.50 g, 9.20 mmol, 15 mol equiv.), CdCO$_3$ (530 mg, 3.11 mmol, 5.0 mol equiv.), acetone (11 cm^3), benzene (2.0 cm^3), and water (0.15 cm^3). After work-up, and purification by use of a silica gel column (hexanes as eluent), acylsilane 17 was obtained in 85% yield (105 mg, 0.53 mmol) as a crystalline solid with m.p. 39.0–40.0 °C; R_f 0.26 (20% EtOAc in hexanes); δ_H(CDCl$_3$; 200 MHz) 0.21 (9 H, s, SiMe$_3$), 1.45–1.75 (4 H, m, COCCH$_2$CH$_2$C), 1.95–2.37 (4 H, m, CH$_2$COCH$_2$ equatorial) and 3.21–3.32 (1 H, m, SiCOCH); ν_{max}(film)/cm^{-1} 2954m, 2860m, 1707s (C=O), 1637s (SiC=O), 1443w, 1414w, 1243s (Si–CH$_3$), 1230w, 1102w, 966w, 845s (Si–CH$_3$), 786m (=CH) and 760m (Found: M$^+$, 198.1087; C, 51.6; H, 9.0%. C$_{10}$H$_{18}$OSi requires M, 198.1076; C, 51.67; H, 8.67%).

2-Phenyl-1-(trimethylsilyl)ethanone 18. The procedure developed by Brook *et al.*[17] was followed by use of the dithiane 16 (319 mg, 1.13 mmol, 1.0 mol equiv.), HgCl$_2$ (4.60 g, 16.9 mmol, 15.0 mol equiv.), CdCO$_3$ (903 mg, 5.22 mmol, 4.62 mol equiv.), acetone (18 cm^3), benzene (4.0 cm^3), and water (0.25 cm^3). After work-up, and purification by use of a silica gel column (hexanes as eluent), acylsilane 18 was obtained as an oil in 75% yield (162 mg, 0.85 mmol); R_f 0.38 (5% EtOAc in hexanes); δ_H(CDCl$_3$; 200 MHz) 0.12 (9 H, s, SiMe$_3$), 3.85 (2 H, s, CCH$_2$Ph) and 7.10–7.32 (5 H, m, C$_6$H$_5$); ν_{max}(film)/cm^{-1} 3029w (C$_6$H$_5$), 2958m, 2903m, 1708m (C=O), 1639m (C=C), 1601w, 1496w, 1453m, 1411w, 1250s (Si–CH$_3$), 1030w, 846s (Si–CH$_3$), 748m (=CH), 701s and 668w (Found: M$^+$, 192.0986; C, 69.0; H, 8.15%. C$_{11}$H$_{16}$OSi requires M, 192.0970; C, 68.72; H, 8.39%).

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