Stereospecific Rearrangement of 2,2-Disubstituted Vinylsilane Epoxides to the Silyl Enol Ethers of 2,2-Disubstituted Aldehydes †

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The Z- and E-2-ethyl-2-methylvinylsilane epoxides (5a) and (5b) rearrange stereospecifically in the presence of boron trifluoride–diethyl ether to the Z- and E-silyl enol ethers, (6a) and (6b), respectively, of 2-methylbutanal. These silyl enol ethers react with t-butyl chloride, with 2-phenylthioalkyl chlorides, with the dimethyl acetal of benzaldehyde, with methyl vinyl ketone, and with 2-nitropropene, each catalysed by an appropriate Lewis acid, to give alkylation products. Since the vinylsilanes were prepared by silyl-cupration of a terminal acetylene, followed by alkylation, the overall result is to convert C-2 of a terminal acetylene into the quaternary carbon of a 2,2,2-trialkylated aldehyde, in which each of the alkyl groups is different.

We reported [1] earlier that our lithium bis(phenyldimethyl-silyl)cuprate reagent (1) reacts with terminal acetylenes (2) to give, regio- and stereo-selectively, a Z-vinyl-copper species (3), which can be alkylated with a wide range of electrophiles. Using this route, we easily prepared, for the work described in this paper, the isomeric vinylsilanes (4a) and (4b) (Scheme 1).

Although vinylsilanes have many uses in synthesis,[2] we have only investigated in this work the chemistry of the corresponding vinylsilane epoxides (5a) and (5b). Vinylsilane epoxides are themselves versatile intermediates. Thus Stork and Colvin showed that they can be hydrolysed regioselectively to carbonyl compounds,[3] and Brook [4] and Hudrlik [5] and their co-workers showed that either thermal or Lewis acid-catalysed rearrangement gave a variety of products, the nature of which depended upon the conditions used and the degree of substitution in the epoxysilane. However, in most of this work, 2,2-disubstituted vinylsilane epoxides were not used, largely because they have only recently become readily available as a result of our work [1] and that of others.[6] We now report that Lewis acid-catalysed rearrangement of the 2,2-disubstituted vinylsilane epoxides (5a) and (5b) leads to the silyl enol ethers (6a) and (6b) respectively (Scheme 2). Not only is this pattern of reaction cleaner and different from that observed [4,5] with less-substituted vinylsilane epoxides, it is also stereo-specific, and leads directly to a useful enol derivative of the very aldehyde which would have been the product of the Stork-Colvin hydrolysis.[3]

In detail, the best Lewis acid was boron trifluoride–diethyl ether at −78 °C for 5 min in dichloromethane, when the epoxysilane (5a) gave the silyl enol ethers (6a) and (6b) in a ratio of *ca.* 96 : 4 and in a 68% yield of isolated products. Similarly, the E-isomer (5b) gave the silyl enol ethers (6a) and (6b) in a ratio of *ca.* 5 : 95 and in 69% yield. At higher temperatures (0 °C) the reaction was non-stereospecific, giving the silyl enol ethers in equal amounts. Dimethylaluminium chloride was nearly as good as boron trifluoride–diethyl ether, but the yields were a little lower.

We think it likely that the reaction takes place by β-opening of the Lewis acid-epoxysilane salt (7), with rotation about the C(1)–C(2) bond in that direction which brings the silyl group most rapidly into position to stabilise the cationic centre as in the drawing (8) (Scheme 3). (This is closely similar to the pathway presumed to be followed in the bromination of β-silylstyrenes.[7]) The oxygen atom then removes the silyl group, in a process which is shown as intramolecular in (8), by analogy with the Brook rearrangement.[8] The unusual
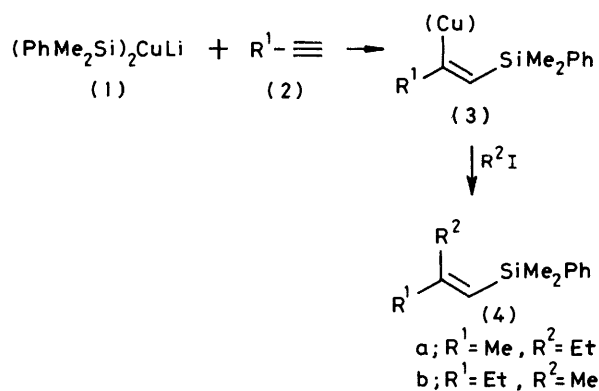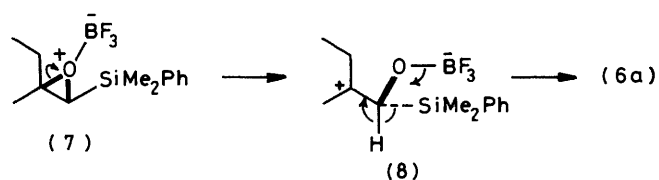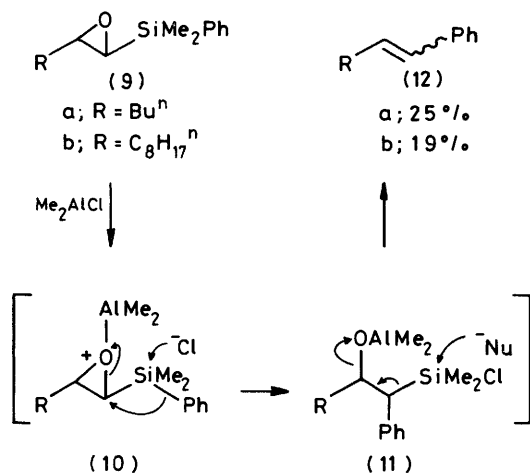

Scheme 1.
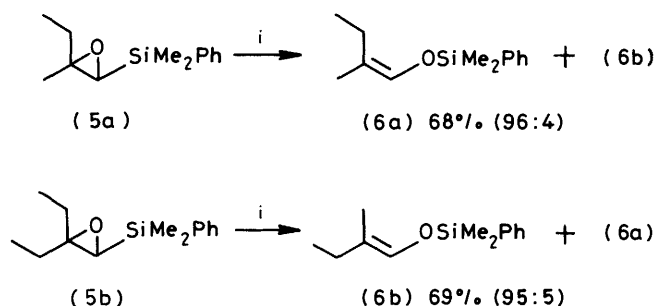
Scheme 2. *Reagent:* BF₃·OEt₂, CH₂Cl₂, −78 °C, 5 min

feature in this sequence is the β-opening, since most epoxy-silanes are known to react thermally or in the presence of acids by α-opening, often assisted by nucleophilic attack on C-1.[4,5,9] Clearly the two alkyl groups on C-2 encourage β-opening, and the absence of good nucleophiles for carbon discourages attack at C-1. Indeed, we observed α-opening when we tried the Lewis acid-catalysed reaction on the epoxysilanes (9a) or (9b), which do not have two β-substituents. As it happens, the actual reaction we observed (Scheme 4) has no parallel in the published work on epoxysilanes, since it stems from the presence of the phenyl group on the silicon atom: α-opening was evidently assisted, not by external nucleophilic attack, but by internal migration of a phenyl group from silicon to the α-carbon (10). Subsequent elimination of the silyl and oxygen groups (11) gave the styrenes (12a) or (12b) as mix-

† *No reprints available.*

Scheme 3.

Scheme 4.

Scheme 5. *Reagents:* i, Bu^{t}Cl, TiCl$_4$; ii, PhSCHMeCl, TiCl$_4$–Ti(OPr^i)$_4$; iii, PhSCHPr^{n}Cl, TiCl$_4$–Ti(OPr^i)$_4$; iv, PhCH(OMe)$_2$, TiCl$_4$; v, CH$_2$=CHCOMe, TiCl$_4$; vi, NaOH; vii, CH$_2$=CMeNO$_2$, TiCl$_4$

Scheme 6.

tures of stereoisomers. The yields in these reactions were not high enough for them to be synthetically interesting.

There is some advantage to the conversion of an epoxy-silane directly into a silyl enol ether rather than to the corresponding aldehyde, as in the Stork–Colvin reaction. Aldehydes are not always easily converted into their enolates, and the enolates are not always well behaved; in contrast, the silyl enol ethers of aldehydes are effective carbon nucleophiles, when suitably activated electrophiles are used.[10] To demonstrate this point, and to establish the usefulness of the whole sequence described above, we treated the silyl enol ethers, (5a) or (5b) (or mixtures of them both), with several standard [10] carbon electrophiles as shown in Scheme 5. Of these, only an acetal [11] and t-butyl chloride [12] have been shown before to work with the silyl enol ethers of 2,2-disubstituted aldehydes, and hence to be effective in setting up quaternary centres α to an aldehyde group. The yields in these reactions were not optimised in any way.

In summary, we note that the whole sequence allows acetylene to be used as an acetaldehyde enolate equivalent three times (Scheme 6) with the introduction of three different electrophiles.

In this work we have not used the remarkable stereospecificity of the rearrangement. We should like simply to draw attention here to the potential for forming the corresponding lithium enolates (and/or their boron equivalents), and for the use of these compounds in stereospecific aldol reactions. Hitherto, there has been no simple way in which such lithium enolates could be made stereospecifically.

Experimental

Light petroleum is the fraction of b.p. 40—60 °C. Throughout ether refers to diethyl ether. Column chromatography was carried out on Merck Kieselgel 60 (70—230 mesh).
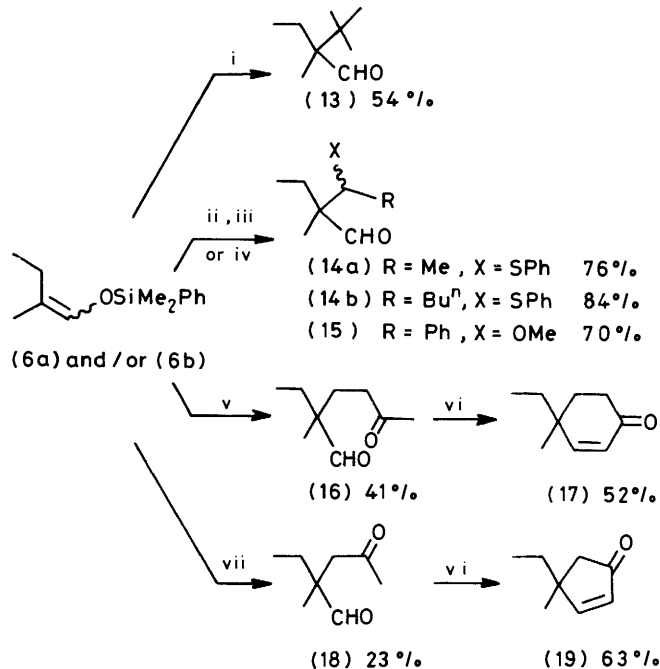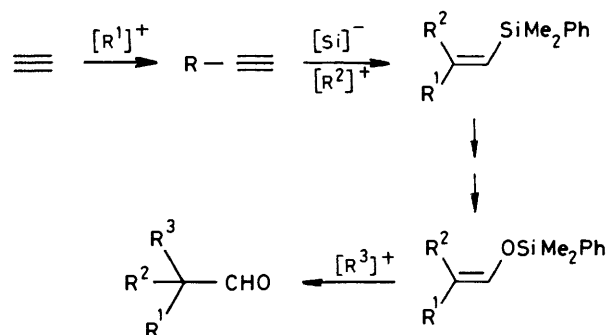
(Z)-1-*Dimethyl(phenyl)silyl*-2-*methylbut*-1-*ene* (4a).—Propyne (120 ml, 5 mmol) was injected over a stirred solution of the silyl-cuprate reagent [1] (1) (5 mmol) under argon at 0 °C and the mixture stirred for 20 min. Hexynyl-lithium, prepared from n-butyl-lithium (38.5 ml of a 1.6M solution in hexane) and hex-1-yne (5.7 ml, 50 mmol) in tetrahydrofuran (THF) (50 ml) under nitrogen at −78 °C, was added at −78 °C. After 5 min, ethyl iodide (8 ml) was added dropwise and the mixture stirred for 30 min at −78 °C and then for 40 h at 0 °C. Saturated ammonium chloride solution (1.0 ml) was added and the mixture diluted with light petroleum and filtered through glass wool. The organic phase was washed with saturated ammonium chloride (3 × 20 ml), dried (MgSO$_4$), and evaporated under reduced pressure. Column chromatography with light petroleum–ether (19 : 1 v/v) as eluant gave the *vinylsilane* (4a) (6.86 g, 67%) as an oil, $\nu_{max.}$ (CCl$_4$) (1 614 (C=C), 1 428 and 1 112 (SiPh), and 1 248 cm^{-1} (SiMe); δ (CCl$_4$) 7.7—7.1 (5 H, m, Ph), 5.40 (1 H, s br, C=CHSi), 2.06 (2 H, q, *J* 8 Hz, CH$_2$), 1.82 (3 H, s, MeC=C), 0.86 (3 H, t, *J* 8 Hz, C*H*$_3$CH$_2$), and 0.40 (6 H, s, SiMe$_2$)

(Found: M^+, 204.1341. $C_{13}H_{20}Si$ requires M, 204.1334), m/z 204 (23%, M^+), 189 (96, M − Me), and 135 (100, Me_2PhSi).

(E)-1-*Dimethyl(phenyl)silyl-2-methylbut-1-ene* (4b).—But-1-yne (0.66 ml, 7.9 mmol) was treated with the silyl-cuprate reagent, as described above, and then methyl iodide (3 ml) was added and the mixture kept at 0 °C for 30 min. Work-up as above gave the *vinylsilane* (4b) (884 mg, 55%) as an oil, $v_{max.}$ (CCl_4) 1 614, 1 428, 1 112, and 1 248 cm⁻¹; δ (CCl_4) 7.7—7.1 (5 H, m), 5.38 (1 H, s), 2.10 (2 H, q, J 7 Hz), 1.68 (3 H, s), 1.02 (3 H, t, J 7 Hz), and 0.40 (6 H, s) (Found: M^+, 204.1339), m/z 204 (9%), 189 (23), and 135 (100).

(Z)-(3-*Ethyl-3-methyloxiranyl)dimethyl(phenyl)silane* (5a).—A solution of *m*-chloroperbenzoic acid (604 mg, 3.5 mmol) in dichloromethane (10 ml) was added to a stirred solution of (Z)-1-dimethyl(phenyl)silyl-2-methylbut-1-ene (4a) (632 mg, 3.1 mmol) in dichloromethane (20 ml) under nitrogen at 0 °C. After 1 h the mixture was washed with 20% aqueous sodium hydrogensulphite (20 ml), 10% aqueous sodium hydrogen-carbonate (20 ml), and 10% aqueous sodium chloride (20 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography (light petroleum–ether, 19 : 1 v/v) gave the *epoxy-silane* (5a) (610 mg, 89%) as a liquid, R_F (light petroleum–ether, 19 : 1 v/v) 0.22, $v_{max.}$ (CCl_4) 1 431 and 1 118 (SiPh) and 1 253 cm⁻¹ (SiMe); δ$_H$ (CCl_4) 7.70—7.48 (2 H, m, Ph) and 7.38—7.20 (3 H, m, Ph), 2.20 (1 H, s, HC–O), 1.62—1.33 (2 H, m, CH_2CH_3), 1.30 (3 H, s, MeC–O), 0.90 (3 H, t, J 7 Hz, CH_3CH_2), and 0.39 (6 H, s, $SiMe_2$); δ$_C$ (CDCl₃) 150.5, 147.1, 142.6, 141.2, 74.9, 72.0, 42.3, 36.4, 23.7, 10.7, and 10.2 (Found: M^+, 220.1287. $C_{13}H_{20}OSi$ requires M, 220.1284), m/z 220 (5%, M^+), 205 (12, M − Me), and 135 (100, Me_2PhSi).

(E)-(3-*Ethyl-3-methyloxiranyl)dimethyl(phenyl)silane* (5b).—(E)-1-Dimethyl(phenyl)silyl-2-methylbut-1-ene (4b) was epoxidised, as described above, to give the *epoxysilane* (5b) (77%) as a liquid, R_F (light petroleum–ether, 19 : 1 v/v) 0.23, $v_{max.}$ (CCl_4) 1 432 and 1 116 (SiPh) and 1 251 cm⁻¹ (SiMe); δ$_H$ (CCl_4) 7.72—7.48 (2 H, m, Ph) and 7.40—7.23 (3 H, m, Ph), 2.17 (1 H, s, HC–O), 1.92—1.26 (2 H, m, CH_2CH_3), 1.18 (3 H, s, MeC–O), 0.93 (3 H, t, J 7 Hz, CH_3CH_2), and 0.39 (6 H, s, $SiMe_2$); δ$_C$ (CDCl₃) 150.5, 147.1, 142.6, 141.2, 75.5, 70.3, 46.5, 32.8, 23.2, 10.6, and 10.2 (Found: M^+, 220.1280. $C_{13}H_{20}OSi$ requires M, 220.1283), m/z 220 (5%, M^+), 205 (11, M − Me), and 135 (100, Me_2PhSi).

(Z)-(2-*Methylbut-1-enyloxy)dimethyl(phenyl)silane* (6a).—Boron trifluoride–ether (0.13 ml, 1.0 mmol) was added drop-wise to a stirred solution of the (Z)-epoxysilane (6a) (220 mg, 1.0 mmol) in dichloromethane (5 ml) under nitrogen at −78 °C and stirred for 5 min. The reaction mixture was quenched with aqueous sodium hydrogencarbonate (1 ml) and allowed to warm gradually to room temperature. The organic phase was washed with aqueous sodium chloride (3 × 5 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography (light petroleum–ether, 19 : 1 v/v) gave the *silyl enol ether* (6a) [contaminated with *ca.* 4% of the (E)-isomer as judged by the n.m.r. spectrum] (150 mg, 68%) as a liquid, R_F (light petroleum–ether, 19 : 1 v/v) 0.56, $v_{max.}$ (CCl_4) 1 680 (C=C), 1 431 and 1 121 (SiPh), and 1 259 cm⁻¹ (SiMe); δ$_H$ (CCl_4) 7.58—7.15 (5 H, m, Ph), 5.81 (1 H, s br, C=CH), 2.03 (2 H, q, J 7 Hz, CH_2), 1.40 (3 H, d, J 1 Hz, CH_3C=C), 0.87 (3 H, t, J 7 Hz, CH_3CH_2), and 0.32 (6 H, s, $SiMe_2$) (Found: M^+, 220.1284, $C_{13}H_{20}OSi$ requires M, 220.1283), m/z 220 (28%, M^+), 205 (19, M − Me), and 135 (100, Me_2PhSi).

The use of dimethylaluminium chloride in place of boron

trifluoride–ether gave a 62% yield of a *ca.* 94 : 6 ratio of (6a) and (6b).

(E)-(2-*Methylbut-1-enyloxy)dimethyl(phenyl)silane* (6b).—The boron trifluoride catalysed rearrangement of the (E)-epoxysilane (5b) was carried out using exactly the same procedure as for the preparation of (6a). Column chromatography (light petroleum–ether, 19 : 1 v/v) gave the *silyl enol ether* (6b) [contaminated with *ca.* 5% of the (Z)-isomer] (152 mg, 69%) as a liquid, R_F (light petroleum–ether, 19 : 1 v/v) 0.56, $v_{max.}$ (CCl_4) 1 680 (C=C), 1 430 and 1 121 (SiPh), and 1 258 cm⁻¹ (SiMe); δ$_H$ (CCl_4) 7.54—7.13 (5 H, m, Ph), 5.91 (1 H, s br, C=CH), 1.80 (2 H, q, J 7 Hz, CH_2CH_3), 1.51 (3 H, s br, CH_3C=C), 0.88 (3 H, t, J 7 Hz, CH_3CH_2), and 0.32 (6 H, s, $SiMe_2$) (Found: M^+, 220.1279. $C_{13}H_{20}OSi$ requires M, 220.1283), m/z 220 (29%, M^+), 205 (20, M − Me), and 135 (100, Me_2PhSi).

The use of dimethylaluminium chloride in place of boron trifluoride–ether gave a 48% yield of a *ca.* 95 : 5 ratio of (6b) and (6a) according to n.m.r.

(E)-(3-*Butyloxiranyl)dimethyl(phenyl)silane* (9a).—A solution of *m*-chloroperbenzoic acid (5.18 g, 30 mmol) in dichloromethane (50 ml) was added to a stirred solution of (E)-1-dimethyl(phenyl)silylhex-1-ene ¹ (5.10 g, 23.4 mmol) in dichloromethane (100 ml) under nitrogen at 0 °C and stirred for 5 h. Work-up as in the preparation of (5a) followed by column chromatography (light petroleum–ether, 19 : 1 v/v) gave the *epoxysilane* (9a) (5.16 g, 94%) as a liquid, R_F (light petroleum–ether, 19 : 1 v/v) 0.27, $v_{max.}$ (CCl_4) 1 428 and 1 119 (SiPh) and 1 251 (cm⁻¹) (SiMe), δ$_H$ (CCl_4) 7.76—7.36 (5 H, m, Ph), 2.78 (1 H, m, OCHCH₂), 2.12 (1 H, d, J 3 Hz, CHSi), 1.8—1.2 (6 H, m, 3 × CH_2), 1.02 (3 H, t, J 7 Hz, CH_3CH_2), and 0.43 and 0.38 (6 H, 2 s, $SiMe_2$) (Found: m/z 219.1213. $C_{13}H_{19}OSi$ requires M − Me, 219.1205), m/z 219 (5%, M − Me) and 135 (100, Me_2PhSi).

(E)-*Dimethyl(3-octyloxiranyl)(phenyl)silane* (9b)—(E)-1-Dimethyl(phenyl)silyldec-1-ene ¹ (767 mg, 2.8 mmol) was epoxidised in the same way to give the *epoxysilane* (9b) (596 mg, 74%) as a liquid, R_F (light petroleum–ether, 19 : 1 v/v) 0.30, $v_{max.}$ (CCl_4) 1 429 and 1 117 (SiPh) and 1 250 cm⁻¹ (SiMe); δ$_H$ (CCl_4) 7.71—7.17 (5 H, m, Ph), 2.74 (1 H, m, OCHCH₂), 2.09 (1 H, d, J 3 Hz, CHSi), 1.90—1.00 (14 H, m, 7 × CH_2), 1.02 (3 H, t, J 7 Hz, CH_3CH_2), and 0.43 and 0.38 (6 H, 2 s, $SiMe_2$) (Found: m/z 275.1820. $C_{17}H_{27}OSi$ requires M − Me, 275.1831), m/z 275 (5%, M − Me) and 135 (100, Me_2PhSi).

(E)- *and* (Z)-*Phenylhex-1-ene* (12a).—Dimethylaluminium chloride (0.36 ml of a 2.8M solution in hexane) was added dropwise to a stirred solution of (E)-(3-butyloxiranyl)dimethyl(phenyl)silane (9a) (234 mg, 1.0 mmol) in dichloromethane (10 ml) under nitrogen at −78 °C. The reaction mixture was allowed to warm gradually to −10 °C and then stirred for 30 min. Work-up and chromatography as in the preparation of (6a) gave the alkenes (12a) ¹³ (40 mg, 25%), as a *ca.* 5 : 1 mixture of (E)- and (Z)-isomers (n.m.r.), R_F (light petroleum–ether, 19 : 1 v/v) 0.64, $v_{max.}$ (CCl_4) 1 602 and 1 497 (Ph) and 967 cm⁻¹ (*trans* CH=CH); δ (CCl_4) (E)-isomer: 7.5—7.0 (5 H, m, Ph), 6.35 (1 H, d, J 15 Hz, PhCH= CH), 6.10 (1 H, dt, J 15 and 7 Hz, PhCH=CH), 2.4—2.0 (2 H, m, CH=CHCH₂), 1.6—1.1 (4 H, m, other CH₂'s), and 0.88 (3 H, t, J 7 Hz, CH₃); (Z)-isomer: 7.5—7.0 (5 H, m, Ph), 6.37 (1 H, d, J 12 Hz, PhCH=CH), 5.59 (1 H, dt, J 12 and 7 Hz, PhCH=CH), 2.5—2.0 (2 H, m, CH=CHCH₂), 1.7—1.1 (4 H, m, other CH₂'s), and 0.89 (3 H, t, J 7 Hz, CH₃). The reaction was also carried out using ethylaluminium dichloride, di-

ethylaluminium chloride, or trimethylaluminium as catalyst to give similar mixtures of styrenes (12a), but with no improvement in yield.

(E)- and (Z)-1-*Phenyldec*-1-*ene* (12b).—(E)-Dimethyl(3-octyloxiranyl)(phenyl)silane (9b) was treated in the same way to give the alkenes (12b) [14] (21 mg, 19%) as a *ca.* 5 : 4 mixture of (E)- and (Z)-isomers according to n.m.r. spectroscopy; R_F (light petroleum–ether, 19 : 1 v/v) 0.64, $v_{max.}$ (CCl_3) 1 600 and 1 496 (Ph), and 965 cm^{-1} (*trans* CH=CH); δ (CCl_4) (E)-isomer: 7.45—7.00 (5 H, m, Ph), 6.37 (1 H, d, *J* 15 Hz, PhC*H*=CH), 6.13 (1 H, dt, *J* 15 and 7 Hz, PhCH=C*H*), 2.5—2.0(2 H, m, CH=CHC*H₂*), 1.7—1.1 (12 H, m, other CH_2's), and 0.89 (3 H, t, *J* 7 Hz, CH_3); (Z)-isomer: 7.45—7.00 (5 H, m, Ph), 6.40 (1 H, d, *J* 12 Hz, PhC*H*=CH), 5.62 (1 H, dt, *J* 12 and 7 Hz, PhCH=C*H*), 2.5—2.0 (2 H, m, CH=CHC*H₂*), 1.7—1.1 (12 H, m, other CH_2's), and 0.89 (3 H, t, *J* 7 Hz, CH_3) (Found: M^+, 216.1875. $C_{16}H_{24}$ requires *M*, 216.1878), *m/z* 216 (13%, M^+), 117 (78, $PhCH=CHCH_2^+$), and 104 (100, $PhCH=CH_2$).

2-*Ethyl*-2,3,3-*trimethylbutanal* (13).—A solution of t-butyl chloride (0.33 ml, 3.0 mmol) in dichloromethane (5 ml) was added to a stirred solution of titanium(IV) chloride (0.33 ml, 3.0 mmol) in dichloromethane (10 ml) under nitrogen at −78 °C. After 10 min, a mixture of silyl enol ethers (6a) and (6b) (660 mg, 3.0 mmol) was added dropwise and the mixture was stirred for 3 h at −78 °C. The reaction mixture was quenched with aqueous sodium hydrogencarbonate (1 ml) and the organic phase was washed with aqueous sodium hydrogencarbonate solution (3 × 10 ml) and water (10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography (light petroleum–ether, 19 : 1 v/v), gave the *aldehyde* (13) (229 mg, 54%) as an oil, R_F (light petroleum–ether, 19 : 1 v/v) 0.80, $v_{max.}$ (CCl_4) 1 725 cm^{-1} (C=O); δ$_H$ (CCl_4) 9.63 (1 H, s, CHO), 2.1—1.2 (2 H, m, C*H₂*CH₃), 1.02 (3 H, s, OHCCC*H₃*), 0.90 (9 H, s, C*Me₃*), and 0.68 (3 H, t br, *J* 7 Hz, C*H₃*CH₂).

1-*Phenylthioethyl Chloride*.—*N*-Chlorosuccinimide (6.2 g, 50 mmol) was added to a stirred solution of 1-phenylthio-ethane (6.4 g, 50 mmol) in carbon tetrachloride (50 ml, AnalaR) under nitrogen at room temperature. After 12 h, the mixture was filtered and evaporated under reduced pressure to give the chloride [15] (7.9 g, 97%) as an oil, δ (CCl_4) 7.6—7.0 (5 H, m, Ph), 5.15 (1 H, q, *J* 6.5 Hz, PhSC*H*), and 1.70 (3 H, d, *J* 6.5 Hz, CH_3). The 1-phenylthioethyl chloride was used without further purification and could be stored at −16 °C.

1-*Phenylthiobutyl Chloride*.—1-Phenylthiobutane (1.66 g) was chlorinated in the same way to give the chloride [15] (*ca.* 100%) as an oil, δ (CCl_4) 7.8—7.3 (5 H, m, Ph), 5.25 (1 H, t, *J* 6 Hz, PhSC*H*), and 2.4—1.9 (7 H, m, $CH_3CH_2CH_2$).

2-*Ethyl*-2-*methyl*-3-*phenylthiobutanal* (14a).—Titanium(IV) isopropoxide (0.06 ml, 0.5 mmol) was added to a stirred solution of titanium(IV) nitrogen at room temperature. This mixture was added to a stirred solution of (Z)-(2-methylbut-1-enyloxydimethyl)(phenyl)silane (6a) (110 mg, 0.5 mmol) and 1-phenylthioethyl chloride (100 mg, 0.65 mmol) in dichloromethane under nitrogen at −78 °C. After the reaction mixture had been stirred for 40 min it was quenched with saturated aqueous sodium hydrogen-carbonate (10 ml) and the crude products were extracted into ether (3 × 10 ml). The organic phase was washed with saturated aqueous sodium chloride (2 × 10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography (light petroleum–ether, 19 : 1 v/v)

gave the *aldehyde* (14a) (161 mg, 76%) as a *ca.* 1 : 1 mixture of diastereoisomers, R_F (light petroleum–ether, 19 : 1 v/v) 0.19, $v_{max.}$ (CCl_4) 1 731 cm^{-1} (C=O); δ$_H$ (CCl_4) 9.45 and 9.39 (1 H, 2s, diastereoisomeric CHO's), 7.5—7.0 (5 H, m, Ph), 3.6—3.1 (1 H, m, C*H*SPh), 1.82 (2 H, q br, *J* 7 Hz, C*H₂*CH₃), 1.32 and 1.25 (3 H, 2 d, *J* 7 Hz, C*H₃*CHSPh), 1.14 (3 H, s, OHCCC*H₃*), and 0.87 (3 H, t br, *J* 7 Hz, C*H₃*CH₂) (Found: M^+, 222.1083. $C_{13}H_{18}OSi$ requires *M*, 222.1078), *m/z* 222 (14%, M^+), 137 (76, $PhS(CH_3)CH^+$), and 110 (100, PhSH)

2-*Ethyl*-2-*methyl*-3-*phenylthiohexanal* (14b).—This compound was prepared by the same procedure that was used for (14a), but with 1-phenylthiobutyl chloride, to give the *aldehyde* (14b) (84%) as a mixture of diastereoisomers, R_F (light petroleum–ether, 19 : 1 v/v) 0.20, $v_{max.}$ (CCl_4) 1 730 cm^{-1} (C=O); δ$_H$ (CCl_4) 9.40 (1 H, s, CHO), 7.5—7.0 (5 H, m, Ph), 3.36—3.03 (1 H, m, C*H*SPh), 1.17 (3 H, s, OHCCC*H₃*), and 2.0—0.6 (12 H, m, other H's) (Found: M^+, 250.1399. $C_{15}H_{22}OSi$ requires *M*, 250.1391), *m/z* 250 (52%, M^+), 165 [91, $C_3H_7(PhS)CH^+$], 123 (95, $PhSCH_2$), and 110 (100, PhSH). The reaction was repeated using the (E)-isomer of the silyl enol ether (6b) to give a similar mixture of isomers (n.m.r.).

2-*Ethyl*-3-*methoxy*-2-*methyl*-3-*phenylpropanal* (15).—A solution of benzaldehyde dimethyl acetal (408 mg, 3.0 mmol) in dichloromethane (3 ml) was added to a stirred solution of titanium(IV) chloride (0.33 ml, 3.0 mmol) in dichloromethane (10 ml) under nitrogen at −78 °C. After 10 min, a mixture of silyl enol ethers (6a) and (6b) (660 mg, 3.0 mmol) was added dropwise and the mixture was stirred for 40 min at −78 °C. Work-up as in the preparation of (13) followed by column chromatography (light petroleum–ether, 9 : 1 v/v) gave the *aldehyde* (15) (435 mg, 70%) as a *ca.* 1 : 1 mixture of diastereoisomers, R_F (light petroleum–ether, 9 : 1 v/v) 0.26 and 0.32, $v_{max.}$ (CCl_4) 1 727 (C=O) and 1 100 cm^{-1} (C–O); δ$_H$ (CCl_4) 9.55 (1 H, s, CHO), 7.4—6.9 (5 H, m, Ph), 4.23 and 4.15 (1 H, 2s, C*H*OMe), 3.14 (3 H, s, OMe), 2.2—1.2 (2 H, m, C*H₂*CH₃), 1.00 (3 H, s, OHCCC*H₃*), and 0.82 (3 H, t, *J* 7 Hz, C*H₃*CH₂) (Found: *m/z* 205.1215. $C_{13}H_{17}O_2$ requires *M* − H, 205.1228), *m/z* 205 (4%, *M* − H) and 121 [100, Ph(MeO)CH].

2-*Ethyl*-2-*methyl*-5-*oxohexanal* (16).—A solution of but-3-en-2-one (0.24 ml, 3.0 mmol) in dichloromethane (5 ml) was added to a stirred solution of titanium(IV) chloride (0.33 ml, 3.0 mmol) in dichloromethane (10 ml) under nitrogen at −78 °C. After 10 min, a mixture of silyl enol ethers (6a) and (6b) (660 mg, 3.0 mmol) was added dropwise and the mixture was stirred for 5 min at −78 °C. Work-up as in the preparation of (13) followed by column chromatography (light petroleum–ether, 7 : 3 v/v) gave the *keto-aldehyde* (16) (191 mg, 41%) as an oil, R_F (light petroleum–ether, 7 : 3 v/v) 0.38, $v_{max.}$ (CCl_4) 1 730 and 1 715 cm^{-1} (C=O); δ (CCl_4) 9.10 (1 H, s, CHO), 2.4—1.8 (2 H, m, C*H₂*CO), 1.97 (3 H, s, CH_3CO), 1.7—1.1 (4 H, m, other CH_2's), 0.90 (3 H, s, OHCCC*H₃*), and 0.74 (3 H, t, *J* 7 Hz, C*H₃*CH₂) (Found: M^+, 156.1160. $C_9H_{16}O_2$ requires *M*, 156.1150), *m/z* 156 (12%, M^+) and 137 (100, *M* − H_2O − H).

4-*Ethyl*-4-*methylcyclohex*-2-*enone* (17).—The cyclisation was carried out by analogy with a literature procedure.[16] 2-Ethyl-2-methyl-5-oxohexanal (16) (135 mg, 0.85 mmol) was stirred vigorously with 10% sodium hydroxide solution (10 ml) at room temperature for 3 h. The products were extracted into ether (3 × 10 ml) and the organic phase was washed with aqueous sodium chloride (2 × 10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography (light petroleum–ether, 7 : 3 v/v) gave the *enone* (17) (80 mg, 52%) as an oil, R_F (light petroleum–ether, 7 : 3 v/v)

0.61, $v_{max.}$ (CCl$_4$) 1 682 (C=O) and 1 620 cm^{-1} (C=C); δ (CCl$_4$) 6.48 (1 H, d, J 10 Hz, CH=CHCO), 5.65 (1 H, d, J 10 Hz, CH=CHCO), 2.5—1.3 (6 H, m, CH$_2$'s), 1.12 (3 H, s, C=CCCH$_3$), and 0.95 (3 H, t, J 7 Hz, CH$_3$CH$_2$) (Found: M^+, 138.1049. C$_9$H$_{14}$O requires M, 138.1045), m/z 138 (13%, M^+), 137 (42, M − H), 110 (30, M − C$_2$H$_4$), and 55 (100, C$_4$H$_7$).

2-*Ethyl*-2-*methyl*-4-*oxopentanal* (18).—This compound was prepared by the general method of Miyashita.[17] The silyl enol ethers (6a) and (6b) (660 mg, 3.0 mmol) in dichloromethane (3 ml) were added dropwise to a stirred solution of titanium-(IV) chloride (0.35 ml, 3.0 mmol) and 2-nitropropene [18] (0.31 ml, 3.6 mmol) in dichloromethane (10 ml) under nitrogen at −78 °C. The mixture was stirred for 1 h at −78 °C and then allowed to warm to 0 °C during 2 h. Water (5 ml) was added and the mixture was refluxed for 2 h. The products, were extracted into ether (3 × 20 ml) and the organic phase was washed with water (2 × 20 ml) and saturated aqueous sodium chloride (20 ml), dried (MgSO$_4$), and evaporated under reduced pressure. Column chromatography (light petroleum–ether, 7 : 3 v/v) gave the *keto-aldehyde* (18) (100 mg, 23%) as an oil, R_F (light petroleum–ether, 7 : 3 v/v) 0.14, $v_{max.}$ (CCl$_4$) 1 730 and 1 715 cm^{-1} (C=O); δ_H (CCl$_4$) 9.34 (1 H, s, CHO), 2.66—2.62 (2 H, s br, CH$_2$CO), 2.10 (3 H, s, CH$_3$CO), 1.51 (2 H, m, CH$_2$CH$_3$), 1.15 (3 H, s, OHCCCH$_3$), and 0.85 (3 H, t br, J 7 Hz, CH$_3$CH$_2$).

4-*Ethyl*-4-*methylcyclopent*-2-*enone*   (19).—2-Ethyl-2-methyl-4-oxopentanal (18) (100 mg, 0.70 mmol) was stirred vigorously with 10% aqueous sodium hydroxide (10 ml) at room temperature for 12 h. Work-up as in the preparation of (17) followed by column chromatography (light petroleum–ether, 7 : 3 v/v) gave the *enone* (19) (55 mg, 63%) as an oil, R_F (light petroleum–ether, 7 : 3 v/v) 0.44, $v_{max.}$ (CCl$_4$) 1 721 (C=O) and 1 596 cm^{-1} (C=C); δ (CCl$_4$) 7.09 (1 H, d, J 6 Hz, CH= CHCO), 5.74 (1 H, d, J 6 Hz, CH=CHCO), 1.98 and 1.94 (2 H, 2 s br, CH$_2$CO), 1.7—1.2 (2 H, m, CH$_2$CH$_3$), 1.12 (3H, s, Me) and 0.80 (3 H, t br, J 7 Hz, CH$_3$CH$_2$) (Found: M^+, 124.0880. C$_8$H$_{12}$O requires M, 124.0888), m/z 124 (66%, M^+) and 95 (100, M − Et).

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