Some Bifunctional Acylsilanes and Their Photochemical Reactions

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The preparation of the αβ-unsaturated acylsilane (1) and some β-functionalised acylsilanes (2)—(5) is described. On irradiation, the β-azidoacylsilane (2) was converted into the enol form (19) of a β-methyliminoacylsilane, and the β-isothiocyanatoacylsilane (4) underwent isomerisation into the thioamide (23; R = SiMe₃).

This paper is concerned with the synthesis of αβ-unsaturated acylsilane (1), some β-functionalised acylsilanes (2)—(5) derived therefrom, and a preliminary survey of their photochemical reactions.

Various synthetic approaches to αβ-unsaturated acylsilanes have been described.[1-3] The isoprenoid αβ-unsaturated acylsilane (1), which was first reported in 1971[2] and derived by hydroboration–oxidation of 3-methyl-1-trimethylsilylbut-3-en-1-yne, turned out to be fairly readily available by the route summarised in the Scheme. This route is based on a procedure developed by S. Julia[4] for the preparation of the lithioallene (6; R = Ph) and related to that used by Bridges[5] in preparing the silylthioallene (7; R = Ph). Attempts to prepare the acylsilane (1) by hydrolysis of the allene (7; R = Ph) only gave poor conversion. Major by-products were the isomeric 1,3-diene (8) under mildly acidic conditions, and the cyclised product (9) under more vigorous conditions. The group R in compound (7) was varied in an attempt to find a more appropriate precursor. The thioallenes (7; R = Et) and (7; R = PhCH₂) proved to be too labile to be readily isolable, but (7; R = Buᵗ) was a convenient intermediate and could be hydrolysed to give the acylsilane (1) in moderate yield under the conditions indicated in the Scheme.

Some attempts were made to prepare related unsaturated acylsilanes by analogous procedures. Thus the pentamethyleneallene (10) was obtained, but on hydrolysis gave a mixture of the αβ- and the βγ-unsaturated acylsilanes (11) and (12). An approach to the tetramethylene analogue of (10) starting from 1-chloro-1-ethynylcyclopentane gave instead the isomeric 1,3-diene (13). Finally, hydrolysis of the allene (14), derived by prototropic rearrangement of 1-t-butylthiopropyne[6] gave the 3-t-butylthio-substituted acylsilane (15) instead of the desired αβ-unsaturated acylsilane.

The β-azidoacylsilane (2), the β-phenylsulphonylacylsilane (3), and the β-isothiocyanatoacylsilane (4) were prepared from the αβ-unsaturated ketone (1) by the addition, under the appropriate conditions, of azide, phenylsulphinate, or thiocyanate respectively. The catalytic hydrogenation of compound (1) gave the saturated acylsilane (5).

Previous investigations[7] into the photochemistry of acylsilanes have shown that products of two main types are formed: (a) 'carbene' products formally derived from siloxycarbenes (16); and (b) radical products originating from the initial cleavage of the acyl–Si bond. Preliminary studies on the irradiation of the acylsilanes (1), (3), and (5) in ether indicated that the predominant products were the corresponding aldehydes (H replacing SiMe₃) presumably derived by acyl–Si cleavage. As we were interested primarily in exploring new types of photochemical reaction, we did not study these substrates further.

U.v. irradiation (Pyrex filter) of the azidoacylsilane (2) in hexane or ether gave a single photoproduct derived by the loss of nitrogen. ¹H and ¹³C N.m.r. data (see Experimental section) indicated that the compound was one of the tautomeric forms
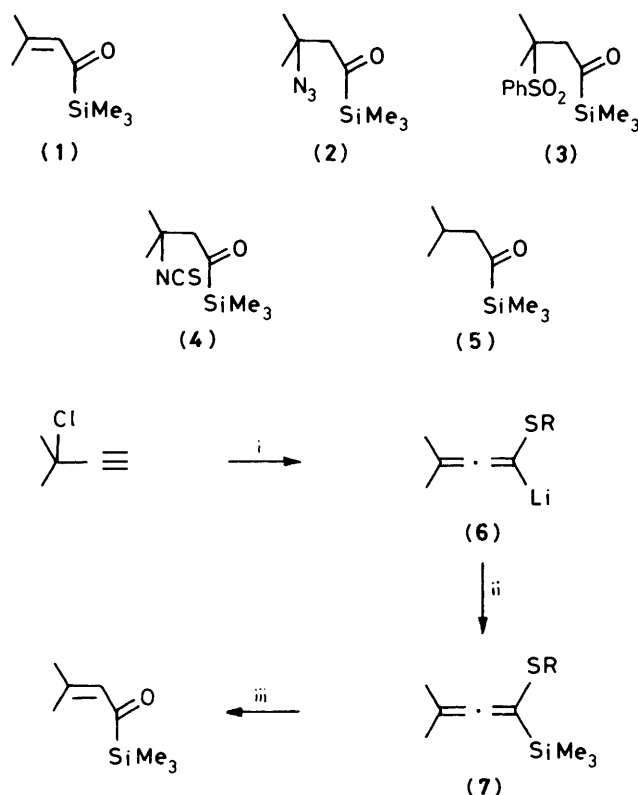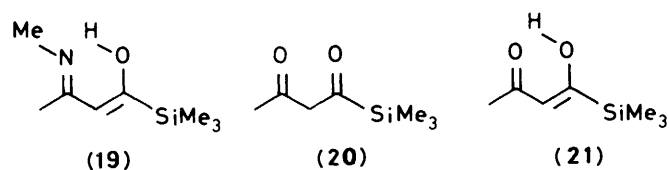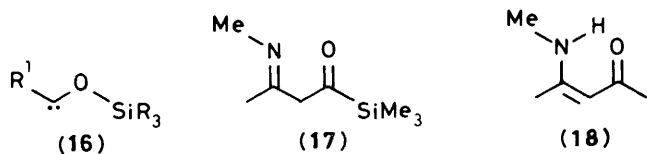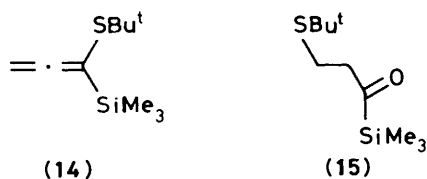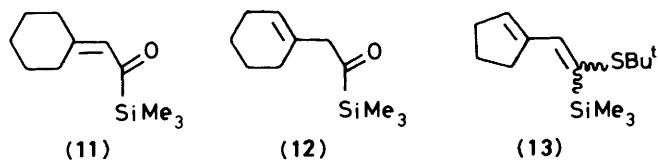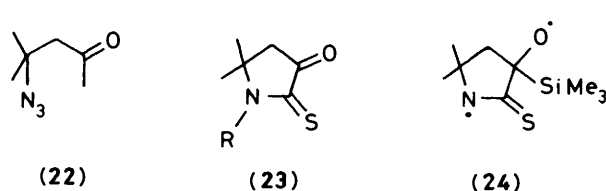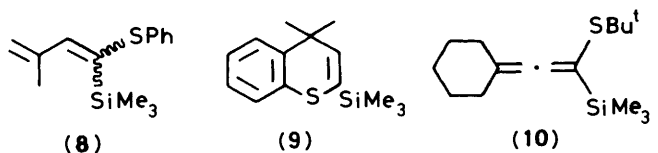

Scheme. *Reagents:* i, RSH–BuLi; ii, Me₃SiCl; iii, for R = Buᵗ, Me₃SiCl–AcOH at 25 °C or FeCl₃–H₂O–Me₂CO at 25 °C

of the β-methylaminoacylsilane (17). The limited amount of ¹³C C=O n.m.r. literature data indicate that the 235—255 p.p.m. range, downfield of the normal ketone region, is characteristic of acylsilanes,[8] and this is corroborated by the ¹³C n.m.r. spectra for compounds (1)—(5), (12), and (15). Thus the finding that the absorption at lowest field in the ¹³C n.m.r. spectrum of the photoproduct is at 220.3 p.p.m. tends to rule out an acylsilane structure. Further it is known that the enaminoketone (18) shows CH₃–N–H coupling (J 5 Hz) in its ¹H n.m.r. spectrum[9] and such coupling is absent in the spectrum of the photoproduct. The most likely structure thus appears to be (19).

For purposes of comparison the β-ketoacylsilane (20) was prepared (in low yield) by treatment of ethyl acetoacetate with Li–Me₃SiCl in tetrahydrofuran. It is concluded that the predominant tautomer present (in CDCl₃) is (21) as the lowest field ¹³C n.m.r. signal is at 201.7 p.p.m. Thus both compounds (19) and (21) demonstrate the marked tendency for the acylsilane group to enolise.

The [1,2]-methyl migration occurring on photolysis of the azidoacylsilane (2) is a typical reaction of simple alkyl azides

(8) (9) (10)

(22) (23) (24)

(11) (12) (13)

(14) (15)

(16) (17) (18)

(19) (20) (21)

molecular photoadditions involving acylsilanes. The reaction appears therefore to be a genuine example of the intramolecular interaction of an excited acylsilane group with another functional group.

Experimental

[1]H N.m.r. spectra were recorded with a Perkin-Elmer R24 (60 MHz) or R32 (90 MHz), or a Bruker WH 300 (300 MHz) instrument. Chemical shifts are quoted in p.p.m. using CH_2Cl_2 (δ 5.25) as internal standard. [13]C N.m.r. spectra were recorded with a Bruker WH 90 (22.63 MHz) or Bruker WH 300 (75.57 MHz) instrument. Chemical shifts are quoted in p.p.m. downfield of Me$_4$Si using the central peak of the solvent (CDCl$_3$) signal (δ 77.00) as internal standard. Ether refers to diethyl ether. Light petroleum refers to the fraction with b.p. 30—40 °C.

Standard Procedure for the Preparation of Allenyl Sulphides from Prop-2-ynyl Chlorides.—Following a procedure very similar to that of Clinet *et al.*,[4] the prop-2-ynyl chloride (1 equiv.) and the thiol (1 equiv.) were dissolved together in dry ether (4—5 mmol in 15 ml) under nitrogen and the resulting solution was immediately cooled to −78 °C. n-Butyl-lithium in hexane (1.6M; 2 equiv.) was then added dropwise at such a rate as to maintain the temperature below −60 °C. After the mixture had been stirred for 1 h at −78 °C, a white precipitate had usually been deposited. The mixture was allowed to warm up to −30 °C during *ca.* 2 h (elimination occurs between −50 and −40 °C) and the precipitate redissolved to give a coloured solution of the α-lithio allenyl sulphide. This solution was recooled to −78 °C and then chlorotrimethylsilane (*ca.* 1.6 equiv.), or another quenching agent, was added. The resulting mixture was allowed to warm up slowly to room temperature under nitrogen (5—6 h) and then brine–water (1:1) was added. The aqueous layer was separated and extracted with ether. The combined organic layers were washed with sodium hydroxide solution (2M) and brine–water (1:1), and then dried (K$_2$CO$_3$). Filtration through Celite followed by evaporation yielded the crude allene as a coloured liquid.

3-Methyl-1-phenylthio-1-trimethylsilylbuta-1,2-diene (7; R = Ph).—Following the standard procedure, 3-chloro-3-methyl-but-1-yne (5.13 g, 50 mmol) and thiophenol (5 ml, 50 mmol) in dry ether (150 ml) gave, after quenching with chlorotrimethyl-silane, a liquid (13.73 g) which was distilled at 73—75 °C and 0.03 mmHg to yield the *phenylthioallene* (7; R = Ph) (6.9 g, 56%) (Found: C, 68.05; H, 8.15; S, 13.25. C$_{14}$H$_{20}$SSi requires C, 67.7; H, 8.1; S, 12.9%); $\nu_{max.}$(film) 1 945 (C=C=C), 1 250 cm^{-1} (SiMe$_3$); δ(CCl$_4$) 7.40—7.05 (5 H, m), 1.55 (6 H, s), and 0.10 (9 H, s); δ_C(CDCl$_3$) 205.8 (s) (C-2), 136.0 (s), 131.5 (d), 128.4 (d), 126.5 (d) (PhS), 95.3 (s), 92.7 (s) (C-1, C-3), 19.6 (q) (Me), −1.2 (q) (SiMe$_3$). The allene became faintly coloured within minutes of being exposed to air, but this was not accompanied by any detectable change in its spectroscopic properties. Samples could be redistilled in good yield even after several months at 0 °C. Crude solutions dried over Na$_2$SO$_4$ (instead of K$_2$CO$_3$) yielded 3-methyl-1-phenylthio-1-trimethylsilylbuta-1,3-diene after evaporation and attempted distillation.

that lack a hydrogen atom in the α-position.[10] In a control experiment the azidoketone (22)[11] was irradiated under the same conditions. The compound was recovered in high yield, only a trace of the enamine (18) being formed. It is presumed that the difference results from the much longer wavelength n—π* absorption for the acylsilane which results in more efficient excitation on irradiation using a Pyrex filter, followed by energy transfer to the β-azido group.

Irradiation of the β-isothiocyanatoacylsilane (4) in ether, acetonitrile, or cyclohexene gave a complex mixture of unstable products which were not investigated in detail. Irradiation (350 nm) in hexane however led to the rapid formation of a yellow crystalline solid. The [1]H n.m.r. spectrum (in CDCl$_3$) of this solid showed a signal at δ 0.08, attributable to SiMe$_3$, which rapidly diminished with time after exposure to air. Treatment with methanol led to complete desilylation and the crystalline product (48% yield) had ^{1}H and [13]C n.m.r. spectra (see Experimental section) compatible with the thioamide structure (23; R = H); this was supported by the u.v. spectrum which showed an apparent π—π* absorption at 335 nm (ε 5 420) and an n—π* absorption at 442 nm (ε 29). On the basis of this structure, the first formed photoproduct is considered to be the silyl analogue (23; R = SiMe$_3$). A possible mechanism for the formation of this compound would involve the formation of the biradical (24) followed by migration of the trimethylsilyl group, presumably within a radical cage. Some precedent for this might be provided by the proposals of Dalton *et al.*[7] for inter-

3-Methyl-1-t-butylthio-1-trimethylsilylbuta-1,2-diene (**7**; R = Bu^t).—Following the standard procedure, 3-chloro-3-methyl-but-1-yne (5 ml, 44 mmol) and 1,1-dimethylethanethiol (5 ml, 44 mmol) in dry ether (150 ml) gave, after quenching with chloro-trimethylsilane, a slightly milky, coloured liquid (10.48 g). Column chromatography on neutral alumina (200 g), using light petroleum–dichloromethane (0→10%) as eluant, yielded the t-butylthioallene (**7**; R = Bu^t) (5.67 g, 56%). The compound distilled poorly over a temperature range, b.p. *ca.* 65—67 °C at 4 mmHg, $v_{max.}$(film) 1 940 cm^{-1}; δ(CCl$_4$) 1.70 (6 H, s), 1.34 (9 H, s), and 0.90 (9 H, s). Satisfactory analytical data were not obtained.

1-t-Butylthio-1-trimethylsilylpropadiene (**14**).—n-Butyl-lith-ium in hexane (1.6M; 3.75 ml, 6 mmol) was diluted with dry tetrahydrofuran (THF) (10 ml), under nitrogen at −20 °C, and di-isopropylamine (0.2 ml, 1.5 mmol) was added dropwise. The mixture was stirred for 20 min at −30 to −20 °C, and then cooled to −78 °C. A solution of 1-t-butylthiopropyne[6] (0.64 g, 5 mmol) in dry THF (6 ml) was added dropwise and the resulting mixture was stirred at −78 °C. After 4 h, chloro-trimethylsilane (1 ml; excess) was added and the mixture was allowed to warm to room temperature under nitrogen (6 h). Brine–water (1:1) (25 ml) and light petroleum (10 ml) were added. The aqueous layer was separated and extracted with light petroleum. The combined organic extracts were washed with aq. HCl, water, aq. NaOH, and brine and then dried (K$_2$CO$_3$). Celite filtration followed by evaporation yielded a liquid (1.17 g), which was distilled at 78—79 °C and 8 mmHg to give the *silylallene* (**14**) as a colourless liquid (0.64 g, 64%) (Found: C, 59.5; H, 10.15; S, 16.15. C$_{10}$H$_{20}$SSi requires C, 59.95; H, 10.05; S, 16.0%); $v_{max.}$(film) 1 930 cm^{-1}; δ(CCl$_4$) 4.55 (2 H, s), 1.40 (9 H, s), and 0.15 (9 H, s).

Reaction of 3-Methyl-1-t-butylthio-1-trimethylsilylbuta-1,2-diene with Iron(III) Chloride.—Iron(III) chloride (4.4 g, 27.1 mmol) was dissolved in water (11 ml), and the cold solution was added to a solution of the allene (5.63 g, 24.4 mmol) in acetone (270 ml) in a foil-wrapped flask. After the mixture had been stirred for 24 h at 20 °C, water (250 ml) and dichloromethane (250 ml) were added. The aqueous layer was separated and extracted with dichloromethane. The combined organic layers were washed with brine–water (1:1) and then dried (MgSO$_4$). The solution was filtered through Celite and then concentrated to yield a brightly coloured liquid (5.77 g). This material was purified by column chromatography on silica gel (100 g), using dichloromethane–light petroleum (20→0%) as eluant. A fraction consisting largely of di-t-butyl disulphide (1.68 g) was eluted first and the αβ-unsaturated acylsilane (**1**) (1.54 g, 41%) was collected (Found: C, 61.5; H, 10.3. Calc. for C$_8$H$_{16}$OSi: C, 61.75; H, 10.3%); $v_{max.}$(film) 1 640, 1 570, 1 440, 1 375, 1 250, 1 095, 1 015, 870, 845, 790, and 750 cm^{-1}; λ(hexane) 412sh (ε 80), 434 (117), 456 (113), and 484sh nm (52); $\lambda_{max.}$ (ether) 432 (ε 102), 452 nm (98); $\lambda_{max.}$(MeCN) 429 nm (ε 104); $\lambda_{max.}$ (EtOH) 430 nm (ε 105); $\lambda_{max.}$(AcOH) 423 nm (ε 108); δ(CCl$_4$) 6.38 (1 H, br s), 2.01 (3 H, br s), 1.82 (3 H, br s), and 0.13 (9 H, s); δ_C(CDCl$_3$) 237.7 (s), 150.2 (s), 126.9 (d), 27.4 (q), 21.0 (q), and −3.3 (q); *m/z* (E.I.) 156 (*M*$^+$, 77%), 141 (*M* − Me, 68), 113 (*M* − C$_3$H$_7$, 100), 83 (Me$_2$C=CHCO$^+$, 79), 73 (Me$_3$Si$^+$, 68), and 59 (C$_4$H$_7$$^+$, 30).

Reaction of 2-Cyclohexylidene-1-t-butylthio-1-trimethylsilyl-ethene (**10**) *with Iron(III) Chloride.*—Following a procedure similar to that used for the reaction of the dimethylallene (**7**; R = Bu^t), a solution of the allene (**10**) (6.56 g, 24.5 mmol) in acetone (270 ml) was mixed with a solution of iron(III) chloride (4.0 g, 24.7 mmol) in water (11 ml) in a foil-wrapped flask. After being refluxed for 1 h, the mixture was worked up as before to

yield a dark liquid (5.09 g). This material was purified by column chromatography on silica gel (110 g) using dichloro-methane–light petroleum (30→0%) as eluant. A mixture of sulphur compounds, including the 1,3-diene isomer of (**10**) (3.15 g), was eluted first followed by a further coloured fraction. This was shown to be a mixture of (cyclohexylideneacetyl)trimethyl-silane (**11**) and (cyclohex-1-enylacetyl)trimethylsilane (**12**) (total 0.99 g, 21%), initially in the ratio *ca.* 5.2. Equilibration of the two isomers was found to occur on standing.

(3-Azido-3-methylbutanoyl)trimethylsilane (**2**).—(3-Methyl-but-2-enoyl)trimethylsilane (**1**) (0.94 g, 6 mmol) was dissolved in glacial acetic acid (12 ml), in a foil-wrapped flask, and solid lithium azide (0.36 g, 7.3 mmol) was added. After the mixture had been stirred for 24 h at 20 °C, ether and brine were added and the aqueous layer was separated and extracted with ether. The combined organic layers were washed with water, aq. Na$_2$CO$_3$, and water and then dried (Na$_2$SO$_4$). The solution was filtered and evaporated to yield the *azide* (**2**) (1.0 g, 83%) as a light coloured liquid. The n.m.r. spectrum showed only trace amounts of the αβ-unsaturated acylsilane and 3-methylbut-2-enal, and the azide was used for subsequent experiments without further purification. An analytical sample was obtained by column chromatography on silica gel, using light petroleum–dichloromethane (1:1) as eluant (Found: C, 48.45; H, 8.8; N, 20.65. C$_8$H$_{17}$N$_3$OSi requires C, 48.2; H, 8.6; N, 21.1%); $v_{max.}$(film) 2 100 cm^{-1}; $\lambda_{max.}$(hexane) 369 (ε 114), 384 nm (111); δ(CCl$_4$) 2.60 (2 H, s), 1.29 (6 H, s), and 0.15 (9 H, s); δ_C(CDCl$_3$) 247.1 (s), 60.2 (s), 56.5 (t), 25.5 (q), and −3.3 (q).

(3-Isothiocyanato-3-methylbutanoyl)trimethylsilane (**4**).—Fol-lowing a procedure analogous to that used for the reaction with lithium azide, (3-methylbut-2-enoyl)trimethylsilane (**1**) (1.41 g, 9 mmol) was treated with lithium thiocyanate (1.0 g, 15.4 mmol) in acetic acid (18 ml). After 46 h at room temperature in the dark, similar work-up yielded a coloured liquid (1.51 g) which was shown (by n.m.r.) to consist of compound (**4**) and unchanged (**1**) in the ratio *ca.* 7:1, together with trace amounts of other components. This material was purified by column chromatography on silica gel (30 g), using dichloromethane–light petroleum (1:1) as eluant, to yield the *isothiocyanate* (**4**) (1.32 g, 68%) (Found: C, 49.9; H, 7.85; N, 6.3. C$_9$H$_{17}$NOSSi requires C, 50.1; H, 7.95; N, 6.5%); $v_{max.}$(film) 2 080 cm^{-1} (strong, br); $\lambda_{max.}$(hexane) 251 (ε 980), 355 (64), 369 (77), and 385 nm (72); δ(CCl$_4$) 2.80 (2 H, s), 1.48 (6 H, s), and 0.20 (9 H, s); δ_C(CDCl$_3$) 245.0 (s), 58.7 (s), 57.0 (t), 29.2 (q), and −3.2 (q).

(3-Methyl-3-phenylsulphonylbutanoyl)trimethylsilane (**3**).—Following a procedure analogous to that used for the reaction with lithium azide, the acylsilane (**1**) (160 mg, 1.02 mmol) was treated with sodium benzenesulphinate (250 mg, 1.52 mmol) in acetic acid (2 ml). After 24 h at room temperature in the dark, similar work-up yielded an oily solid (270 mg). This was dissolved in the minimum amount of ether and then purified by column chromatography on silica gel (6 g), using light petroleum–ether (4:1) as eluant. An initial fraction (74 mg) was shown to consist of a *ca.* 2:1 mixture of compound (**3**) and unchanged (**1**), together with trace amounts of other com-ponents. The major fraction then yielded the *sulphone* (**3**) (166 mg, 54%) as a white, crystalline solid, m.p. 78—80 °C. An analytical sample had m.p. 80—81 °C (Found: C, 56.15; H, 7.55; S, 10.8. C$_{14}$H$_{22}$O$_3$SSi requires C, 56.35; H, 7.45; S, 10.75%); $\lambda_{max.}$(hexane) 216 (ε 9 200), 257 (830), 264 (870), 271 (707), 367 (98), and 382 nm (75); δ_C(CDCl$_3$) 244.7 (s), 134.4 (s), 133.7 (d), 130.7 (d), 62.6 (s), 48.3 (t), 20.1 (q), and −3.5 (q).

(3-Methylbutanoyl)trimethylsilane (**5**).—An initial attempt to hydrogenate the unsaturated silane (**1**) (205 mg, 1.31 mmol) in ethyl acetate (35 ml), using 10% Pd–C (101 mg) as catalyst,

yielded only unchanged compound (**1**). Repeating the process on the same sample, with fresh catalyst, yielded a liquid (172 mg), which was purified by column chromatography on silica gel (4 g), using dichloromethane–light petroleum (1:1) as eluant, to give the *saturated acylsilane* (**5**) (58 mg, 28%) as an almost colourless liquid. An analytical sample was repurified by column chromatography (Found: C, 61.15; H, 11.15. $C_8H_{18}OSi$ requires C, 60.7; H, 11.45%); $v_{max.}$(film) 1 648 cm^{-1}; $\lambda_{max.}$(hexane) 367 (ε 83), 382 (75); $\lambda_{max.}$(EtOH) 367 nm (ε 120); δ(CCl$_4$) 2.34 (2 H, br d, J 6 Hz), 2.26—1.85 (1 H, m), 0.85 (6 H, d, J 6 Hz), and 0.09 (9 H, s); δ_C(CDCl$_3$) 249.0 (s), 57.4 (t), 23.0 (d), 22.7 (q), and -3.2 (q); m/z (E.I.) 158 (M^+, 3%), 143 (M – Me, 2), 116 (M – C_3H_6, 2), 101 (M – C_4H_9, 4), and 73 (Me$_3$Si$^+$, 100); m/z (C.I.) 159 (M + 1, 32%), 143 (M – Me, 4), 90 (Me$_3$SiOH$^{·+}$, 47), and 73 (Me$_3$Si, 100).

(3-Oxobutanoyl)trimethylsilane (**20**).—By analogy to the general literature procedure for the use of Li–THF–Me$_3$SiCl,^{12} chlorotrimethylsilane (32 ml, 0.25 mol) was added to a cooled (ice–salt bath) mixture of lithium wire (*ca.* 1.5 g, 0.22 mol, 1—2 mm lengths) and dry THF (50 ml) under argon, and then ethyl acetoacetate (6.4 ml, 0.05 mol) was added dropwise during 1 h, maintaining the temperature below 10 °C. After being stirred at room temperature for 15 h, the solution was filtered, and the solid removed was washed several times with ether. The combined filtrate and washings were concentrated and the residue obtained was quenched with hydrochloric acid (6M; 75 ml). The resulting dark mixture was extracted with ether and the combined extracts were washed with aq. HCl, water, and brine and then dried (MgSO$_4$). Filtration through Celite followed by evaporation yielded a liquid (6.94 g) which was separated into several fractions (total 3.03 g) by column chromatography on silica gel (200 g), using light petroleum–ether (4→16%) as eluant. Attention was concentrated on a small, relatively slow-moving fraction (0.78 g) showing $v_{max.}$ 1 620, 1 575 cm^{-1}. Flash distillation at room temperature and 0.15 mmHg, followed by distillation at 69—71 °C and 15 mmHg, yielded the β-*ketoacylsilane* (**20**) (103 mg) as a faintly coloured liquid. An analytical sample was further purified by column chromatography on silica gel (4 g), using ether–light petroleum (1:9) as eluant (Found: C, 53.3; H, 8.95. C$_7$H$_{14}$O$_2$Si requires C, 53.1; H, 8.9%). The compound was considered to exist as 4-hydroxy-4-trimethylsilylbut-3-en-2-one, on the basis of the following data: $v_{max.}$(film) 1 620, 1 575, 1 390, 1 250, 1 207, 1 125, 988, 915, 860, 845, 795, and 760 cm^{-1}; $\lambda_{max.}$(hexane) 272 nm (ε 8 220); δ(CDCl$_3$) *ca.* 14.4 (1 H, br s), 5.69 (1 H, s), 2.04 (3 H, s), and 0.12 (9 H, s); δ_C(CDCl$_3$) 201.7 (s), 191.6 (s), 109.1 (d), 28.5 (q), and -3.3 (q).

Photolysis of (3-*Azido-3-methylbutanoyl*)*trimethylsilane* (**2**).—A solution of the azide (**2**) (300 mg, 1.5 mmol) in hexane (300 ml) was irradiated through Pyrex (100-W medium-pressure mercury vapour lamp) for 15 min. After removal of the solvent, dry ether (25 ml) was added, and some polymeric material was removed by filtration through Celite. The solution was evaporated to yield a liquid (250 mg). Column chromatography on silica gel (10 g), using ether as eluant, gave (3-*methyliminobutanoyl*)*trimethylsilane* (**17**) (131 mg, 51%) as an oil which, on one occasion, crystallised as platelets melting at about room temperature. An analytical sample was further purified by column chromatography on silica gel, using ethyl acetate–light petroleum (50→30%) as eluant (Found: C, 56.35; H, 9.85; N, 7.75. C$_8$H$_{17}$NOSi requires C, 56.1; H, 10.0; N, 8.2%). The compound was considered to exist as 1-hydroxy-3-methyl-imino-1-trimethylsilylbut-1-ene (**19**) on the basis of the following data: $v_{max.}$(CHCl$_3$) 1 595, 1 520, 1 440, 1 380, 1 290, 1 250, 1 080, 895, and 850 cm^{-1}; $\lambda_{max.}$(hexane) 328 (ε 9 000), 334 (9 000), and 376 nm (123); δ(CDCl$_3$) *ca.* 12.2 (1 H, br s), 5.46 (1

H, s), 2.94 (3 H, s), 1.96 (3 H, s), and 0.17 (9 H, s); δ_C(CDCl$_3$) 220.3 (s), 162.9 (s), 102.6 (d), 29.2 (q), 18.0 (q), and -2.8 (q). A faster-moving fraction from the column (86 mg) was shown to consist largely of unchanged azide (**2**).

Photolysis for 30 min gave more complete conversion of (**2**) into the product (**19**), but led also to by-products that were difficult to separate by chromatography. Photolysis of compound (**2**) for 3 h caused complete degradation to a complex mixture of products.

Photolysis of (3-*Isothiocyanato-3-methylbutanoyl*)*trimethyl-silane* (**4**).—A solution of the isothiocyanate (505 mg, 2.35 mmol) in hexane (250 ml) was irradiated at 350 nm (Rayonet apparatus) for 1 h, during which time yellow needles were deposited. In a separate experiment, the n.m.r. spectrum of this material showed δ(CDCl$_3$) 2.72 (2 H, br s), 1.50 (6 H, s), and 0.08 (<9 H, s). Further loss of the Me$_3$Si absorption occurred on leaving the sample in solution overnight, thus producing compound (**23**; R = H) with no distinguishable shift in the position of the CH$_2$–CMe$_2$ signals. The initial solid product was considered to be 5,5-dimethyl-1-trimethylsilyl-3-oxopyrrolidine-2-thione (**23**; R = SiMe$_3$).

The almost colourless solution was decanted and the solid was washed with small portions of light petroleum. The combined solutions were evaporated to yield an oily residue which was washed with further light petroleum. The solid obtained, and the crystals removed earlier, were combined, dissolved in methanol (30 ml), and left overnight in the dark. Meanwhile the final light petroleum extracts were evaporated to yield a liquid (194 mg), which was shown to consist largely of unchanged isothiocyanate. On evaporation of the methanol solution, 5,5-*dimethyl-3-oxopyrrolidine-2-thione* (**23**; R = H) was obtained (225 mg, 61%) as a bright yellow solid showing only trace amounts of other components. Polar impurities were removed by column chromatography on silica gel (10 g) using ethyl acetate–light petroleum (4:1) as eluant (the material was applied to the column in 100% ethyl acetate). The sample of compound (**23**; R = H) obtained (175 mg, 48%) was re-crystallised from chloroform and then had m.p. 170—171.5 °C (Found: C, 49.8; H, 6.75; N, 9.5; S, 22.55. C$_6$H$_9$NOS requires C, 50.3; H, 6.35; N, 9.8; S, 22.4%); $v_{max.}$ (CHCl$_3$, saturated) 3 380, 1 762, 1 496, 1 460, 1 408, 1 376, 1 145, and 1 013 cm^{-1}; $\lambda_{max.}$(EtOH) 335 (ε 5 420), 442 nm (29); δ(CDCl$_3$) 9.58 (1 H, br s), 2.76 (2 H, s), and 1.46 (6 H, s); δ_C (CD$_3$OD; relative to solvent peak at δ 49.00) 196.6 (s), 188.0 (s), 58.9 (s), 50.0 (t), and 28.9 (q); m/z (C.I.) 144 (M + 1, 100%), 143 (M^+, 82), 128 (M – Me, 18), 83 (Me$_2$C=CHCO$^+$, 19), 60 (H$_2$NCS$^+$, 22), 56 (MeCNMe$^+$, 61), 55 (C$_4$H$_7^+$, 28), 41 (50), and 39 (36).

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