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SIMPLE PREPARATION OF α-BROMO ACYL SILANES, α-KETOACYL SILANES, AND α-KETOESTERS FROM SILYL ACETYLENES

Philip C. Bulman Page* and Stephen Rosenthal

Robert Robinson Laboratories, Department of Chemistry,
University of Liverpool, P.O. Box 147, Liverpool, L69 3BX, U.K.

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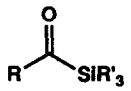
Abstract : α-Bromo- and α-keto-acyl silanes may simply and efficiently be prepared in short reaction schemes from silyl acetylenes; α-ketoacyl silanes are also implicated in a one-pot synthesis of α-ketoesters from silyl acetylenes.

Introduction

Acyl silanes (1) exhibit unusual spectroscopic properties and possess interesting chemistry.[1,2] While a number of methods for the preparation of simple acyl silanes are now available,[1] more highly functionalised acyl silanes are much less well-known. This is perhaps because the sensitivity of acyl silanes, particularly towards basic conditions and light, makes them poor substrates for functionalisation: the most satisfactory preparative routes are those which do not involve acyl silanes as intermediates, that is those in which a potential acyl silane moiety is unmasked in the last step. To this end we have developed useful syntheses of α-bromo- (2)[3] and α-keto- (3)[4] acyl trimethylsilanes in which the halo and carbonyl functions respectively are introduced concomitantly with the formation of the acyl silane unit. We have also discovered a simple and efficient synthetic method for α-ketoesters (4) in which α-ketoacyl silanes are implicated as reaction intermediates.[5] All of these new reactions involve trimethylsilyl acetylenes (5) as the common starting materials.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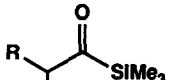
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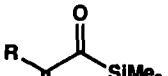
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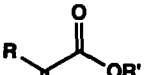
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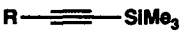
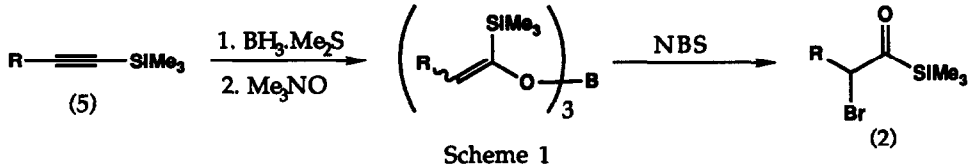

(5)

α-Bromoacylsilanes

α-Haloacyl silanes have previously been prepared by a number of different routes including bromination of 1,1-bis-trimethylsilyl alkan-1-ols[6] and bromination of the silyl enol ethers of acyl silanes;[7] however, these methods suffer from multi-step sequences, variable yields, or sensitive intermediates. We have devised a convenient synthesis of α-bromoacyl silanes from silyl acetylenes using hydroboration methodology.[8] Enol borinates of simple aldehydes and ketones are known to react with N-bromosuccinimide at 0 °C to give the corresponding α-brominated

species.[9] We have shown that enol borinates of acyl trimethylsilanes, readily derived directly from trimethylsilyl acetylenes using hydroboration - oxidation, undergo an analogous reaction to provide α-bromoacyl silanes (2, R^1 = Me) in reasonable yields (Scheme 1, Table I). The entire sequence may be carried out in one-pot and tolerates the presence of silyl ether and halide groups in the substrate (Table I, entries c - e).



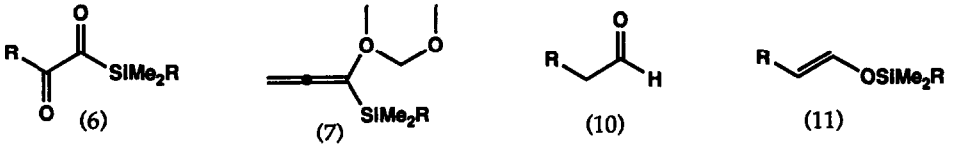
Scheme 1

Table I. Preparation of α-bromoacyl silanes

Entry	R	Yield/%
a	$^nC_5H_{11}$	61
b	$^nC_4H_9$	60
c	$Cl(CH_2)_3$	61
d	$^tBuMe_2Si(CH_2)_3$	54
e	$^tBuMe_2Si(CH_2)_2$	52

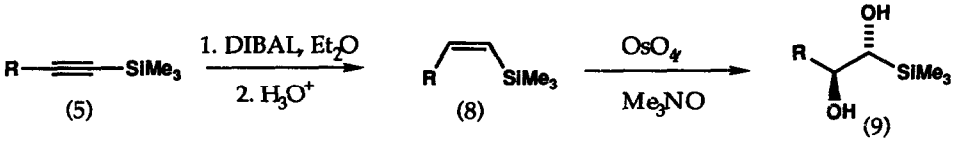
α-Ketoacyl silanes

Prior to our 1986 communication[4] only one report of α-ketoacyl silane preparation had appeared in the literature. Reich had reported the isolation of α-ketoacyl silanes (6) from the epoxidation and rearrangement of α-silyl allenyl ethers (7) (derived in turn from the corresponding allenyl ethers by metallation and silylation),[10] a procedure which does not allow the preparation of α-ketoacyl silanes not possessing β-hydrogen atoms.



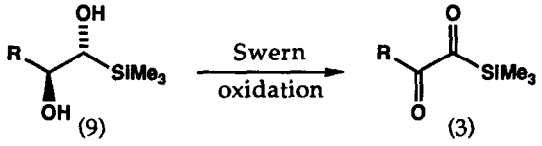
Osmium tetroxide-catalysed oxidation of Z-alkenyl trimethylsilanes (8) (coupling constant ca. 12.5 Hz, selectively prepared by kinetically-controlled hydroalumination using diisobutyl aluminium hydride reduction of trimethylsilyl acetylenes in ethereal solution[11]) occurs to give the corresponding anti-1,2-diols (9) in reasonable yields when trimethylamine-N-oxide is used as the reoxidant (Scheme 2);[4,12] use of alternative reoxidants such as *tert*-butyl hydroperoxide results in formation of aldehydes (10) and silyl enol ethers (11) as the sole products due to the facile acid- and base-mediated decomposition pathways.[12-15] Z-Alkenyl silane substrates are necessary for a high yield of diol; the thermodynamically more stable E-alkenyl silanes (coupling

constant ca. 19 Hz), which may be prepared by hydroalumination using diisobutyl aluminium hydride reduction of silyl acetylenes in hexane solution, are not efficiently syn-dihydroxylated.[12]



Scheme 2

While pyridinium chlorochromate oxidation of diol (9a) gave only aldehyde (10a), we were pleased to find that use of the Swern procedure[16] allowed the isolation of the highly light-sensitive deep crimson α-ketoacyl trimethylsilanes (3) from diols (9) in useful yields (Scheme 3, Table II).[4] Purification was conducted in the dark by dry flash-column chromatography at -78 °C or by vacuum distillation. This sequence provides a simple and reliable three-step route to a very sensitive species.



Scheme 3

Table II. Preparation of α-ketoacyl silanes

Entry	R	Yield/%
a	Ph	55
b	$^{n}C_5H_{11}$	39
c	$^{n}C_4H_9$	41

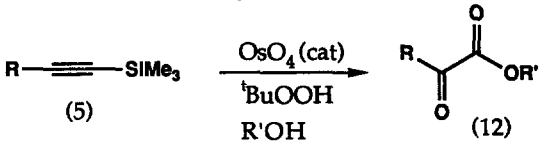
α-Ketoesters

α-Ketoacids are important intermediates in several biosynthetic pathways, for example the biosynthesis of α-amino acids, fats, carbohydrates, proteins, porphyrins, and nucleic acids.[17] Several synthetic routes for the preparation of α-ketoacids and α-ketoesters,[18-24] including synthesis *via* metalloaldimines,[18] Ritter reactions,[19] oxidative decarboxylation of β-ketoesters,[20] hydrolysis of thioacetal derivatives[21] and α-amino esters,[22] and Pummerer rearrangement[23] are available in the literature. These methods may have the disadvantages of length, lack of generality, or experimental inconvenience.

We have discovered a simple and general procedure for the preparation of α-ketoesters in good yields from silyl acetylenes.[5] Treatment of trimethylsilyl acetylenes (5) with osmium tetroxide under catalytic conditions (5% w/w) using *tert*-butyl hydroperoxide as reoxidant in an alcoholic solvent at 0 °C directly provides α-ketoesters (12) in which the alkoxy group is derived from the

solvent used (Scheme 4, Table III).

The osmium tetroxide-catalysed oxidation of dialkyl acetylenes is known to afford the corresponding α-diketones[15] and we believe the present reaction to proceed through the intermediacy of an α-ketoacyl silane. Reaction mixtures display the deep pink colour characteristic of α-ketoacyl silanes; and indeed when 2-oxo-2-phenylethanoyl trimethylsilane (3a) was subjected to identical reaction conditions using methanol as solvent, methyl phenylglyoxylate (12a) could be isolated in 45% yield.

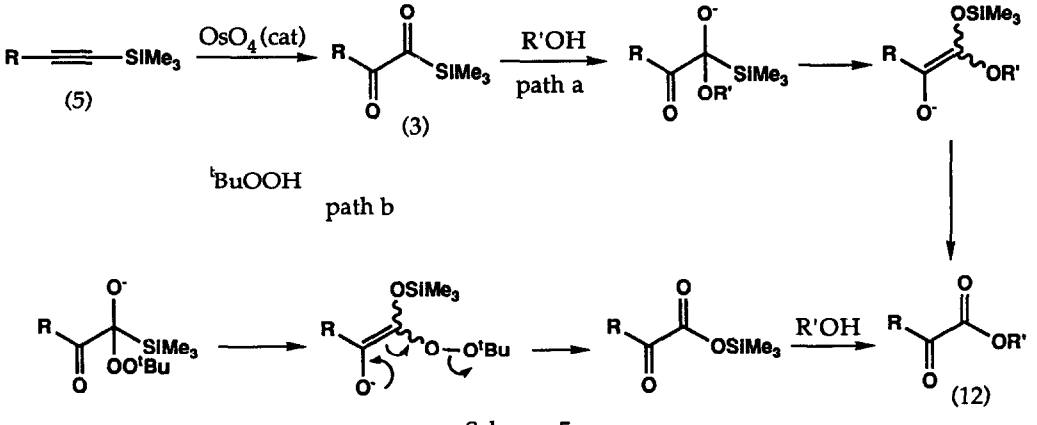


Scheme 4

Table III. Preparation of α-keto esters

Entry	R	R'	Yield/%
a	Ph	Me	74
b	Ph	^{t}Bu	70
c	$^{n}C_6H_{13}$	Me	52
d	$^{n}C_4H_9$	Me	54

Two mechanisms for this reaction seem feasible: the intermediate α-ketoacyl silane could be attacked at the more electrophilic carbonyl group either by alcoholic solvent or by hydroperoxide. In the first case, Brook rearrangement followed by further oxidation could produce α-ketoester directly (Scheme 5, path a), while in the case of attack by hydroperoxide, Brook rearrangement followed by a peroxide cleavage pathway could give rise to silyl ester, transformed under the reaction conditions into α-ketoester (Scheme 5, path b).



Scheme 5

Unhappily, we find that neither the presence of water in the reaction mixtures nor the use of water in place of solvent results in the formation of α-ketoacids, only oxidative cleavage to give carboxylic acids being observed. In accordance with the report by Griffith,[25] similar osmium tetroxide-catalysed oxidation of phenyl acetylene in alcoholic solution also gave only benzoic acid.

Acknowledgements
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Experimental section

General experimental
Petroleum ether (b.p. 40-60°C and b.p. 60-80°C) was distilled prior to use. Hexane and benzene were dried by distillation from sodium. Dichloromethane was dried by distillation from calcium hydride. Diethyl ether and tetrahydrofuran were dried by distillation from the sodium benzophenone ketyl radical. Dimethylformamide was distilled from calcium hydride; the distillate was flash distilled from alumina activated by heating to 150 °C overnight; the dried DMF was stored over 4 Å molecular sieve. Pyridine was dried by storage over potassium hydroxide pellets and distilled before use. Toluene was dried by distillation from calcium hydride and stored over 4Å molecular sieve. Methanol was dried by distillation from magnesium. Trimethylamine-*N*-oxide was dried by azeotropic distillation with toluene.

Commercially available reagents were used as supplied unless otherwise stated.

Butyl-lithium was purchased from the Lithium Corporation of Europe in one-gallon quantities and decanted into glass bottles fitted with septum caps, and was stored at 0 °C. The reagent was dispensed by syringe under argon and standardised by the method of Gilman.

Reactions requiring rigorously anhydrous conditions were carried out in glassware which had been dried for a minimum of four hours at 150 °C and allowed to cool in a desiccator. Reactions were maintained in an atmosphere of argon and reagents and solvents introduced, *via* syringe or using cannula techniques, through a septum cap.

Silica-gel refers to Merck Art 9385 Kieselgel 60 (flash column chromatography) or to Merck Art 15111 Kieselgel 60 (dry flash column chromatography).

Infrared spectra were recorded on Perkin Elmer SP298 or SP1025 infrared spectrophotometers and were calibrated against the 1602 cm^{-1} absorption of polystyrene.

^1H Nuclear magnetic resonance spectra were recorded on Perkin Elmer R 34 (220 MHz) or Bruker WM 250 (250 MHz) spectrometers. ^{13}C N.M.R. spectra were recorded on a Bruker WM 250 spectrometer operating at 62.8 MHz. All spectra were recorded using tetramethylsilane as internal standard.

Electron impact (EI) and chemical ionisation (CI) mass spectra were recorded on a VG Micromass 7070E instrument.

Capillary gas chromatography was performed on a Dani 3800 gas chromatograph. Melting points were determined on a Kofler block apparatus and are uncorrected. Microanalyses were carried out by the Department of Chemistry microanalytical service.

2-PHENYL-1-TRIMETHYLSILYL ETHYNE (5a)

To a solution of phenyl ethyne (20.0 g, 0.196 mol) in anhydrous tetrahydrofuran (150 ml) under a nitrogen atmosphere at -78 °C was added a 1.58 M solution of butyl-lithium in hexane (148.9 ml, 0.235 mol) was added and the mixture was stirred at -78 °C for two hours. Trimethyl chlorosilane (29.60 ml, 0.235 mol) was added, and the reaction mixture allowed to reach room temperature over one hour. The solution was poured into saturated ammonium chloride solution (150 ml) and extracted with dichloromethane (3 x 150 ml). The combined organic layers were washed with water (2 x 40 ml) and brine (2 x 10 ml), and dried over magnesium sulphate. Evaporation of the solvent, followed by bulb-to-bulb distillation (Kugelrohr) gave (5a) as a colourless oil (28.70 g, 85%), bp 55-60 °C (2 mmHg); ν_{max} (film) 2850, 2180, 1600, 1490, 1250, 850, and 760 cm^{-1}; δ (^1H, $CDCl_3$) 7.49-7.43 (2H, m), 7.30-7.25 (3H, m), and 0.25 (9H, s); m/z (EI) 174 (M^+).

1-TRIMETHYLSILYL OCT-1-YNE (5b)

To a solution of oct-1-yne (5.0 g, 45.4 mmol) in anhydrous tetrahydrofuran (100 ml) at -78 °C under a nitrogen atmosphere was added a 1.58 M solution of butyl-lithium in hexane (34.5 ml, 54.5 mmol), and the mixture was stirred at -78 °C for two hours. Trimethyl chlorosilane (6.9 ml, 54.5 mmol) was added, and the reaction mixture allowed to reach room temperature over one hour. Work-up as described above for (5a) followed by bulb-to-bulb distillation (Kugelrohr) gave (5b) as a colourless oil (7.27 g, 88%), bp 65-70 °C (15 mmHg); ν_{max} (film) 2840, 2190, 1250, and 845 cm^{-1}; δ (^1H, $CDCl_3$) 2.23 (2H, t, J 7 Hz), 1.58-1.28 (8H, m), 0.94-0.87 (3H, m), and 0.14 (9H, s); m/z (CI, NH_4^+) 183 (M^++1).

1-TRIMETHYLSILYL HEPT-1-YNE (5c)

To a solution of hept-1-yne (20.0 g, 0.208 mol) in anhydrous tetrahydrofuran (150 ml) at -78 °C under a nitrogen atmosphere was added a solution of butyl-lithium in hexane (1.2 equiv.), and the mixture was stirred at -78 °C for two hours. Trimethyl chlorosilane (31.4 ml, 0.25 mol) was added, and the reaction mixture allowed to reach room temperature over one hour. Work-up as described above for (5a) followed by bulb-to-bulb distillation (Kugelrohr) gave (5c) as a colourless oil (30.40 g, 87%), bp 45-50 °C (2 mmHg); ν_{max} (film) 2850, 2190, 1250, and 845 cm^{-1}; δ (^1H, $CDCl_3$) 2.20 (2H, t, J 7 Hz), 1.54-1.30 (6H, m), 0.93-0.87 (3H, m), and 0.14 (9H, s); m/z (CI, NH_4^+), 186 (M^++18) and 169 (M^++1).

1-TRIMETHYLSILYL HEX-1-YNE (5d)

To a solution of hex-1-yne (10.0g, 0.122 mol) in anhydrous tetrahydrofuran (100 ml) at -78 °C under a nitrogen atmosphere was added a 1.50 M solution of butyl-lithium in hexane (92.6 ml, 0.146 mol), and the mixture was stirred at -78 °C for two hours. Trimethyl chlorosilane (18.4 ml, 0.146 mol) was added, and the reaction mixture allowed to reach room temperature over one hour. Work-up as described above for (5a) followed by bulb-to-bulb distillation (Kugelrohr) gave (5d) as a colourless oil (15.97 g, 85%), bp 35-40 °C (12 mmHg); ν_{max} (film) 2850, 2190, 1250, and 845

cm^{-1}; δ (^1H, $CDCl_3$) 2.25 (2H, t, J 7 Hz), 1.57-1.35 (4H, m), 0.95-0.88 (3H, m), and 0.15 (9H, s); m/z (CI, NH_4^+) 155 (M^++1).

1-TRIMETHYLSILYL-5-CHLOROPENT-1-YNE (5e)

To a solution of 5-chloropent-1-yne (6.50 g, 65.37 mmol) in anhydrous tetrahydrofuran (60 ml) at -78 °C under a nitrogen atmosphere was added a 1.58 M solution of butyl-lithium in hexane (48.13 ml, 76.04 mol), and the mixture was stirred at -78 °C for two hours. Trimethyl chlorosilane (8.3 ml, 76.06 mmol) was added, and the reaction mixture allowed to reach room temperature over one hour. Work-up as described above for (5a) followed by bulb-to-bulb distillation (Kugelrohr) gave (5e) as a colourless oil (8.16 g, 74%), bp 65-75 °C (3 mmHg); ν_{max} (film) 2980, 2180, 1250, 1040, 850, and 760 cm^{-1}; δ (^1H, $CDCl_3$) 3.65 (2H, t, J 6.5 Hz), 2.40 (2H, t, J 6.8 Hz), 1.99-1.91 (2H, m), and 0.15 (9H, s); m/z (CI, NH_4^+), 172 (M^++18); (Found: C, 55.27; H, 8.87. $C_8H_{15}SiCl$ requires C, 54.98; H, 8.65%).

1-TRIMETHYLSILYL-5-*tert*-BUTYLDIMETHYLSILYLOXY PENT-1-YNE (5f)

Pent-4-yn-1-ol (3.0 g, 35 mmol) was dissolved in anhydrous tetrahydrofuran (30 ml) under a nitrogen atmosphere at 0 °C. A 1.58 M solution of butyl-lithium in hexane in hexane (49.57 ml, 78 mmol) was added over a period of thirty minutes. The solution was vigorously stirred for three hours at 0 °C and trimethyl chlorosilane (9.85 ml, 0.078 mol) added. Stirring was continued under a nitrogen atmosphere for fourteen hours at room temperature, 1 M hydrochloric acid (100 ml) added, and the solution stirred for a further twelve hours at room temperature. The layers were separated and the aqueous layer was extracted with diethyl ether (3 x 100 ml). The combined organic layers were washed with water (2 x 50 ml) and brine (10 ml), and dried over magnesium sulphate. Evaporation of the solvent gave 5-trimethylsilyl pent-4-yn-1-ol (4.87 g), which was used without further purification.

5-Trimethylsilyl pent-4-yn-1-ol (4.87 g, 31 mmol) was dissolved in anhydrous DMF (30 ml). Imidazole (5.30 g, 78 mmol) and *tert*-butyldimethyl chlorosilane (5.64 g, 37 mmol) were added and the mixture stirred for twelve hours at room temperature. Saturated aqueous ammonium chloride (100 ml) was added and the layers separated. The aqueous layer was extracted with dichloromethane (3 x 50 ml), and the combined organic layers washed with water (2 x 50 ml), brine (10 ml), and dried over magnesium sulphate. Evaporation of the solvent followed by column chromatography on silica-gel using petroleum ether as the eluant gave (5f) as a colourless oil (6.15 g, 64%), ν_{max} (film) 2900, 2190, 1250, 1100, and 850 cm^{-1}; δ (^1H, $CDCl_3$) 3.70 (2H, t, J 7 Hz), 2.41 (2H, t, J 7 Hz), 1.90-1.75 (2H, m), 0.90 (9H, s), 0.15 (9H, s), and 0.10 (6H, s); m/z (CI, NH_4^+) 271 (M^++1); (Found: C, 60.94; H, 11.27. $C_{14}H_{30}OSi_2$ requires C, 60.86; H, 11.00%).

1-TRIMETHYLSILYL-4-*tert*-BUTYLDIMETHYL SILYLOXY BUT-1-YNE (5g)

But-3-yn-1-ol (2.50 g, 35 mmol) was dissolved in anhydrous tetrahydrofuran (20 ml) under a nitrogen atmosphere at 0 °C. A 1.58 M solution of butyl-lithium in hexane in hexane (49.60 ml, 78 mmol) was added and the solution vigorously stirred for three hours at 0 °C. Trimethyl chlorosilane (9.94 ml, 78 mmol) was added and stirring continued under a nitrogen atmosphere for fourteen hours at room temperature. Work-up as described above for (5f) and evaporation of the solvent gave 4-trimethylsilyl but-3-yn-1-ol (4.14 g) which was used without further purification.

4-Trimethylsilyl but-3-yn-1-ol (4.14 g, 29 mmol) was dissolved in anhydrous DMF (30 ml). Imidazole (4.93 g, 72 mmol) and *tert*-butyldimethyl chlorosilane (5.24 g, 34 mmol) were added and the solution stirred for twelve hours at room temperature. Work-up as described above for (5f) followed by column chromatography on silica-gel gave (5g) as a colourless oil (5.0 g, 58%), ν_{max} (film) 2900, 2190, 1250, 1100, and 850 cm^{-1}; δ (^1H, $CDCl_3$) 3.72 (2H, t, J 7 Hz), 2.43 (2H, t, J 7 Hz), 0.90 (9H, s), 0.14 (9H, s), and 0.07 (6H, s); m/z (CI, NH_4^+), 257 (M^++1); (Found: C, 58.84; H, 10.84. $C_{12}H_{26}OSi_2$ requires C, 58.61; H, 10.81%).

Z-2-PHENYL-1-TRIMETHYLSILYL ETHENE (8a)

To a stirred solution of 2-phenyl-1-trimethylsilyl ethyne (5a) (10.0 g, 57.5 mmol) and *N*-methyl morpholine (7.60 ml, 69 mmol) in anhydrous ether (50 ml) at room temperature, was added dropwise a 1 M diisobutyl aluminium hydride solution in hexane (70.0 ml, 69 mmol). The solution was stirred for eight hours at room temperature under an argon atmosphere. The mixture was then poured into a separating funnel containing cold 10% hydrochloric acid (50 ml) and ice. The layers were separated, and the aqueous layer was extracted with ether (3 x 100 ml). The combined organic extracts were washed with water (2 x 30 ml) and brine (10 ml), and dried over magnesium sulphate. Evaporation of the solvent followed by bulb-to-bulb distillation of the residue (Kugelrohr) gave (8a) as a colourless oil (8.40 g, 83%), bp 80-85 °C (6 mmHg); ν_{max} (film) 2980, 1600, 1580, 1450, 1250, and 850 cm^{-1}; δ (^1H, $CDCl_3$) 7.50-7.22 (6H, m), 5.85 (1H, d, J 15 Hz), and 0.02 (9H, s); m/z (EI) 176 (M^+). Glc analysis indicated a 90:10 Z-E ratio.

Z-1-TRIMETHYLSILYL HEPT-1-ENE (8b)

To a stirred solution of 1-trimethylsilyl hept-1-yne (5c) (10.0 g, 60 mmol) and *N*-methylmorpholine (7.91 ml, 72 mmol) in anhydrous ether (50 ml) at room temperature, was added dropwise a 1 M diisobutylaluminium hydride solution in hexane (72.0 ml, 72 mmol). The solution was stirred for eight hours at room temperature under an argon atmosphere. Work-up as described above for (8a) followed by bulb-to-bulb distillation of the residue (Kugelrohr) gave (8b) as a colourless oil (8.77 g, 86%), bp 95-100 °C (60 mmHg); ν_{max} (film) 2990, 1605, 1470, 1250, 850, and 780 cm^{-1}; δ (^1H, $CDCl_3$) 6.35-6.24 (1H, m), 5.45 (1H, d, J 14 Hz), 2.12-2.06 (2H, m), 1.54-1.25 (6H, m), 0.91-0.86 (3H, m), and 0.10 (9H, s); m/z (CI, NH_4^+) 188 (M^++18). Glc analysis indicated a 93:7 Z-E ratio.

Z-1-TRIMETHYLSILYL HEX-1-ENE (8c)

To a stirred solution of 1-trimethylsilyl hex-1-yne (5d) (10.0 g, 65 mmol) and *N*-methylmorpholine (8.60 ml, 78 mmol) in anhydrous ether (50 ml) at room temperature, was added dropwise a 1 M diisobutylaluminium hydride solution in hexane (78.0 ml, 78 mmol). The solution was stirred for eight hours at room temperature under an argon atmosphere. Work-up as described above for (8a) followed by bulb-to-bulb distillation of the residue (Kugelrohr) gave (8c) as a colourless oil (8.82 g, 87%), bp 54-60 °C (15 mmHg); ν_{max} (film) 2990, 1610, 1470, 1250, 850, and 780 cm^{-1}; δ (^1H, $CDCl_3$) 6.37-6.26 (1H, m), 5.47 (1H, d, J 14 Hz), 2.15-2.01 (2H, m), 1.57-1.29 (4H, m), 0.91-0.86 (3H, m), and 0.10 (9H, s); m/z CI, NH_4^+) 174 (M^++18). Glc analysis indicated a 85:15 Z-E ratio.

E-2-PHENYL-1-TRIMETHYLSILYL ETHENE (13)

To a stirred solution of 2-phenyl-1-trimethylsilyl ethyne (5a) (10.0 g, 57 mmol) in anhydrous hexane (15 ml) at room temperature was added dropwise a 1 M diisobutylaluminium hydride

solution in hexane (70.0 ml, 69 mmol). The solution was stirred for eight hours at room temperature under an argon atmosphere. Work-up as described above for (8a) followed by bulb-to-bulb distillation of the residue (Kugelrohr) gave (13) as a colourless oil (9.00 g, 89%), bp 65-70 °C (0.5 mmHg); ν_{max} (film) 2985, 1610, 1256, 990, and 850 cm^{-1}; δ (^1H, $CDCl_3$) 7.52-7.26 (5H, m), 6.95 (1H, d, J 19 Hz), 6.54 (1H, d, J 19 Hz), and 0.23 (9H, s). Glc analysis indicated a 10:90 Z-E ratio.

***syn*-2-HYDROXY-2-PHENYL-1-TRIMETHYLSILYL ETHANOL (14)**

E-2-Phenyl-1-trimethylsilyl ethene (13) (4.00 g, 22 mmol) was added to a solution of *tert*-butanol (50 ml), water (15 ml), and pyridine (2 ml). Trimethylamine *N*-oxide dihydrate (3.53 g, 32 mmol) and osmium tetroxide (100 mg, 0.39 mmol) were added to the solution and the mixture boiled under reflux under an argon atmosphere for twelve hours. Aqueous sodium bisulphite (20 ml) was added and the solvent removed under reduced pressure. The residue was added to saturated aqueous ammonium chloride (100 ml) and extracted with dichloromethane (20 ml) in a continuous extractor. The organic layer was dried with magnesium sulphate. Evaporation of the solvent followed by column chromatography on florisil gave (14) as a colourless solid (2.30 g, 48%), mp 73-75 °C; ν_{max} (nujol mull) 3300, 2920, 1460, 1250, 1000, 850, and 700 cm^{-1}; δ (^1H, $CDCl_3$) 7.36-7.29 (5H, m), 4.75 (1H, d, J 7 Hz), 3.50 (1H, d, J 7 Hz), 2.54 (1H, br s), 2.07 (1H, br s), and -0.09 (9H, s); (Found: C, 63.07; H, 8.88. $C_{11}H_{18}O_2Si$ requires C, 62.81; H, 8.62%).

***anti*-2-HYDROXY-2-PHENYL-1-TRIMETHYLSILYL ETHANOL (9a)**

Z-2-Phenyl-1-trimethylsilyl ethene (8a) (4.00 g, 22.7 mmol) was added to a solution of *tert*-butanol (50 ml), water (15 ml), and pyridine (2 ml). Trimethylamine *N*-oxide dihydrate (3.53 g, 32 mmol) and osmium tetroxide (100 mg, 0.39 mmol) were added to the solution and the mixture boiled under reflux under an argon atmosphere for twelve hours. Work-up as described above for compound (14) followed by column chromatography on florisil gave (9a) as a colourless solid (2.75 g, 61%), mp 70-72 °C; ν_{max} (nujol mull) 3300, 2920, 1460, 1250, 1000, 850, and 700 cm^{-1}; δ (^1H, $CDCl_3$) 7.37-7.30 (5H, m), 4.90 (1H, d, J 3 Hz), 3.66 (1H, d, J 3 Hz), 2.45 (1H, br s), 2.01 (1H, br.s.), and -0.04 (9H, s).

***anti*-2-HYDROXY-1-TRIMETHYLSILYL HEPTANOL (9b)**

Z-1-Trimethylsilyl hept-1-ene (8b) (4.50 g, 27 mmol) was added to a solution of *tert*-butanol (50 ml), water (15 ml), and pyridine (2 ml). Trimethylamine-*N*-oxide dihydrate (4.12 g, 37 mmol) and osmium tetroxide (100 mg, 0.39 mmol) were added to the solution and the mixture boiled under reflux under an argon atmosphere for twelve hours. Work-up as described above for compound (14) followed by bulb-to-bulb distillation of the residue (Kugelrohr) gave (9b) as a colourless oil (3.34 g, 61%), bp 85-90 °C (0.5 mmHg); ν_{max} (film) 3450, 2985, 1480, 1250, 1050, and 850 cm^{-1}; δ (^1H, $CDCl_3$) 3.94-3.90 (1H, m), 3.56 (1H, d, J 3 Hz), 2.23 (2H, br s), 1.72-1.39 (8H, m), 1.06-1.01 (3H, m), and 0.24 (9H, s); δ (^{13}C, $CDCl_3$) 75.8, 71.8, 33.9, 32.6, 26.9, 23.5, 14.5, and -1.6.

***anti*-2-HYDROXY-1-TRIMETHYLSILYL HEXANOL (9c)**

Z-1-Trimethylsilyl hex-1-ene (8c) (5.0 g, 32 mmol) was added to a solution of *tert*-butanol (50 ml), water (15 ml), and pyridine (2 ml). Trimethylamine-*N*-oxide dihydrate (5.00 g, 45 mmol) and osmium tetroxide (100 mg, 0.39 mmol) were added to the solution and the mixture boiled under reflux under an argon atmosphere for twelve hours. Work-up as described above for compound (14) followed by bulb-to-bulb distillation of the residue (Kugelrohr) gave (9c) as a colourless oil (3.90 g, 63%), bp 65-70 °C (0.4 mmHg); ν_{max} (film) 3450, 2980, 1480, 1250, 1050, and 850 cm^{-1}; δ (^1H,

$CDCl_3$) 3.98-3.95 (1H, m), 3.57 (1H, d, J 3 Hz), 2.25 (2H, br s), 1.77-1.41 (6H, m), 1.08-1.02 (3H, m), and 0.24 (9H, s); δ (^{13}C, $CDCl_3$) 76.8, 72.4, 34.9, 33.7, 24.5, 14.90, and -1.1.

REACTION OF *anti*-2-HYDROXY-2-PHENYL-1-TRIMETHYLSILYL ETHANOL (9a) WITH PYRIDINIUM CHLOROCHROMATE

anti-2-Hydroxy-2-phenyl-1-trimethylsilyl ethanol (9a) (1.0 g, 5.02 mmol) was dissolved in anhydrous dichloromethane (30 ml) at 0 °C. To this solution was added pyridinium chlorochromate (2.38 g, 11.04 mmol) and the resulting mixture stirred at 0 °C for two hours. Anhydrous ether (100 ml) was added and the supernatant liquid decanted from the black gum. The insoluble residue was washed with anhydrous ether (3 x 50 ml) and the combined organic solution was passed through a short pad of florisil. Evaporation of the solvent gave phenylacetaldehyde (0.54 g, 90%).

2-OXO-2-PHENYL ETHANOYL TRIMETHYLSILANE (3a)

To a magnetically stirred solution of oxalyl chloride (0.96 ml, 11.04 mmol) in anhydrous dichloromethane (25 ml) at -60 °C was added dropwise dimethylsulphoxide (1.56 ml, 22.1 mmol) dissolved in anhydrous dichloromethane (15 ml). The solution was stirred under a nitrogen atmosphere for two minutes at -60 °C. A solution of *anti*-2-hydroxy-2-phenyl-1-trimethylsilyl ethanol (9a) (1.0 g, 5.02 mmol) in anhydrous dichloromethane (30 ml) was added dropwise to the solution and the resulting mixture stirred for thirty minutes at -60 °C. Triethylamine (2.0 ml, 14.35 mmol) was added and the flask was wrapped with silver foil. The solution was then allowed to warm to room temperature over forty-five minutes. The resulting red solution was diluted with water (50 ml) and the layers separated. The organic layer was dried over magnesium sulphate. Evaporation of the solvent and purification by dry flash column chromatography at -78 °C on silica-gel gave (3a) as a reddish-purple liquid (0.54 g, 55%); ν_{max} (film) 2990, 1680, 1610, 1590, 1250, and 850 cm^{-1}; δ (^1H, $CDCl_3$) 7.47-7.27 (5H, m) and 0.26 (9H, s); δ (^{13}C, $CDCl_3$) 220.4, 191.2, 136.2, 134.2, 129.4, 128.7, and -0.8; m/z (CI, NH_4^+) 213 (M^++18) and 196 (M^++1); λ_{max} (cyclohexane) 518 (117), 328 (45), and 275 (6500).

2-OXOHEPTANOYL TRIMETHYLSILANE (3b)

To a magnetically stirred solution of oxalyl chloride (0.93 ml, 10.63 mmol) in anhydrous dichloromethane (25 ml) at -60 °C was added dropwise dimethylsulphoxide (1.51 ml, 21.25 mmol) dissolved in anhydrous dichloromethane (15 ml). The solution was stirred under a nitrogen atmosphere for two minutes at -60 °C. A solution of *anti*-2-hydroxy-1-trimethylsilyl heptanol (9b) (1.0 g, 4.83 mmol) in anhydrous dichloromethane (30 ml) was added dropwise to the solution and the resulting mixture stirred for thirty minutes at -60 °C. Triethylamine (2.0 ml, 14.35 mmol) was added and the flask was wrapped with silver foil. The solution was then allowed to warm to room temperature over forty-five minutes. The resulting red solution was diluted with water (50 ml) and the layers separated. The organic layer was dried over magnesium sulphate. Evaporation of the solvent and purification by dry flash column chromatography at -78 °C on silica-gel gave (3b) as a reddish-purple liquid (0.38g, 39%); ν_{max} (film) 2980, 1710, 1660, 1250, and 850 cm^{-1}; δ (^1H, $CDCl_3$) 2.55 (2H, t, J 7 Hz), 1.73-1.41 (6H, m), 1.01-0.91 (3H, m), and 0.31 (9H, s); δ (^{13}C, $CDCl_3$) 235.1, 198.3, 63.6, 31.5, 27.7, 23.0, 14.7, and -2.9; m/z (CI, NH_4^+) 221 (M^++18) and 204 (M^++1); λmax (cyclohexane) 530 (96) and 284 (43).

2-OXOHEXANOYL TRIMETHYLSILANE (3c)

To a magnetically stirred solution of oxalyl chloride (1.00 ml, 11.44 mmol) in anhydrous dichloromethane (25 ml) at -60 °C was added dropwise dimethylsulphoxide (1.62 ml, 22.88 mmol) dissolved in anhydrous dichloromethane (15 ml). The solution was stirred under a nitrogen atmosphere for two minutes at -60 °C. A solution of *anti*-2-hydroxy-1-trimethylsilyl hexanol (9c) (1.0 g, 5.2 mmol) in anhydrous dichloromethane (30 ml) was added dropwise to the solution and the resulting mixture stirred for thirty minutes at -60 °C. Triethylamine (2.0 ml, 14.35 mmol) was added and the flask was wrapped with silver foil. The solution was then allowed to warm to room temperature over forty-five minutes. The resulting red solution was diluted with water (50 ml) and the layers separated. The organic layer was dried over magnesium sulphate. Evaporation of the solvent and purification by dry flash column chromatography at -78 °C on silica-gel gave (3c) as a reddish-purple liquid (0.41 g, 41%); ν_{max} (film) 2980, 1710, 1660, 1250, and 850 cm^{-1}; δ (^1H, $CDCl_3$) 2.58 (2H, t, J 7 Hz), 1.77-1.46 (4H, m), 1.03-0.94 (3H, m), and 0.30 (9H, s); m/z (CI, NH_4^+) 211 (M^++18) and 194 (M^++1); λmax (cyclohexane) 528 (98) and 284 (45).

METHYL PHENYLGLYOXYLATE (12a)

2-Phenyl-1-trimethylsilyl ethyne (5a) (2.0 g, 11.5 mmol) was dissolved in methanol (50 ml) and the solution cooled to 0 °C under an argon atmosphere. A 7.5 M solution of *tert*-butyl hydroperoxide in cyclohexane (7.7 ml, 57.6 mmol) was added followed by osmium tetroxide (100 mg, 0.39 mmol). The reaction mixture was stirred at 0 °C until all the starting material was consumed (tlc analysis). Saturated aqueous sodium metabisulphite (10 ml) was added and the bulk of the solvents removed *in vacuo*. Saturated aqueous ammonium chloride (50 ml) was added to the residue and the mixture was extracted with dichloromethane (3 x 50 ml). The combined organic layers were washed with water (2 x 20 ml) and dried over magnesium sulphate. The solvents were removed under reduced pressure, and the residue purified by flash chromatography on silica-gel to give (12a) as a colourless oil (1.39 g, 74%), bp 85-90 °C (1.5 mmHg); ν_{max} (film) 2985, 1750, 1700, 1210, and 910 cm^{-1}; δ (^1H, $CDCl_3$) 8.0 (2H, d, J 7 Hz), 7.70-7.40 (3H, m), and 3.90 (3H, s); m/z (CI, NH_4^+) 165 (M^++1).

***tert*-BUTYL PHENYLGLYOXYLATE (12b)**

2-Phenyl-1-trimethylsilyl ethyne (5a) (2.0 g, 11.5 mmol) was dissolved in *tert*-butanol (50 ml) and the solution cooled to 0 °C under an argon atmosphere. A 7.5 M solution of *tert*-butyl hydroperoxide in cyclohexane (7.7 ml, 57.6 mmol) was added followed by osmium tetroxide (100 mg, 0.39 mol). The reaction mixture was stirred at 0 °C until all the starting material was consumed (tlc analysis). Work-up as described above for (12a) and purification of the residue by flash chromatography on silica-gel gave (12b), (1.65 g, 70%); ν_{max} (film) 3000, 1740, 1700, 1150, 890, and 700 cm^{-1}; δ (^1H, $CDCl_3$) 7.90 (2H, d, J 7 Hz), 7.70-7.41 (3H, m), and 1.57 (9H, br s); δ (^{13}C, $CDCl_3$) 186.7, 162.3, 134.6, 132.6, 129.8, 128.8, 84.6, and 28.0; m/z (CI, NH_4^+) 207 (M^++1); (Found: C, 69.93; H, 6.86. $C_{12}H_{14}O_3$ requires C, 69.88; H, 6.84%).

METHYL HEXYL GLYOXYLATE (12c)

1-Trimethylsilyl oct-1-yne (5b) (2.0 g, 10.99 mmol) was dissolved in methanol (50 ml) and the solution cooled to 0 °C under an argon atmosphere. A 7.5 M solution of *tert*-butyl hydroperoxide in cyclohexane (7.3 ml, 54.95 mmol) was added followed by osmium tetroxide (100 mg, 0.39 mmol). The reaction mixture was stirred at 0 °C until all the starting material was consumed (tlc analysis). Work-up as described above for (12a) and purification of the residue by flash chromatography on silica-gel gave (12c) as a colourless oil (0.98 g, 52%), bp 80-85 °C (5 mmHg);

ν_{max} (film) 2910, 1735, 1460, 1440, 1270, and 1070 cm^{-1}; δ (^1H, $CDCl_3$) 3.86 (3H, s), 2.84 (2H, t, J 7 Hz), 1.66-1.28 (8H, m), and 0.90-0.85 (3H, m); m/z (CI, NH_4^+) 186 (M^++18). Methyl heptanoate was also isolated (0.38 g, 24%).

METHYL BUTYL GLYOXYLATE (12d)

1-Trimethylsilyl hex-1-yne (5d) (2.0 g, 12.98 mmol) was dissolved in methanol (50 ml) and the solution cooled to 0 °C under an argon atmosphere. A 7.5 M solution of *tert*-butyl hydroperoxide in cyclohexane (8.6 ml, 64.9 mmol) was added followed by osmium tetroxide (100 mg, 0.39 mmol). The reaction mixture was stirred at 0 °C until all the starting material was consumed (tlc analysis). Work-up as described above for (12a) and purification of the residue by flash chromatography on silica-gel gave (12d) as a colourless oil (1.01 g, 54%), bp 45-50 °C (10 mmHg); ν_{max} (film) 2920, 1735, 1460, 1440, 1270, and 1070 cm^{-1}; δ (^1H, $CDCl_3$) 3.88 (3H, s), 2.87 (2H, t, J 7 Hz), 1.68-1.30 (4H, m), and 0.91-0.87 (3H, m).

REACTION OF 2-OXO-2-PHENYL ETHANOYL TRIMETHYLSILANE WITH OSMIUM TETROXIDE

2-Oxo-2-phenyl ethanoyl trimethylsilane (3a) (1.00 g, 5.13 mmol) was dissolved in methanol (50 ml) and the solution cooled to 0 °C under an argon atmosphere. A 7.5 M solution of *tert*-butyl hydroperoxide in cyclohexane (3.42 ml, 25.65 mmol) was added followed by osmium tetroxide (100 mg, 0.39 mmol). The reaction mixture was stirred at 0 °C until all the starting material was consumed. Work-up as described above for (12a) and purification of the residue by flash chromatography on silica-gel gave (12a), (0.37 g, 45%).

2-BROMOHEPTANOYL TRIMETHYLSILANE (2a)

A 2 M solution of borane-dimethyl sulphide complex in thf (13 ml, 26 mmol) was added dropwise to 1-trimethylsilyl hept-1-yne (5c) (10 g, 60 mmol) in an inert atmosphere below 20 °C. The mixture was stirred for two hours at 0-5 °C, diluted with thf (100 ml), and anhydrous trimethylamine-*N*-oxide (9.33 g, 84 mmol) added. The mixture was stirred at room temperature for five minutes and the resulting slurry boiled under reflux for four hours. The reaction mixture, containing enol borinate, was cooled to 0 °C and *N*-bromosuccinimide (14.95 g, 84 mmol) added. The resulting slurry was stirred for three hours at 0 °C. The solvent was removed under reduced pressure, and saturated aqueous ammonium chloride (100 ml) added. The mixture was extracted with hexane (3 x 100 ml) and the combined organic layers were washed with water (2 x 30 ml), brine (2 x 20 ml), and dried over magnesium sulphate. Evaporation of the solvent followed by column chromatography on silica-gel gave (2a) (9.66 g, 61%); ν_{max} (film) 2900, 1650, 1250, and 850 cm^{-1}; δ (^1H, $CDCl_3$) 4.37 (1H, dd, J 6 and 2 Hz), 1.80-1.10 (8H, m), 0.85-0.76 (3H, m), and 0.20 (9H, s); δ (^{13}C, $CDCl_3$) 234.8, 59.9, 31.9, 27.6, 23.0, 14.6, and -1.2; m/z (CI, NH_4^+) 265 (M^++1); λ_{max} (cyclohexane) 374 (142).

2-BROMOHEXANOYL TRIMETHYLSILANE (2b)

A 2 M solution of borane-dimethyl sulphide complex in thf (3.65 ml, 7.3 mmol) was added dropwise to 1-trimethylsilyl hex-1-yne (5d) (3.08 g, 20 mmol) in an inert atmosphere below 20 °C. The mixture was stirred for two hours at 0-5 °C, diluted with thf (30 ml), and anhydrous trimethylamine-*N*-oxide (2.67 g, 24 mmol) added. The mixture was stirred at room temperature for five minutes and the resulting slurry boiled under reflux for four hours. The reaction mixture, containing enol borinate, was cooled to 0 °C and *N*-bromosuccinimide (4.27 g, 24 mmol)

added. The resulting slurry was stirred for three hours at 0 °C. Work-up as described above for (2a) followed by column chromatography on silica-gel gave (2b) (3.0 g, 60%); ν_{max} (film) 2900, 1645, 1250, and 850 cm^{-1}; δ (^1H, $CDCl_3$) 4.39 (1H, dd, J 6 and 2 Hz), 1.84-1.15 (6H, m), 0.87-0.78 (3H, m), and 0.21 (9H, s); m/z (CI, NH_4^+) 251 (M^++1).

2-BROMO-5-CHLOROPENTANOYL TRIMETHYLSILANE (2c)

A 2 M solution of borane-dimethyl sulphide complex in thf (7.1 ml, 14.2 mmol) was added dropwise to 1-trimethylsilyl 5-chloropent-1-yne (5e) (5.30 g, 30 mmol) in an inert atmosphere below 20 °C. The mixture was stirred for two hours at 0-5 °C, diluted with thf (50 ml), and anhydrous trimethylamine-*N*-oxide (4.66 g, 42 mmol) added. The mixture was stirred at room temperature for five minutes and the resulting slurry boiled under reflux for four hours. The reaction mixture, containing enol borinate, was cooled to 0 °C and *N*-bromosuccinimide (7.47 g, 42 mmol) added. The resulting slurry was stirred for three hours at 0 °C. Work-up as described above for (2a) followed by column chromatography on silica-gel gave (2c) (4.94 g, 61%); ν_{max} (film) 2900, 1645, 1250, and 850 cm^{-1}; δ (^1H, $CDCl_3$) 4.32 (1H, dd, J 6 and 2 Hz), 3.36 (2H, t, J 6 Hz), 1.98-1.61 (4H, m), and 0.10 (9H, s); δ (^{13}C, $CDCl_3$) 235.2, 57.9, 44.1, 30.1, 28.4, and -2.0; m/z (CI, NH_4^+) 271 (M^++1).

2-BROMO-5-*tert*-BUTYLDIMETHYSILYLOXY PENTANOYL TRIMETHYL SILANE (2d)

A 2 M solution of borane-dimethyl sulphide complex in thf (2.77 ml, 5.54 mmol) was added dropwise to 1-trimethylsilyl 5-*tert*-butyldimethylsilyloxy pent-1-yne (5f) (3.20 g, 11.8 mmol) in an inert atmosphere below 20 °C. The mixture was stirred for two hours at 0-5 °C, diluted with thf (15 ml), and anhydrous trimethylamine-*N*-oxide (1.84 g, 16.6 mmol) added. The mixture was stirred at room temperature for five minutes and the resulting slurry boiled under reflux for four hours. The reaction mixture, containing enol borinate, was cooled to 0 °C and *N*-bromosuccinimide (2.95 g, 16.6 mmol) added. The resulting slurry was stirred for three hours at 0 °C. Work-up as described above for (2a) followed by column chromatography on silica-gel gave (2d) (2.34 g, 54%); ν_{max} (film) 2850, 1640, 1250, 1090, and 840 cm^{-1}; δ (^1H, $CDCl_3$) 4.33 (1H, dd, J 6 and 2 Hz), 3.55-3.65 (2H, m), 2.60 (2H, t, J 6 Hz), 1.97-1.70 (2H, m), 0.85 (9H, s), 0.26 (9H, s), and 0.08 (6H, s); m/z (CI, NH_4^+) 367 (M^++1).

2-BROMO-4-*tert*-BUTYLDIMETHYSILYLOXY BUTANOYL TRIMETHYLSILANE (2e)

A 2 M solution of borane-dimethyl sulphide complex in thf (2.46 ml, 4.92 mmol) was added dropwise to 1-trimethylsilyl 4-*tert*-butyldimethylsilyloxy but-1-yne (5g) (2.70 g, 10.5 mmol) in an inert atmosphere below 20 °C. The mixture was stirred for two hours at 0-5 °C, diluted with thf (15 ml), and anhydrous trimethylamine-*N*-oxide (1.64 g, 14.65 mmol) added. The mixture was stirred at room temperature for five minutes and the resulting slurry boiled under reflux for four hours. The reaction mixture, containing enol borinate, was cooled to 0 °C and *N*-bromosuccinimide (2.63 g, 14.65 mmol) added. The resulting slurry was stirred for three hours at 0 °C. Work-up as described above for (2a) followed by column chromatography on silica-gel gave (2e) (1.93 g, 52%); ν_{max} (film) 2850, 1640, 1250, 1090, and 845 cm^{-1}; δ (^1H, $CDCl_3$) 4.35 (1H, dd, J 6 and 2 Hz), 3.70-3.63 (2H, m), 2.39 (2H, t, J 6 Hz), 0.87 (9H, s), 0.17 (9H, s), and 0.09 (6H, s); m/z (CI, NH_4^+) 353 (M^++1).

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