*Tetrahedron* Vol. 37, No. 23, pp. 4027 to 4034, 1981
Printed in Great Britain.

0040-4020/81/234027-08$02.00/0


# THE SYNTHESIS OF αβ-UNSATURATED KETONES FROM β-SILYLENONES AND β-SILYLYNONES

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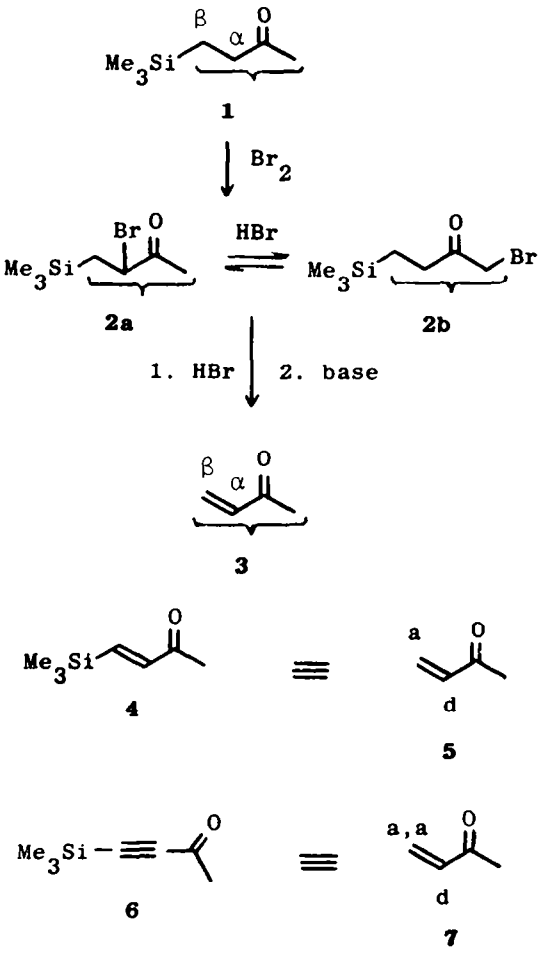
(*Received in USA 23 April 1981*)

**Abstract**—Conjugate addition, followed by alkylation, bromination and desilyl-bromination make the β-silylketone (**4**) an $a^3d^2$-synthon (**5**) and the β-silylynone (**6**) a $2a^3d^2$-synthon (**7**).

We established earlier[1] that a β-silylketone (**1**) is a masked αβ-unsaturated ketone (**3**); bromination (**1**→**2**) and desilylbromination (**2**→**3**) place a double bond specifically between the β-C carrying the silyl group and the α-C, but the β-silylketone group is stable to many synthetic operations before the bromination step. In this paper, we show how this capability makes it possible to use a β-silylenone such as **4** as an $a^3d^2$-synthon[2] (**5**), and a β-silylnone (**6**) as a $2a^3d^2$-synthon (**7**).

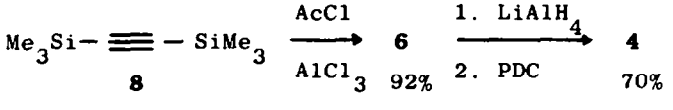


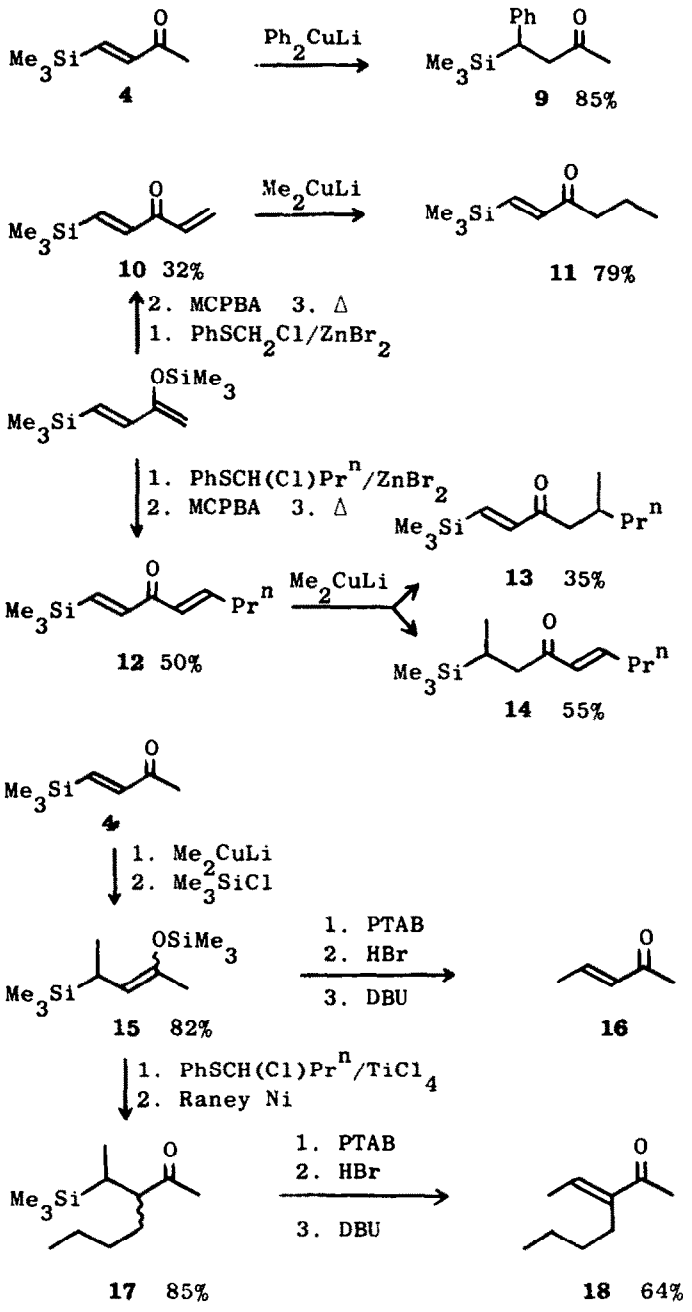

The β-silylynone (**6**) was made by the method of Birkofer *et al.*[3] (**8**→**6**), and reduction and oxidation (**6**→**4**) gave us the β-silylenone (**4**). We find this route more convenient than any of the earlier routes to this compound.[4-7]

We first investigated the conjugate addition of cuprates to the enone (**4**). The silyl group did not seriously interfere with this well-established type of reaction, as shown by the formation of the ketone (**9**). The effect of the silyl group on the conjugate addition appears to be about the same as that of a simple alkyl group, as we were able to show using the dienones (**10** and **12**). The former underwent conjugate addition exclusively on the unsubstituted double bond, and the latter underwent conjugate addition more or less equally on both sides. The dienones (**10** and **12**) were prepared by phenylthioalkylidenation[8] of the silyl enol ether of **4**.

The conjugate addition to **4** gave an enolate as an intermediate. In principal, this has the necessary $d^2$-reactivity, but enolates are fairly restricted in the range of electrophiles which will react cleanly with them.[9] We therefore isolated the silyl enol ether (**15**) and alkylated it using Paterson's phenylthioalkylation-desulphurisation reaction[8] (**15**→**17**). The bromination-desilylbromination of **15** and **17** then gave the enones (**16** and **18**) uneventfully. Thus we have demonstrated that the enone (**4**) is an $a^3$- and an $a^3d^2$-synthon, the whole point being that the silyl group, unlike an electronegative heteroatom, can be relied upon to stay in the molecule during the stage when the $d^2$-reaction is being carried out.

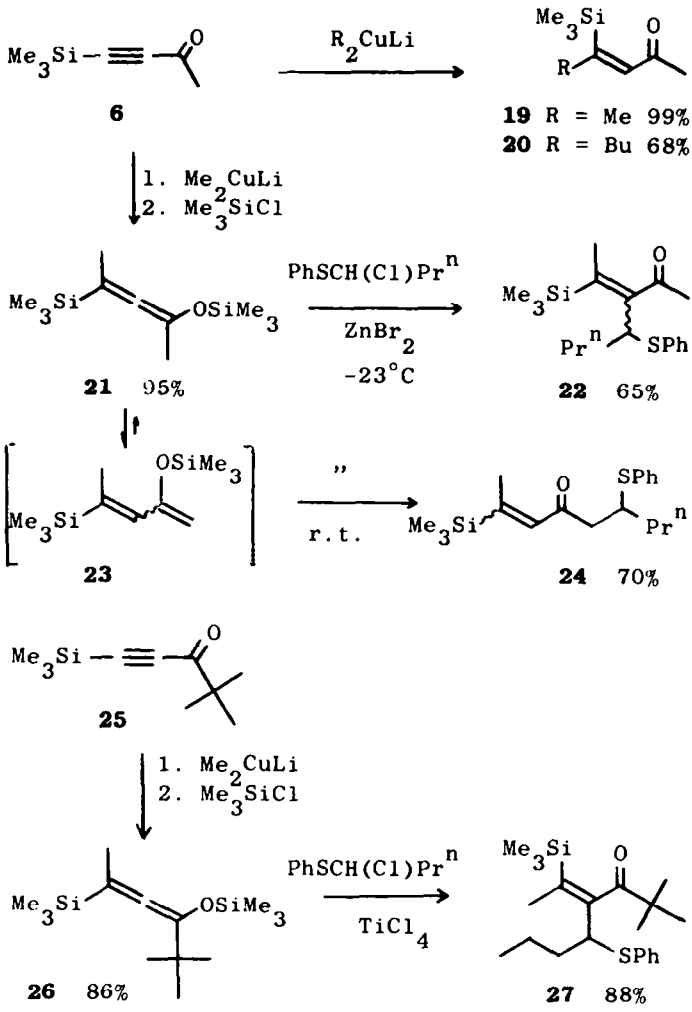
Sulphenylation of the silyl enol ether (**15**), oxidation, and pyrolysis gave the β-silylenone (**19**) in a reaction we discuss elsewhere.[10] However, a better method of making this compound was by conjugate addition to the ynone (**6**). The intermediate in this reaction could be trapped as a silyl enol ether (**21**), and we briefly investigated this unusual, but not unknown,[11,12] kind of silyl enol ether. It could be phenylthioalkylated (**21**)→**22**) in tolerable yield using zinc bromide as the catalyst at −23°, but the product was accompanied by that of hydrolysis (**19**), the amount of which was not reduced by careful exclusion of water. Negligible "hydrolysis" occurred when titanium tetrachloride was used as catalyst, but, as with zinc bromide at room temperature, unusually easy equilibration (**21**⇌**23**) led to the formation






of the regioisomer (**24**) of the desired alkylation product (**22**). Certainly when this equilibration was impossible, we got clean phenylthioalkylation (**25**→**26**→**27**).

Having prepared the β-silylenone (**19**), we found that it reacted with lithium dimethylcuprate in the usual way, and the silyl enol ether (**28**) could be phenylthioalkylated to give **30**. Similarly, we made the β-phenylthioketone (**31**) by successive conjugate addition of dibutylcuprate and dimethylcuprate, followed by phenylthioethylation (**29**→**31**). We got better yields using this order, since the less-stable dibutylcuprate added to the enone (**19**) in only 57% yield. However, we met here our first set-back: desulphurisation of **31** gave the β-silylketone (**32**), but we were quite unable to carry out the bromination–desilylbromination reaction on this compound. Presumably the bromine was very reluctant to attach itself to the now highly hindered side of the ketone. We got round this difficulty by using oxidative desulphurisation to give the enones (**33** from **30** and **34** from **31**). Protodesilylation of these compounds, which are allylsilanes,[13] then gave the enones (**37** and **38**, respectively). The only problem with this route was that the sulphoxide-eliminations gave some of the unconjugated ketones (**35** and **36**), and these survived our attempts to convert them in acid or base into the conjugated enones (**33** and **34**). If the phenylthioalkylation step was omitted, the double conjugate addition gave the ketone (**39**). This presented no problems in the bromination–desilylbromination reaction, which gave the enone (**42**). However this sequence gave us a rare opportunity to use the sulphoxide group to remove the silicon. Conjugate addition to **20** and sulphenylation of the derived silyl enol ether (**29**) gave the

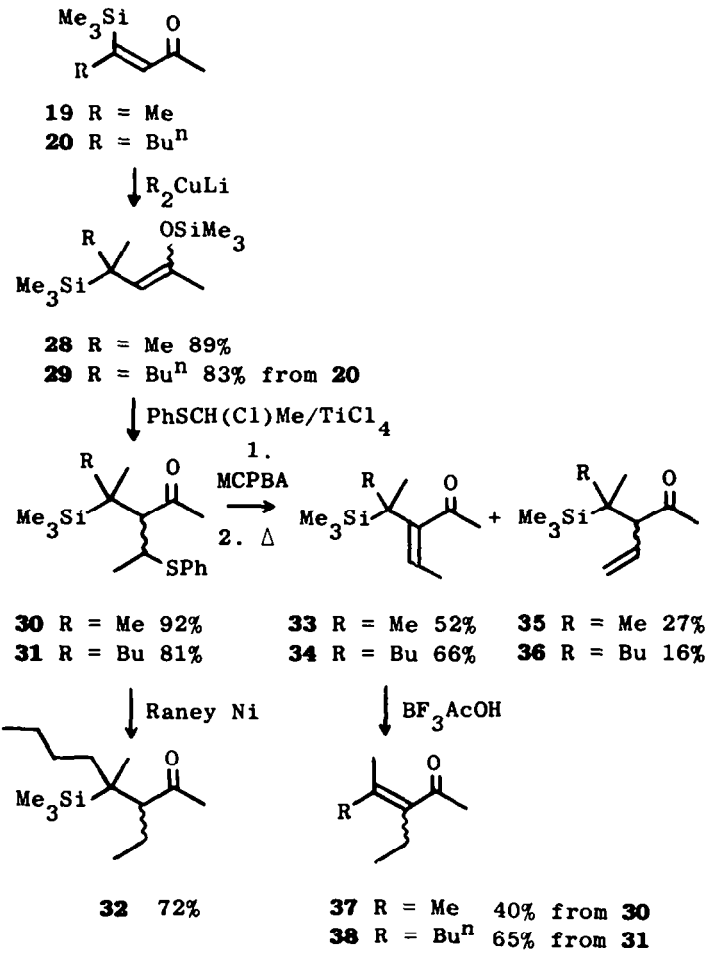


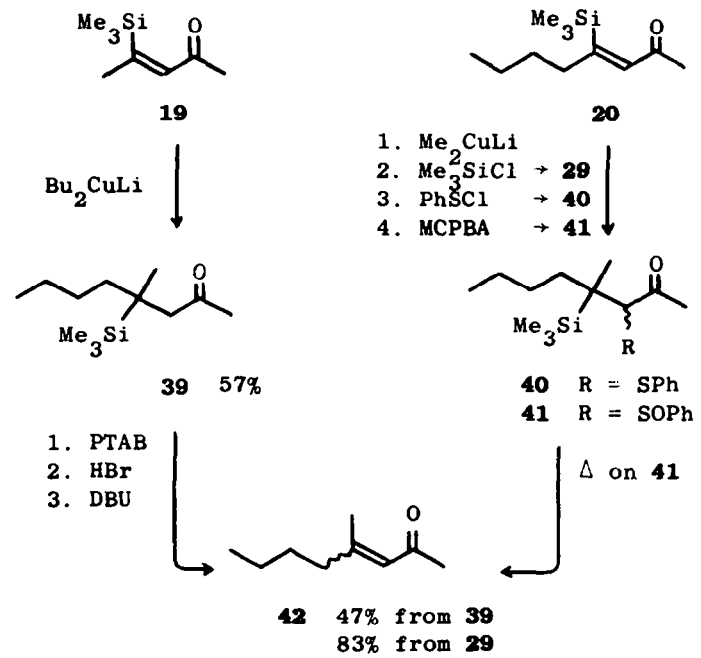

α-thioketone (**40**); oxidation and heating then gave the enone (**42**) in better yield than by bromination-desilybromination. This method for removing the silyl group is only feasible, as we discuss elsewhere,[10] when there is no hydrogen available for the sulphoxide to abstract.

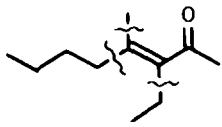
These reactions demonstrate the $2a^3d^2$- and $2a^3$-reactivity of the ynone (**6**), and the final products (**16**, **18**, **37**, **38** and **42**) are all mixed-aldol products, which can be assembled (**43**) from an ynone framework and the corresponding alkyl halides. It is unlikely that anyone would choose to synthesise these particular mixed-aldol products using the reactions described in this paper; however, as model reactions, they do have some virtue in demonstrating one aspect of the synthetic potential of β-silylenones. For this reason, we should like to draw attention to some of the other methods by which β-silylenones have been, and can be synthesised, in addition to those already mentioned above. They have been made by acylation of β-silylvinyl-metal reagents,[4] by the electrolytic reduction of β-silylnones,[6] by the reductive silylation of ynones,[11] by the reaction of oxygen on cyclic allylsilanes,[14] by the dehydrogenation of β-silylketones,[5,15] by the hydrosilation of ynones,[16] by the base-catalysed isomerisation of 3-silylpropargyl ethers,[17] and by silocupration and acylation of acetylenes.[18] To these methods we now add two others: first, our phenyldimethylsilyl-cuprate[18] reacts with β-chloroenones (**44** and **45**) to give β-silylenones (**46** and **47**), and second, phenylthiotrimethylsilylmethylation (**48**→**49**) followed by oxidation and base-catalysed elimination (**49**→**51**→**52**) gave the product (**52**) of trimethylsilylmethylenation. In this last method, the oxidation must be taken to the sulphone stage, since the corresponding sulphoxide (**50**) largely underwent a sila-Pummerer reaction[19] on heating, and elimination was only a minor pathway.

Although we have only used the β-silyl ketones produced in this work to make αβ-unsaturated ketones, we should like to draw attention to their potential as alkene precursors: Baeyer–Villiger oxidation and treatment with fluoride ion should give di- or tri-substituted alkenes.[20]

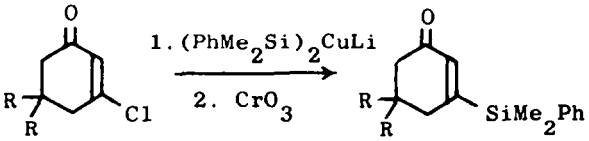
Finally, we should comment on some reactions which failed. In particular, we were much less successful in extending the idea to carbon nucleophiles other than cuprates. The lithium enolate of cyclohexanone gave some conjugate addition to the enone (**4**). The silyl enol ether of cyclohexanone reacted with **4** and **6** in the presence of Lewis acids, but the yield of conjugate addition to **4** was low, and the ynone reacted directly at the CO group. The enamine of cyclohexanone appeared not to react at all, and the dimethylhydrazone-cuprate


Me3Si
O
R
19 R = Me
20 R = Bu^n
R2CuLi
R
OSiMe3
Me3Si
28 R = Me 89%
29 R = Bu^n 83% from 20
PhSCH(Cl)Me/TiCl4
1.
MCPBA
2. Δ
SPh
30 R = Me 92%
31 R = Bu 81%
33 R = Me 52%
34 R = Bu 66%
35 R = Me 27%
36 R = Bu 16%
Raney Ni
BF3AcOH
32 72%
37 R = Me 40% from 30
38 R = Bu^n 65% from 31


Me3Si
O
19
20
Bu2CuLi
1. Me2CuLi
2. Me3SiCl → 29
3. PhSCl → 40
4. MCPBA → 41
39 57%
40 R = SPh
41 R = SOPh
1. PTAB
2. HBr
3. DBU
Δ on 41
42 47% from 39
83% from 29

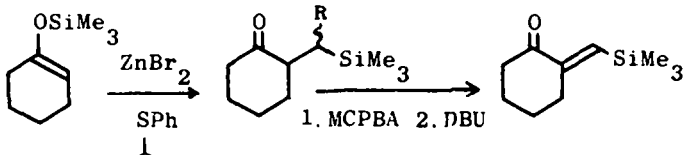


43

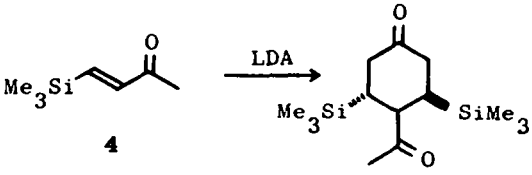



**44** R = H
**45** R = Me

**46** R = H 70%
**47** R = Me 99%




**48** **49** R = SPh 84% **52** 67%
**50** R = SOPh
**51** R = $SO_2Ph$ 67%




4

**53** 74%

did not add, but catalysed instead the dimerisation of **4** to give **53**. The dimer (**53**) could more easily be made by treating **4** with lithium diisopropylamide.

## EXPERIMENTAL

Light petroleum is the fraction of b.p. 30–40°.

(*E*)-4-*Trimethylsilylbut*-3-*ene*-2-*one* (**4**). The ynone **6**[3] (14 g) in dry THF was added dropwise to a stirred suspension of $LiAlH_4$ (3.05 g) in THF (250 ml) under $N_2$ at 0°; after 30 min the mixture was refluxed for 3 hr. The crude (*E*)-4-silylbutenol was dissolved in dry $CH_2Cl_2$ (150 ml), pyridinium dichromate[21] (56.5 g) was added and the suspension stirred for 24 hr. Pentane (100 ml) was added, the mixture filtered through celite, evaporated and chromatographed on silica to give the enone (**4**)[4–7] (10 g, 70%), b.p. 56–60°/13 mmHg.

*Conjugate addition of cuprates.* The enone or ynone (typically 5 mmol) in dry ether (5 ml) was added dropwise to the cuprate[22] (6 mmol) in ether (15 ml) at −78°. The reaction was followed by tlc and the mixture allowed to warm slowly to 0° when necessary.

*Work-up procedure A.* The enolate soln was poured into sat $NH_4Cl$ aq, filtered through celite and extracted with ether. Drying ($MgSO_4$), evaporation *in vacuo*, and chromatography on silica, eluting with light petroleum–ether (9:1) gave the following ketones (**9**,[23] **11**, **13** and **14**, **19**, **20** and **39**).

*Work-up procedure B.*[24] The enolate soln was recooled to −78° and $Me_3SiCl$ (typically 15 mmol) followed by $Et_3N$ (15 mmol) were added. The mixture was warmed to room temp, stirred for 1 hr, poured onto ice and light petroleum, and filtered through celite. Extraction with light petroleum, drying ($Na_2SO_4$), evaporation *in vacuo*, and rapid chromatography on silica, eluting with light petroleum-ether (19:1) gave **15**, **21**, **26**, **28** and **29**.

*Preparation of other silyl enol ethers.* The silyl enol ether of **4** was known[7] and the silyl enol ether (**23**) was made by keeping the silyl enol ether (**21**) at room temp in $CCl_4$ in the light for 24 hr. It was a mixture of (*E*)- and (*Z*)-isomers (*ca.* 1:1) IR (film) 1605 and 1568 $cm^{-1}$, NMR ($CCl_4$) δ 6.38 and 5.97 (1 H, q, $J$ = 2 Hz), 4.34 and 4.24 (2 H, s), 2.01 and 1.90 (3 H, d, $J$ = 2 Hz), 0.34 and 0.30 (9 H, s), and 0.20 and 0.17 (9 H, s).

*Phenylthioalkylation of silyl enol ethers*

*Method A.* Anhyd $ZnBr_2$ (*ca.* 25 mg) was added to a stirred soln of the silyl enol ether (typically 10 mmol) and 1-phenylthioalkyl chloride[8] (10 mmol) in dry $CH_2Cl_2$ (80 ml) under $N_2$ at room temp. After 0.5 hr, an aqueous work-up and chromatography on silica, eluting with light petroleum-ether (9:1) gave **22**, **24**, and **49** and the phenylthioketones which were the precursors of **10** and **12**.

*MethodB.* The silyl ether (typically 15 mmol) and the phenylthioalkyl chloride[8] (15 mmol) in dry $CH_2Cl_2$ (20 ml) were added dropwise to a stirred soln of $TiCl_4$ (1.71 ml, 15 mmol) in dry $CH_2Cl_2$ (100 ml) at −78° under Ar, and kept for 2 hr. Aqueous work-up and chromatography on silica, eluting with light petroleum-ether (9:1) gave **22** and **24**, **27**, **30**, and **31** and the phenylthioketone which was the precursor of **17**.

*Reductive desulphurisations.* The ketones (**17** and **32**) were prepared by the method of Ireland and Marshall.[25]

*Oxidative desulphurisations.* *m*-Chloroperbenzoic acid (MCPBA) (typically 11 mmol) in dry $CH_2Cl_2$ was added dropwise to a stirred soln of the β-phenylthioketone (10 mmol) in $CH_2Cl_2$ (50 ml) at −78° under $N_2$. After 10 min, a basic aqueous work-up gave the sulphoxide, which was dissolved in $CCl_4$ (AR, 30 ml) and refluxed until no further sulphoxide remained (tlc or NMR). Distillation (bulb-to-bulb) gave **10**, **12**, **33** and **35**, and **34** and **36**.

*Bromination-desilylbromination.* Phenyltrimethylammonium tribromide (PTAB) (typically 2.5 mmol) in dry THF (5 ml) was added dropwise to a stirred soln of either the silyl enol ether or the saturated ketone (2.5 mmol) in dry THF (5 ml) at room temp. The soln was filtered, evaporated, and the residue dissolved in $CCl_4$ (AR, 10 ml). A slow stream of dry HBr was passed through at reflux for 1 hr (following by NMR, using the $SiMe_3$ signal), and then $N_2$ was passed through to flush out the excess HBr. Careful evaporation of the solvent gave the β-bromo ketone, which was dissolved in $CCl_4$ (1 ml) and then 1,5-diazabicyclo-[5,4,0]undec-5-ene (DBU) (2.5 mmol) in $CCl_4$ was added. There was an immediate precipitation of ammonium salt. Distillation gave **16**,[26] **18**, and **42**.[27]

*Protodesilylation of the allylsilanes.* The mixture **33** + **35** or **34** + **36** (2 mmol) and $BF_3AcOH$ (380 mg) was kept in dry EtOH-free $CDCl_3$ (1.5 ml) in an NMR tube for 15 min at 70°. Basic aqueous work-up and chromatography on silica eluting with light petroleum-ether (9:1) gave the recovered **35** or **36** (32% and 20%, respectively) and **37**[28] or **38** (50% and 79%, respectively).

4-*Methyloct*-3-*en*-2-*one* (**42**). PhSCl (0.7 M in $CH_2Cl_2$) was added dropwise to **29** (575 mg) in dry $CH_2Cl_2$ (10 ml) under $N_2$ at −78° until a yellow colour persisted. MCPBA (400 mg) in dry $CH_2Cl_2$ (5 ml) was then added dropwise at −78° and after 5 min the mixture poured into 10% $Na_2CO_3$ aq and extracted with $CH_2Cl_2$. The solvent was evaporated and the residue distilled (bulb-to-bulb) at 0.1 mmHg with the oven temp rising to 130°. Redistillation to remove S-containing by-products gave **42** (231 mg, 83%) identical to the sample prepared earlier.

*The β-silylenones* (**46** *and* **47**). Phenyldimethylsilyl-lithium[29] (10 mmol) in THF (10 ml) was added slowly to a stirred suspension of CuCN (450 mg) in dry THF (10 ml) at 0° under Ar. After 20 min, the soln was cooled to −78° and **44** or **45** (5 mmol) in dry THF (5 ml) was added dropwise. Aqueous work-up gave crude product which showed evidence of additional attack at the CO group (NMR). Jones oxidation of the crude product in acetone removed this product of over-reaction and gave, after chromatography on silica eluting with light petroleum-ether (7:3), the pure **46** or **47**).

2-*Trimethylsilylmethylenecyclohexanone* (**52**). MCPBA (545 mg) in dry $CH_2Cl_2$ (7 ml) was added to a stirred soln of **49** (440 mg) in dry $CH_2Cl_2$ (5 ml) at −78° under Ar. The mixture was allowed to warm to room temp and after 0.5 hr a basic aqueous work-up gave **51**, which was dissolved in $CCl_4$ (7 ml) and DBU (260 mg) added. Evaporation of the solvent and chromatography on silica eluting with light petroleum-ether (7:3) gave the *enone* **52** (163 mg, 67%).

trans - 4 - *Acetyl* - 3,5 - *bis*(*trimethylsilyl*)*cyclohexanone* (**53**). The enone **4** (712 mg) in dry THF (2 ml) was added dropwise to a stirred soln of LDA (2.5 mmol) in THF (10 ml) at −78°. After 1.75 hr, the soln was allowed to come to 0° over 2 hr, and then poured into $NH_4Cl$ aq. Work-up and chromatography on silica eluting with light petroleum-ether (7:3) gave the *diketone* **53** (526 mg, 74%), m.p. 77–77.5° (from light petroleum).

*Spectroscopic data on new compounds*

(E)-1-*Trimethylsilyl*-5-*phenylthiopent*-1-*en*-3-*one* (69% from the silyl enol ether of **4**), IR (film) 1678 and 1587 $cm^{-1}$; NMR ($CCl_4$) δ 7.55–7.15 (5 H, m), 7.02 (1 H, d, *J* = 20 Hz), 6.48 (1 H, d, *J* = 20 Hz), 3.07 (4 H, m), and 0.25 (9 H, s); MS (Found $M^+$, 264.1003. $C_{14}H_{20}OSSi$ requires *M*, 264.1003) *m*/*z* 264 (60%), 231 (12) and 123 (100). (E)-*Trimethylsilylpenta*-1,4-*diene*-3-*one* (**10**) (47%), IR (film) 1682 sh, 1669, 1618, and 1590 $cm^{-1}$; NMR ($CCl_4$) δ 7.12 (1 H, d, *J* = 19 Hz), 6.72 (1 H, d, *J* = 19 Hz), 6.72 (1 H, dd, *J* = 17 and 10 Hz), 6.30 (1 H, dd, *J* = 17 and 2 Hz), 5.84 (1 H, dd, *J* = 10 and 2 Hz), and 0.26 (9 H, s); MS (Found $M^+$ − Me, 139.0584. $C_7H_{11}OSi$ requires *M* − Me, 139.0579) *m*/*z* 139 (27%), 119 (100), and 117 (100). (E)-1-*Trimethylsilyl*-5-*phenylthiooct*-1-*en*-3-*one* (83% from the silyl enol ether of **4**), IR (film) 1674 and 1583 $cm^{-1}$; NMR ($CCl_4$) δ 7.55–7.15 (5 H, m), 6.98 (1 H, d, *J* = 19 Hz), 6.44 (1 H, d, *J* = 19 Hz), 3.70 (1 H, m), 2.94 (1 H, dd, *J* = 17.5 and 5.5 Hz), 2.78 (1 H, dd, *J* = 17.5 and 7 Hz), 1.75–1.40 (4 H, m), 1.00 (3 H, m), and 0.23 (9 H, s); MS (Found: $M^+$, 306.1473. $C_{17}H_{26}OSSi$ requires *M*, 306.1473) *m*/*z* 306 (15%), 221 (5), 127 (95), and 110 (100). (E,E)-1-*Trimethylsilylocta*-1,4-*dien*-3-*one* (**12**) (59%), IR (film) 1679 sh, 1665, 1623, and 1587 $cm^{-1}$; NMR ($CCl_4$) δ 7.08 (1 H, d, *J* = 19 Hz), 6.68 (1 H, d, *J* = 19 Hz), 6.91 (1 H, dt, *J* = 15.5 and 6.5 Hz), 6.39 (1 H, dt, *J* = 15.5 and 1 Hz), 2.29 (2 H, m), 1.80–1.40 (2 H, m), 1.02 (3 H, t, *J* = 7 Hz), and 0.23 (9 H, s); MS (Found: $M^+$, 196.1294. $C_{11}H_{20}OSi$ requires 196.1283) *m*/*z* 196 (1.4%), 181 (35), 153 (60), and 73 (100). (E)-1-*Trimethylsilylhex*-1-*en*-3-*one* (**11**) (79% and no other Michael addition production was present), IR (film) 1682 and 1594 $cm^{-1}$; NMR ($CCl_4$) δ 6.99 (1 H, d, *J* = 19 Hz), 6.44 (1 H, d, *J* = 19 Hz), 2.58 (2 H, t, *J* = 7 Hz), 1.70 (2 H, sextet, *J* = 7 Hz), 1.01 (3 H, t, *J* = 7 Hz), and 0.24 (9 H, s); MS (Found: $M^+$ − Me, 155.0883. $C_8H_{15}OSi$ requires 155.0892) *m*/*z* 155 (2%) and 69 (100). (E)-2-*Trimethylsilylnon*-5-*en*-4-*one* (**13**) (55%), IR (film) 1697, 1679, and 1634 $cm^{-1}$; NMR ($CCl_4$) δ 6.77 (1 H, dt, *J* = 16 and 6.5 Hz), 6.03 (1 H, dt, *J* = 16 and 1 Hz), 2.55–1.95 (4 H, m), 1.85–0.70 (9 H, m), and 0.03 (9 H, s); MS (Found: $M^+$, 212.1590. $C_{12}H_{24}OSi$ requires *M*, 212.1596) *m*/*z* 212 (0.35%), 197 (10), 169 (30), and 73 (100). (E)-1-*Trimethylsilyl*-5-*methyloct*-1-*en*-3-*one* (**14**) (35%), IR (film) 1680 and 1595 $cm^{-1}$; NMR ($CCl_4$) δ 7.00 (1 H, d, *J* = 19.5 Hz), 6.42 (1 H, d, *J* = 19.5 Hz), 2.40 (2 H, m), 2.3–0.7 (11 H, m), 0.22 (9 H, s); MS (Found: $M^+$, 212.1586. $C_{12}H_{24}OSi$ requires 212.1596) *m*/*z* 212 (1.7%) 197 (10), 169 (20), and 73 (100). 2-*Trimethylsiyloxy*-4-*trimethylsilylpent*-2-*ene* (**15**) (82%) (a mixture of *E*- and *Z*-stereoisomers in the ratio 2:1), IR (film) 1660 $cm^{-1}$; NMR ($CCl_4$) δ 4.40 and 4.22 (1 H, dq, *J* = 11 and 1 Hz), 1.77 and 1.65 (3 H, d, *J* = 1 Hz), 1.1–1.6 (1 H, dq, *J* = 11 and 7.5 Hz), 0.95 and 0.90 (3 H, d, *J* = 7.5 Hz), 0.14 (9 H, s), and −0.05 (9 H, s); MS (Found: $M^+$, 230.1523. $C_{11}H_{26}OSi_2$ requires *M*, 230.1522) *m*/*z* 230 (37%), 215 (26), and 157 (100). 3-(1-*Trimethylsilylethyl*)-4-*phenylthioheptan*-2-*one* (the precursor of **17**) (97%), as a mixture of diastereoisomers; IR (film) 1710 and 1585 $cm^{-1}$; NMR ($CCL_4$) δ 7.45–7.10 (5 H, m), 3.35 (1 H, m), 2.80 (1 H, m), 2.22 (3 H, s), 1.8–0.7 (11 H, m), 0.01 and −0.10 (9 H, s); MS (Found: $M^+$, 322.1777. $C_{18}H_{30}OSSi$ requires *M*, 322.1786) *m*/*z* 322 (1.4%), 307 (1), and 213 (100). 3-(1-*Trimethylsilylethyl*)*heptan*-2-*one* (**17**) (88%), as a mixture of diastereoisomers; IR (film) 1710 $cm^{-1}$; NMR ($CCl_4$) δ 2.51 (1 H, m), 2.06 (3 H, s), 1.4–0.7 (13 H, m), 0.02 and −0.04 (9 H, s); MS (Found: $M^+$, 214.1760. $C_{12}H_{26}OSi$ requires *M*, 214.1753) *m*/*z* 214 (1.2%), 199 (30), and 157 (100). (E)-3-*Butylpent*-3-*en*-2-*one* (**18**) (64%), IR (film) 1671 and 1643 $cm^{-1}$; NMR ($CCl_4$) δ 6.65 (1 H, q, *J* = 7 Hz), 2.23 (3 H, s), 2.45–2.05 (2 H, m), 1.89 (3 H, d, *J* = 7 Hz), and 1.55–0.70 (7 H, m); MS (Found: $M^+$, 140.1201. $C_9H_{16}O$ requires 140.1201) *m*/*z* 140 (11%). 4-*Trimethylsilylpent*-3-*en*-2-*one* (**19**) (99%), as a mixture of *Z*- and *E*-isomers, initially *ca.* 11:1, respectively, but equilibrating at room temp in $CCl_4$ to *ca.* 1:1; IR (film) 1690 and 1580 $cm^{-1}$; NMR ($CCl_4$) δ 6.73 and 6.43 (1 H, q, *J* = 2 Hz), 2.21 (3 H, s), 2.2–2.05 (3 H, d, *J* = 2 Hz), and 0.19 (9 H, s); MS (Found: $M^+$, 156.0963. $C_8H_{16}OSi$ requires *M*, 156.0971) *m*/*z* 156 (4%), 141 (100), and 83 (13). 4-*Trimethylsilyloct*-3-*en*-2-*one* (**20**) (68%), initially as almost pure *Z*-isomer but rapidly equilibrating in $CCl_4$ at room temp to *ca.* 1:1 *E*:*Z*; IR (film) 1693 and 1588 $cm^{-1}$; NMR ($CCl_4$) δ 6.53 and 6.25 (1 H, t, *J* = 1.5 Hz), 2.45 (2 H, m), 2.08 (3 H, s), 1.5–0.6 (7 H, m), and 0.03 (9 H, s); MS (Found: $M^+$, 198.1447. $C_{11}H_{22}OSi$ requires *M*, 198.1440) *m*/*z* 198 (0.75%), 183 (3), and 125 (0.5%). 4-*Trimethylsilyl*-2-*trimethylsiloxypenta*-2,3-*diene* (**21**) (95%); IR (film) 1945 $cm^{-1}$; NMR ($CCl_4$) δ 1.85 (3 H, s), 1.80 (3 H, s), 0.20 (9 H, s), and 0.15 (9 H, s); MS (Found: $M^+$, 228.1344. $C_{11}H_{24}OSi_2$ requires 228.1322) *m*/*z* 228 (3%), 213 (90), and 147 (100). 4-*Trimethylsilyl*-3-(1-*phenylthiobutyl*)*pent*-3-*en*-2-*one* (**22**) (65%), as a mixture of *E*- and *Z*-isomers *ca.* 4:1; IR (film) 1696 and 1586 $cm^{-1}$; NMR ($CCl_4$) δ 7.6–7.2 (5 H, m), 4.29 (1 H, m), 2.47 (3 H, s), 1.9–0.8 (7 H, m), 1.55 (3 H, s), and 0.14 (9 H, s); MS (Found: $M^+$, 320.1614. $C_{18}H_{28}OSSi$ requires 320.1630) *m*/*z* 320 (1%), 305 (10), and 195 (100). 2-*Trimethylsilyl*-

6-*phenylthionon*-2-*en*-4-*one* (**24**) (70% from 23), as a mixture of *E*- and *Z*-isomers *ca.* 4:1; IR (film) 1686 and 1586 $cm^{-1}$; NMR ($CCl_4$) δ 7.7–7.2 (5 H, m), 6.68 and 6.35 (1 H, q, $J$ = 2 Hz), 3.70 (1 H, m), 2.85–2.65 (2 H, m), 2.25 and 2.07 (3 H, d, $J$ = 2 Hz), 1.8–0.8 (7 H, M), and 0.23 (9 H, s); MS (Found: $M^+$, 320.1609. $C_{18}H_{28}OSSi$ requires $M$, 320.1630) $m/z$ 320 (12%). 5 - *Trimethylsilyl* - 3 - *trimethylsilyloxy* - 2,2 - *dimethylhexa* - 3,4 - *diene* (**26**) (86% from the known[11] **25**); IR (film) 1939 $cm^{-1}$; NMR ($CCl_4$) δ 1.85 (3 H, s), 1.08 (9 H, s), 0.21 (9 H, s), and 0.19 (9 H, s); MS (Found: $M^+$, 270.1819. $C_{14}H_{30}OSi_2$ requires $M$, 270.1803) $m/z$ 270 (9%), 187 (55), and 73 (100). 5 - *Trimethylsilyl* - 2,2 - *dimethyl* - 4 - (1 - *phenylthiobutyl*)*hex* - 4 - *en* - 3 - *one* (**27**) (88%), apparently one stereoisomer, presumably (*E*)-; IR (film) 1683 and 1588 $cm^{-1}$; NMR ($CCl_4$) δ 7.7–7.2 (5 H, m), 3.97 (1 H, dd, $J$ = 6.5 and 6 Hz), 2.10 (3 H, s), 2.05–0.8 (7 H, m), 1.42 (9 H, s), and 0.23 (9 H, s); MS (Found: $M^+$, 362.2109. $C_{21}H_{34}OSSi$ requires M, 362.2100) $m/z$ 362 (8%), 305 (45), and 253 (100). 4 - *Trimethylsilyl* - 2 - *trimethylsilyloxy* - 4 - *methylpent* - 2 - *ene* (**28**) (89%), as a mixture of *E*- and *Z*-isomer *ca.* 6:1: IR (film) 1655 $cm^{-1}$; NMR ($CCl_4$) δ 4.63 and 4.10 (1 H, s), 1.85 (3 H, s), 1.17 (6 H, s), 0.24 (9 H, s), and 0.08 (9 H, s); MS (Found: $M^+$, 244.1666. $C_{12}H_{28}OSi_2$ requires $M$, 244.1653) $m/z$ 244 (5%), 171 (100), and 147 (43). 4 - *Trimethylsilyl* - 2 - *trimethylsilyloxy* - 4 - *methyloct* - 2 - *ene* (**29**) (83% from **20**, 53% from **19**), largely one stereoisomer; IR (film) 1655 $cm^{-1}$; NMR ($CCl_4$) δ 4.53 (1 H, s), 1.75 (3 H, s), 1.4–0.7 (9 H, m), 1.10 (3 H, s), 0.15 (9 H, s), and −0.05 (9 H, s); MS (Found: $M^+$, 286.2137. $C_{15}H_{34}OSi_2$ requires $M$, 286.2148) $m/z$ 286 (2%) and 213 (100). 4 - *Methyl* - 3 - (1 - *phenylthioethyl*) - 4 - *trimethylsilylpentan* - 2 - *one* (**30**) (92%) as a mixture of diastereoisomers *ca.* 2:1; IR (film) 1710 $cm^{-1}$; NMR ($CCl_4$) δ (major, less polar diastereoisomer) 7.7–7.2 (5 H, m), 3.65 (1 H, dq, $J$ = 2 and 7 Hz), 3.00 (1 H, d, $J$ = 2 Hz), 2.37 (3 H, s), 1.34 (3 H, d, $J$ = 7 Hz), 1.10 (3 H, s), 1.00 (3 H, s), and 0.08 (9 H, s), and (minor, more polar diastereoisomer) 7.6–7.15 (5 H, m), 3.48 (1 H, dq, $J$ = 5.5 and 7 Hz), 2.80 (1 H, d, $J$ = 5.5 Hz), 2.35 (3 H, s), 1.50 (3 H, d, $J$ = 7 Hz), 1.22 (3 H, s), 1.18 (3 H, s), and 0.15 (9 H, s); MS (Found: $M^+$, 308.1633. $C_{17}H_{28}OSSi$ requires 308.1630) $m/z$ 308 (0.2%), 198 (100), and 172 (75). 4-Methyl-3-(1-phenylthioethyl)-4-trimethylsilyloctan-2-one (**31**) (81%) as a mixture of diastereoisomers; IR (film) 1713 $cm^{-1}$; NMR ($CCl_4$) δ 7.6–7.26 (5 H, m), 3.60 (1 H, m), 3.19 (1 H, m), 2.37 and 2.35 (3 H, s), 1.7–0.8 (9 H, m), 1.29 (3 H, d, $J$ = 7 Hz), 1.08 and 1.00 (3 H, s), and 0.08 and 0.06 (9 H, s); MS (Found: $M^+$ − Me, 335.1871. $C_{19}H_{31}OSSi$ requires $M$ − Me, 335.1865) $m/z$ 335 (0.25%) and 241 (100). 3-*Ethyl*-4-*methyl*-4-*trimethylsilyloctan*-2-*one* (**32**) (72%), as a mixture of diastereoisomers *ca.* 3:2; IR (film) 1715 $cm^{-1}$; NMR ($CCl_4$) δ 2.42 (1 H, m), 2.18 and 2.08 (3 H, s), 1.8–1.0 (14 H, m), 0.85 (3 H, t, $J$ = 7 Hz), and 0.09 (9 H, s); MS (Found: $M^+$ − Me, 227.1821. $C_{13}H_{27}OSi$ requires$M$ − Me, 227.1831) $m/z$ 227 (1%) and 185 (100). (E)-3-(2-*Trimethylsilyl*-2-*propyl*)*pent*-3-*en*-2-*one* (**33**) (52%) contaminated with the ketone (**35**) (27%); IR (film) 1700 and 1632 $cm^{-1}$; NMR ($CCl_4$) δ 5.18 (1 H, q, $J$ = 7 Hz), 2.23 (3 H, s), 1.68 (3 H, d, $J$ = 7 Hz), 1.10 (6 H, s), and 0.04 (9 H, s); MS (Found: $M^+$, 198.1437. $C_{11}H_{22}OSi$ requires 198.1434) $m/z$ 198 (5%), 183 (25), and 73 (100). (E)-3-(2-*Trimethylsilylhex*-2-*yl*)*pent*-3-*en*-2-*one* (**34**) (66%) contaminated with the ketone (**36**) (16%); IR (film) 1700 and 1632 $cm^{-1}$; NMR ($CCl_4$) δ 5.12 (1 H, q, $J$ = 7 Hz), 2.15 (3 H, s), 1.63 (3 H, d, $J$ = 7 Hz), 1.4–0.7 (9 H, m), 0.95 (3 H, s), and −0.03 (9 H, s); MS (Found: $M^+$, 240.1924. $C_{14}H_{28}OSi$ requires 240.1909) $m/z$ 240 (2%), 225 (32), and 73 (100). 3-(2-*Trimethylsilyl*-2-*propyl*)*pent*-4-*en*-2-*one* (**35**), isolated after protodesilylation; IR (film) 1717 and 1633 $cm^{-1}$; NMR ($CCl_4$) δ 6.25–5.6 (1 H, m), 5.3–4.9 (2 H, m), 2.10 (3 H, s), 1.03 (6 H, s), and 0.04 (9 H, s). 3-(2-*Trimethylsilyl*-2-*hexyl*)*pent*-4-*en*-2-*one* (**36**), isolated after protodesilylation as a mixture of diastereoisomers; IR (film) 1718 and 1633 $cm^{-1}$; NMR ($CCl_4$) δ 6.2–5.6 (1 H, m), 5.25–4.95 (2 H, m), 3.33 and 3.24 (1 H, d, $J$ = 9.5 Hz), 2.03 and 2.05 (3 H, s), 1.4–0.7 (9 H, m), 0.98 and 0.93 (3 H, s), and −0.06 (9 H, s). 3-*Ethyl*-4-*methyl*-*oct*-3-*en*-2-*one* (**38**) (79%) probably as a mixture of stereoisomers; IR (film) 1693 and 1620 $cm^{-1}$; NMR ($CCl_4$) δ 2.5–1.9 (4 H, m), 2.32 (3 H, s), 1.78 (3 H, br, s), and 1.65–0.7 (8 H, m); MS (Found: $M^+$, 168.1511. $C_{11}H_{20}O$ requires 168.1514) $m/z$ 168 (3%) and 151 (100). 4-*Methyl*-4-*trimethylsilyloctan*-2-*one* (**39**) (57%); IR (film) 1718 $cm^{-1}$; NMR ($CCl_4$) δ 2.39 (2 H, s), 2.11 (3 H, s), 1.55–0.84 (9 H, m), 1.00 (3 H, s), and 0.06 (9 H, s); MS (Found: $M^+$, 214.1769. $C_{12}H_{26}OSi$ requires $M$, 214.1753) $m/z$ 214 (0.2%), 199 (1), and 157 (100). 4-*Methyloct*-3-*en*-2-*one* (**42**) (59% from bromination–desilylbromination of **29**, 47% from bromination–desilylbromination of **39**, 83% by sulphenylation–oxidation), as a mixture of stereoisomers *E*:*Z* *ca.* 3:1; IR (film) 1692 and 1620 $cm^{-1}$; NMR ($CCl_4$) δ 6.24 and 6.00 (1 H, m), 2.4–2.05 (2 H, m), 2.15 and 2.10 (3 H, s), and 2.0–0.7 (10 H, m); MS (Found: $M^+$, 140.1208. $C_9H_{16}O$ requires M, 140.1201) $m/z$ 140 (2%) and 69 (100). 3-(*Phenyldimethylsilyl*)*cyclohex*-2-*enone* (**46**) (70%): IR (film) 1672 and 1591 $cm^{-1}$; NMR ($CCl_4$) δ 7.75–7.25 (5 H, m), 6.29 (1 H, t, $J$ = 1.5 Hz), 2.65–1.75 (6 H, s), and 0.56 (6 H, s); MS (Found: $M^-$, 230.1127. $C_{14}H_{18}OSi$ requires 230.1127) $m/z$ 230 (38%), 215 (30), and 135 (100). 5,5-*Dimethyl*-3-(*phenyldimethylsilyl*)-*cyclohex*-2-*enone* (**47**) (99%); IR (film) 1679 and 1589 $cm^{-1}$; NMR ($CCl_4$) δ 7.75–7.25 (5 H, m), 6.30 (1 H, t, $J$ = 2 Hz), 2.25 (4 H, s), 1.06 (6 H, s), and 0.53 (6 H, s); MS (Found: $M^+$, 258.1443. $C_{16}H_{22}OSi$ requires 258.1440) $m/z$ 258 (3%), 243 (100), and 135 (95). 2-(*Trimethylsilyl*)(*phenylthio*)*methylcyclohexanone* (**49**) (84%);[30] m.p. 75–76°, but a mixture of diastereoisomers; IR (film) 1715 and 1585 $cm^{-1}$; NMR ($CCl_4$) δ 7.4–7.10 (5 H, m), 3.40 and 3.17 (1 H, d, 1.5 and 4.5 Hz, respectively) 2.80–1.30 (9 H, m) and 0.23 (9 H, s); MS (Found: $M^+$, 292.1320. $C_{16}H_{24}OSSi$ requires $M$, 292.1323) $m/z$ 292 (3%), 277 (5), and 183 (100). (E)-2-*Trimethylsilylmethylenecyclohexanone* (**52**) (67%); IR (film) 1694 and 1590 $cm^{-1}$; NMR ($CCl_4$) δ 6.49 (1 H, t, $J$ = 2 Hz), 2.85–1.45 (8 H, m), and 0.27 (9 H, s); MS (Found: $M^+$, 182.1115. $C_{10}H_{18}OSi$ requires $M$, 182.1127) $m/z$ 182 (4%), 167 (80), and 73 (100). trans-4-*Acetyl*-3,5-*bis*(*trimethylsilyl*)*cyclohexanone* (**53**) (74%); IR ($CHCl_3$) 1703 $cm^{-1}$; NMR ($CCl_4$) 3.07–2.76 and 2.5–2.0 (5 H, m), 2.21 (3 H, s), 1.58 (1 H, ddd, $J$ = 7.5, 4, and 2 Hz), 1.23 (1 H, dt, $J$ = 14 and 4 Hz), 0.10 (9 H, s), and 0.04 (9 H, s); MS (Found: $M^+$, 284.1641. $C_{14}H_{28}O_2Si_2$ requires 284.1628) $m/z$ 284 (0.2%), 143 (40), and 73 (100); Found: C, 59.2; H, 9.8%. $C_{14}H_{28}O_2Si_2$ requires C, 59.1; H, 9.9%.

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