The Peterson Olefination Using the *tert*-Butyldiphenylsilyl Group: Stereoselective Synthesis of Di- and Trisubstituted Alkenes

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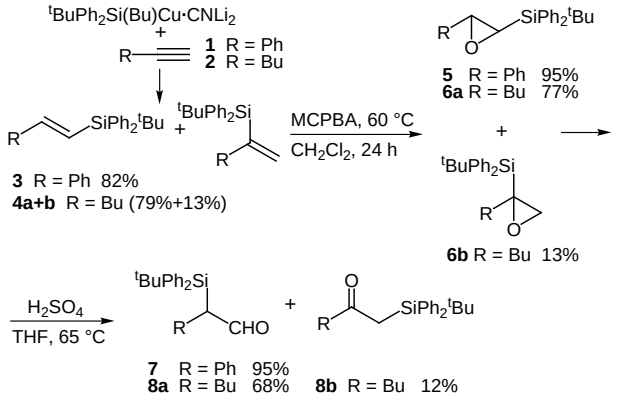
Abstract: The reaction of α-*tert*-butyldiphenylsilyl carbonyl compounds with organometallics leads with a high diastereoselectivity to *erythro*-β-hydroxysilanes, which under acidic or basic elimination conditions give *E* or *Z* di- and trisubstituted alkenes.

Key words: Peterson olefination, *tert*-butyldiphenylsilyl group, stereoselective synthesis, alkenes, silicon

α-Silyl carbonyl compounds are very important intermediates in organic synthesis as it has been well documented.[1] Several procedures have been described for their synthesis involving enolate anion displacement of chlorine from chlorosilanes,[2] reaction of Grignard or lithium reagents derived from α-halosilanes with acetic anhydrides, ethyl carboxylates or acid chlorides,[3] oxidation of vinylsilanes[4] and more recently C-silylation of hydrazones.[5] However, there are several difficulties associated with their preparation mainly due to the lability of some of these compounds.[6] One of the most interesting applications of these compounds lies in their ability to get converted into *Z*- and *E*-alkenes, through the stereospecific *syn*- and *anti*-elimination reactions of the intermediate β-hydroxysilane resulting from nucleophilic addition to the carbonyl group.[7] However, the diastereoselectivity associated to the formation of the β-hydroxysilane is not always high and strongly depends on the nature of the silyl group.[8] Apart from a brief example[9a] that we have reported some time ago, the *tert*-butyldiphenylsilyl group has not been tested before in the Peterson reaction. Obviously, its steric hindrance could promote highly Cram-selective reactions. The *tert*-butyldiphenylsilyl group has been widely used in our group for the preparation of vinylsilanes.[9b]

We report here on the synthesis of α-silyl aldehydes and ketones carrying the bulky *tert*-butyldiphenylsilyl group, and their reaction with organolithium and Grignard reagents as an efficient and easy route to stereodefined β-hydroxysilanes, which can be used in the stereoselective synthesis of di- and trisubstituted olefins via Peterson olefination. Preparation of the starting α-silyl carbonyl compounds has been achieved using our silylcuprate chemistry.[9c] We have recently described[9a] that silylcupration of acetylenes is an excellent method for the stereoselective synthesis of vinylsilanes with a wide substitution pattern. As we have shown,[9a] monosubstituted acetylenes react with bis(*tert*-butyldiphenylsilyl)cuprate to give vinylsilanes in which the silyl group is placed at the terminus. The mixed *tert*-butyldiphenylsilyl(butyl)cuprate reacts in the same way with acetylenes **1** and **2** to give vinylsilanes **3** and **4** in high yield. The reaction with hex-1-yne **(2)** was only moderately regioselective leading to both isomers **4a** and **4b** in a ratio of 6:1 which could not be well separated (Scheme 1).

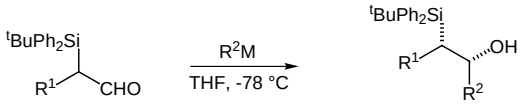


Scheme 1

Reaction of vinylsilanes **3** and **4** with MCPBA gave epoxysilanes **5** and **6** in good yield (Scheme 1). Epoxysilanes **6a** and **6b** were difficult to separate by chromatography and the mixture was carried forward in the next step. The acid-catalyzed rearrangement of **5** and **6** with protic acid provided cleanly α-silyl aldehydes **7** and **8a** and α-silyl ketone **8b** (Scheme 1). Contrarily to other reported examples where the Stork−Colvin reaction occurs predominantly,[10] it should be noted that in our reaction the α-silyl group is retained, as it has been observed with other epoxides having bulky silyl groups.[11] On the other hand, the use of *tert*-butyldiphenylsilyl group is very advantageous because it is known that only α-silyl aldehydes bearing crowded silyl groups are stable enough to be isolated.[12]

The silyl aldehydes thus obtained arise from mechanisms involving cleavage of either the α or β C−O bond of the epoxide. Previous studies have shown that the cleavage α to silicon is more probable,[13] however, the formation of ketone **8b** by the acid-catalyzed rearrangement of epoxysilane **6b**, can be explained only if cleavage of the C−O bond β to silicon takes place with migration of the silyl group.[14]

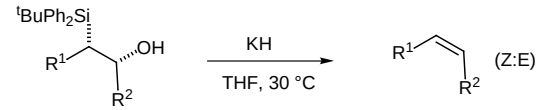
The lack of methods for the synthesis and isolation of α-trimethylsilyl aldehydes has lowered the potential of these compounds in the stereospecific synthesis of olefins, although in some cases they have been generated and trapped in situ with Grignard reagents.[13,15] However, the bulky *tert*-butyldiphenylsilyl group allows the corresponding aldehydes to be stable, opening a potential general method for the stereospecific synthesis of alkenes. Thus, reaction of aldehydes **7** and **8a** with organolithium and Grignard reagents provides stereoselectively β-hydroxysilanes **9a–g** in an addition reaction according to the Felkin–Anh model[16] (Scheme 2). The addition takes place with a high degree of diastereoselectivity to form almost exclusively *erythro*-β-hydroxysilanes (after chromatographic purification no *threo*-isomer could be detected).



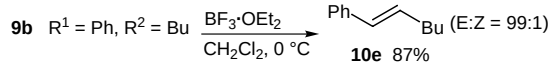
7	R^1 = Ph	R^2 = Me, M = Li	**9a**	(87%)
7	R^1 = Ph	R^2 = Bu, M = Li	**9b**	(85%)
7	R^1 = Ph	R^2 = Ph, M = Li	**9c**	(90%)
7	R^1 = Ph	R^2 = vinyl, M = MgBr	**9d**	(83%)
8a	R^1 = Bu	R^2 = Me, M = Li	**9e**	(72%)
8a	R^1 = Bu	R^2 = i-Pr, M = MgBr	**9f**	(60%)
8a	R^1 = Bu	R^2 = Ph, M = Li	**9g**	(70%)

Scheme 2

Fortunately the bulky *tert*-butyldiphenylsilyl group is still capable of taking part in a β-elimination step, under mild conditions, using the standard acidic (BF_3) or basic conditions (KH).[17] The so-called Peterson olefination can be used in the stereoselective preparation of *Z*- or *E*-disubstituted alkenes by *syn*- or *anti*-elimination as shown in Scheme 3. The *Z* to *E* ratio was determined by GC and/or NMR (Scheme 3).

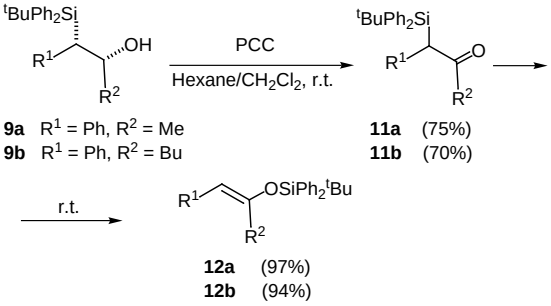


9a	R^1 = Ph, R^2 = Me	**10a**	(92:8) 86%
9b	R^1 = Ph, R^2 = Bu	**10b**	(97:3) 90%
9c	R^1 = Ph, R^2 = Ph	**10c**	(85:15) 91%
9d	R^1 = Ph, R^2 = vinyl	**10d**	(95:5) 93%
9g	R^1 = Bu, R^2 = Ph	**10b**	(96:4) 80%



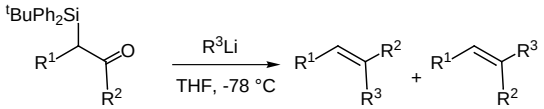
Scheme 3

We have also explored the possibility of obtaining trisubstituted alkenes via reaction of β-*tert*-butyldiphenylsilyl ketones with lithium reagents. Silyl ketones **11a,b** were prepared by oxidation of β-hydroxysilanes **9a** and **9b** with pyridinium chlorochromate (PCC). These ketones showed to be very unstable, isomerizing to *tert*-butyldiphenlsilyl enol ethers **12a,b** after standing at room temperature for several hours. It is noteworthy that, the rearrangement ocurred with high stereocontrol leading exclusively to the *E*-isomers (Scheme 4). The high *E*-selectivity observed should be the result of the concerted intramolecular migration of the silyl group via a four-membered transition state similar to the one proposed in the thermal isomerization of silylmethyl ketones.[18]



Scheme 4

Nevertheless ketones **11a,b** could be prepared, purified and used within a short time. Thus, treatment of these silyl ketones with organolithium reagents led to the corresponding trisubstituted alkenes, without isolation of the β-hydroxysilane intermediates, in a process where the β-alkoxysilane seems to be sufficiently reactive to undergo "in situ" a *syn* β-elimination giving **13** and **14** (Scheme 5). The reaction of alkyllithium reagents with ketones **11a,b** is acceptably stereoselective following the Felkin–Anh model. However, reaction with PhLi is not very selective, as it was reported for similar ketones by Utimoto.[19]



11a	R^1 = Ph, R^2 = Me	R^3 = Bu	**13a =14c**	(85:15)	**14a = 13c**	(70%)
11a	R^1 = Ph, R^2 = Me	R^3 = Ph	**13b**	(55:45)	**14b**	(75%)
11b	R^1 = Ph, R^2 = Bu	R^3 = Me	**13c =14a**	(80:20)	**14c = 13a**	(71%)
11b	R^1 = Ph, R^2 = Bu	R^3 = Ph	**13d**	(60:40)	**14d**	(90%)

Scheme 5

In summary, the *tert*-butyldiphenylsilyl group is a novel and useful silyl goup to be utilized in Peterson reactions. The corresponding α-silyl aldehydes undergo highly diastereoselective organometallic addition leading to *erythro*-β-hydroxysilanes which under typical Peterson elimination conditions give *E* or *Z* disubstituted alkenes with a high stereocontrol. The behaviour of the analogous α-silyl ketones is less stereroselective but still favouring

the trisubstituted alkenes expected according to the Felkin−Anh model.

Melting points are uncorrected. All reagents were of commercial quality from freshly opened containers or were purified before use. THF was distilled under N_2 from purple solutions of sodium benzophenone ketyl. IR spectra were recorded on a PU97400 or Mattson Cygnus-100 spectrophotometer. NMR spectra were obtained with a Bruker AM-300 spectrometer. GC/MS were recorded on a Hewlett-Packard 5988. Purification of products was performed by flash chromatography on silica gel 60 (Merck, 230−400 mesh).

Silylcupration of Acetylenes; General Procedure

tert-Butyldiphenylsilyl choride (0.80 mL, 3 mmol) was stirred with lithium shots (0.126 g, 18 mmol) under N_2 in THF (10 mL) for 4 h at 0 °C. The solution of *tert*-butyldiphenylsilyllithium[9a] thus formed was added by a syringe to a suspension of CuCN (0.269 g, 3 mmol) in THF (15 mL) at 0 °C, and then BuLi (1.9 mL, 3 mmol) was added to the mixture which was stirred at this temperature for 45 min and then cooled to −78 °C. A solution of the acetylene **1** or **2** (3 mmol) in THF (1 mL) was added at −78 °C and the mixture stirred for 1 h. The mixture was quenched with aq sat. basic NH_4Cl solution (20 mL) and allowed to warm to r.t. The residue was extracted with Et_2O (3 × 15 mL), the combined organic fractions washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure to give after chromatography the following vinylsilanes: for the silylcupration of phenylacetylene (*E*)-1-*tert*-butyl(diphenyl)silyl-2-phenylethene[9a] (**3**) (82%), and for the silylcupration of hex-1-yne 92% of a 6:1 mixture of (*E*)-1-*tert*-butyl(diphenyl)silylhex-1-ene[9a] (**4a**) and 2-*tert*-butyl(diphenyl)silylhex-1-ene (**4b**). Componds **3** and **4a** have been previously described.[9a] NMR data of **4b** were obtained from a mixture of **4a** and **4b**.

2-*tert*-Butyl(diphenyl)silylhex-1-ene (4b)

Colorless oil (13%); R_f (hexane) 0.54.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70−7.54 (m, 4 H, C_6H_5), 7.30-7.20 (m, 6 H, C_6H_5), 6.04 (s with fine couplings, 1 H, H_2C=), 5.67 (s with fine couplings, 1 H, H_2C=), 2.2 (t with fine couplings, *J* = 7 Hz, 2 H, CH_2C=), 1.45−1.21 (m, 4 H, CH_2CH_2) 1.20 [s, 9 H, $SiC(CH_3)_3$], 0.85 (t, *J* = 7 Hz, 3 H, CH_2CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.8 (SiC=), 136.3, 135.0 (C_6H_5), 129.3 (=CH_2), 128.9, 127.5 (C_6H_5), 36.5 (CH_2C=), 30.7 (CH_2), 28.7 [C(CH_3)$_3$], 22.5 (CH_2), 18.5 [C(CH_3)$_3$], 13.9 (CH_3).

Epoxidation of Vinylsilanes; General Procedure

A solution of *m*-chloroperoxybenzoic acid (0.27 g, 1.31 mmol) in anhyd CH_2Cl_2 (10 mL) was added to a stirred solution of the vinylsilane **3** or **4** (0.88 mmol) in anhyd CH_2Cl_2 (15 mL) containing solid $NaHCO_3$ (0.14 g, 1.75 mmol). The mixture was refluxed for 24 h, until completion of the reaction and then allowed to cool down. The solution was washed with aq $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed (hexane/Et_2O) to give the epoxysilanes **5** and a mixture of **6a** and **6b**. Compound **6a** had been previously described.[9a]

***(E)*-1-*tert*-Butyldiphenylsilyl-2-phenyl-1,2-epoxyethane (5)**

Colorless oil (95%); R_f (hexane/Et_2O, 35:1) 0.3.

IR (neat): ν = 1110 cm^{-1} (Si−Ph).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72−7.31 (m, 15 H, 3 × C_6H_5), 3.61 (d, *J* = 3.3 Hz, 1 H, C*H*Ph), 2.9 (d, *J* = 3.3 Hz, 1 H, CHSi), 1.25 [s, 9 H, $SiC(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.9, 136.1, 136.0, 132.3, 132.0, 129.73, 129.68, 128.5, 127.9, 127.8, 125.2 (C_6H_5), 55.7 (CHO), 54.7 (CHO), 27.8 [C(CH_3)$_3$], 18.7 [C(CH_3)$_3$].

MS (EI): *m*/*z* (%) = 358 (9, M), 301 (33, M − *t*-Bu), 239 (100, *t*-$BuPh_2Si$).

Anal. $C_{24}H_{26}SiO$ (358.6): calcd C 80.40, H 7.31; found: C 80.68, H 7.50.

2-*tert*-Butyldiphenylsilyl-1,2-epoxyhexane (6b)

Colorless oil (13%); R_f (hexane/ Et_2O, 20:1) 0.24.

IR (neat): ν = 1110 cm^{-1} (Si−Ph).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.7−7.3 (m, 10 H, 2 × C_6H_5), 2.76 (d, *J* = 5.2 Hz, 1 H, C*H*HO), 2.61 (d, *J* = 5.2 Hz, 1 H, CH*H*O), 2.04−1.94 (m, 1H, C*H*HCSi), 1.73−1.55 (m, 1 H, CH*H*CSi), 1.45-1.1 (m, 4 H, CH_2CH_2), 1.2 [s, 9 H, $SiC(CH_3)_3$], 0.8 (t, *J* = 7.2 Hz, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.1, 136.0, 133.7, 133.2, 129.4, 129.2, 127.8, 127.6 (C_6H_5), 51.2 (SiCO), 48.7 (OCH_2), 34.5 (CH_2), 28.8 [C(CH_3)$_3$], 26.0 (CH_2), 22.9 (CH_2), 19.1 [C(CH_3)$_3$], 13.9 (CH_3).

MS (EI): *m*/*z* (%) = 338 (0.5, M), 281 (46, M − *t*-Bu), 199 (100, Ph_2SiOH).

Acid Rearrangement of Epoxysilanes; General Procedure

To a solution of the epoxide **5** or **6** (1.8 mmol) in THF (20 mL) was added H_2SO_4 (1 mL) and heated at 65 °C for 5 h. The mixture was quenched with aq $NaHCO_3$ solution. The organic layer was washed with brine (3 × 10 mL), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane/Et_2O, 10:1) to give the silyl carbonyl compounds **7** and **8a,b**. The silyl aldehyde **8a** has been previously described.[9a]

2-*tert*-Butyldiphenylsilyl-2-phenylethanal (7)

Colorless crystals (95%); R_f (hexane/Et_2O, 9:1) 0.24; mp 115−116 °C (MeOH).

IR (KBr): δ = 1700 (C=O), 1100 cm^{-1} (Si−Ph).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.9 (d, *J* = 3.5 Hz, 1 H, CHO), 7.68−6.96 (m, 15 H, 3 C_6H_5), 4.45 (d, *J* = 3.5 Hz, 1 H, C*H*Ph), 0.97 [s, 9 H, $SiC(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.1 (CO), 136.7, 134.1, 132.3, 131.5, 129.9, 129.8, 129.5, 128.4, 127.8, 127.6, 126.2 (C_6H_5), 53.7 (*C*HCHO), 27.7 [C(CH_3)$_3$], 19.6 [C(CH_3)$_3$].

MS (EI): *m*/*z* (%) = 301 (64, M − *t*-Bu), 239 (18, *t*-$BuPh_2Si$), 199 (100, Ph_2SiOH).

Anal. $C_{24}H_{26}SiO$ (358.6): calcd C 80.40, H 7.31; found: C 80.62, H 7.42.

1-*tert*-Butyldiphenylsilylhexan-2-one (8b)

Colorless oil (12%); R_f (hexane/EtOAc, 13:1) 0.4.

IR (neat): ν = 1720 (C=O), 1245 (C−Si), 1100 cm^{-1} (Ph−Si).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65−7.25 (m, 10 H, 2 × C_6H_5), 2.75 (s, 2 H, CH_2Si), 1.9 (t, *J* = 7.4 Hz, 2 H, CH_2CO), 1.3−0.8 (m, 4 H, 2 × CH_2), 1.1 [s, 9 H, $SiC(CH_3)_3$], 0.7 (t, *J* = 7.2 Hz, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.8 (CO), 136.1, 133.1, 129.6, 127.8 (C_6H_5), 44.2 (Si*C*H_2CO), 32.3 (*C*H_2CO), 27.5 [C(CH_3)$_3$], 25.7 (CH_2), 22.0 (CH_2), 18.7 [C(CH_3)$_3$], 13.7 (CH_3).

MS (EI): *m*/*z* (%) = 338 (9, M), 281 (100, M − *t*-Bu), 239 (4, *t*-$BuPh_2Si$), 199 (83, Ph_2SiOH).

Reaction of Silyl Aldehydes with Organometallic Reagents; General Procedure

The organometallic reagent (1.0 mmol) was added to a stirred solution of the aldehyde **7** or **8a** (0.65 mmol) in anhyd THF at −78 °C under N_2. After 1 h at this temperature the reaction was quenched with MeOH (2 mL), allowing the mixture to warm up to r.t. Sat. aq NH_4Cl solution (15 mL) was added, and the aqueous layer extracted

with Et_2O (3 × 15 mL). The organic layers were combined, washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane/Et_2O, 9:1) to give the alcohols **9a–g** (Scheme 2). In the case of **9g**, purification was not desirable because much elimination occurred during column elution. The crude **9g** [70% yield, roughly determined; ^{1}H NMR: δ = 5.1 (d, C*H*OH)] was directly treated with KH to give the alkene **10b**.

(1*SR*,2*RS*)-1-*tert*-Butyldiphenylsilyl-1-phenylpropan-2-ol (9a)
Colorless oil (87%); R_f (hexane/Et_2O, 9:1) 0.2.

IR (neat): ν = 3600 (OH), 1100 cm^{-1} (Si–Ph).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.8–7.1 (m, 15 H, 3 × C_6H_5), 4.37 (qd, *J* = 6.1, 5.9 Hz, 1 H, C*H*OH), 3.0 (d, *J* = 5.9 Hz, 1 H, C*H*Ph), 1.29 (br s, 1 H, OH), 1.1 (d, *J* = 6.1 Hz, 3 H, CH_3), 0.8 [s, 9 H, $SiC(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): ν = 139.3, 136.9, 136.7, 134.8, 133.9, 130.9, 129.5, 129.2, 128.4, 127.7, 127.4, 126.0 (C_6H_5), 68.7 (CHOH), 41.5 (CHSi), 27.9 [C(*C*H_3)$_3$], 23.8 (CH_3), 19.1 [*C*(CH_3)$_3$].

MS (EI): *m*/*z* (%) = 317 (2, M – *t*-Bu), 239 (2, *t*-BuPh_2Si), 199 (100, Ph_2SiOH).

Anal. $C_{25}H_{30}SiO$ (374.6): calcd C 80.16, H 8.07; found: C 80.41, H 8.29.

(1*SR*,2*RS*)-1-*tert*-Butyldiphenylsilyl-1-phenylhexan-2-ol (9b)
Colorless oil (85%); R_f (hexane/Et_2O, 11:1) 0.22.

IR (neat): ν = 3600 (OH), 1100 cm^{-1} (Si–Ph).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.8–7.1 (m, 15 H, 3 × C_6H_5), 4.25–4.15 (m, 1 H, C*H*OH), 3.1 (d, *J* = 3.5 Hz, 1 H, C*H*Ph), 1.4–1.1 (m, 7 H, 3 × CH_2 and OH), 0.9–0.75 (m, 3 H, CH_3), 0.8 [s, 9 H, $SiC(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.1, 137.0, 136.8, 134.6, 134.3, 131.2, 129.4, 128.2, 127.7, 127.4, 125.8 (C_6H_5), 72.0 (CHOH), 39.3 (CHSi), 36.9 (*C*H_2CHOH), 28.5 (CH_2), 28.0 [C(*C*H_3)$_3$], 22.5 (CH_2), 19.1 [*C*(CH_3)$_3$], 14.0 (CH_3).

MS (EI): *m*/*z* (%) = 399 (0.2, M – OH), 359 (3, M – *t*-Bu), 239 (2, *t*-BuPh_2Si), 199 (100, Ph_2SiOH).

Anal. $C_{28}H_{36}SiO$ (416.7): calcd C 80.71, H 8.71; found: C 80.96, H 8.82.

(1*RS*,2*SR*)-2-*tert*-Butyldiphenylsilyl-1,2-diphenylethan-1-ol (9c)
Colorless crystals (90%); R_f (hexane/Et_2O, 10:1) 0.3; mp 124.4–125.1 °C (MeOH).

IR (neat): ν = 3580 (OH), 1100 cm^{-1} (Si–Ph).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.9–6.9 (m, 20 H, 4 × C_6H_5), 5.5 (dd, *J* = 4.3, 1.9 Hz, 1 H, C*H*OH), 3.2 (d, *J* = 1.9 Hz, 1 H, CHSi), 1.68 (d, *J* = 4.3 Hz, 1 H, OH), 0.9 [s, 9 H, $SiC(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.5, 137.3, 137.1, 136.9, 134.4, 134.2, 131.9, 129.6, 129.3, 127.8, 127.6, 126.7, 125.8, 125.6 (C_6H_5), 73.5 (CHOH), 42.0 (CHSi), 28.0 [C(*C*H_3)$_3$], 19.1 [*C*(CH_3)$_3$].

MS (EI): *m*/*z* (%) = 379 (1, M – *t*-Bu), 239 (5, *t*-BuPh_2Si), 199 (100, Ph_2SiOH).

Anal. $C_{30}H_{32}SiO$ (436.7): calcd C 82.52, H 7.39; found: C 82.61, H 7.44.

(1*SR*,2*RS*)-1-*tert*-Butyldiphenylsilyl-1-phenylbut-3-en-2-ol (9d)
Colorless oil (83%); R_f (hexane/Et_2O, 10:1) 0.17.

IR (neat): ν = 3580 (OH), 1255 (Si–C), 1100 cm^{-1} (Si–Ph).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.8–7.1 (m, 15 H, 3 × C_6H_5), 5.8 (ddd, *J* = 16.9, 10.4, 6.1 Hz, 1 H, CHOHC*H*=), 5.1 (dt, *J* = 16.9, 1.5 Hz, 1 H, C*H*H=), 4.9 (dt, *J* = 10.4, 1.5 Hz, 1 H, CH*H*=), 4.8 (dd, *J* = 6.1, 4.1 Hz, 1 H, C*H*OH), 3.1 (d, *J* = 4.1 Hz, 1 H, CHSi), 1.3 (br s, 1 H, OH), 0.9 [s, 9 H, $SiC(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.8 (CH=), 138.4, 137.2, 136.9, 134.4, 134.0, 131.2, 129.5, 129.2, 128.2, 127.6, 127.4, 126.0 (C_6H_5), 114.2 (CH_2=), 73.2 (CHOH), 40.2 (CHSi), 28.1 [C(*C*H_3)$_3$], 19.1 [*C*(CH_3)$_3$].

MS (EI): *m*/*z* (%) = 329 (3, M – *t*-Bu), 239 (3, *t*-BuPh_2Si), 199 (100, Ph_2SiOH).

Anal. $C_{26}H_{30}SiO$ (386.6): calcd C 80.78, H 7.82; found: C 81.12, H 8.08.

(2*RS*,3*SR*)-3-*tert*-Butyldiphenylsilylheptan-2-ol (9e)
Colorless oil (72%); R_f (hexane/Et_2O, 8:1) 0.32.

IR (neat): ν = 3540 (OH), 1255 (Si–C), 1100 cm^{-1} (Si–Ph).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.8–7.2 (m, 10 H, 2 × C_6H_5), 4.3 (dq, *J* = 7.1, 6.4 Hz, 1 H, C*H*OH), 1.69–1.23 (m, 8 H, 3 × CH_2 + CHSi + OH), 1.2 (d, *J* = 6.4 Hz, 3 H, C*H*$_3$CHOH), 1.1 [s, 9 H, $SiC(CH_3)_3$], 0.84 (t, *J* = 7 Hz, 3 H, C*H*$_3$CH$_2$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.5, 136.4, 135.1, 134.9, 129.1, 129.0, 127.7, 127.5 (C_6H_5), 68.1 (CHOH), 35.7 (CH_2), 32.2 (CHSi), 28.9 [C(*C*H_3)$_3$], 24.7 (CH_2), 23.9 (*C*H_3CHOH), 23.2 (CH_2), 18.9 [*C*(CH_3)$_3$], 14.0 (CH_3).

MS (EI): *m*/*z* (%) = 336 (3, M - H_2O), 279 (64, M - H_2O – *t*-Bu), 239 (56, *t*-BuPh_2Si), 199 (22, Ph_2SiOH).

Anal. $C_{23}H_{34}SiO$ (354.6): calcd C 77.90, H 9.66; found: C 78.29, H 9.95.

(3*RS*,4*SR*)-4-*tert*-Butyldiphenylsilyl-2-methyloctan-3-ol (9f)
Colorless oil (60%); R_f (hexane/Et_2O, 8:1) 0.3.

IR (neat): ν = 3580 (OH), 1255 (Si–C), 1100 cm^{-1} (Si–Ph).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.7–7.3 (m, 10 H, 2 × C_6H_5), 3.6 (br d, *J* = 9.4 Hz, 1 H, C*H*OH), 1.8-1.2 [m, 9 H, 3 × CH_2 + C*H*(CH_3)$_2$ + CHSi + OH], 1.1 [s, 9 H, $SiC(CH_3)_3$], 0.9 [d *J* = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$], 0.8 (t, *J* = 7.2 Hz, 3 H, C*H*$_3$CH$_2$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.6, 136.5, 135.2, 134.6, 129.1, 129.0, 127.6, 127.4 (C_6H_5), 78.1 (CHOH), 35.2 (CH_2), 32.3 (CHSi), 28.9 [C(*C*H_3)$_3$], 26.8 [*C*H(CH_3)$_2$], 24.2 (CH_2), 23.4 (CH_2), 20.1 [CH(*C*H_3)$_2$], 19.9 [CH(*C*H_3)$_2$], 19.0 [*C*(CH_3)$_3$], 13.9 (CH_3).

MS (EI): *m*/*z* (%) = 325 (2, M – *t*-Bu), 281 (2, M – *t*-Bu – *i*-Pr), 239 (3, *t*-BuPh_2Si), 199 (100, Ph_2SiOH).

Anal. $C_{25}H_{38}SiO$ (382.7): calcd C 78.47, H 10.01; found: C 78.23, H 9.92.

Elimination Reactions of β-Hydroxysilanes; General Procedures (Scheme 3)

Basic Conditions: KH (0.103 g of a 50% slurry in oil, 1.25 mmol) was stirred with hexane (3 × 4 mL), and the supernatant layer was removed by syringe. To the residue was added anhyd THF (5 mL), and a solution of the β-hydroxysilane **9a–d,g** (0.4 mmol) in anhyd THF (2 mL). After stirring for 1 h at r.t., the mixture was added to cold 10% NH_4Cl solution and Et_2O. The Et_2O layer was separated and dried ($MgSO_4$).

Acidic conditions: To an ice-cooled solution of the β-hydroxysilane **9b** (0.32 mmol) in anhyd CH_2Cl_2 (7 mL) was added BF_3.OEt_2 (4 mmol). The mixture was stirred for 1 h at 0 °C, then added to aq sat. $NaHCO_3$ and extracted with Et_2O. The Et_2O layer was separated and dried ($MgSO_4$).

(*Z*)-1-Phenylprop-1-ene (10a)[20]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.5–7.2 (m, 5 H, C_6H_5), 6.5 (dq, *J* = 11.6, 1.8 Hz, 1 H, C*H*Ph), 5.8 (dq, *J* = 11.6, 7.1 Hz, 1 H, C*H*CH_3), 1.9 (dd, *J* = 7.1, 1.8 Hz, 3 H, CH_3).

(*Z*)-1-Phenylhex-1-ene (10b)[21]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.5−7.2 (m, 5 H, C_6H_5), 6.4 (br d, *J* = 11.6 Hz, 1 H, C*H*Ph), 5.7 (dt, *J* = 11.6, 7.2 Hz, 1 H, C*H*CH_2), 2.4−2.3 (m, 2 H, CH_2C=), 1.5−1.3 (m, 4 H, 2 × CH_2), 0.9 (t, *J* = 7.2 Hz, 3 H, CH_3).

(*E*)-1-Phenylhex-1-ene (10e)[21]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.5−7.3 (m, 5 H, C_6H_5), 6.38 (br d, *J* = 15 Hz, 1 H, C*H*Ph), 6.24 (dt, *J* = 15, 7.1 Hz, 1 H, C*H*CH_2), 2.3−2.2 (m, 2 H, CH_2C=), 1.5−1.3 (m, 4 H, 2 × CH_2), 0.89 (t, *J* = 7.2 Hz, 3 H, CH_3).

(*Z*)-1,2-Diphenylethene (10c)[22]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4−7.2 (m, 10 H, 2 × C_6H_5), 6.7 (s, 2 H, 2 × C*H*).

(*Z*)-1-Phenylbuta-1,3-diene (10d)[23]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.8−7.7 (m, 5 H, C_6H_5), 6.8 (ddd, *J* = 16.8, 11.0, 10.1 Hz, 1 H, C*H*=CH_2), 6.5 (d, *J* = 11.3 Hz, 1 H, C*H*Ph), 6.3 (dd, *J* = 11.3, 11.3 Hz, 1 H, CHC=), 5.4 (dd, *J* = 16.8, 2.0 Hz, 1 H, =C*H*H), 5.2 (dd, *J* = 10.1, 2.0 Hz, 1 H, =CH*H*).

Oxidation of β-Hydroxysilanes; General Procedure
To a suspension of PCC/aluminum oxide (2.54 g, 2.1 mmol) in hexane/CH_2Cl_2 (50%) was added a solution of the β-hydroxysilane **9a,b** (0.6 mmol) in hexane/CH_2Cl_2, and the mixture stirred for 16 h at r.t. The solution was filtered and the solid residue washed with Et_2O (3 × 10 mL). The combined filtrates were evaporated and the crude product was chromatographed (hexane/Et_2O).

1-*tert*-Butyldiphenylsilyl-1-phenylpropan-2-one (11a)
Colorless crystals (75%); R_f (hexane/EtOAc, 20:1) 0.3; mp 119−120 °C (hexane).

IR (KBr): ν = 1700 (C=O), 1255 (Si−C), 1100 cm^{-1} (Si−Ph).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72−7.11 (m, 15 H, 3 × C_6H_5), 4.52 (s, 1 H, C*H*Ph), 2.07 (s, 3 H, CH_3CO), 0.96 [s, 9 H, $SiC(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.5 (CO), 137.0, 136.9, 136.2, 133.4, 132.2, 130.2, 129.6, 129.5, 128.1, 127.4, 126.1 (C_6H_5), 53.2 (CHSi), 32.2 (CH_3CO), 28.2 [$C(CH_3)_3$], 19.6 [$C(CH_3)_3$].

MS (EI): *m*/*z* (%) = 372 (8, M), 315 (51, M – *t*-Bu), 237 (100, M – *t*-BuPh), 199 (10, Ph_2SiOH).

Anal. $C_{25}H_{28}SiO$ (372.6): calcd C 80.59, H 7.57; found: C 80.72, H 7.66.

1-*tert*-Butyldiphenylsilyl-1-phenylhexan-2-one (11b)
Colorless crystals (70%); R_f (hexane/EtOAc, 25:1) 0.6; mp 72−73 °C (MeOH).

IR (KBr): ν = 1700 (C=O), 1100 cm^{-1} (Si−Ph).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89−7.06 (m, 15 H, 3 × C_6H_5), 4.45 (s, 1 H, C*H*Ph), 2.42−2.29 (m, 2 H, CH_2CO). 1.44−1.02 (m, 4 H, 2 × CH_2), 0.96 [s, 9 H, $SiC(CH_3)_3$], 0.75 (t, *J* = 7.2 Hz, 3 H, CH_3CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.7 (CO), 137.1, 136.9, 136.2, 133.3, 132.4, 130.0, 129.3, 128.0, 127.3, 125.9 (C_6H_5), 52.3 (CHSi), 44.3 (CH_2CO), 28.3 [$C(CH_3)_3$], 25.8 (CH_2), 22.0 (CH_2), 19.5 [$C(CH_3)_3$], 13.7 (CH_3).

MS (EI): *m*/*z* (%) = 414 (4, M), 357 (85, M − *t*-Bu), 199 (15, Ph_2SiOH).

Anal. $C_{28}H_{34}SiO$ (414.7): calcd C 81.10, H 8.26; found: C 80.98, H 8.20.

The silyl ketones **11a,b** on standing at r.t., easily isomerized in high yield to the following silyl enol ethers (Scheme 4).

(*E*)-2-*tert*-Butyldiphenylsilyloxy-1-phenylprop-1-ene (12a)[24]
Colorless oil (97% conversion); R_f (hexane/EtOAc, 20:1) 0.6.

IR (neat): ν = 1650 (C=C), 1240 and 1180 (SiOC=), 1100 cm^{-1} (Si−Ph).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87−7.43 (m, 10 H, 2 × C_6H_5Si), 7.28−7.0 (m, 5 H, C_6H_5), 5.78 (s, 1 H, CH=), 2.04 (s, 3 H, CH_3C=), 1.17 [s, 9 H, $SiC(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.2 (=C−O), 137.5, 135.5, 133.3, 129.8, 128.4, 128.0, 127.7, 125.2 (C_6H_5), 111.0 (CH=), 26.6 [$C(CH_3)_3$], 19.5 (CH_3), 19.4 [$C(CH_3)_3$].

MS (EI): *m*/*z* (%) = 372 (8, M), 315 (61, M – *t*-Bu), 237 (100, M – *t*-BuPh), 199 (5, Ph_2SiOH).

(*E*)-2-*tert*-Butyldiphenylsilyloxy-1-phenylhex-1-ene (12b)
Colorless oil (94% conversion); R_f (hexane) 0.4.

IR (neat): ν = 1640 (C=C), 1240 and 1180 (SiOC=), 1100 cm^{-1} (Si−Ph).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81−7.38 (m, 10 H, 2 × C_6H_5Si), 7.21−6.87 (m, 5 H, C_6H_5), 5.51 (s, 1H, CH=), 2.37 (t, *J* = 7.7 Hz, 2 H, CH_2C=), 1.72, (quintet, *J* = 7.7 Hz, 2 H, CH_2CH_2C=), 1.49−1.26 (m, 2 H, CH_3CH_2), 1.09 [s, 9 H, $SiC(CH_3)_3$], 0.92 (t, *J* = 7.4 Hz, 3 H, CH_3CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.6 (=C−O), 137.4, 135.5, 133.0, 129.7, 128.3, 127.9, 127.6, 125.1 (C_6H_5), 110.3 (CH=), 31.9 (CH_2), 29.5 (CH_2), 26.6 [$C(CH_3)_3$], 22.5 (CH_2), 19.4 [$C(CH_3)_3$], 14.0 (CH_3).

MS (EI): *m*/*z* (%) = 414 (8, M), 357 (98, M – *t*-Bu), 279 (100, M – *t*-Bu-Ph), 199 (19, Ph_2SiOH).

Reaction of the α-Silyl Ketones with Organolithium Reagents; General Procedure
To a stirred solution of the α-silyl ketone **11a,b** (0.11 mmol) in anhyd THF (3 mL) was added the appropriate organolithium reagent (0.22 mmol)) at −78 °C under N_2. After 2 h at this temperature, the reaction was quenched with MeOH (2 mL) at −78 °C, allowing the mixture to warm up to r.t. Aq satd NH_4Cl solution (15 mL) was added, and the aqueous layer extracted with Et_2O (3 × 15mL). The organic layers were combined, washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed (SiO_2, pentane) to give the alkenes **13a−d** and **14a−d** in the ratio shown in Scheme 5. The ratio was determined by ^{1}H NMR and GC.

From silyl ketone **11a** and PhLi, a mixture of (*E*)- and (*Z*)-1,2-diphenylprop-1-enes[24] (75%) was obtained.

(*E*)-1,2-Diphenylprop-1-ene (14b)[25]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63−6.98 (m, 10 H, 2 × C_6H_5), 6.87 (br s, 1 H, C*H*Ph), 2.33 (d, *J* = 1.3 Hz, 3 H, CH_3).

(*Z*)-1,2-Diphenylprop-1-ene (13b)[25]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63−6.98 (m, 10 H, 2 × C_6H_5), 6.5 (br s, 1 H, C*H*Ph), 2.25 (d, *J* = 1.5 Hz, 3 H, CH_3).

From silyl ketone **11b** and PhLi, a mixture of (*E*)- and (*Z*)-1,2-diphenylhex-1-enes[25] (90%) was obtained.

***(E)*-1,2-Diphenylhex-1-ene (14d)**[26]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89−7.39 (m, 10 H, 2 × C_6H_5), 6.77 (s, 1 H, C*H*Ph), 2.79 (t, *J* = 7 Hz, 2 H, CH_2C=), 1.52−1.1 (m, 4 H, 2 × CH_2), 0.92 (t, *J* = 7 Hz, 3 H, CH_3).

(*Z*)-1,2-Diphenylhex-1-ene (13d)[26]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89−7.39 (m, 10 H, 2 × Ph), 6.51 (s, 1 H, C*H*Ph), 2.56 (t, *J* = 7 Hz, 2 H, CH_2C=), 1.52-1.1 (m, 4 H, 2 × CH_2), 0.92 (t, *J* = 7 Hz, 3 H, CH_3).

From silyl ketone **11a** and BuLi and from silyl ketone **11b** and Me-Li, a mixture of (*E*)- and (*Z*)-2-methyl-1-phenylhex-1-enes[26] in 71−75% yield was obtained.

(*E*)-2-Methyl-1-phenylhex-1-ene (14a = 13c)[27]
^{1}H NMR (300 MHz, $CDCl_3$): d = 7.34−7.19 (m, 5 H, C_6H_5), 6.29 (s, 1 H, C*H*Ph), 2.24 (t *J* = 7 Hz, 2 H, CH_2C=), 1.89 (s, 3 H, CH_3C=), 1.52−1.2 (m, 4 H, 2 × CH_2), 0.91 (t, *J* = 7 Hz, 3 H, CH_3).

(*Z*)-2-Methyl-1-phenylhex-1-ene (13a = 14c)[27]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34−7.19 (m, 5 H, C_6H_5), 6.29 (s, 1 H, C*H*Ph), 2.24 (t, *J* = 7 Hz, 2 H, CH_2C=), 1.82 (s, 3 H, CH_3C=), 1.52−1.2 (m, 4 H, 2 × CH_2), 0.87 (t, *J* = 7 Hz, 3 H, CH_3).

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References

(1) (a) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: New York, 1988.
(b) Tietze, L. F.; Neumann, T.; Kajino, M.; Pretor, M. *Synthesis* **1995**, 1003.
(c) Bhushan, V.; Lohray, B. B.; Enders, D. *Tetrahedron Lett.* **1993**, *34*, 5067.
(2) (a) Larson, G. L.; Fuentes, L. M. *J. Am. Chem. Soc*. **1981**, *103*, 2418.
(b) Fessenden, R.J.; Fessenden, J. S. *J. Org. Chem*. **1967**, *32*, 3535.
(3) (a) Hauser, C. R.; Hance, C. R. *J. Am. Chem. Soc*. **1952**, *74*, 5091.
(b) Demuth, M. *Helv. Chim. Acta* **1978**, *61*, 3136.
(c) Seitz, D. E.; Zapata, A. *Synthesis* **1981**, 557.
(4) (a) Hudrlik, P. F. *Tetrahedron Lett*. **1976**, 1453.
(b) Eisch, J. J.; Galle, J. E. *J. Org. Chem*. **1976**, *41*, 2615.
(c) Sato, S.; Okada, H.; Matsuda, Y.; Izumi, Y. *Tetrahedron Lett.* **1986**, *27*, 4269.
(d) Cunico, R. F. *Tetrahedron Lett*. **1986**, *27*, 4269.
(e) Fristad, W. E.; Bailey, T. R.; Paquette, L. A. *J. Org. Chem*. **1980**, *45*, 3028.
(5) (a) Enders, D.; Lohray, B. B. *Angew. Chem. Int. Ed. Engl*. **1987**, *26*, 351.
(b) Enders, D.; Lohray, B. B.; Burkamp, F.; Bhushan, V.; Hett, R. *Liebigs Ann. Chem.* **1996**, 189.
(c) Corey, E. J.; Enders, D. *Chem. Ber*. **1978**, *111*, 1362.
(6) (a) Hudrlik, P. F.; Misra, R. N.; Withers, G. P.; Hudrlik, A. M.; Rona, R. J.; Arcoleo, J. P. *Tetrahedron Lett*. **1976**, 1453.
(b) Chauret, D. C.; Chang, J. M. *Tetrahedron Lett.* **1993**, *34*, 3695.
(7) (a) Hudrlik, P. F.; Peterson, D. *Tetrahedron Lett.* **1974**, 1133.
(b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer: Heidelberg, 1983.
(8) (a) Obayashi, M; Utimoto, K.; Nonaki, H. *Bull Chem. Soc. Jpn*. **1979**, *52*, 1760.
(b) Hudrlik, P. F.; Peterson, D. *Tetrahedron Lett.* **1972**, 1785.
(9) (a) Barbero, A.; Cuadrado, P.; Fleming, I.; Gonzalez, A. M.; Pulido, F. J.; Sanchez, A. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1525.
(b) Blanco, F. J.; Cuadrado, P.; González, A. M.; Pulido, F. J. *Synthesis* **1996**, 42.
(c) Barbero, A.; Pulido, F. J. *Recent Research Developments in Synthetic Organic Chemistry*, Vol. 2; Pandalai, S. G., Ed.; T.R.N: Trivandrum, 1999; pp 1−22.
(10) Stork, G.; Colvin, E. *J. Am. Chem. Soc*. **1971**, *93*, 2080.
(11) Muchowski, M.; Naef, R.; Maddox, M. L. *Tetrahedron Lett.* **1985**, *26*, 5375.
(12) Hudrlik, P. F.; Kulkarni, A. K. *J. Am. Chem. Soc*. **1981**, *103*, 6251.
(13) Hudrlik, P. F.; Hudrlik, A. M.; Misra, R. N.; Peterson, D.; Withers, G. P.; Kulkarni, A. K. *J. Org. Chem*. **1980**, *45*, 4444.
(14) The assumption that **8b** comes from **6b** is based on the fact that the acid-catalyzed rearrangement of a pure sample of **6a** yields **8a** without contamination of **8b**.
(15) Sato, T.; Abe, T.; Kuwajima, I. *Tetrahedron Lett*. **1978**, *19*, 259.
(16) (a) Cherest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett*. **1968**, 2119.
(b) Anh, N. T.; Eisenstein, O. *Nouv. J. Chim.* **1977**, *1*, 61.
(17) (a) Peterson, D. J. *J. Org. Chem*. **1968**, *33*, 780.
(b) Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc*. **1975**, *97*, 1464.
(18) (a) Brook, A. G.; MacRae, D. M.; Bassindale, A. R. *J. Organometal. Chem*. **1975**, *86*, 185.
(b) Bassindale, A. R.; Brook, A. G.; Chen, P.; Lennon, J. *J. Organometal. Chem*. **1975**, *94*, C21.
(19) Utimoto, K.; Obayashi, M.; Nozaki, H. *J. Org. Chem*. **1976**, *41*, 2940.
(20) Davidson, A. H.; Fleming, I.; Grayson, J. Y.; Pearce, A.; Snowden, R. L.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1977**, 550.
(21) Fleming, I.; Newton, T. W. *J. Chem. Soc., Perkin Trans. I* **1984**, 119.
(22) Aldrich Catalogue of Fine Chemicals 1999−2000. *Beilstein 5*, 630.
(23) Baldry, P. J. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1913
(24) Sakurai, H.; Miyoshi, K.; Nakadaira, Y. *Tetrahedron Lett*. **1977**, 2671.
(25) Reeve, W.; Doherty, R. M. *J. Org. Chem*. **1975**, *40*, 1662.
(26) Mulvaney, J. E.; Gardlund, Z. G.; Gardlund, S. L.; Newton, D. J. *J. Am. Chem. Soc*. **1966**, 476.
(27) Crandall, J. K.; Collonges, F. *J. Org. Chem*. **1976**, *41*, 4089.

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