Supporting Information

**Efficient Synthesis of 1,2,4-Dithiazolidine-3,5-diones [Dithiasuccinoyl-Amines] from Bis(chlorocarbonyl)disulfane Plus Bis(trimethylsilyl)amines**

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**General**

Unless indicated otherwise, solvents and chemicals were reagent grade from Aldrich and/or Fluka, and were used without further purification. In particular, it was not critical to scrupulously dry solvents further, e.g., by storage over 3- or 4-Å molecular sieves or by passage through activated neutral alumina, nor was it necessary to run reactions (even silylations) under N₂ atmosphere. [Occasionally, such precautions were followed out of force of habit.] Reactions and workups were run at 25 °C, unless noted otherwise. When organic solutions of mono(silyl) or bis(silyl)amines were subjected to aqueous workup, i.e., carrying out several washes with 1.0 N aqueous HCl, the silyl group(s) was readily removed and transformed to hydrolysis products [long-term, hexamethyldisiloxane (Tms₂O) in the organic phase, although a relatively unstable species assigned to Tms-OH, ¹H NMR δ 0.13; ¹³C NMR δ 1.3, was sometimes detectable; meanwhile, the amine hydrochloride was extracted into the aqueous phase].

NMR spectra were recorded, with CDCl₃ as solvent, on Varian instruments operating for ¹H at 200 or 300 MHz and for ¹³C at 50 or 75 MHz. The reported chemical shifts (¹H // ¹³C) were referenced, depending on context, to tetramethylsilane (δ 0.00 // δ 0.0), CHCl₃ (δ 7.27 // δ 77.0), or p-xylene internal standard (δ 7.04, 2.29 // δ 134.6, 128.9, 20.9) and are considered accurate to ± 0.02 (¹H) and ± 0.5 (¹³C) depending on the exact conditions. Relative shifts were more accurate, and absolute identifications of compounds were confirmed by NMR spectra of ‘doped’/‘spiked’ samples, i.e., the appropriate authentic reference compound(s) was added to reaction mixtures believed to contain said compound(s). Carbon resonances for ¹³CCl₃ or for O=⁻¹³C=N– were sometimes very weak, or not picked up at all. Exchangeable protons, which give rise to broad peaks at variable chemical shifts, were not tabulated. Coupling constants were measured but are not reported; they were ~ 7 Hz for adjacent aliphatic C–H, and ~ 5 to 6 Hz for C–H split by adjacent N–H.

**Starting Materials and Reference Compounds**

*Chemical Abstracts* compound registry numbers are given in brackets next to each compound name, whenever that compound has been previously reported in the chemistry literature. These registry numbers can be readily used to retrieve reference physical properties and relevant literature citations.

1. **Bis(chlorocarbonyl)disulfane [51615-88-4]**, C₂Cl₂O₂S₂, MW 191.05, ρ 1.60, bp 44-46 °C (0.2 mm), was prepared as described in text ref. 11c. Material synthesized and purified in the early 1980’s, and stored since then under ambient conditions, was still completely unchanged (and mostly colorless) when used in experiments conducted in the summer of 2003. Two new batches were made in 2004, each reproducing on a 0.2 mol scale the procedures and yields of the cited publication. More specifically, bis(ethoxythiocarbonyl)disulfane was converted by sulfuryl chloride treatment to ethoxythiocarbonyl chloride (cracking distillation), which was reacted for 5 days at 25 °C with chlorocarbonylsulfenyl chloride to provide an adduct, which was treated with catalytic FeCl₃ to effect loss of ethyl chloride, whereupon two successive vacuum distillations provided the title product: ¹³C NMR δ 161.4. Purity of 1 was confirmed by previously described N-methylaniline assays and methanol quenches (text ref. 11c).
2 (R = H). Hexamethyldisilazane [999-97-3], C₆H₁₉NSi₂, MW 161.40, δ 0.77. ¹H NMR δ 0.055 (s); ¹³C NMR δ 2.5.

2 (R = Me), Heptamethyldisilazane = N,N-Bis(trimethylsilyl)methylamine [920-68-3], C₇H₂₁NSi₂, MW 175.43, δ 0.80. ¹H NMR δ 2.46 (s, 3H), 0.07 (s, 18H); ¹³C NMR δ 30.9, 1.2.

2 (R = allyl), N,N-Bis(trimethylsilyl)allylamine [7688-51-9], C₇H₁₉NSi₂, MW 201.46, δ 0.82. ¹H NMR δ 5.80 (ddt, 1H), 5.13 (dq, 1H), 5.00 (dq, 1H), 3.46 (dt, 2H), 0.10 (s, 18H); ¹³C NMR δ 141.2, 113.3, 47.3, 2.0.

2 (R = Bn), N,N-Bis(trimethylsilyl)benzylamine [18406-59-2], C₉H₂₇NSi₂, MW 249.51, δ 0.91. Following Bestmann, H. J.; Wölfel, G. Chem. Ber. 1984, 117, 1250-1254, benzyl bromide (3.0 mL, δ 1.44, 25 mmol) was added at 25 °C to a suspension of sodium bis(trimethylsilyl)amide (4.6 g, 25 mmol) together with hexamethyldisilazane (12.5 mL). After 6 h stirring under N₂, the reaction mixture was filtered to remove salts, rinsed with dry tetrahydrofuran (~ 10 mL), and concentrated to provide a clear, yellow liquid, which was distilled, bp 78-81 °C (1.2 mm) [lit. bp 67 °C (0.4 mm)]. The title compound was obtained after distillation as a clear, colorless liquid (3.3 g, 53%), δ 7.27 (m, 4H), 7.18 (m, 1H), 4.11 (s, 2H), 0.07 (s, 18H), δ 144.4, 127.9, 126.3, 125.9, 48.5, 1.9, with no additional peaks diagnostic of unreacted starting materials or other contaminants. This distilled material was stable under ambient conditions for several months. After standing for several weeks, a portion of the title product settled as a solid, which had identical spectral data and is presumably of greater purity; nevertheless, the liquid form was the one used for reactions.

2 (R = Ph). N,N-Bis(trimethylsilyl)phenylamine [4147-89-1], C₁₂H₂₃NSi₂, MW 237.49, δ 0.89. Following Hamada, Y.; Yamamoto, Y.; Shimizu, H. J. Organomet. Chem. 1996, 510, 1-6, iodomethane (9.8 g, 69 mmol) was added to a mixture of N-(trimethylsilyl)diethylamine (10.0 g, 69 mmol) and toluene (11.5 mL), leading to an immediate milky white appearance. The mixture was stirred for 4 h at 50 °C, and took on an orange appearance with some solid orange beads settling. Next, aniline (2.7 g, 29 mmol) was added, and the mixture was heated, with stirring, at 75 °C. Within 10 min of heating, an upper yellow phase and a lower brown phase separated. The reaction continued for 6 h, at the end of which time the salts were removed by filtration, and the filtrate (along with a toluene rinse of the salts) was concentrated and vacuum distilled as a clear, colorless liquid (3.3 g, 70%), δ 7.07 (m, 2H), 7.07 (m, 1H), 6.90 (dd, 2H), 0.05 (s, 18H), δ 130.2, 128.4, 123.5, 2.0.

2 (R = Tms). Nonamethyltrisilazane = N,N,N-tris(trimethylsilyl)amine [1586-73-8], C₃H₂₇NSi₃, MW 233.58, mp 67-69 °C. ¹H NMR δ 0.18 (s); ¹³C NMR δ 5.5.

3 (R = Me). N-Methyl-1,2,4-dithiazolidine-3,5-dione [18137-43-4], C₅H₅NO₂S₂, MW 149.18, mp 33-35 °C. This compound has been made by several different procedures [text refs. 2, 3a, 3b, 4d, 4e]. Depending on the details of initial purity and of storage, the title compound can be stable for > 30 years, or undergo partial decomposition over a period of several years. The decomposition product was readily identified as N,N’-dimethylurea, matching a reference compound [¹H NMR δ 2.74 (d); ¹³C NMR δ 160.6, 26.9]. The specific standard of title compound used in the present investigation was prepared freshly in 2003, according to text ref. 4d. ¹H NMR δ 3.28 (s); ¹³C NMR: 167.5, 31.9.

3 (R = allyl). N-Allyl-1,2,4-dithiazolidine-3,5-dione [21597-11-5], C₅H₅NO₂S₂, MW 175.22, viscous oil. As of 2003, this compound is new to our laboratory, and – independent of the title procedure of this paper – was made by an alternate two-step procedure that started with allyl isothiocyanate and followed the general procedure of text ref. 4d. ¹H NMR δ 5.82 (dtt, 1H), 5.33 (dq, 1H), 5.29 (dq, 1H), 4.36 (dt, 2H); ¹³C NMR δ 167.0, 129.1, 120.1, 47.9. The physical
and spectroscopic data match exactly [except for what is undoubtedly a typographical error] what was reported by Wood, M. E.; Cane-Honeysett, D. J.; Dowle, M. D.; Coles, S. J.; Hursthouse, M. B. Org. Biomol. Chem. 2003, 1, 3015-3023, who used allyl bromide to alkylate “dithiasuccinimide” (3, R = H).

3 (R = Bn), N-Benzyl-1,2,4-dithiazolidine-3,5-dione [21597-13-7], C₉H₉NO₂S₂, MW 225.28, mp 90-92 °C. A roughly 20 year old standard stored under ambient conditions had decomposed partially (~15%) to N,N'-dibenzylurea [1466-67-7] [characteristic ¹H NMR δ 4.39 (d)], but the spectral features characteristic of the title compound were readily discernible. ¹H NMR δ 7.42 (m, 2H), 7.34 (m, 2H), 7.28 (m, 1H), 4.90 (s, 2H); ¹³C NMR δ 167.5, 134.1, 129.0, 128.7, 127.4, 49.3. More recently, analytically and spectroscopically pure material was synthesized in our hands by following the protocol of text ref. 9.

3 (R = Ph), N-Phenyl-1,2,4-dithiazolidine-3,5-dione [21597-12-6], C₁₀H₁₀NO₂S₂, MW 211.25, mp 164-167 °C. Several approximately 20-year-old standards prepared for the manuscript of text ref. 4d, and stored since then under ambient conditions, had not changed [same mp, same spectral data]. ¹H NMR δ 7.52 (m, 3H), 7.28 (dd, 2H); ¹³C NMR δ 166.9, 130.0, 129.3, 127.6.

3 (R = CH₃CO₂C₂H₅), Ethyl 3,5-dioxo-1,2,4-dithiazolidine-4-acetate = DtsGlyOEt [70711-36-3], C₇H₇NO₂S₂, MW 221.25. This compound is mentioned in text refs. 3a, 4a, 4e, and 9. ¹H NMR δ 4.48 (s, 2H), 4.25 (q, 2H), 1.30 (t, 3H); ¹³C NMR δ 167.0, 165.5, 62.6, 45.5, 14.0.

4. Chlorotrimethylsilane (TmsCl) [75-77-4], C₃H₇ClSi, MW 108.64, ρ 0.86. ¹H NMR δ 0.43 (s); ¹³C NMR δ 3.1. Upon aqueous workup, this compound was transformed quantitatively to hexamethyldisiloxane (Tms₂O), which later was removed by evaporation in vacuo.

9 (R = Me), Methyl isocyanate [624-83-9], C₂H₅NO, MW 57.02, ρ 0.97. During the 1970’s and early 1980’s, this compound was obtained inexpensively from any of several suppliers. Reference spectra were recorded, and the presence of a presumed isocyanurate impurity [¹H NMR δ 3.30 (s)] was noted. Post-Bhopal, the isocyanate was generated in situ by taking an approximately 0.2 M CDCl₃ solution of N-methyl-1,2,4-dithiazolidine-3,5-dione (3, R = Me), and adding a few drops (~2 molar equiv) of tri-n-butylphosphine. Within minutes, the methyl singlet due to the presence of Dts had metamorphed to a singlet due to quantitative conversion to the title isocyanate. ¹H NMR δ 7.02 (s); ¹³C NMR δ 121.7 (weak), 28.2. A similar reaction with triphenylphosphine (solid used) required overnight treatment to reach completion.

9 (R = Bn), Benzyl isocyanate [3173-56-6], C₉H₉NO, MW 133.15, ρ 1.08. ¹H NMR δ 7.30 (m, 5H), 4.44 (s, 2H); ¹³C NMR δ 136.8, 128.8, 127.9, 126.6, 46.4. The aforementioned spectral data were determined on newly acquired material; upon long-term storage extensive decomposition occurred, with presumed isocyanurate [partial ¹H NMR δ 5.06 (s)] and N,N'-dibenzylurea among the components recognized.

9 (R = Tms), Trimethylsilyl isocyanate [1118-02-1], C₆H₁₃NO, MW 115.21, ρ 0.85. ¹H NMR δ 0.25 (s, along with s for Tms₂O at 0.06); ¹³C NMR δ 123.4 (weak), 0.7.

9 (R = CH₂CO₂C₂H₅), Ethyl isocyanatoacetate [2949-22-6], C₆H₁₀NO₂, MW 129.11, ρ 1.15. ¹H NMR δ 4.28 (q, 2H), 3.94 (s, 2H), 1.32 (t, 3H); ¹³C NMR δ 169.2, 127.5 (weak), 62.6, 44.5, 14.1.

10. (Trichloromethyl)dithiodicyanomethane [51615-91-9], C₂Cl₂OS₂, MW 245.95, ρ 1.69, bp 55 °C (0.6 mm), was prepared as described in text ref. 11c. Material synthesized and purified in the early 1980’s, and stored since then under ambient conditions, was short-path redistilled (two batches) before use in the 2004 experiments. ¹³C NMR δ 162.2, 98.5.
12. Trichloromethyl N-methycarbamoyl disulfane [90010-79-0], C₈H₇Cl₃NOS₂, MW 240.55, mp 57-60 °C, was prepared first in the mid-1970’s (text ref. 3a) following the precedent of Harris (text ref. 15). When re-examined in 2004, the sample was unaltered. ¹H NMR δ 2.99 (d); ¹³C NMR δ 161.6, 99.3, 28.6.

14. N-Trimethylsilyl N-benzylamine [14856-79-2], C₁₈H₁₇NSi, MW 179.34, ρ 0.90. ¹H NMR δ 7.4 (m, 4H), 7.3 (m, 1H), 3.90 (d, 2H), 0.07 (s, 9H); ¹³C NMR δ 144.3, 128.5, 127.2, 126.6, 45.9, 0.0. Compound 14 hydrolyzed completely upon standard aqueous workup.

15. Trichloromethyl N-benzylcarbamoyl disulfane, C₈H₇Cl₃NOS₂, MW 316.55, mp 83-87 °C, is new from this work (see later), and was prepared independently by homologating the Harris procedure (text ref. 15; already cited) for preparation of compound 12. ¹H NMR δ 7.25-7.4 (m, 5H), 4.54 (d, 2H); ¹³C NMR δ 161.1, 136.4, 128.9, 128.1, 127.9, 99.2, 46.0.

Hexamethyldisiloxane (Tms₂O) [107-46-0], C₆H₁₈Si₂O, MW 162.38, ρ 0.76. ¹H NMR δ 0.064 (s); ¹³C NMR δ 1.9.

Ethyl 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane-1-acetate (STABASE-GlyOEt) [78605-23-9], MW 245.47, ρ 0.95, ¹H NMR δ 4.12 (q, 2H), 3.50 (s, 2H), 1.26 (t, 3H), 0.74 (s, 4H), 0.06 (s, 12H); ¹³C NMR δ 173.7, 60.3, 44.3, 14.2, 8.0, -0.7.

1,2-Bis(chlorodimethylsilyl)ethane [13528-93-3], C₆H₁₆Si₂Cl₂, MW 215.27, mp 35-38 °C. ¹H NMR δ 0.82 (s, 4H), 0.42 (s, 12H); ¹³C NMR δ 10.7, 1.0. Upon standard aqueous workup, these peaks were replaced by ones due to hydrolysis, i.e., ¹H NMR δ 0.74 (s, 4H), 0.14 (s, 12H).

Reactions of bis(chlorocarbonyl)disulfane (1) with heptamethyldisilazane (2, R = Me)

The overall design and salient conclusions of these studies are outlined in the text. Reactions were conducted either in NMR tubes (reaction volume typically ~ 0.8 mL) or in screw-capped test tubes [reaction volume typically ~ 2 to 3 mL]. Typically, 1.0 M stock solutions of 1 and 2 (R = Me) were prepared in CDCl₃, with a p-xylene internal standard (~ 0.5 M) included in the stock solution of 2. Unless indicated otherwise, the stock solution of 2 was added rapidly under ambient conditions to the stock solution of 1, testing various ratios [2:1, 1:1, and 1:2]. More concentrated, as well as more dilute, overall final concentrations [i.e., sum = 2.0, 0.5, 0.1, and even 0.01 M] were also tested. Progress of reactions at 25 °C was monitored by direct ¹H and ¹³C NMR spectroscopy (e.g., Supporting Figure 1, top of next page). Data for starting materials 1 and 2, product 3 (R = Me), and co-product 4 have been stated earlier in this Supporting Information. Intermediate 5 was deduced to have ¹H NMR δ 2.92 (s, 3H); 0.32 (s, 9H); ¹³C NMR δ 168.7, 31.6, 1.9, whereas diacylated, disilylated adduct 6, detected especially when 2 was in excess, was assigned ¹H NMR δ 3.01 (s, 3H), 0.29 (s, 9H); ¹³C NMR δ 168.9, 31.4, 1.0.

At appropriate times, either an aliquot or the entire reaction mixture was subjected to aqueous workup, which consisted of three washes with 1.0 N aqueous HCl, and NMR re-examination of the CDCl₃ phase. Later, the organic layer was dried (MgSO₄) and concentrated in vacuo. Isolated yields were comparable to what had been deduced in situ by comparison of NMR integrations of products with respect to the p-xylene internal standard. In those experiments were 2 had been in excess, the final aqueous workup provided spectroscopic evidence for compound 7 [¹H NMR δ 2.94 (d); ¹³C NMR δ 162.6, 28.4; 4% NH₃/CH₃CIMS (probe insertion) m/z 213 (MNa⁺), 198 (MNH₃⁺), 181 (base peak, MH⁺)].
Supporting Figure 1. Time course of title reaction, conducted at 25 °C, of bis(chlorocarbonyl)disulfane (1) plus heptamethyldisilazane (2, R = Me) [0.5 M each] to form, via intermediate 5 (R = Me), N-methyl-1,2-4-dithiazolidine-3,5-dione product (3, R = Me) plus 2 equiv of co-product TmsCl (4) (text Scheme 1). The relative amounts of 2 (●), 3 (◆), 4 (■), and intermediate 5 (▲) were normalized with respect to a p-xylene internal standard. Calculations take into account theoretical reaction stoichiometry and balance of Tms groups [two in starting material 2 vs. 2 equiv of co-product 4]; relative quantification of intermediate 5 was on the basis of the Me group and confirmed by the Tms group balance. The endpoint yields are indicated by the dashed line for 3 and the dotted line for 4.

Alternatively, reaction mixtures were quenched by addition into 20 volumes of methanol in a chilled, tared round-bottom flask. After 30 min at 25 °C, the solvent was removed on a rotary evaporator, and the residue was dissolved in CDCl₃ for NMR characterization. Observation of bis(methoxycarbonyl)disulfane [MeO(C=O)SS(C=O)OMe], with ¹H NMR δ 3.92 (s); ¹³C NMR δ 166.7, 55.8, was diagnostic of excess 1 which had not been transformed during the title reaction.

One experiment was conducted at 25 °C, using 1 and 2 (R = Me) in a 1:1 ratio (2.0 mmol each), in CHCl₃ (2 mL total) [Note: external ice-chilling applied when combining reactants, and slight spontaneous exotherm/evolution of white gas were noted]. After 18 h, the reaction was quenched by washings (3 x) with 1.0 N aqueous HCl, and the organic phase was dried (MgSO₄) and concentrated in vacuo to provide a yellow oil (211 mg, nominally 71% yield) that was ~85% of the Dts product 3 (R = Me) as judged by ¹H and ¹³C NMR [taken both before and after methanol quench]. In addition, the identity of 3 (R = Me) was readily confirmed by i-C₄H₁₀-CIMS (probe insertion): m/z 150 (base peak, MH⁺).

Some reactions were carried out on a 1.0 mmol scale in refluxing CDCl₃, i.e., 62 °C. When the sum of reactant concentrations was 1.0 M, these reactions reached endpoints within 30 min, and the major co-products 3 (R = Me) and TmsCl (4) represented > 90% of the signals in the ¹H and ¹³C NMR spectra.
Reaction of ((trichloromethyl)dithio)carbonyl chloride (10) with heptamethyldisilazane (2, R = Me)

The earlier procedure was followed on a 2.0 mmol scale, substituting 10 (1 equiv) for 1. The final concentration of both reactants was 0.5 M, and the reaction temperature was 25 °C. Monoadduct 11 formed with an approximate half-time of 3 h, and was assigned $^1$H NMR $\delta$ 2.99 (s, 3H), 0.32 (s, 9H); $^{13}$C NMR $\delta$ 165.7, 99.8, 31.4. An equivalent amount of TmsCl (4) formed at the same rate. As reported in the main text, conversion of 2 to 11 plus 4 was, at the endpoint, quantitative [confirmed in pilot studies by $^1$H NMR integrations in the presence of $p$-xylene internal standard]. After 18 h at 25 °C, aqueous workup and concentration in vacuo gave 12 (477 mg, nominal 99%) as a clear oil that exactly matched the $^1$H and $^{13}$C NMR of an authentic standard [a small amount of hexamethyldisiloxane was also noted]. “Chasing” on a rotary evaporator with methanol induced formation of white crystals (408 mg, 85%), which were scraped out (320 mg, 67% isolated). This product material gave mp 56–61 °C, which matches what was measured on compound 12 material made in our hands by the Harris reaction.

Reactions of bis(chlorocarbonyl)disulfane (1) or ((trichloromethyl)dithio)carbonyl chloride (10) with additional bis(trimethylsilyl)amines (2, R = allyl, Bn, and Ph)

The same general procedures already stated for the R = Me system were followed, with final concentrations of both reactants in CDCl$_3$ set at 0.5 M, and the reaction temperature at 25 °C. Results were as follows:

R = allyl, with 1 (0.5 mmol scale; no $p$-xylene internal reference). After 16 h reaction, $^1$H and $^{13}$C NMR examination revealed that ~ 75% of the integration of peaks in the silyl region were TmsCl (4), and the diagnostic peaks of desired 3 (R = allyl) represented ~ 80% of the integration in the remainder of the spectrum. Aqueous workup, followed by non-optimized silica gel column chromatography [eluent CH$_2$Cl$_2$–hexanes (1:1)], gave NMR-pure title product that matched exactly a reference sample made by the two-step procedure referred to earlier in this Supporting Information.

R = Bn, with 10 (2.5 mmol scale). A smooth but slow in situ reaction occurred to produce CCl$_3$SS(C=O)N(Tms)Bn [$^1$H NMR $\delta$ 7.4 (m, 5H), 4.6 (s, 3H), 0.31 (s, 9H)] plus TmsCl (4). After 70 h reaction and aqueous workup, a white powder [600 mg, nominal yield 75%], of which the desired Dts derivative was the major component, ~ 75%, as estimated by $^1$H and $^{13}$C NMR.

R = Ph, with 1 (1 mmol scale). Dts derivative 3 (R = Ph) formed with a half-time of ~ 30 h and few, if any, discernible intermediates; after 140 h reaction and aqueous workup, a powder (143 mg, nominal yield 68%) was obtained with estimated 80% purity as judged by $^1$H and $^{13}$C NMR.

R = Ph, with 10 (1 mmol scale). After 140 h, conversion of starting material, with concomitant formation of TmsCl (4), was less than 20%. A new diagnostic N-Tms peak with partial $^1$H NMR $\delta$ at 0.25 was assigned tentatively to CCl$_3$SS(C=O)N(Tms)Ph. Aqueous workup after 190 h led to the complete transformation of any unreacted Tms$_2$NPh (2, R = Ph) to aniline [removed by
Reactions of bis(chlorocarbonyl)disulfane (1) or ((trichloromethyl)dithio)carbonyl chloride (10) with hexamethyldisilazane (2, R = H) and nonamethyltrisilazane (2, R = Tms)

Experiments used standard concentrations and ratios, along with p-xylene as an internal standard; variations and results are outlined in the main text, including footnote 16. The outcome of the rapid exothermic reaction of 1 plus 2 (R = H) was indicated by a sulfur precipitate of elemental sulfur, and signals in the silyl region of the $^1$H and $^{13}$C NMR spectrum corresponding to TmsCl (4) [integration equal to half of the Tms moieties in the starting 2], Tms-N=C=O, Tms$_2$O, and one more species [all of these hydrolyzed to Tms$_2$O upon aqueous workup]. The corresponding reaction of 10 plus 2 (R = H) was more controlled, and after 4 h showed clearly the stoichiometric formation of CCl$_2$SS(C=O)NHTms (13) [$^1$H NMR $\delta$ 0.30 (s); $^{13}$C NMR $\delta$ 165.1, 99.5, -1.1], plus TmsCl (4). No attempt was made to follow up with an aqueous workup that would be expected to lead to CCl$_2$SS(C=O)NH$_2$, a known albeit unstable compound [117122-86-8] that was described previously by Harris (text ref. 15).

The bulky nonamethyltrisilazane (2, R = Tms) reacted very sluggishly, even at CDCl$_3$, reflux. Consequently, the solvent for these reactions was switched to tetrachloroethylene [$^{13}$C NMR $\delta$ 128.5], and reactions were conducted for 3 h at reflux, bp 121 °C. Relative to p-xylene internal standard ($\delta$ 7.04, 2.29 // $\delta$ 133.8, 120.1, 20.6) in this solvent, starting 2 ($\delta$ 0.23 // $\delta$ 5.1) was transformed with 1 to TmsCl (4) ($\delta$ 0.43 // $\delta$ 2.7), COS ($^{13}$C NMR $\delta$ 152.9, matches standard), and Tms-N=C=O ($\delta$ 0.26 // $\delta$ 0.3). Stoichiometry was as indicated in the main text discussion. The corresponding reaction with 10 went to ~20% conversion [experiment should be repeated with longer reaction time] and gave TmsCl (4) plus what is likely to be CCl$_2$SS(C=O)NTms$_2$: $^1$H NMR $\delta$ 0.26; $^{13}$C NMR $\delta$ 0.4.

Reactions of bis(chlorocarbonyl)disulfane (1) or ((trichloromethyl)dithio)carbonyl chloride (10) with N-trimethylsilyl N-benzylamine (14)

For the title experiments, standard conditions were followed, working again with CDCl$_3$, as solvent, and 1:1 molar ratios (each reactant final concentration 0.5 M). The mono(silyl)amine substrate 14 was considerably more reactive than the corresponding bis(silyl)amine 2 (R = Bn), as evidenced by the fact that reactions with the former gave significant spontaneous exotherms, as well as sulfur precipitates.

Reaction of 10 plus 14 was complete as of the first time point examined (2 h), and gave TmsCl (4) plus CCl$_2$SS(C=O)NH$_2$ (15). Transformation was quantitative, based on integrations with respect to p-xylene internal standard. Spectral data for 15 obtained by this method was superimposable on that reported earlier in this Supporting Information section for an authentic standard made by the Harris reaction (text ref. 15).

Similarly, reaction of 1 plus 14 gave TmsCl (4) plus Cl(C=O)SS(C=O)NH$_2$ (16). The assignment of structure 16 was supported by the following spectral data: $^1$H NMR $\delta$ 7.3 (m, 5H), 4.45 (d, 2H); $^{13}$C NMR $\delta$ 161.6, 134.6, 128.8, 128.0, 127.8, 46.4. This reaction mixture was re-examined 2 days later, and was unchanged; specifically, no Dts derivative 3 (R = Bn) had formed.
Reaction of bis(chlorocarbonyl)disulfane (1) with ethyl 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane-1-acetate (STABASE-GlyOEt)

Conditions corresponded to those already reported, except that instead of 2, STABASE-GlyOEt was used. There was usually a very slight spontaneous exotherm at the start, and reactions required ~18 h at 25 °C to reach completion. $^1$H and $^{13}$C NMR spectral examinations clearly revealed that the predominant process was formation of DtsGlyOEt (3, $R = \text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$) plus 1,2-bis(chlorodimethylsilyl)ethane; the latter species hydrolyzed upon aqueous workup. Authentications of compounds followed data presented earlier in this Supporting Information.