# ORGANIC SYNTHESIS WITH REAGENTS DERIVED FROM $3R_3SiMgMe$ AND $MnCl_2$

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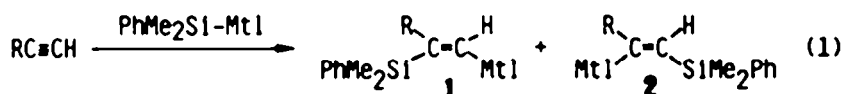Koichiro Oshima,[*] Kiitiro Utimoto, and Hitosi Nozaki[1]

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**Summary**: Synthetically useful reactions mediated by reagents
derived from 3 equiv. of $R_3SiMgMe$ and $MnCl_2$ are disclosed.
(1) The manganese species reacted with terminal acetylenes to
give 1,2-disilylated 1-alkenes. Mono- and bis(trimethyl-
silyl)acetylenes gave tri- and tetrasilylated ethenes,
respectively, in good yields. Highly strained tetrakis(tri-
methylsilyl)ethene has now become easily accessible by this
technique. (2) The reaction of alkenyl halides, alkenyl
sulfides, and enol phosphates with the title reagents
provides vinylsilanes in good yields. The method is also
applicable to the synthesis of allylsilanes from allylic
sulfides and ethers. (3) Treatment of 1,3-dienes with the
manganese reagents provides silylated allylmanganese
compounds which add to the carbonyl moiety with high regio-
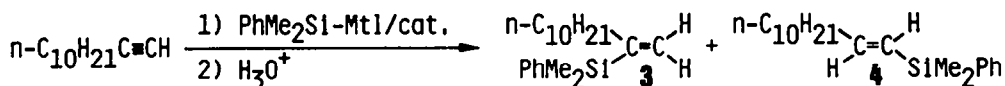selectivity.

## Introduction

In connection with an investigation of the stereoselective synthesis of the
side chain of a plant growth steroidal hormone, brassinolide, we required a
method for the formation of alkenylmetal species (1) containing trialkylsilyl
group. Regio- and stereoselective addition of Si-Metal reagent[2] to acetylenes
was an attracted possibility to obtain this compound (eq. 1). Although
exclusive formation of 2-metallo-1-silyl-1-alkenes (2) by silylalumination,[3]
silylcupration[4] or silyltitanation[5] was previously reported, the selective gen-
eration of 1-metallo-2-silyl isomers 1 hitherto has not been described to our
knowledge.

$$RC\equiv CH \xrightarrow{\quad PhMe_2Si-Mtl \quad} \underset{\underset{\textstyle 1}{PhMe_2Si}}{\overset{\textstyle R}{\phantom{x}}} C=C \overset{\textstyle H}{\underset{\textstyle Mtl}{\phantom{x}}} \; + \; \underset{\underset{\textstyle 2}{Mtl}}{\overset{\textstyle R}{\phantom{x}}} C=C \overset{\textstyle H}{\underset{\textstyle SiMe_2Ph}{\phantom{x}}} \qquad (1)$$
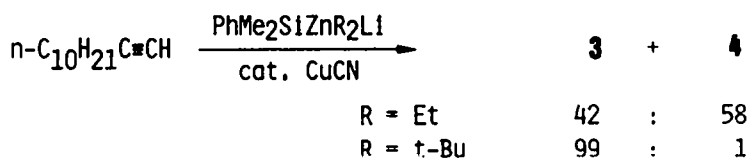
First we investigated simultaneous addition of a silyl group and a metal to
acetylenes with regioselectivity using $PhMe_2SiLi$ and metal compounds such as

MeMgI, Et$_2$AlCl, ZnBr$_2$, and Et$_3$B, in the presence of transition-metal catalysts.[6,7] Platinum- or copper-catalyzed silylmagnesation (PhMe$_2$SiMgMe) followed by aqueous quenching provided exclusively (E)-1-silyl-1-alkenes, which have the same regiochemistry as the products prepared from stoichiometric silyl-cupration or silyltitanation. On the other hand, palladium catalyzed silyl-alumination (PhMe$_2$SiAlEt$_2$) afforded the regioisomer 2-silyl-1-alkenes with high regioselectivity.[8]

$$\text{n-C}_{10}\text{H}_{21}\text{C}\equiv\text{CH} \xrightarrow[\text{2) H}_3\text{O}^+]{\text{1) PhMe}_2\text{Si-Mtl/cat.}} \quad \begin{matrix} \text{n-C}_{10}\text{H}_{21} \\ \text{PhMe}_2\text{Si} \end{matrix}\text{C}=\text{C}\begin{matrix}\text{H}\\\text{H}\end{matrix} \ \mathbf{3} \ + \ \begin{matrix} \text{n-C}_{10}\text{H}_{21}\\\text{H} \end{matrix}\text{C}=\text{C}\begin{matrix}\text{H}\\\text{SiMe}_2\text{Ph}\end{matrix}\ \mathbf{4}$$

| | | |
|---|---|---|
| MeMgI-cis-PtCl$_2$(P-n-Bu$_3$)$_2$ or CuI | <1 : | >99 |
| Et$_2$AlCl- PdCl$_2$(P(o-CH$_3$C$_6$H$_4$)$_3$)$_2$ | 85 : | 15 |

Dialkyl(dimethylphenylsilyl)zinclithium[9] added effectively to internal acetylenes as well as to terminal ones to provide vinylsilanes with high stereo- and regioselectivities. The regioselectivity of the reaction was strongly affected by the nature of the dialkylzinc employed. The use of a bulky alkyl group on zinc favours the formation of 2-silyl-1-alkenes.

$$\text{n-C}_{10}\text{H}_{21}\text{C}\equiv\text{CH} \xrightarrow[\text{cat. CuCN}]{\text{PhMe}_2\text{SiZnR}_2\text{Li}} \quad \mathbf{3} \ + \ \mathbf{4}$$

| | | |
|---|---|---|
| R = Et | 42 : | 58 |
| R = t-Bu | 99 : | 1 |

Organocuprates have been extensively studied and widely applied to organic synthesis.[10] In contrast, little attention has been paid to the related reactions of triorganomanganese compounds, although the addition of 3 equiv of BuLi to MnCl$_2$ is known to give Bu$_3$MnLi which adds to α,β-unsaturated carbonyl compounds in 1,4-fashion.[11] Here we describe the behaviour of silylmanganese reagents which are derived from 3 equiv of R$_3$SiMgMe and MnCl$_2$ and are believed to be (R$_3$Si)$_3$MnMgMe. The reactions involve (1) acetylenes, (2) alkenyl halides, alkenyl sulfides, and enol phosphates, and (3) dienes as the acceptor components. The formulation of the reagents, for example as (R$_3$Si)$_3$MnMgMe, has no evidence to support it and represents the stoichiometry of the components rather than an explicit structural formula.

## Results and Discussion
(1) Disilylation of Acetylenes with Si-Mn Reagent

Palladium(0) catalyzed reaction of acetylenes with disilanes such as HMe$_2$SiSiMe$_2$H, FMe$_2$SiSiMe$_2$F, and (MeO)Me$_2$SiSiMe$_2$(OMe) produces the corresponding disilylated olefins in good yield.[12] In contrast, hexamethyldisilane gives less than 10% yield of doubly silylated products.

We have examined the reaction of the Si-Mn reagent with acetylenes[13] and observed the rather unexpected formation of disilylated products.[14] (Trimethylsilyl)lithium[15] was treated with methylmagnesium iodide and anhydrous manganese(II) chloride.[16] Addition of 1-alkyne to the resulting reagent provided an E, Z mixture of 1,2-bis(trimethylsilyl)-1-alkene. The reaction proceeded smoothly with silylacetylenes as well as terminal acetylenes to give

tri- and tetrasilylated ethenes.

Although the role of MeMgI is not clear, its presence is essential for the formation of disilylated products. Without MeMgI, monosilylated products were obtained predominantly after aqueous workup. For instance, treatment of 4-(benzyloxy)-1-butyne with 3Me₃SiLi-MnCl₂ gave a mixture of 4-(benzyloxy)-2-(trimethylsilyl)-1-butene, 4-(benzyloxy)-1-(trimethylsilyl)-1-butene, and disilylated product in 1:1:1 ratio (65% combined yield). The reaction has been extended to distannylation of acetylenes.[17] The representative results are shown in Table 1.

Treatment of 5-(benzyloxy)-2-pentyne with the reagent which is believed to be (Me₃Si)₃MnMgMe (5a) gave 2,3-bis(trimethylsilyl)-2-alkene 6a in 78% yield. Meanwhile, the addition of H₂O (or D₂O, MeI) to the reaction mixture after stirring at 0°C for 20 min without warming up to room temperature gave monosilylated product 6b (71%) (or 6c (71%), 6d (70%)) along with the disilylated one 6a (13-20%).[18] Thus, the formation of disilylated alkenes may be explained as follows: (1) Addition of the reagent 5a to the triple bond in a <u>cis</u> fashion giving silylated alkenylmanganese A and (2) reductive elimination of manganese affording disilylated olefin. The <u>cis</u> addition of the Si-Mn component was confirmed by the following experiment. A monosilylated alkene, 5-(benzyloxy)-2-(dimethylphenylsilyl)-2-pentene was prepared from (PhMe₂Si)₃MnMgMe (5b) and 5-

Table 1. Disilylation or distannylation of acetylenes with Si-Mn or Sn-Mn reagent

$$RC{\equiv}CR^1 \xrightarrow[\text{(Me}_3\text{SnLi, MeMgI, MnCl}_2\text{)}]{\text{R}^2{}_3\text{SiLi, MeMgI, MnCl}_2} \begin{array}{c} R \quad\quad R^1 \\ {}^{\backslash}C{=}C^{\diagup} \\ R^2{}_3\text{Si} \quad \text{SiR}^2{}_3 \\ \text{(Me}_3\text{Sn)} \quad \text{(SnMe}_3\text{)} \end{array}$$

| Acetylene RC≡CR¹ | Reagent R²₃Si | Product Yield(%) | Product Z/E |
|---|---|---|---|
| HC≡CSiMe₃ | Me₃SiLi | 72 | ——— |
| n-C₆H₁₃C≡CH | Me₃SiLi | 66 | 33/67 |
| PhC≡CH | Me₃SiLi | 65 | 50/50 |
| n-C₆H₁₃C≡CSiMe₃ | Me₃SiLi | 80 | ——— |
| PhCH₂OCH₂CH₂C≡CH | Me₃SiLi | 55 | 50/50 |
| PhCH₂OCH₂CH₂C≡CH | PhMe₂SiLi | 51 | 42/58 |
| PhCH₂OCH₂CH₂C≡CD | PhMe₂SiLi | 55 | 42/58[a] |
| PhCH₂OCH₂CH₂C≡CSiMe₃ | Me₃SiLi | 59 | ——— |
| THPOCH₂CH₂C≡CH | Me₃SiLi | 63 | 65/35 |
| THPOCH₂CH₂C≡CH | PhMe₂SiLi | 70 | 65/35 |
| THPOCH₂CH₂C≡CSiMe₃ | Me₃SiLi | 83 | ——— |
| HOCH₂CH₂C≡CSiMe₃ | Me₃SiLi[b] | 58 | ——— |
| n-C₁₀H₂₁C≡CH | Me₃SnLi[c] | 56 | 100/0 |
| n-C₁₀H₂₁C≡CD | Me₃SnLi | 55 | 100/0 |
| THPOCH₂CH₂C≡CH | Me₃SnLi | 54 | 100/0 |
| THPOCH₂CH₂C≡CH | n-Bu₃SnLi[c] | 48 | 90/10 |
| PhCH₂OCH₂CH₂C≡CH | Me₃SnLi | 52 | 90/10 |

a) Deuterium was retained completely, thus reagents did not cause the acetylenic proton-metal exchange. b) Three millimoles of manganese reagent and 1.0 mmol of substrate were employed. c) Prepared from SnCl₂ and 3 equiv of alkyllithium. See Ref. 20.

(benzyloxy)-2-pentyne in the same way as **6b**. Protodesilylation with n-Bu$_4$NF[18] gave 5-(benzyloxy)-2-pentene. The $^1$H NMR spectra proved that the olefin had $\underline{Z}$ configuration (>95%, $\underline{J}$ = 11 Hz). Similar desilylation of **6b** failed.[19]
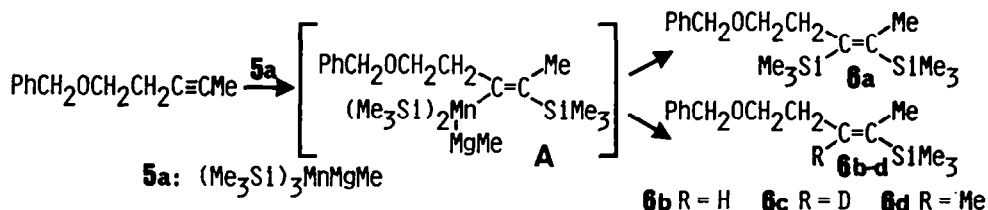


The reaction can be successfully applied to the synthesis of highly strained tetrakis(trimethylsilyl)ethene, which is not readily available by known methods.[20]
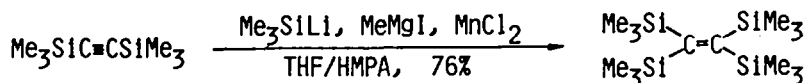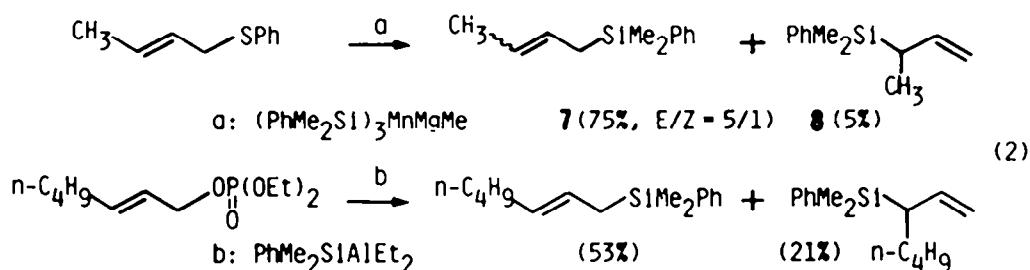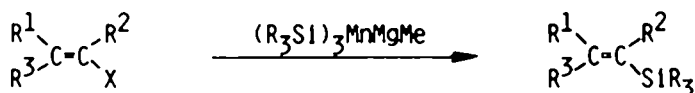


## (2) Synthesis of Vinylsilanes and Allylsilanes by Cross-coupling of Manganese Reagents with Alkenyl and Allylic Compounds

The organoaluminium reagent, PhMe$_2$SiAlEt$_2$, is effective for the transformation of enol phosphates or allylic phosphates into vinylsilanes or allylsilanes,[21] respectively.[22] Treatment of alkenyl halides (or alkenyl sulfides, or enol phosphates) or allylic sulfides (or allylic ethers)[23,24] with the Si-Mn reagent provides vinylsilanes or allylsilanes in an alternative way. Representative results are summarized in Table 2.

Points to be noted are as follows. (1) The reaction proceeded stereospecifically. Whereas (E)-1-iodo-1-dodecene gave (E)-dimethylphenylsilyl-1-dodecene exclusively upon treatment with the reagent **5b**, (Z)-1-iodo-1-dodecene provided the (Z) vinylsilane preferentially. In the latter case, low reaction temperature such as -95°C was essential in order to obtain high stereospecificity (Entry 4). (2) Not only alkenyl halides[25] but also alkenyl sulfides and enol phosphates were easily converted into the corresponding vinylsilanes. A vinyl ether such as 1-methoxycyclohexene reacted sluggishly with the manganese reagent to provide a trace of the desired vinylsilane (<5%). (3) The use of MeMgI was essential for the reaction. The reaction of cyclohexenyl diethyl phosphate with (R$_3$Si)$_3$MnLi gave cyclohexanone, possibly due to the nucleophilic attack of the reagent on the phosphorus atom. (4) The amount of Li$_2$MnCl$_4$ could be reduced to a catalytic amount. For instance, treatment of diethylcyclohexenyl phosphate with PhMe$_2$SiMgMe in the presence of 10 mol% of Li$_2$MnCl$_4$ gave the desired vinylsilane in 66% yield.

Allylic sulfides also smoothly coupled with **5b** to give the corresponding allylic silanes in good yields.[26,27] The results are shown in Table 3. The reaction proceeded with high regioselectivity. Both (E)-1-phenylthio-2-butene and 3-phenylthio-1-butene gave a 95:5 mixture of 1-dimethylphenylsilyl-2-butene (**7**) and the regioisomer, 3-dimethylphenylsilyl-1-butene (**8**). The silylanion appears to attack the less hindered site of the allylic system. Geranyl benzyl sulfide afforded geranylsilane exclusively. The selectivity is much higher than the reaction of allylic phosphates with PhMe$_2$SiAlEt$_2$[22] (eq. 2). Allylic ethers and halides such as 1-benzyloxy-2-butene, 1-tert-butyldimethylsiloxy-2-butene, and crotyl bromide easily reacted with the manganese reagent to give the corre-

corresponding allylsilanes.



$$\text{(2)}$$

Table 2. Synthesis of vinylsilanes with Si-Mn reagents[a]



| Entry | Substrate | | | | Reaction Conditions | | Product | |
|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | X | Temp(°C) | Time(h) | Y(%)[b] | E/Z |
| (PhMe₂Si)₃MnMgMe | | | | | | | | |
| 1 | Me(H) | H | H(Me) | Br[c] | 0 | 3 | 100 | 47/53 |
| 2 | n-C₆H₁₃ | H | H | I | 0 | 0.5 | 88 | 100/0 |
| 3 | n-C₁₀H₂₁ | H | H | I | 0 | 0.5 | 72 | 100/0 |
| 4 | H | H | n-C₁₀H₂₁ | I | 0 | 0.5 | 73 | 20/80 |
| 5 | H | H | n-C₁₀H₂₁ | I | -95 | 1.3 | 40[d] | 0/100 |
| 6 | H | H | Ph | Br | 25 | 1 | 70 | 39/61 |
| 7 | H | H | Ph | Br | -78 | 3 | 50 | 0/100 |
| 8 | Me | H | Me | Br | 0 | 0.5 | 70 | —— |
| 9 | n-C₁₀H₂₁ | H | Me | I | 0 | 2 | 75[e] | 100/0 |
| 10 | n-C₅H₁₁ | n-C₅H₁₁ | Me | I | 0 | 2 | 47[f] | 80/20 |
| 11 | -(CH₂)₄- | | H | Br | 0 | 2 | 93 | —— |
| 12 | (naphthalene, Br) | | | | 0 | 2 | 65 | —— |
| 13 | Ph | H | H | SMe | 0 | 1 | 70 | 100/0 |
| 14 | -(CH₂)₄- | | H | SMe | 0 | 1 | 75 | —— |
| 15 | H | n-C₆H₁₃ | H | OP(O)(OPh)₂ | 25 | 5 | 74 | —— |
| 16 | -(CH₂)₄- | | H | OP(O)(OEt)₂ | 0 | 1 | 66 | —— |
| 17 | H | n-C₃H₇ | H | OSO₂CF₃ | 0 | 1 | 99 | —— |
| (Me₃Si)₃MnMgMe | | | | | | | | |
| 18 | H | n-C₁₀H₂₁ | H | I | 0 | 3 | 100 | —— |
| 19 | n-C₁₀H₂₁ | H | H | I | -95 | 2 | 100 | 30/70 |
| 20 | -(CH₂)₆- | | H | SPh | 0 | 3 | 89 | —— |

a) Manganese reagent (1.5 mmol) and substrate (1.0 mmol) were employed. b) Isolated yields. c) Commercially available 1-bromo-1-propene (Aldrich Chemical Co.) was used ($E/Z$ = 40/60). d) Starting material was recovered (30%). e) 2-Methyl-1-dodecene was obtained as byproduct (5% yield). f) ($Z$)-6-Methyl-6-dodecene was also obtained (25% yield).

Table 3.   Synthesis of allylsilanes by cross coupling of allylic sulfides and ethers with Si-Mn reagent[a]



| Starting Material | Product Yield(%)[b] | Starting Material | Product Yield(%)[b] |
|---|---|---|---|
|  |  (91) |  |  [c,d] (84) |
|  |  (60) |  |  (98) |
|  | 7(88)[e]  8(2) |  R" = CH₂Ph | 7 (65)[f]  8 (5) |
| | | R" = SiMe₂ᵗBu | 7 (71)[g]  8 (2) |
|  |  (89) | | |
|  |  (56) [c] |  | 7 (80)  8 (2) |

a) Reactions were performed at 0°C for 30 min.  Two mmol of the reagent and one mmol of substrate were employed.   b) Isolated yields.   c) (Me₃Si)₃MnMgMe was used instead of (PhMe₂Si)₃MnMgMe.   d) Reaction mixture was stirred for 15 h.   e) E/Z = 2/1.   f) E/Z = 20/1.   g) E/Z = 20/1.

(3) Silylmanganation of 1,3-dienes

    In the first section of this paper, we have reported addition reactions of (R₃Si)₃MnMgMe reagents to acetylenic compounds to give disilylated alkenes.  In further extension, we have examined the reaction of 1,3-dienes with (R₃Si)₃MnMgMe and observed the selective formation of vinylsilanes after quenching with carbonyl compounds.[28,29]  Table 4 summarizes further examples.  Quenching with MeI gave a mixture of

    Treatment of isoprene with the reagent (PhMe₂Si)₃MnMgMe gave a mixture of (E)-3-deuterio-1-dimethylphenylsilyl-3-methyl-1-butene (9) and 1-deuterio-1-dimethylphenylsilyl-3-methyl-2-butene (10) (9:10 = 1:5) after quenching with D₂O.  Table 4 summarizes further examples.  Quenching with MeI gave a mixture of (E)-3,3-dimethyl-1-dimethylphenylsilyl-1-butene 11 (E = Me) and 4-dimethyl-phenylsilyl-2-methyl-2-pentene 12 (E = Me) (11:12 = 1:2) in 90% combined yield.  In contrast, addition of aldehyde or ketone to the silylated allylmanganese intermediate gave (E)-vinylsilane 11 as a single product.
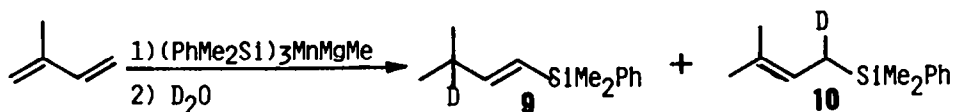


    The reagent 5b possibly adds to isoprene in 1,2-fashion (or 1,4 fashion) to give the hypothetical intermediates B and C, the latter being produced by β-

elimination of Mn-H and successive readdition. Alicyclic dienes such as cyclo-pentadiene and 1,3-cyclooctadiene were reluctant to react. The reagents PhMe$_2$SiLi or PhMe$_2$SiMgMe did not react with isoprene and the manganese atom played a key role in the reaction. The addition of MeMgI was essential for the complete isomerization of **B** to **C**. Treatment of isoprene with (PhMe$_2$Si)$_3$MnLi derived from PhMe$_2$SiLi and MnCl$_2$ gave 4-dimethylphenylsilyl-2-methyl-1-butene (30%) arising from **B** along with 11 (E ⁼ H, 10%) and 12 (E = H, 39%) after quenching with water.



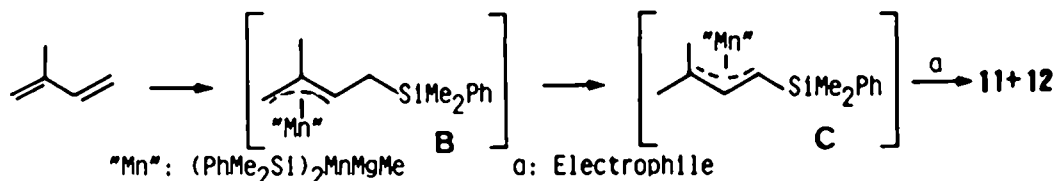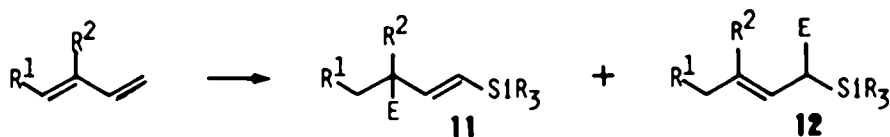"Mn": (PhMe$_2$Si)$_2$MnMgMe          a: Electrophile

Table 4. Silylmanganation of 1,3-dienes with Si-Mn reagent



| Entry | Diene R$^1$ | R$^2$ | Reagent | Electrophile | Product 11 | Y(%) 12 |
|---|---|---|---|---|---|---|
| 1 | H | H | (PhMe$_2$Si)$_3$MnMgMe | D$_2$O | 44 | 25 |
| 2 | | | | MeI | 11 | 69 |
| 3 | | | | PhCHO | 70[a) | 0 |
| 4 | | | | PhCH=CHCHO | 44[b) | 0 |
| 5 | | | | CH$_3$CH=CHCHO | 88[b) | 0 |
| 6 | | | | Me$_2$CO | 95 | 0 |
| 7 | | | (Me$_3$Si)$_3$MnMgMe | PhCHO | 82 | 0 |
| 8 | | | | CH$_3$CH=CHCHO | 50[b) | 0 |
| 9 | H | Me | (PhMe$_2$Si)$_3$MnMgMe | D$_2$O | 13 | 65 |
| 10 | | | | MeI | 30 | 60 |
| 11 | | | | n-BuCHO | 85 | 0 |
| 12 | | | | PhCHO | 78 | 0 |
| 13 | | | | PhCH=CHCHO | 74[b) | 0 |
| 14 | | | (Me$_3$Si)$_3$MnMgMe | n-C$_8$H$_{17}$CHO | 52 | 0 |
| 15 | | | | PhCHO | 77 | 0 |
| 16 | | | | CH$_3$CH=CHCHO | 75[b) | 0 |
| 17 | | | | Me$_2$CO | 76 | 0 |
| 18 | Me | H | (PhMe$_2$Si)$_3$MnMgMe | D$_2$O | 46 | 46 |
| 19 | | | | PhCHO | 68 | 0 |

a) Erythro/threo = 1/1.   b) Only 1,2-adducts were obtained.

The presence of a large excess (10 equiv) of the carbonyl electrophiles such as PhCHO and PhCH=CHCHO caused Oppenauer type oxidation to give ketones as the main products. For instance, treatment of a solution of 13 (1.0 mmol) derived from isoprene and 5a with PhCHO (10 mmol) afforded 2,2-dimethyl-1-phenyl-4-(trimethylsilyl)-3-buten-1-one (14) in 68% yield along with 2,2-dimethyl-1-phenyl-4-(trimethylsilyl)-3-buten-1-ol (24%) and PhCH$_2$OH.
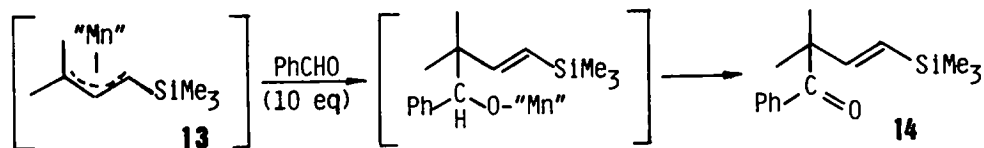


## Experimental

Distillation of the products were performed by use of Kugelrohr (Büchi), and boiling points are indicated by an air bath temperature without correction. ^{1}H-NMR spectra were taken on a Varian XL-200 spectrometer, CDCl$_3$ was used as solvent, chemical shifts being given in δ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl.

General Procedure for the Generation of Silylmanganate Reagents. An ethereal solution of MeMgI (1.1 M, 4.1 ml, 4.5 mmol) was added to a THF solution of Me$_2$PhSiLi[30] (0.75 M, 6.0 ml, 4.5 mmol) (or a THF-HMPA (10 ml, 4:1) solution of Me$_3$SiLi (prepared in situ from 6.0 mmol of hexamethyldisilane and 4.5 mmol of MeLi-LiBr complex[15]) at 0 °C under an argon atmosphere. After stirring for 15 min, a THF solution of Li$_2$MnCl$_4$[31] (1.0 M, 1.5 ml, 1.5 mmol) was added. The resulting dark brown mixture was stirred for an additional 15 min before use.

General Procedure for the Disilylation of Acetylenes. A solution of tetrahydropyranyl ether of 4-(trimethylsilyl)-3-butyn-1-ol (0.23 g, 1.0 mmol) in THF (3.0 ml) was added to a solution of (Me$_3$Si)$_3$MnMgMe (1.5 mmol) in THF-HMPA and the resulting mixture was stirred for 3 h at 0 °C. The mixture was diluted with ether and poured into saturated NH$_4$Cl. Purification by preparative tlc on silica-gel gave tetrahydropyranyl ether of 3,4,4-tris(trimethylsilyl)-3-buten-1-ol (0.31 g) in 83% yield as a colourless oil: bp 150 °C (1.0 Torr, bath temp); IR (neat) 1440, 1350, 1260, 1250, 1200, 1140, 1120, 1030, 840 cm$^{-1}$; NMR (CDCl$_3$) δ 0.19 (s, 9H), 0.22 (s, 9H), 0.23 (s, 9H), 1.5-1.9 (m, 1H), 2.89 (t, J = 8 Hz, 2H), 3.36 (dt, J = 8, 10 Hz, 1H), 4.61 (t, J = 3 Hz, 1H); MS, m/z 372 (M$^+$, 1), 270 (64), 197 (43), 155 (48), 85 (100), 73 (99). Found: C, 58.02; H, 11.06%. Calcd for C$_{18}$H$_{40}$O$_2$Si$_3$: C, 58.00; H, 10.82%.

Tris(trimethylsilyl)ethene: bp 85 °C (15 Torr, bath temp); IR (neat) 2950, 1250, 900, 840, 680 cm$^{-1}$; NMR (CDCl$_3$) δ 0.09 (s, 9H), 0.16 (s, 9H), 0.17 (s, 9H), 7.34 (s, 1H); MS, m/z 244 (M$^+$, 3), 229 (2), 156 (11), 73 (100), 45 (14). Found: C, 54.20; H, 11.79%. Calcd for C$_{11}$H$_{28}$Si$_3$: C, 54.02; H, 11.54%.

(E)-1,2-Bis(trimethylsilyl)-1-octene: bp 90 °C (2 Torr, bath temp); IR (neat) 2950, 2930, 2850, 1250, 840, 760, 690 cm$^{-1}$; NMR (CDCl$_3$) δ 0.07 (s, 9H), 0.11 (s, 9H), 0.89 (t, J = 4 Hz, 3H), 1.25-1.37 (m, 8H), 2.21-2.27 (m, 2H), 5.97 (s, 1H); MS, m/z 256 (M$^+$, 1), 241 (6), 186 (40), 167 (23), 98 (39), 73 (100). Analytical sample was prepared by preparative glc (t$_r$ = 3 min, Silicone OV 17, 3% on Uniport HP, 2 m, 120 °C). Found: C, 65.53; H, 12.76%. Calcd for C$_{14}$H$_{32}$Si$_2$: C, 65.54; H, 12.57%.

(Z)-1,2-Bis(trimethylsilyl)-1-octene: bp 90 °C (2 Torr, bath temp); IR (neat)

2950, 2930, 2850, 1250, 840, 760, 690 cm$^{-1}$; NMR (CDCl$_3$) δ 0.13 (s, 9H), 0.15 (s, 9H), 0.88 (t, $J$ = 4 Hz, 3H), 1.4-1.6 (m, 8H), 2.17 (dt, $J$ = 1, 4 Hz, 2H), 6.27 (d, $J$ = 1 Hz, 1H); MS, $m/z$ 241 (M$^+$-CH$_3$, 6), 186 (20), 167 (16), 98 (35), 73 (100); $t_r$ = 5 min, Silicone OV 17, 3% on Uniport HP 2m, 120 °C. Found: C, 65.65; H, 12.82%. Calcd for C$_{14}$H$_{32}$Si$_2$: C, 65.54; H, 12.57%.

1,1,2-Tris(trimethylsilyl)-1-octene: bp 120 °C (3 Torr, bath temp); IR (neat) 2950, 2920, 1470, 1410, 1380, 1250, 870, 840 cm$^{-1}$; NMR (CDCl$_3$) δ 0.19 (s, 18H), 0.20 (s, 9H), 0.89 (t, $J$ = 7 Hz, 3H), 1.21-1.36 (m, 8H), 2.50 (t, $J$ = 9 Hz, 2H); MS, $m/z$ 328 (M$^+$, 8), 313 (8), 255 (41), 167 (100), 155 (34), 131 (37), 73 (51). Found: C, 62.29; H, 12.37%. Calcd for C$_{17}$H$_{40}$Si$_3$: C, 62.11; H, 12.26%.

(E)-1,2-Bis(trimethylsilyl)-4-benzyloxy-1-butene: bp 120 °C (1 Torr, bath temp); IR (neat) 2950, 2890, 2850, 1450, 1360, 1250, 1100, 840 cm$^{-1}$; NMR (CDCl$_3$) δ 0.05 (s, 9H), 0.11 (s, 9H), 2.63 (t, $J$ = 8 Hz, 2H), 3.41 (t, $J$ = 8 Hz, 2H), 4.52 (s, 2H), 6.11 (s, 1H), 7.26-7.37 (m, 5H); MS, $m/z$ 291 (M$^+$-CH$_3$, 1), 200 (4), 179 (17), 147 (5), 112 (32), 91 (100), 73 (71). Pure sample was obtained by preparative glc, $t_r$ = 6 min, Silicone OV 17, 3% on Uniport HP 2 m, 170 °C. Found: C, 66.60; H, 9.98%. Calcd for C$_{17}$H$_{30}$Si$_2$: C, 66.60; H, 9.86%.

(Z)-1,2-Bis(trimethylsilyl)-4-benzyloxy-1-butene: bp 120 °C (1 Torr, bath temp); IR (neat) 2950, 2900, 2850, 1450, 1360, 1250, 1100, 860, 830, 750, 730, 690 cm$^{-1}$; NMR (CDCl$_3$) δ 0.13 (s, 9H), 0.15 (s, 9H), 2.52 (dt, $J$ = 1, 8 Hz, 2H), 3.47 (t, $J$ = 8 Hz, 2H), 4.51 (s, 2H), 6.38 (t, $J$ = 1 Hz, 1H), 7.27-7.36 (m, 5H); MS, $m/z$ 291 (M$^+$-CH$_3$, 1), 179 (20), 147 (6), 112 (33), 91 (100), 73 (71); $t_r$ = 10 min, Silicone OV 17, 3% on Uniport HP 2 m, 170 °C. Found: C, 66.85; H, 10.10%. Calcd for C$_{17}$H$_{30}$Si$_2$: C, 66.60; H, 9.86%.

1,2-Bis(dimethylphenylsilyl)-4-benzyloxy-1-butene (E/Z = 1/1): bp 160 °C (0.3 Torr, bath temp); IR (neat) 2950, 1430, 1250, 1110, 840, 820, 730, 700 cm$^{-1}$; NMR (CDCl$_3$) δ 0.19 (s, 3H), 0.25 (s, 3H), 0.35 (s, 3H), 0.39 (s, 3H), 2.58 (t, $J$ = 8 Hz, 1H), 2.60 (t, $J$ = 8 Hz, 1H), 4.18 (s, 1H), 4.44 (s, 1H), 6.40 (s, 0.5H), 6.72 (s, 0.5H), 7.2-7.6 (m, 15H); MS, $m/z$ 415 (M$^+$-CH$_3$, 0.2), 324 (5), 135 (100), 91 (60). Found: C, 75.38; H, 8.11%. Calcd for C$_{27}$H$_{34}$OSi$_2$: C, 75.29; H, 7.96%.

4-Benzyloxy-1,1,2-tris(trimethylsilyl)-1-butene: bp 140 °C (1 Torr, bath temp); IR (neat) 1450, 1360, 1260, 1250, 1100, 870, 830 cm$^{-1}$; NMR (CDCl$_3$) δ 0.16 (s, 9H), 0.17 (s, 9H), 0.19 (s, 9H), 2.90 (t, $J$ = 7 Hz, 2H), 3.38 (t, $J$ = 7 Hz, 2H), 4.49 (s, 2H), 7.3-7.4 (m, 5H); MS, $m/z$ 278 (M$^+$, 2), 205 (4), 199 (9), 155 (21), 143 (19), 91 (100), 73 (73). Found: C, 63.48; H, 10.33%. Calcd for C$_{20}$H$_{38}$Si$_3$: C, 63.42; H, 10.11%.

Tetrahydropyranyl Ether of (E)-3,4-Bis(trimethylsilyl)-3-buten-1-ol: bp 105 °C (3 Torr, bath temp); IR (neat) 2950, 1250, 1140, 1120, 1040, 840 cm$^{-1}$; NMR (CDCl$_3$) δ 0.08 (s, 9H), 0.14 (s, 9H), 1.5-1.6 (m, 6H), 2.62 (t, $J$ = 8 Hz, 2H), 3.34 (dt, $J$ = 8, 8 Hz, 1H), 3.4-3.55 (m, 1H), 3.69 (td, $J$ = 8, 10 Hz, 1H), 3.8-3.95 (m, 2H), 4.61 (t, $J$ = 3 Hz, 1H), 6.12 (s, 1H); MS, $m/z$ 227 (M$^+$-SiMe$_3$, 1), 173 (11), 85 (100), 73 (41); $t_r$ = 4 min, Silicone OV 17 3% on Uniport HP 2 m, 160 °C. Found: C, 59.70; H, 10.96%. Calcd for C$_{15}$H$_{32}$O$_2$Si$_2$: C, 59.94; H, 10.73%.

Tetrahydropyranyl Ether of (Z)-3,4-Bis(trimethylsilyl)-3-buten-1-ol: bp 105 °C (3 Torr, bath temp); IR (neat) 2900, 1250, 1140, 1120, 1040, 860, 840 cm$^{-1}$; NMR (CDCl$_3$) δ 0.13 (s, 9H), 0.17 (s, 9H), 1.5-1.6 (m, 6H), 2.49 (dt, $J$ = 1, 8 Hz, 2H), 3.38 (dt, $J$ = 8, 8 Hz, 1H), 3.4-3.55 (m, 1H), 3.66 (td, $J$ = 8, 10 Hz, 1H), 3.8-3.95 (m, 2H), 4.60 (t, $J$ = 3 Hz, 1H), 6.40 (t, $J$ = 1 Hz, 1H); MS, $m/z$ 285 (M$^+$-CH$_3$, 0.1), 201 (7), 173 (22), 85 (100), 73 (42); $t_r$ = 6.5 min, Silicone OV 17 3% on Uniport HP 2 m, 160 °C. Found: C, 60.10; H, 10.96%. Calcd for C$_{15}$H$_{32}$O$_2$Si$_2$: C, 59.94; H, 10.73%.

Tetrahydropyranyl Ether of 3,4-Bis(dimethylphenylsilyl)-3-buten-1-ol (E/Z =
2/1): bp 160 °C (0.3 Torr, bath temp); IR (neat) 2950, 1430. 1250, 1110, 1030,
840, 820, 700 cm$^{-1}$; NMR (CDCl$_3$) E-isomer: δ 0.39 (s, 6H), 0.42 (s, 6H), 1.4-1.6
(m, 6H), 3.09 (dt, J = 8, 10 Hz, 1H), 3.3-3.6 (m, 3H), 3.6-3.9 (m, 2H), 4.24 (t,
J = 3 Hz, 1H), 6.41 (s, 1H), 7.2-7.4 (m, 3H), 7.4-7.6 (m, 2H). Z-isomer: δ
0.18 (s, 6H), 0.28 (s, 6H), 1.4-1.6 (m, 6H), 3.1 (m, 1H), 3.3-3.6 (m, 3H), 3.6-
3.9 (m, 2H), 4.54 (t, J = 3 Hz, 1H), 6.73 (s, 1H), 7.2-7.4 (m, 3H), 7.4-7.6 (m,
2H); MS, m/z 409 (M$^+$-CH$_3$, 0.1), 235 (50), 135 (64), 85 (100). Found: C, 70.92;
H, 8.77%. Calcd for C$_{25}$H$_{36}$O$_2$Si$_2$: C, 70.70; H, 8.54%.

(Z)-Tetrahydropyranyl Ether of 1,2-Bis(trimethylstannyl)-3-buten-1-ol: bp 110
°C (0.1 Torr, bath temp); IR (neat) 2950, 2920, 1350, 1120, 1030, 730 cm$^{-1}$; NMR
(CDCl$_3$) δ 0.16 (s, 9H), 0.19 (s, 9H), 1.5-1.8 (m, 6H), 3.62 (dt, J = 1, 5 Hz,
2H), 3.4-3.5 (m, 2H), 3.7-3.9 (m, 2H), 4.59 (t, J = 3 Hz, 1H), 6.75 (d, J = 1
Hz, 1H).

2,3-Bis(dimethylphenylsilyl)-5-benzyloxy-2-pentene: bp 120 °C (1 Torr, bath
temp); IR (neat) 2920, 1240, 1090, 840, 830 cm$^{-1}$; NMR (CDCl$_3$) δ 0.15 (s, 9H),
0.16 (s, 9H), 1.85 (s, 3H), 2.67 (t, J = 7 Hz, 2H), 3.34 (t, J = 7 Hz, 2H), 4.51
(s, 2H), 7.25-7.35 (m, 5H); MS, m/z 305 (M$^+$-CH$_3$, 0.1), 179 (53), 91 (99), 73
(100). Found: C, 67.39; H, 10.33%. Calcd for C$_{18}$H$_{32}$OSi$_2$: C, 67.43; H,
10.06%.

(E)-5-Benzyloxy-2-trimethylsilyl-2-pentene: bp 100 °C (2 Torr, bath temp); IR
(neat) 2950, 2850, 1620, 1250, 1100, 840 cm$^{-1}$; NMR (CDCl$_3$) δ 0.04 (s, 9H), 1.68
(dt, J = 1, 1 Hz, 3H), 2.44 (qdt, J = 1, 6, 7 Hz, 2H), 3.51 (t, J = 7 Hz, 2H),
4.54 (s, 2H), 5.73 (qt, J = 1, 6 Hz, 1H), 7.27-7.37 (m, 5H); MS, m/z 233 (M$^+$-
CH$_3$, 1), 143 (20), 99 (20), 91 (100), 73 (42). Found: C, 72.52; H, 10.02%.
Calcd for C$_{15}$H$_{24}$OSi: C, 72.52; H, 9.74%.

(E)-5-Benzyloxy-3-deuterio-2-trimethylsilyl-2-pentene: bp 100 °C (2 Torr, bath
temp); IR (neat) 2950, 2850, 1600, 1250, 1100, 840 cm$^{-1}$; NMR (CDCl$_3$) δ 0.04 (s,
9H), 1.68 (s, 3H), 2.43 (t, J = 7 Hz, 2H), 3.51 (t, J = 7 Hz, 2H), 4.53 (s, 2H),
7.27-7.37 (m, 5H); MS, m/z 234 (M$^+$-CH$_3$, 1), 144 (11), 100 (12), 91 (100), 73
(61). Found: C, 72.21; H, 10.31%. Calcd for C$_{15}$H$_{23}$DOSi: C, 72.23; H, 10.10%.

(E)-5-Benzyloxy-3-methyl-2-trimethylsilyl-2-pentene: bp 160 °C (1 Torr, bath
temp); IR (neat) 2900, 2800, 1600, 1440, 1350, 1240, 1090, 830 cm$^{-1}$; NMR (CDCl$_3$)
δ 0.11 (s, 9H), 1.5 (m, 3H), 1.8 (m, 3H), 2.46 (t, J = 9 Hz, 2H), 3.50 (t, J = 9
Hz, 2H), 4.52 (s, 2H), 7.3 (m, 5H); MS, m/z 247 (M$^+$-CH$_3$, 1), 179 (37), 156 (25),
91 (65), 73 (100). Found: C, 73.09; H, 10.07%. Calcd for C$_{16}$H$_{26}$OSi: C,
73.22; H, 9.98%.

Tetrakis(trimethylsilyl)ethene. The compound was obtained following the
general procedure described above (76% yield). The physical data of the sample
were identical with those in the literature.[20] mp 102 °C; $^1$H-NMR (CDCl$_3$) δ 0.06
(s, 36H); $^{13}$C-NMR (CDCl$_3$) δ 4.3, 195.4; MS, m/z 316 (M$^+$, 1), 155 (56), 131 (23),
73 (100). Found: m/z 316.1873. Calcd for C$_{14}$H$_{36}$Si$_4$: M$^+$, 316.1895.

The Reaction between Silylmanganate Reagents and Hetero Substituted Olefinic
Compounds. Following procedure is representative. A THF solution of 1-cyclo-
hexenyl diethyl phosphate (0.12 g, 0.50 mmol) was added to a THF solution of
(PhMe$_2$Si)$_3$MnMgMe (1.5 mmol) and resulting mixture was stirred for 2 h at room
temperature. Workup and purification by preparative tlc gave 1-(dimethylphenyl-
silyl)-1-cyclohexene (70 mg, 65% yield): bp 67 °C (2 Torr, bath temp); IR
(neat) 2924, 1615, 1428, 1247, 1112, 1062, 827, 807, 769, 728, 698, 650 cm$^{-1}$;
NMR (CDCl$_3$) δ 0.31 (s, 6H), 1.5-1.7 (m, 4H), 1.9-2.1 (m, 4H), 6.0-6.1 (m, 1H),
7.3-7.4 (m, 3H), 7.5-7.6 (m, 2H). Found: C, 77.81; H, 9.47%. Calcd for
C$_{14}$H$_{20}$Si: C, 77.71; H, 9.32%. The physical data of 1-(dimethylphenylsilyl)-1-
propene,[32] (E) and (Z)-2-(dimethylphenylsilyl)styrene[4,5], and 1-(dimethylphenyl-

silyl)-2-methyl-1-dodecene[19] were identical with those of authentic samples.

6-(Dimethylphenylsilyl)-7-methyl-6-dodecene (E:Z = 80:20): bp 133 °C (0.1 Torr, bath temp); IR (neat) 2954, 2930, 2854, 1466, 1428, 1247, 1110, 830, 814, 770, 728, 698 cm$^{-1}$; NMR (CDCl$_3$) δ 0.24 (s, 1.2H), 0.34 (s, 4.8H), 0.7-1.0 (m, 6H), 1.0-1.5 (m, 12H), 1.61 (s, 2.4H), 1.72 (s, 0.6H), 1.9-2.2 (m, 4H), 7.3-7.4 (m, 3H), 7.4-7.6 (m, 2H). Found: C, 79.62; H, 11.60%. Calcd for C$_{21}$H$_{36}$Si: C, 79.67; H, 11.46%.

(E)-1-(Dimethylphenylsilyl)-1-octene: bp 66 °C (2 Torr, bath temp); IR (neat) 2954, 2924, 2852, 1617, 1428, 1247, 1114, 989, 840, 821, 728, 698 cm$^{-1}$; NMR (CDCl$_3$) δ 0.31 (s, 6H), 0.88 (t, J = 6.8 Hz, 3H), 1.2-1.5 (m, 8H), 2.13 (ddt, J = 6.2, 1.4, 6.0 Hz, 2H), 5.76 (dt, J = 18.5, 1.4 Hz, 1H), 6.12 (dt, J = 18.5, 6.2 Hz, 1H), 7.3-7.4 (m, 3H), 7.5-7.6 (m, 2H). Found: C, 77.74; H, 10.77%. Calcd for C$_{16}$H$_{26}$Si: C, 77.97; H, 10.63%.

2-(Dimethylphenylsilyl)-1-octene: bp 80 °C (2 Torr, bath temp); IR (neat) 2954, 2924, 2852, 1459, 1428, 1248, 1112, 924, 832, 816, 774, 729, 698 cm$^{-1}$; NMR (CDCl$_3$) δ 0.36 (s, 6H), 0.85 (t, J = 6.8 Hz, 3H), 1.1-1.7 (m, 8H), 2.11 (tm, J = 7.6 Hz, 2H), 5.39 (dt, J = 3.0, 1.0 Hz, 1H), 5.67 (dt, J = 3.0, 1.5 Hz, 1H), 7.3-7.4 (m, 3H), 7.5-7.6 (m, 2H). Found: C, 77.75; H, 10.90%. Calcd for C$_{16}$H$_{26}$Si: C, 77.97; H, 10.63%.

2-(Dimethylphenylsilyl)-1-pentene: bp 70 °C (2 Torr, bath temp); IR (neat) 2954, 2924, 2854, 1460, 1428, 1248, 1111, 831, 728, 697 cm$^{-1}$; NMR (CDCl$_3$) δ 0.36 (s, 6H), 0.83 (t, J = 7.1 Hz, 3H), 1.2-1.4 (m, 4H), 2.11 (tm, J = 7.5 Hz, 2H), 5.39 (dt, J = 3.0, 1.0 Hz, 1H), 5.68 (dt, J = 3.0, 1.5 Hz, 1H), 7.3-7.4 (m, 3H), 7.5-7.6 (m, 2H). Found: C, 76.12; H, 10.07%. Calcd for C$_{13}$H$_{20}$Si: C, 76.40; H, 9.86%.

2-(Trimethylsilyl)-1-dodecene: bp 95 °C (2 Torr, bath temp); IR (neat) 2952, 2922, 2852, 1466, 1459, 1247, 922, 836, 754, 688 cm$^{-1}$; NMR (CDCl$_3$) δ 0.08 (s, 9H), 0.88 (t, J = 6.8 Hz, 3H), 1.27 (br.s, 14H), 1.2-1.5 (m, 2H), 2.12 (t, J = 6.3 Hz, 2H), 5.30 (dt, J = 3.1, 1.0 Hz, 1H), 5.55 (dt, J = 3.1, 1.5 Hz, 1H). Found: C, 74.90; H, 13.69%. Calcd for C$_{15}$H$_{32}$Si: C, 74.91; H, 13.41%.

5-(Dimethylphenylsilyl)-4-nonene: bp 123 °C (2 Torr, bath temp); IR (neat) 2954, 2924, 2856, 1611, 1466, 1459, 1427, 1247, 1109, 830, 814, 770, 728, 698 cm$^{-1}$; NMR (CDCl$_3$) δ 0.33 (s, 6H), 0.82 (t, J = 6.6 Hz, 3H), 0.90 (t, J = 6.8 Hz, 3H), 1.19 (br.s, 6H), 1.3-1.4 (m, 4H), 2.0-2.2 (m, 4H), 5.80 (t, J = 6.9 Hz, 1H), 7.3-7.4 (m, 3H), 7.5-7.6 (m, 2H). Found: C, 78.86; H, 11.44%. Calcd for C$_{19}$H$_{32}$Si: C, 79.09; H, 11.18%.

The Reaction of Silylmanganate Reagents with Conjugated Dienes. A typical procedure is as follows. To a THF solution of (PhMe$_2$Si)$_3$MnMgMe (1.5 mmol) was added a THF solution of 1,3-butadiene (1.5 M, 1.0 ml, 1.5 mmol) at 0 °C and the mixture was stirred for 15 min. Benzaldehyde (0.16 g, 1.5 mmol) was added to the solution and stirring was continued for 1 h at room temperature. The reaction mixture was diluted by hexane and 0.5 ml of saturated aqueous ammonium chloride was added. After additional stirring for 10 min, the supernatant was decanted, dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. Purification by preparative tlc on silica-gel afforded (E)-4-(dimethyl-phenylsilyl)-2-methyl-1-phenyl-3-buten-1-ol (1:1 mixture of diastereoisomers): bp 140 °C (2 Torr, bath temp); IR (neat) 3370 (broad), 2956, 1612, 1453, 1427, 1248, 1112, 1019, 998, 842, 730, 698 cm$^{-1}$; NMR (CDCl$_3$) δ 0.26 (s, 1.5H), 0.27 (s, 1.5H), 0.34 (s, 3.0H), 0.88 (d, J = 6.8 Hz, 1.5H), 1.04 (d, J = 6.8 Hz, 1.5H), 2.01 (br.s, 0.5H), 2.12 (br.s, 0.5H), 2.53 (ddq, J = 7.6, 7.1, 6.8 Hz, 0.5H), 2.61 (ddq, J = 6.6, 5.8, 6.8 Hz, 0.5H), 4.40 (d, J = 7.6 Hz, 0.5H), 4.56 (d, J = 5.8 Hz, 0.5H), 5.74 (dd, J = 18.9, 1.1 Hz, 0.5H), 5.95 (d, J = 18.8 Hz, 0.5H), 5.99 (dd, J = 18.9, 6.6 Hz, 0.5H), 6.10 (dd, J = 18.8, 7.1 Hz, 0.5H),

7.2-7.6 (m, 10H).  Found: C, 77.10; H, 8.36%.  Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16%.

A 1:6 Mixture of (E)-1-(Dimethylphenylsilyl)-3-methyl-1-butene and 4-(Dimethyl-phenylsilyl)-2-pentene:  bp 115 °C (22 Torr, bath temp); IR (neat) 2956, 1428, 1249, 1113, 834, 776, 729, 699 cm$^{-1}$; NMR (CDCl$_3$) δ 0.25 (s, 2.58H), 0.27 (s, 2.58H), 0.32 (s, 0.84H), 1.00 (d, J = 7.0 Hz, 3.42H), 1.46 (dd, J = 6.5, 1.4 Hz, 2.58H), 2.09 (dq, J = 10.5, 7.2 Hz, 0.86H), 2.2-2.4 (m, 0.14H), 5.1-5.5 (m, 1.72H), 5.71 (dd, J = 18.7, 1.4 Hz, 0.14H), 6.10 (dd, J = 18.7, 5.8 Hz, 0.14H), 7.3-7.4 (m, 3H), 7.5-7.6 (m, 2H).  Found: C, 76.59; H, 9.97%.  Calcd for $C_{13}H_{20}Si$: C, 76.40; H, 9.86%.

(1E, 5E)-6-(Dimethylphenylsilyl)-4-methyl-1-phenyl-1,5-hexadien-3-ol (1:1 mixture of diastereoisomers):  bp 160 °C (2 Torr, bath temp); IR (neat) 3348 (br), 2958, 1613, 1450, 1428, 1249, 1113, 966, 843, 828, 787, 762, 731, 693, 663 cm$^{-1}$; NMR (CDCl$_3$) δ 0.32 (s, 1.5H), 0.33 (s, 1.5H), 0.35 (s, 3H), 1.07 (d, J = 6.8 Hz, 1.5H), 1.10 (d, J = 6.8 Hz, 1.5H), 2.4-2.6 (m, 1H), 4.10 (dd, J = 6.9, 6.3 Hz, 0.5H), 4.2-4.3 (m, 0.5H), 5.91 (dd, J = 18.7, 0.9 Hz, 0.5H), 5.96 (d, J = 18.8 Hz, 0.5H), 6.0-6.3 (m, 2H), 6.57 (dd, J = 16.0, 1.1 Hz, 0.5H), 7.2-7.5 (m, 8H), 7.5-7.7 (m, 2H).  Found: C, 78.47; H, 8.24%.  Calcd for $C_{21}H_{26}OSi$: C, 78.21; H, 8.13%.

(1E, 5E)-1-(Dimethylphenylsilyl)-3-methyl-1,5-heptadien-4-ol (1:1 mixture of diastereoisomers):  bp 88 °C (2 Torr, bath temp); IR (neat) 3352 (br), 2956, 1613, 1428, 1248, 1114, 998, 966, 842, 824, 730, 698 cm$^{-1}$; NMR (CDCl$_3$) δ 0.32 (s, 3H), 0.33 (s, 3H), 0.99 (d, J = 7.4 Hz, 1.5H), 1.04 (d, J = 6.4 Hz, 1.5H), 1.6-1.7 (m, 3H), 2.2-2.5 (m, 1H), 3.82 (dd, J = 7.8, 7.2 Hz, 0.5H), 3.96 (dd, J = 6.8, 6.0 Hz, 0.5H), 5.4-5.8 (m, 2H), 5.85 (dd, J = 19.0, 1.1 Hz, 0.5H), 5.92 (d, J = 19.0 Hz, 0.5H), 6.05 (dd, J = 19.0, 6.9 Hz, 0.5H), 6.08 (dd, J = 19.0, 6.6 Hz, 0.5H), 7.3-7.4 (m, 3H), 7.4-7.6 (m, 2H).  Found: C, 73.82; H, 9.54%.  Calcd for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29%.

(E)-2,3-Dimethyl-5-(dimethylphenylsilyl)-4-penten-2-ol:  bp 90 °C (2 Torr, bath temp); IR (neat) 3372 (br), 2968, 1612, 1428, 1371, 1248, 1114, 843, 825, 728, 698 cm$^{-1}$; NMR (CDCl$_3$) δ 0.34 (s, 6H), 1.05 (d, J = 6.9 Hz, 3H), 1.17 (d, J = 4.3 Hz, 3H), 1.56 (br.s, 1H), 2.27 (ddq, J = 7.7, 0.6, 6.9 Hz, 1H), 5.88 (dd, J = 18.7, 0.6 Hz, 1H), 6.10 (dd, J = 18.7, 7.7 Hz, 1H), 7.3-7.4 (m, 3H), 7.5-7.6 (m, 2H).  Found: C, 72.79; H, 9.95%.  Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74%.

(E)-2-Methyl-1-phenyl-4-(trimethylsilyl)-3-buten-1-ol (60:40 diastereomeric mixture):  bp 91 °C (2 Torr, bath temp); IR (neat) 3368 (br), 2954, 1612, 1453, 1247, 1020, 996, 865, 837, 699 cm$^{-1}$; NMR (CDCl$_3$) δ 0.01 (s, 5.4H), 0.07 (s, 3.6H), 0.85 (d, J = 6.8 Hz, 1.2H), 0.99 (d, J = 6.8 Hz, 1.8H), 1.97 (br.s, 0.6H), 2.14 (br.s, 0.4H), 2.48 (ddq, J = 7.9, 7.1, 6.8 Hz, 0.4H), 2.54 (dddq, J = 6.5, 5.5, 1.2, 6.8 Hz, 0.6H), 4.36 (d, J = 7.9 Hz, 0.4H), 4.61 (d, J = 5.5 Hz, 0.6H), 5.65 (dd, J = 18.8, 1.2 Hz, 0.6H), 5.84 (d, J = 18.8 Hz, 0.4H), 5.92 (dd, J = 18.8, 6.5 Hz, 0.6H), 5.97 (dd, J = 18.8, 7.1 Hz, 0.4H), 7.2-7.4 (m, 5H). Found: C, 71.66; H, 9.68%.  Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46%.

(1E, 5E)-3-Methyl-1-(trimethylsilyl)-1,5-heptadien-4-ol (57:43 diastereomeric mixture):  bp 65 °C (2 Torr, bath temp); IR (neat) 3362 (br), 2954, 1613, 1248, 995, 965, 866, 837 cm$^{-1}$; NMR (CDCl$_3$) δ 0.06 (s, 5.13H), 0.06 (s, 3.87H), 0.97 (d, J = 6.8 Hz, 1.29H), 1.01 (d, J = 6.9 Hz, 1.71H), 1.71 (dm, J = 7.2 Hz, 3H), 2.22 (ddq, J = 7.2, 7.0, 6.8 Hz, 0.43H), 2.34 (ddq, J = 6.8, 6.0, 6.9 Hz, 0.57H), 3.79 (dd, J = 7.4, 7.2 Hz, 0.43H), 3.95 (dd, J = 6.1, 6.0 Hz, 0.57H), 5.4-5.5 (m, 1H), 5.6-5.8 (m, 1H), 5.73 (dd, J = 18.8, 1.1 Hz, 0.57H), 5.79 (d, J = 18.8 Hz, 0.43H), 5.92 (dd, J = 18.8, 7.0 Hz, 0.43H), 5.97 (dd, J = 18.8, 6.8 Hz, 0.57H).  Found:  C, 66.36; H, 11.48%.  Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18%.

A 1:2 Mixture of (E)-3,3-dimethyl-1-(dimethylphenylsilyl)-1-butene and 2-Methyl-4-(dimethylphenylsilyl)-2-pentene: bp 65 °C (2 Torr, bath temp); IR (neat) 2956, 2922, 2856, 1427, 1247, 1113, 830, 729, 697 cm$^{-1}$; NMR (CDCl$_3$) δ 0.22 (s, 2.01H), 0.25 (s, 2.01H), 0.31 (s, 1.98H), 0.97 (d, $J$ = 7.2 Hz, 2.01H), 1.02 (s, 2.97H), 1.44 (d, $J$ = 1.2 Hz, 2.01H), 1.68 (d, $J$ = 1.0 Hz, 2.01H), 1.93 (dq, $J$ = 10.9, 7.3 Hz, 0.67H), 4.93 (dm, $J$ = 10.9 Hz, 0.67H), 5.66 (d, $J$ = 19.0 Hz, 0.33H), 6.13 (d, $J$ = 19.0 Hz, 0.33H), 7.3-7.5 (m, 3H), 7.5-7.6 (m, 2H). Found: C, 76.89; H, 10.41%. Calcd for C$_{14}$H$_{22}$Si: C 76.99; H, 10.15%.

(E)-3,3-Dimethyl-1-(dimethylphenylsilyl)-1-octen-4-ol: bp 100 °C (2 Torr, bath temp); IR (neat) 3450 (br), 2954, 2930, 2860, 1466, 1248, 1113, 999, 844, 827, 731, 698 cm$^{-1}$; NMR (CDCl$_3$) δ 0.34 (s, 6H), 0.91 (t, $J$ = 7.1 Hz, 3H), 1.02 (s, 6H), 1.2-1.8 (m, 7H), 3.28 (br.d, $J$ = 9.0 Hz, 1H), 5.83 (d, $J$ = 19.5 Hz, 1H), 6.08 (d, $J$ = 19.5 Hz, 1H), 7.3-7.5 (m, 3H), 7.5-7.7 (m, 2H). Found: C, 74.17; H, 10.60%. Calcd for C$_{18}$H$_{30}$OSi: C, 74.42; H, 10.41%.

(E)-2,2-Dimethyl-4-(dimethylphenylsilyl)-1-phenyl-3-buten-1-ol: bp 140 °C (2 Torr, bath temp); IR (neat) 3420 (br), 2958, 1611, 1453, 1427, 1248, 1113, 999, 844, 826, 731, 699 cm$^{-1}$; NMR (CDCl$_3$) δ 0.34 (s, 6H), 0.98 (s, 3H), 1.03 (s, 3H), 1.93 (br.s, 1H), 4.45 (s, 1H), 5.81 (d, $J$ = 19.1 Hz, 1H), 6.17 (d, $J$ = 19.1 Hz, 1H), 7.26 (br.s, 5H), 7.3-7.5 (m, 3H), 7.5-7.6 (m, 2H). Found: C, 77.21; H, 8.59%. Calcd for C$_{20}$H$_{26}$OSi: C, 77.36; H, 8.44%.

(1E, 5E)-4,4-Dimethyl-6-(dimethylphenylsilyl)-1-phenyl-1,5-hexadien-3-ol: bp 150 °C (2 Torr, bath temp); IR (neat) 3440 (br), 2958, 2868, 1670, 1612, 1494, 1450, 1427, 1248, 1113, 998, 968, 844, 824, 735, 697 cm$^{-1}$; NMR (CDCl$_3$) δ 0.35 (s, 6H), 1.08 (s, 6H), 1.68 (br.s, 1H), 4.01 (d, $J$ = 6.6 Hz, 1H), 5.88 (d, $J$ = 19.1 Hz, 1H), 6.19 (d, $J$ = 19.1 Hz, 1H), 6.21 (dd, $J$ = 16.5, 6.9 Hz, 1H), 6.91 (dd, $J$ = 16.5, 1.0 Hz, 1H), 7.2-7.4 (m, 8H), 7.5-7.6 (m, 2H). Found: C, 78.36; H, 8.53%. Calcd for C$_{22}$H$_{28}$OSi: C, 78.51; H, 8.39%.

(E)-3,3-Dimethyl-1-(trimethylsilyl)-1-dodecen-4-ol: bp 124 °C (2 Torr, bath temp); IR (neat) 3450 (br), 2954, 1247, 1113, 999, 844, 826, 730, 698 cm$^{-1}$; NMR (CDCl$_3$) δ 0.06 (s, 9H), 0.88 (t, $J$ = 6.3 Hz, 3H), 0.98 (s, 6H), 1.28 (br.s, 12H), 1.3-1.5 (m, 2H), 1.55 (br.s, 1H), 5.70 (d, $J$ = 19.2 Hz, 1H), 5.97 (d, $J$ = 19.2 Hz, 1H). Found: C, 71.51; H, 12.84%. Calcd for C$_{17}$H$_{36}$OSi: C, 71.76; H, 12.75%.

(E)-2,2-Dimethyl-1-phenyl-4-(trimethylsilyl)-3-buten-1-ol: bp 113 °C (2 Torr, bath temp); IR (neat) 3448 (br), 2952, 1609, 1453, 1248, 1041, 1026, 1001, 866, 837, 731, 700 cm$^{-1}$; NMR (CDCl$_3$) δ 0.07 (s, 9H), 0.95 (s, 3H), 1.00 (s, 3H), 5.70 (d, $J$ = 19.2 Hz, 1H), 6.06 (d, $J$ = 19.2 Hz, 1 H), 7.2-7.4 (m, 5H). Found C, 72.27; H, 9.94%. Calcd for C$_{15}$H$_{24}$OSi: C, 72.52, H, 9.74%.

(E)-3,3-Dimethyl-1-(trimethylsilyl)-1,5-heptadien-4-ol: bp 87 °C (2 Torr, bath temp); IR (neat) 3386 (br), 2956, 1611, 1449, 1377, 1247, 996, 966, 866, 838, 727, 689 cm$^{-1}$; NMR (CDCl$_3$) δ 0.08 (s, 9H), 0.99 (s, 6H), 1.73 (dm, $J$ = 6.0 Hz, 3H), 3.75 (br.d, $J$ = 7.0 Hz, 1H), 5.4-5.8 (m, 2H), 5.73 (d, $J$ = 19.2 Hz, 1H), 6.02 (d, $J$ = 19.2 Hz, 1H). Found: C, 67.99; H, 11.56%. Calcd for C$_{12}$H$_{24}$OSi: C, 67.86; H, 11.56%.

(E)-2,3,3-Trimethyl-5-(trimethylsilyl)-4-penten-2-ol: bp 60 °C (2 Torr, bath temp); IR (neat) 3448 (br), 2970, 1375, 1248, 839, 689 cm$^{-1}$; NMR (CDCl$_3$) δ 0.05 (s, 9H), 1.03 (s, 6H), 1.15 (s, 6H), 5.70 (d, $J$ = 19.3 Hz, 1H), 6.19 (d, $J$ = 19.3 Hz, 1H). Found: C, 65.63; H, 12.35%. Calcd for C$_{11}$H$_{24}$OSi: C, 65.93; H, 12.07%.

A 1:1 Mixture of (E)-1-(Dimethylphenylsilyl)-1-pentene and 1-(Dimethylphenylsilyl)-2-pentene (stereoisomeric ratio 58:42): bp 67 °C (2 Torr, bath temp); IR (neat) 3004, 2958, 1427, 1248, 1113, 834, 726, 698 cm$^{-1}$; NMR (CDCl$_3$) δ 0.26 (s,

1.74H), 0.27 (s, 1.26H), 0.32 (s, 3.0H), 0.89 (t, $\underline{J}$ = 8.2 Hz, 0.63H), 0.90 (t, $\underline{J}$ = 7.0 Hz, 0.58H), 0.93 (t, $\underline{J}$ = 8.0 Hz, 0.87H), 1.4-1.6 (m, 1H), 1.64 (dt, $\underline{J}$ = 6.6, 1.1 Hz, 1H), 1.71 (d, $\underline{J}$ = 7.2 Hz, 0.42H), 1.8-2.2 (m, 2H), 5.2-5.5 (m, 1.80H), 5.75 (dt, $\underline{J}$ = 18.4, 1.4 Hz, 0.50H), 6.12 (dt, $\underline{J}$ = 18.4, 6.2 Hz, 0.50H), 7.3-7.4 (m, 3H), 7.4-7.6 (m, 2H). Found: C, 76.54; H, 10.09%. Calcd for $C_{13}H_{20}Si$: C, 76.40; H, 9.86%.

(E)-2-Ethyl-4-(dimethylphenylsilyl)-1-phenyl-3-buten-1-ol (diastereomeric ratio 65:35): bp 123 °C (2 Torr, bath temp); IR (neat) 3396 (br), 3064, 2956, 2894, 1612, 1453, 1428, 1247, 1113, 1027, 995, 840, 826, 730, 698 $cm^{-1}$; NMR (CDCl$_3$) δ 0.24 (s, 1.05H), 0.25 (s, 1.05H), 0.35 (s, 3.90H), 0.80 (t, $\underline{J}$ = 7.6 Hz, 1.95H), 0.87 (t, $\underline{J}$ = 7.4 Hz, 1.05H), 1.1-1.4 (m, 2H), 1.97 (d, $\underline{J}$ = 4.4 Hz, 0.35H), 2.09 (d, $\underline{J}$ = 2.4 Hz, 0.65H), 2.2-2.5 (m, 1H), 4.47 (dd, $\underline{J}$ = 7.6, 2.4 Hz, 0.65H), 4.61 (dd, $\underline{J}$ = 6.4, 4.4 Hz, 0.35H), 5.7-5.8 (m, 0.70H), 5.9-6.0 (m, 1.30H), 7.2-7.5 (m, 8H), 7.5-7.6 (m, 2H). Found: C, 77.52; H, 8.63%. Calcd for $C_{20}H_{26}OSi$: C, 77.36; H, 8.44%.

(E)-2-Methyl-1-phenyl-4-(dimethylphenylsilyl)-3-buten-4-one: bp 140 °C (2 Torr, bath temp); IR (neat) 3066, 2958, 1685, 1598, 1448, 1435, 1248, 1225, 1113, 991, 968, 845, 830, 730, 698 $cm^{-1}$; NMR (CDCl$_3$) δ 0.28 (s, 3H), 0.30 (s, 3H), 1.34 (d, $\underline{J}$ = 6.8 Hz, 3H), 4.24 (ddq, $\underline{J}$ = 7.2, 1.0, 6.8 Hz, 1H), 5.97 (dd, $\underline{J}$ = 18.7, 1.0 Hz, 1H), 6.24 (dd, $\underline{J}$ = 18.7, 7.2 Hz, 1H), 7.2-7.7 (m, 8H), 8.0-8.1 (m, 2H). Found: C, 77.40; H, 7.57%. Calcd for $C_{19}H_{22}OSi$: C, 77.50; H, 7.53%.

(E)-2-Methyl-1-phenyl-4-(trimethylsilyl)-3-buten-1-one: bp 90 °C (2 Torr, bath temp); IR (neat) 2954, 1687, 1608, 1249, 1226, 990, 970, 867, 839, 699 $cm^{-1}$; NMR δ 0.02 (s, 9H), 1.32 (d, $\underline{J}$ = 6.8 Hz, 3H), 4.20 (ddq, $\underline{J}$ = 7.1, 1.1, 6.8 Hz, 1H), 5.84 (dd, $\underline{J}$ = 18.6, 1.1 Hz, 1H), 6.14 (dd, $\underline{J}$ = 18.6, 7.1 Hz, 1H), 7.4-7.6 (m, 3H), 7.9-8.1 (m, 2H). Found: C, 72.22; H, 8.85%. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67%.

(E)-2,2-Dimethyl-1-phenyl-4-(trimethylsilyl)-3-buten-1-one: bp 95 °C (2 Torr, bath temp); IR (neat) 2956, 1682, 1599, 1249, 866, 839, 711, 696 $cm^{-1}$; NMR (CDCl$_3$) δ 0.06 (s, 9H), 1.37 (s, 6H), 5.89 (d, $\underline{J}$ = 19.1 Hz, 1H), 6.33 (d, $\underline{J}$ = 19.1 Hz, 1H), 7.3-7.6 (m, 3H), 7.8-7.9 (m, 2H). Found: C, 73.27; H, 9.22%. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00%.

(E)-2-Ethyl-4-(dimethylphenylsilyl)-1-phenyl-3-buten-1-one: bp 117 °C (2 Torr, bath temp); IR (neat) 3064, 1958, 1872, 1682, 1598, 1448, 1427, 1249, 1217, 1113, 993, 836, 821, 730, 698 $cm^{-1}$; NMR (CDCl$_3$) δ 0.29 (s, 3H), 0.31 (s, 3H), 0.93 (t, $\underline{J}$ = 7.4 Hz, 3H), 1.6-1.8 (m, 1H), 1.8-2.0 (m, 1H), 4.04 (dt, $\underline{J}$ = 7.8, 7.4 Hz, 1H), 5.98 (d, $\underline{J}$ = 18.7 Hz, 1H), 6.16 (dd, $\underline{J}$ = 18.7, 7.8 Hz, 1H), 7.2-7.6 (m, 8H), 7.9-8.1 (m, 2H). Found: C, 78.14; H, 8.06%. Calcd for $C_{20}H_{24}OSi$: C, 77.87; H, 7.84%.

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